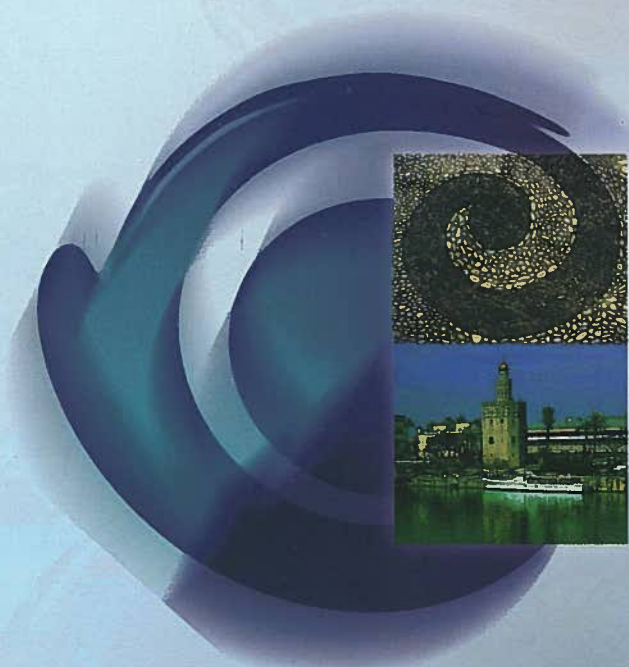


**BOOK OF ABSTRACTS OF THE 14th  
SYMPOSIUM ON ENVIRONMENTAL  
POLLUTION AND ITS IMPACT ON LIFE IN  
THE MEDITERRANEAN REGION WITH  
FOCUS ON ENVIRONMENT AND HEALTH**



**October 10-14, 2007**

**Seville – Spain**



JUNTA DE ANDALUCÍA

Instituto de Investigación y Formación Agraria y Pesquera  
**CONSEJERÍA DE INNOVACIÓN, CIENCIA Y EMPRESA**  
**CONSEJERÍA DE AGRICULTURA Y PESCA**



**MESAEP**  
**MEDITERRANEAN SCIENTIFIC ASSOCIATION**  
**OF ENVIRONMENTAL PROTECTION**

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SYMPOSIUM ON ENVIRONMENTAL POLLUTION AND ITS  
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J.Cornejo, D.Sarigiannis and W.Bergheim (Ed.)

**BOOK OF ABSTRACTS** of the 14th International Symposium on Environmental Pollution and its Impact on Life in the Mediterranean Region with focus on Environment and Health

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## **PREFACE**

The Mediterranean Scientific Association of Environmental Protection (MESAEP) was founded in October 1979 as a non-profit scientific organization engaged in research and development in the field of environmental technology and chemistry as well as ecotoxicology.

The objective of the MESAEP is to provide a forum for interested persons from the field of the environmental sciences carrying out research related to chemical contamination and the other sources of pollution in the Mediterranean environment, and also those in economics and politics. One of the main activities of MESAEP is to organise biennial symposia on "Environmental Pollution and its Impact on Life in the Mediterranean Region". MESAEP has organized since 1981 together with national and international organizations symposia on "Environmental Pollution and its Impact on Life in the Mediterranean Region", in Athens / Greece (1981), Crete / Greece (1983), Istanbul / Turkey (1985), Kavala / Greece (1987), Blanes / Spain (1989), Como / Italy (1991), Juan Les Pin-Antibes / France (1993), Rhodes / Greece (1995), S. Agnello di Sorrento / Italy (1997), Alicante / Spain (1999), Limassol / Cyprus (2001), Antalya / Turkey (2003) and Thessaloniki/Greece (2005).

The objectives of these symposia are to give the opportunity to scientists of different countries:

- to examine the current problems of environmental protection in the Mediterranean region.
- to investigate solutions to these problems on regional, national and international basis.
- to discuss on the problems concerning the protection of man, animals and plants in the Mediterranean region from harmful effects of chemicals and physical agents, both natural and manmade.
- to give suggestions and recommendations to the regulatory bodies of the various Mediterranean Countries to make proper decisions regarding the evaluation of safety of chemicals and physical agents.

In the 14th Symposium have been presented 363 papers as oral and poster presentations by environmental scientist from 32 countries: Albania, Algeria, Argentina, Austria Belgium, Brazil, China, Croatia, Cyprus, Czech Republic, Egypt , France, Germany, Greece ,Hungary, Israel, Italy, Libya, Lithuania, Morocco, Netherlands, Norway, Poland, Portugal, Russia, Slovak Republic, Slovenia, Spain, Switzerland, Turkey, UK and USA

The abstracts of the 14th Symposium papers are included in the present book, while the full papers will be published in successive issues of the international journal "Fresenius Environmental Bulletin" (FEB) contributing to an actual knowledge of the problems and possible solutions to the Mediterranean region environment.

We would like to acknowledge the contribution of the authors of the papers presented in this volume, the scientific work of whom made this edition feasible. Many thanks are due to all members of the Executive Committee of MESAEP and special thanks to Werner Berheim (GSF, Munich) and Dr. Denis Sarigiannis (IRC, Ispra, Italy) for their outstanding work and close collaboration during the preparation of this volume.

*Prof. Dr. Juan Cornejo  
President of MESAEP*

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- 04-p-110      EVALUATION OF POTENTIAL POLLUTION FROM AGRICULTURAL ACTIVITIES AT DURRES REGION (ALBANIA)  
S. Sulce and E. Veizaj
- 04-p-111      AIR PREDICTION MODELS OF POLLUTANTS IN AN INDUSTRIALISED AREA OF THE MEDITERRANEAN BASIN  
A.B. Vicente, A. Sánchez, T. Sanfeliu, M.M. Jordan, and M.D. Esteban
- 04-p-112      HEAVY METAL SPECIATION OF ESTUARINE SEDIMENTS AFFECTED BY ACID MINE DRAINAGE IN THE TINTO AND ODIEL ESTUARY, SPAIN. RELATIONSHIP TO BIOACCUMULATION OF FISH TISSUES.  
J.J. Vicente-Martorell, M.D. Galindo-Riaño, M. García-Vargas, and M.D. Granado-Castro
- 04-p-113      ADSORPTION AND DEGRADATION OF FOUR ACIDIC PESTICIDES IN SOILS FROM SEVILLE  
J. Villaverde, M. Kah, and C. Brown

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- 04-p-114 SURFACE SEDIMENTS IN THE OPEN AEGEAN SEA  
F. Voutsinou-Taliadouri and H. Kaberi
- 04-p-115 DETERMINATION AND EVALUATION OF SURFACE OZONE LEVELS IN  
ESKISEHIR, TURKEY  
O.D. Yay, H. Altug, O. Ozden, and T. Dogeroglu
- 04-p-116 MONITORING OF PESTICIDE RESIDUES IN RIVER WATER OF ALIAK-  
MONAS RIVER IN THE REGION OF IMATHIA (N. GREECE) BY MEANS  
OF SOLIDPHASE EXTRACTION DISKS AND GAS CHROMATOGRAPY  
I. V. Zioris, D.A. Lambropoulou, and T. A. Albanis

### **Session 5 - Endocrine disrupters**

- 05-o-01 ANALYTICAL DETERMINATION OF SYNTHETIC ESTROGENS IN  
ENVIRONMENTAL WATERS, SLUDGE AND SEDIMENTS: STATE OF THE  
ART  
A. Leal-Cerro and A. G. González
- 05-o-02 IN SILICO SCREENING OF ESTROGEN-LIKE CHEMICALS BASED ON  
QSAR MODELS  
H. Liu, E. Papa, and P. Gramatica
- 05-o-03 PROGRESS WITH THE PBT EVALUATION, UNCERTAINTIES AND PBT  
ASSESSMENT UNDER REACH  
A.B. Payá Pérez, H. Magaud, P. Lepper, and B. Schwarz-Schulz
- 05-p-01 ROLE OF POLICYCLIC AROMATIC HYDROCARBONS AS ENDOCRINE  
DISRUPTORS IN A COHORT OF URBAN TRAFFIC POLICEMEN IN SOU-  
THERN EUROPE  
R. Bono, S. Ghittori, P. Piccioni, D. Traversi, C. Pignata, and L. Chiovato
- 05-p-02 POLYCHLORINATED BIPHENYLS (PCBs) IN THE MEDITERRANEAN  
SEA ATMOSPHERE AND SEAWATER  
J. Castro Jiménez, M. Ghiani, G. Hanke, G. Mariani, H. Skejo, G. Umlauf, J.  
Wollgast, N. Berrojalbiz, M. Carmen Valle, S. Lacorte, and J. Dachs
- 05-p-03 DIETARY INTAKE IN PREGNANCY AND THE RISK OF HYPOSPADIAS  
IN 12 EUROPEAN COUNTRIES  
F. Giannandrea, F. Giordano, and I. Figa'-Talamanca

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- 05-p-04      SEX STEROIDS IN TAPES PHILIPPINARUM (ADAMS AND REEVE 1850) DURING THE GAMETOGENIC CYCLE: PRELIMINARY RESULTS  
E. Negrato, M. G. Marin, D. Bertotto, C. Simontacchi, V. Matozzo, and C. Poltronieri
- 05-p-05      DO REPRODUCTIVE CONDITIONS INFLUENCE RESPONSIVENESS OF VITELLOGENIN-LIKE PROTEIN INDUCTION IN CLAMS (TAPES PHILIPPINARUM) EXPOSED TO 4-NONYLPHENOL?  
M.G. Marin, F. Ricciardi, and V. Matozzo
- 05-p-06      DETERMINATION OF THE METABOLITES OF ALKYLPHENOL ETHOXYLATES AND BISPHENOL A IN WATER SAMPLES USING SPE/LC/ MS  
M. Tiggiridou, M. Christodoulidou, and St. Canna-Michaelidou
- 05-p-07      FATE OF ENDOCRINE DISRUPTING COMPOUNDS IN WASTEWATER TREATMENT PLANT  
D. Voutsas and P. Pothitou
- 05-p-08      PASSIVE SAMPLING OF SELECTED ENDOCRINE DISRUPTING COMPOUNDS USING POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLERS  
A. Arditoglou and D. Voutsas
- 05-p-09      ENDOCRINE DISRUPTING COMPOUNDS IN THE COASTAL ENVIRONMENT OF THERMAIKOS GULF, NORTHERN GREECE  
A. Arditoglou and D. Voutsas

#### **Session 6 - Indoor air**

- 06-o-01      CONCENTRATIONS OF VOCs AND OZONE IN INDOOR ENVIRONMENTS: A CASE STUDY IN TWO MEDITERRANEAN CITIES DURING WINTER PERIOD  
J.G. Bartzis, C. Michael, S. Michaelidou, D. Missia, D. Saraga, E. Tolis, S. Psoma, C. Petaloti, D. Kotzias, and J.M. Barero-Moreno
- 06-o-02      AN EVACUATION SYSTEM FOR EXTRAORDINARY INDOOR AIR POLLUTION CIRCUMSTANCES  
I. R. Karas and F. Batuk
- 06-o-03      TOXICOGENOMIC STUDY OF INDOOR AND OUTDOOR AIR CHEMICAL MIXTURES  
E. Marafante, G. Cimino Reale, and D. Sarigiannis

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- 06-o-04      RADIOLOGICAL UNDERGROUND EXPOSURE: THE TAV TUNNEL IN VALLE DI SUSIA (ITALY)  
L. Bonavigo, M. Zucchetti
- 06-p-01      FLIES (FLANDERS INDOOR EXPOSURE SURVEY): THE INFLUENCE OF CONTAMINANTS IN AMBIENT AIR ON THE INDOOR AIR QUALITY AND CHILDREN'S EXPOSURE  
K. De Brouwere, E. Goelen, R. Torfs, M. Spruyt, and M. Van Holderbeke
- 06-p-02      ESTIMATING THE ECOLOGICAL PREFERENCE ON BUILDINGS. THE GREEK ENVIRONMENTAL BUILDING ASSESSMENT  
E. Antoniou and P. Gavriil
- 06-p-03      INDOOR AND OUTDOOR NO<sub>2</sub> & OZONE LEVELS IN SCHOOLS OF ESKISEHIR, TURKEY  
O. Ozden, E. Gaga, and T. Dogeroglu
- 06-p-04      BENZENE EXPOSURE OF SEVERAL POPULATION GROUPS IN A MEDIUM SIZED SOUTHEASTERN EUROPEAN CITY  
G.A. Pilidis, S. P. Karakitsios, and M.A. Papatheodorou
- 06-p-05      INFLUENCE OF GAS ENVIRONMENT WITH THE INCREASED CONTENTS OF CARBONIC GAS ON SLEEP OF HUMAN  
T.A. Shustanova and A.A. Burikov
- 06-p-06      INDOOR AIR QUALITY IN A PRINTERY INDUSTRY IN ATHENS, GREECE  
I. Michopoulos, Th. Maggos, S. Pateraki, D. Saraga, K. Bairachtari, and Ch. Vasilakos

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- 07-o-00      ADVERSE IMPACTS OF WASTE WATER TREATMENT – A CASE STUDY  
W. C. Koskinen and D. S. DeVault
- 07-o-01      CORRELATION STRUCTURE AMONG CHEMICAL-PHYSICAL VARIABLES MEASURED IN MUNICIPAL SOLID WASTE DISPOSAL  
R. Caggiano, R. Coppola, M. D'Emilio, M. Macchiato, S. Martire, M. Ragosta, and S. Sabia

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- 07-o-02 FINGERPRINTING THE ORGANIC MATTER CONTENT OF WASTEWATERS: SEQUENTIAL FILTRATION/ULTRAFILTRATION FOR PARTICLE SIZE DISTRIBUTION-BASED COD FRACTIONATION  
E. Dulekgurgen, S. Dogruel, T. Ölmez, S. Arslan-Alaton, and D. Orhon
- 07-o-03 WASTE MANAGEMENT PRAXIS IN THE AUTOMOTIVE INDUSTRY ACCORDING TO ISO 14001  
O. Hanhan Tikin
- 07-o-04 IMPLEMENTATION OF THE DENITRIFYING PHOSPHORUS REMOVAL PROCESS IN MUNICIPAL WASTEWATER TREATMENT  
A. G. Kapagiannidis and A. Aivasidis
- 07-o-05 TiO<sub>2</sub>-PHOTOCATALYZED DEGRADATION OF PHENOLIC ACID CONTAMINANTS PRESENT IN OLIVE MILL WASTEWATER  
M. Boumhara, B. Tabyaoui, I.T. Lançar, M. Tabyaoui, and M. Bakasse
- 07-o-06 THE DETERMINATION OF ANTIBIOTICS AND DEGRADATION PRODUCTS IN WASTE WATER  
M. Vávrová, J. Cáslavsky, L. Vydrová, H. Vítecková, and R. Opatrilová
- 07-p-001 WASTEWATER TREATMENT AND REUSE BY CONSTRUCTED WETLAND SYSTEMS  
L. Akça, S. Ç. Ayaz, and C. Kınacı
- 07-p-002 ADSORPTION-DESORPTION OF PESTICIDES BY SOILS AMENDED WITH WOOD RESIDUES AFTER DIFFERENT INCUBATION TIMES  
M.S. Rodríguez-Crúz, M.S. Andrades, and M.J. Sánchez-Martín
- 07-p-003 MONITORING OF DI-(2-ETHYLHEXYL)PHTHALATE, NONYLPHENOL, NONYLPHENOL ETHOXYLATES AND POLYCHLORINATED BIPHENYLS IN ANAEROBIC AND AEROBIC SEWAGE SLUDGE BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY  
J. L. Santos, M. M. González, I. Aparicio, and E. Alonso
- 07-p-004 TREATABILITY OF A SIMULATED SPENT DISPERSE DYE BATH WITH ELECTROCOAGULATION  
I. Arslan-Alaton, G. Turkoglu, and I. Kabdasi
- 07-p-005 STREAM AND SOLID WASTE POLLUTION ASSESSMENT AT THE EASTERN BLACK SEA REGION, TURKEY  
S.S. Nas and A. Bayram

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- 07-p-006      INTEGRATION OF GIS, RS AND MULTI CRITERIA ANALYSIS FOR  
LANDFILL SITE SELECTION: ISTANBUL EUROPEAN SITE CASE  
STUDY  
F. Bektas Balçık, A.Ö. Dogru, B. Sener, F B. Sanlı, Ç. Göksel, N. Ulugtekin, and  
S. Sözen
- 07-p-007      SOURCE SEPARATED URINE AS A SOURCE OF PLANT NUTRIENTS  
AND A SUGGESTION FOR ITS USE VIA INDIRECT ROUTE  
B. Beler Baykal, S. Bayram, and A. D. Allar
- 07-p-008      PIG SLURRY DEPURATED BY CONSTRUCTED WETLAND  
A. Caballero, A. Faz, and J.B. Lobera
- 07-p-009      “IN SITU” AMENDMENTS AND REVEGETATION REDUCE TRACE ELE-  
MENT LEACHING IN A CONTAMINATED SOIL  
A. Pérez de Mora, P. Burgos, F. Cabrera, and E. Madejón
- 07-p-010      PERSISTENCE OF DIURON IN AN ORGANIC AMENDED SOIL: A FIELD  
STUDY  
A. Cabrera, L. Cox, P. Velarde, and J. Cornejo
- 07-p-011      TOTAL RECYCLING OF OLIVE MILL WASTES BY INTEGRATED PHYSI-  
CAL, PHYSICO-CHEMICAL, CHEMICAL AND BIOLOGICAL TECHNO-  
LOGIES  
R. Capasso, A. De Martino, F. Sannino, and M. Iorio
- 07-p-012      WASTE MANAGEMENT PRACTICE IN TURKISH SHIPYARDS  
U.B. Celebi, F.T. Akanlar, and N. Vardar
- 07-p-013      THE FATE OF KINETIC PARAMETERS ON BIOLOGICAL TREATMENT  
OF RAW AND ANAEROBICALLY PRE- TREATED WASTEWATER  
E. Cetin
- 07-p-014      THE POTENTIAL USE OF VEGETABLE OIL REFINING SLUDGE IN  
AGRICULTURE  
D. Dolgen, M.N. Alpaslan, and N. Delen
- 07-p-015      TROUBLESHOOTING FOR COD EXPERIMENTS: COMPARATIVE EVA-  
LUATION OF OPEN AND CLOSED REFLUX PROCEDURES FOR DETER-  
MINATION OF COD FROM ACETATE  
E. Dulekgurgen

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- 07-p-016 PREPARATION, CHARACTERIZATION AND APPLICATION OF ACTIVATED CARBON DERIVED FROM OLIVE STONE IN WASTEWATER TREATMENT  
G.E.Sharaf El-Deen and A.A.M. Daifullah
- 07-p-017 INVESTIGATION OF IN-SEWER TREATMENT PROCESSES  
E.Buyuk, E.Erdim, and L.Akca
- 07-p-018 ADSORPTION PROPERTIES OF ACTIVATED CARBONS FROM PEACH STONES PREPARED BY CHEMICAL ACTIVATION WITH  $K_2CO_3$   
H.F. Gerçel and Ö. Gerçel
- 07-p-019 COMBINED ANAEROBIC TREATMENT OF DOMESTIC WASTEWATER AND LANDFILL LEACHATE AT PSYCHROPHILIC TEMPERATURES  
C. Y. Gomec, D. I. Cifci, and C. Kinaci
- 07-p-020 A NEW APPROACH FOR WASTEWATER AND SEWAGE SLUDGE DISINFECTION: INACTIVATION OF SALMONELLA SPP. BY LOW-FREQUENCY ELECTROMAGNETIC FIELDS  
C. Keles, G. Tugrul-Icemer, and S. Ozen
- 07-p-021 BATHING WATER QUALITY ASSESSMENT IN ANTALYA BEACHES: LEVELS AND HEALTH RISKS OF FECAL INDICATORS IN SEAWATER AND BEACH SAND  
G. Tugrul-Icemer, S. Minta, A. Pekiylmaz, C. Keles
- 07-p-022 TREATMENT OF NAPHTHALENE SULPHONIC ACIDS USED AS DYE ASSISTING IN TEXTILE INDUSTRY BY ELECTROCOAGULATION  
I. Arslan-Alaton, I. Kabdashli, O. Tunay, and Z. Çekirge
- 07-p-023 PROPOSALS ON THE CITY OF NIKEA REFORM OF STREETCLEANING COLLECTION SYSTEM. APPLICATION OF CLEAN INDICATORS METHODOLOGY  
P. Konstantinidis, K. Markanastasaki, M. Sideri, and J.K. Kaldellis
- 07-p-024 CHARACTERIZATION AND TREATMENT OF GOLD REFINERY EFFLUENTS  
Ö. Karahan
- 07-p-025 USAGE OF TREATED DOMESTIC WASTEWATER IN IRRIGATION: AN EXAMPLE OF TURKEY  
C. Kınacı, M. Çakmakçı, M. Yazgan, and Ö. Çınar

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- 07-p-026 TREATMENT OF PULP BLEACHING EFFLUENT BY CATALYTIC OZONATION PROCESS  
Ç. Kivılcımdan and I. Akmehtmet Balcıoglu
- 07-p-027 GENERAL PLAN FOR THE INTEGRAL TREATMENT, MANAGEMENT AND VALORISATION OF WASTE GENERATED DURING THE PRODUCTION PROCESS OF VIRGIN OLIVE OIL  
A. Lara, J. R. Perán, A. Calvo, J. López, and P. Gatón
- 07-p-028 EFFECTS OF DE-OILED TWO-PHASE OLIVE MILL WASTE ADDITION TO SOIL ON SORPTION, DEGRADATION AND LEACHING OF THE HERBICIDE TERBUTILAZINE  
A. López-Piñeiro, D. Cabrera, A. Albarrán, and A. Muñoz
- 07-p-029 LONG-TERM IMPACTS OF SUGAR CANE WASTERWATER IRRIGATION ON FERRALITIC SOILS  
C. Maqueda, A. Rosabal, E. Morillo, and T. Undabeytia
- 07-p-030 RECYCLING OF WET OLIVE CAKE "ALPERUJO" THROUGH TREATMENT WITH FUNGI AND SUBSEQUENT VERMICOMPOSTING  
R. Nogales, M. Saavedra, and E. Benítez
- 07-p-031 ENHANCED DIURON SOIL SORPTION USING MEDITERRANEAN AGROINDUSTRIAL WASTES  
E. Romero, J. D., Fernández-Bayo and R. Nogales
- 07-p-032 THE BULKING AND BULGING PROBLEMS THAT CAUSING BY FILAMENTOUS MICROORGANISMS  
N. Ogleni, A. Aras, and O. Ogleni
- 07-p-033 INVESTIGATION OF ACID PHASE PRODUCTS USING COW RUMEN BASED ANAEROBIC MIXED CULTURE  
Y.A. Oktem, N. Sivri, and S. G. Pozan
- 07-p-034 WITHIN BOG VARIATION OF 210PB PROFILES: IMPLICATIONS FOR DATING PEAT CORES  
C. Olid, J. Garcia Orellana, P. Masqué Barri, A. Martínez Cortizas, and E. Peiteado
- 07-p-035 EFFECT OF CHEMICAL TREATMENT ON THE AROMATIC CARBON CONTENT AND PARTICLE SIZE DISTRIBUTION-BASED ORGANIC MATTER PROFILE OF OLIVE MILL WASTEWATERS  
T. Ölmez, E. Dulekgurgen, S. Arslan-Alaton, and D. Orhon



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- 07-p-036 PHOTOCATALYTIC TREATMENT OF PHENOL WITH VISIBLE LIGHT IRRADIATION  
T. Ölmez
- 07-p-037 OZONATION OF OXYTETRACYCLINE IN MANURE AND WASTEWATER  
M. Otker Uslu and I.A. Balcioglu
- 07-p-038 OZONATION OF ANTIBIOTICS IN SYNTHETIC PHARMACEUTICAL WASTEWATER  
M. Otker Uslu and I.A. Balcioglu
- 07-p-039 THE ADSORPTION OF MTBE ON COALS  
M. Ozmak, S. Bal, and Z. Aktas
- 07-p-040 NUTRIENT CONCENTRATIONS IN THE INNER SARONIKOS GULF AFTER THE SEWAGE SECONDARY TREATMENT  
A. Pavlidou and R. Psyllidou – Giouranovits
- 07-p-041 STABILIZATION OF HEAVY METALS BY USE OF CONSTRUCTION AND DEMOLITION RESIDUES (CDRS): A PRELIMINARY APPROACH  
C. Pérez-Sirvent, M.J. Martínez-Sánchez, M.J. Martínez- Pujante, J. López, and M.L.García-Lorenzo
- 07-p-042 PRODUCTION OF METHANE FROM DISTILLERY WASTEWATER USING ANAEROBIC CO- DIGESTION  
G.A. Pilidis, X.A. Boutsiadou, and I.S. Zarkadas
- 07-p-043 BIOSORPTION OF COPPER (II) FROM AQUEOUS SOLUTIONS BY USING SACCHAROMYCES CEREVISIAE  
M. Sarioglu and U.A. Guler
- 07-p-044 A STUDY ON THE TOXIC SUBSTANCES IN A STREAM ORIGINATING FROM DUMPSITE OF A TOWN ( Sivrice, Türkiye)  
B. Sen, O. Canpolat, and M.A.T. Kocer
- 07-p-045 SOIL FACTORS RELATED TO HEAVY METAL BIOAVAILABILITY AFTER SEWAGE SLUDGE APPLICATION  
J.M. Soriano-Disla, I. Gómez, C. Guerrero, M. Jordan, and J. Navarro-Pedreño
- 07-p-046 EFFECTS OF EXTRACELLULAR POLYMERIC SUBSTANCES (EPS) AND PHYSICO-CHEMICAL PROPERTIES OF ANAEROBIC GRANULES ON SLUDGE SETTLING D.T.  
Sponza and H. Atalay

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- 07-p-047      PROGRESS IN USE OF FERRATE (VI) AS AN OXIDANT WASTEWATER TREATMENT: OXIDATION OF P-COUMARIC ACID AND VANILLIC ACID BY FERRATES K<sub>3</sub>FEMNO<sub>8</sub>  
I. Bouhssine, A. Tazi, M. Boumhara, B. Tabyaoui, M. Tabyaoui, I.T. Lançar, and M. Azzi
- 07-p-048      HEALTH-CARE WASTE MANAGEMENT IN COASTAL AREAS  
I. C. Genç, H. Taskınsoy, and B. Topkaya
- 07-p-049      COMBATING BULKING SLUDGE WITH PHYSICAL AND CHEMICAL METHODS  
I.Yilmaz, G.T. Icemer, and B. Topkaya
- 07-p-050      SLUDGE MANAGEMENT PROPOSAL FOR TOURISTIC COASTAL AREAS  
I.Yilmaz and B.Topkaya
- 07-p-051      THE USAGE OF GIS IN LANDFILL SITE SELECTION      I.Bahçeci and B.Topkaya
- 07-p-052      PACKAGING WASTE MANAGEMENT: ANTALYA CITY CASE STUDY  
S. Uçaroglu, D. Ünver, and B. Topkaya
- 07-p-053      THE DETERMINATION OF SELECTED „MUSK“ COMPOUNDS IN WASTE WATER AND SEWAGE SLUDGES  
M. Vávrová, J. Cáslavsky, J. Mares, and M. Másová
- 07-p-054      A RAPID METHOD FOR DETERMINATION OF TOTAL LAS IN SEWAGE SLUDGE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) AND CAPILLARY ELECTROPHORESIS (CE) AFTER MICROWAVE EXTRACTION  
M. Villar, P. Villar, M. Callejón, J.C. Jiménez, E. Alonso, and A. Guiráum
- 07-p-055      EVOLUTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND HEAVY METALS IN SLUDGE SAMPLES FROM CONVENTIONAL WASTEWATER TREATMENT PLANTS  
P. Villar, M. Villar, M. Callejón, E. Alonso, J. C. Jiménez, and A. Guiráum
- 07-p-056      ARSENIC REMOVAL FROM WATERS BY ZERO-VALENT IRON: COLUMN STUDIES  
D. Voutsas, L. Antonoglou, and E. Lazou

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- 07-p-057 HEAVY METALS SPECIATION IN SEWAGE SLUDGE STABILISED WITH FENTON'S REAGENT  
E. Wisniowska, M. Wlodarczyk-Makula, and M. Janosz-Rajczyk
- 07-p-058 CHANGES OF SELECTED MICROPOLLUTANTS CONTENT IN CHEMICALLY STABILISED SEWAGE SLUDGE  
E. Wisniowska and M. Janosz-Rajczyk
- 07-p-059 IMPACT OF SEWAGE SLUDGE ADDED TO THE SOIL ON LEACHING PAHs, PCBs AND AOX  
M. Wlodarczyk-Makula and M. Janosz-Rajczyk
- 07-p-060 SPECIATION OF HEAVY METALS IN SOIL AMENDED WITH SEWAGE SLUDGE  
M. Wlodarczyk-Makula, E. Wisniowska, and M. Janosz-Rajczyk
- 07-p-061 THE ANAEROBIC PRE-TREATMENT OF HIGH STRENGTH LANDFILL LEACHATE  
G. Yilmaz
- 07-p-062 SURFACTANT DEGRADATION BY MEANS OF PEROXI - ELECTROCOAGULATION  
E. Yüksel and A. Sengil
- 07-p-063 COMPARISON AND MODELING OF THE HYDRAULIC PERFORMANCE OF A MEMBRANE SEQUENCING BATCH REACTOR (MSBR) FED WITH SYNTHETIC WASTEWATER AND LANDFILL LEACHATE  
A. Zouboulis, J. Tsilogeorgis, P. Samaras, and D. Zamboulis
- 07-p-064 COPPER AND ZINC CONCENTRATIONS IN FEEDSTUFFS OF DIFFERENT LIVESTOCK ACTIVITIES IN MIDDLE GREECE  
C. Makridis, G. Pilidis, C. Svarnas, N. Rigas, and L. Roka
- 07-p-065 THE PORT WASTE MANAGEMENT SYSTEM: EVALUATION OF TURKISH PORTS  
G.B. Alkan, G. Aydin, and C. Bayat

**Session 8 – Ecosystem function – Ecotoxicology**

- 08-o-00 CLIMATIC DISTURBANCES TO THE WATER CYCLE IN THE WESTERN MEDITERRANEAN BASIN: ORIGIN AND PROPAGATION TO REGIONAL - EUROPEAN AND GLOBAL SCALES  
M.M. Millán

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- 08-o-01 EFFECTS OF NEW ANTIFOULING PAINTS ON THE MACROFOULING BIOCOENOSIS OF HARD SUBSTRATUM IN THE LAGOON OF VENICE  
F. Cima and L. Ballarin
- 08-o-02 PROTEOMICS AND ABSOLUTE TRANSCRIPT EXPRESSION SIGNATURES IN FREE-LIVING MUS SPRETUS TO MONITOR TERRESTRIAL ECOSYSTEMS  
J. Ruiz-Laguna, R. Montes-Nieto, C.A. Fuentes-Almagro, N. Abril, J.L. Gómez-Ariza, J. López-Barea, and C. Pueyo
- 08-o-03 3D COASTAL EROSION ANALYSIS OF KILYOS-KARABURUN REGION USING MULTI-TEMPORAL SATELLITE IMAGE DATA  
S. Kaya, D.Z. Seker, E. Sertel, R.M. Alkan, and H. Maras
- 08-o-04 CONDITIONS OF ELIMINATION OF ENVIRONMENTAL POLLUTION IN INSECT MANAGEMENT  
R.Tykva, J.Hlavacek, B.Bennettova, J.Slaninova, J.Novak, V.Nemec, J.Cerny, V.Vlasakova, and J.Holik
- 08-p-01 TOXICITY OF FUNGICIDE TEBUCONAZOLE TO AN ESTUARINE AND A FRESHWATER ORGANISM  
O. Andreu-Sánchez and J.M. Carrasco-Dorrien
- 08-p-02 USE OF CULTURE COLLECTION (GAZI MACC/TURKEY) FOR HEAVY METAL EFFECTS, TOXINS AND PRESERVATION OF MICROALGAE  
T. Atıcı, H. Katircioglu, and B.S. Akin
- 08-p-03 A DIFFERENT WAY FOR A EARLIER BIO-INDICATION OF ENVIRONMENTAL POLLUTION  
P. Bassi and A. Basile
- 08-p-04 IDENTIFICATION OF ANTHROPOGENIC PRESSURES ON ANTINIOTI LAGOON, A NATURA 2000 SITE IN NORTHERN CORFU (GREECE)  
E. Aperi, F. Botsou, B. Mantzara, D. Faloutsos, and M. Scoullas
- 08-p-05 ENVIRONMENTAL RESIDUES IN GAME ANIMALS. 5 YEARS IN RESEARCH EVALUATION  
C. Brini, R. Orusa, M.C. Abete, S. Robetto, and L. Sala
- 08-p-06 HEMATOLOGICAL INDICES OF THE AZOV SEA ROUND GOBY NEOGOBIUS MELANOSTOMUS  
O.A. Rudnitskaya, L.A. Bugayov and A.S. Zasyad'ko

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- 08-p-07      MODELING THE MOBILITY OF Mn IN COASTAL SEDIMENTS COVERED WITH CYANOBACTERIAL MATS  
M. Ladakis, S. Triantafyllaki, E. Rousaselaki, and M. Dassenakis
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# **SESSIONS**



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## OUR ENVIRONMENT – OUR FUTURE

Manfred Grasserbauer

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The presentation will - referring to the concept of sustainable development as a basic principle for the further evolution of the European Union – discuss major environmental issues of the Mediterranean Region.

Specific results of research activities will be presented focusing on:

- the quality of air and the role of transport for air pollution, sustainable management of the inland and marine water resources,
- the challenge of combating climate change via mitigation and adaptation measures,
- the increasing role of renewable energies, and global issues relating to the sustainable consumption of natural resources.

The presentation will be based on research results obtained in the Joint Research Centre of the European Commission.

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## SUSTAINABILITY IN ORGANIC CHEMISTRY LAB COURSES

On behalf of the NOP-Team: Bahadir, M.,

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### Sustainable development needs chemical research

Research and innovation are preconditions for the transformation of economic and social processes in favor of a sustainable development. Chemistry, the science and practice of the transformation of matter, is of central importance. Everyone dealing with chemistry can contribute substantially to sustainable development and holds special responsibility. Already in education the links between reactions and substances with the consumption of energy and resources, toxicology and environmental pollution have to be treated consciously, so that graduates can provide for them in their professional life.

### Organic chemistry lab courses are central for chemical education

Organic chemistry lab courses are obligatory in university courses in chemistry, biochemistry, biology, pharmacy, physics, medicine and even in some engineering science courses. Most of these courses are being carried out in the traditional manner: Students learn basic experimental techniques of synthesis and analysis as well as dealing with dangerous chemical substances. The efficiency of a reaction is generally only looked at in terms of its stoichiometric yield. Students don't learn to evaluate the overall efficiency of a chemical transformation which is a direct measure of its sustainability. Procedures for possible improvements of their efficiency are not taught in an explicit way.

### Education contents must be complemented

In order for future generations of scientists to pay more attention to the topic of sustainable development already during their education, traditional contents and concepts of chemical education in schools, vocational schools, academies and universities have to be changed. Important contents of organic chemistry lab courses have to be preserved: Experiencing the joys of experimental activities, practicing of experimental skills, getting to know substances, equipment and reactions, safe handling of dangerous substances complying with legal regulations. These topics shall be complemented by aspects of efficiency and sustainability of a reaction. From this broader perspective students learn to plan, conduct and analyse organic synthesis reactions, including effects of the reaction on man and environment into the scope of their activities. Sustainability starts with planning the reaction!

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Course material offered in a new way...

Depending on aim and level of studies the contents to be conveyed differ strongly. Therefore, a new format was chosen for the new organic chemistry lab course. Not a textbook but an interactive database was designed to offer all relevant information. The offer is meant for lab instructors and teachers responsible for practical education in organic chemistry in universities, academia and vocational schools. The NOP material is intended to help set up modern lab courses and seminars, to get concepts and tools of sustainable chemistry across to generations of scientists to come. Lab experiments with experimental instructions, security information, safety information and analytical data have been amended with non-classical issues like life cycle assessment (LCA), energy consumption and (eco-)toxicological evaluations.

...and open for your contributions

Contrary to the "closed" nature of a textbook, only evolving by new editions in a confined way, this lab course is "open", meaning that authors not belonging to the original team can contribute. All materials are free of charge for students as well as teachers. For their application in a specific course, the instructor chooses adequate parts of the NOP collection. A pre-selection of topics, amplitude and structure of a course has been deliberately avoided. We hope that this open form of offering course material will widely be accepted and used on the different levels of education. Classical contents like experimental instructions are directly linked to, but not mixed with information, articles and data concerning sustainability, environmental protection and (eco)toxicology. In this way it is envisioned to convey these contents together with the classical "program".



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## FULL-CHAIN AND UNCERTAINTY APPROACHES FOR ASSESSING HEALTH RISKS IN FUTURE ENVIRONMENTAL SCENARIOS: THE 2-FUN PROJECT

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We present here the program of 2-FUN: an integrated project funded by the European Commission 6th Framework Subprogram on Global Change and Ecosystems. 2-FUN aims to provide decision-makers with state of the art tools to analyse trends in environmental conditions that may lead to health problems. It will support the evaluation and ranking of management options through a range of capabilities of high interest in health risk assessment: building of long-term environmental and socio-economic scenarios, exposure and effects assessment, provision of uncertainty margins, and identification of sensitive pathways and risks.

Specific scientific actions will be set up to develop methodologies, databases, models, and software on the following topics:

- Building future realistic socio-economic, environmental and health scenarios;
- Integrated exposure and effect assessment of multi-stressors via multiple routes;
- Integration of children's issues in health risk assessments;
- Development of uncertainty models and advanced data analyses for improved health management;
- Demonstrations of a full-chain approach for health risk assessment.

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2-FUN will engage in a structured dialogue with all interested parties (stakeholders, policy-makers and researchers) to monitor large environment- and health-focused scientific initiatives and to incorporate stakeholders' vision and needs regarding the development of tools for health risk assessment.

The tools developed will be tested on three contrasted case studies covering a range of temporal, spatial, sectorial, environmental, and societal contexts requiring comprehensive health risk assessments. Those case studies are: i. Evolution of air pollutants and thermal stress in Portugal and implications for future health risk scenarios; ii. Selection of alternative industrial technologies for the management of a river watershed (Loire or Seine River – France; iii. Land management in a heavy industry region (Upper Silesia region – Poland). They will provide policy-makers with relevant and easy-to-use information.

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## MULTIVARIATE TECHNIQUES FOR THE ANALYSIS OF PARTIAL EQUILIBRIUM ENERGY MODELS RESULTS

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The energy sector is of outstanding importance for defining sound planning strategies on supra-national, national and local scale, because of its direct and indirect consequences on environment as well as on socioeconomic development. In this framework, a valuable tool is represented by the TIMES energy models generators, developed under the aegis of IEA, that allow a comprehensive representation of complex energy systems based on a linear programming approach, individuating the optimal configuration of energy activities that fulfill the commodities demand at the minimum feasible cost. The solutions provide a large amount of results concerning energy consumption, levels of utilisation of technologies, emissions of main atmospheric pollutants, equilibrium prices of energy resources, etc. Some of the investigated parameters are usually combined in trade-off curves to point out the effects of variations of exogenous boundary conditions on energy systems and to derive the best suited solutions for the achievement of prefixed targets (scenario analysis). However, most of the information contained in the solutions are not completely exploited and there is a need of individuating the parameters with the high informational content, in order to derive "the robust strategies" and the priorities for the implementation of the energy technology roadmap, taking also into account the social acceptance of the envisaged measures.

In this context, a powerful method to investigate in depth the data correlation structure is represented by multivariate statistical procedures, currently used in many environmental studies. In fact, the evaluation and characterization of the correlation patterns underlying a multidimensional data set represents an important step for data analysis and their interpretation. These statistical methods, based on the analysis of [samples x descriptors] matrices, allow to reduce the original data set without losing important information (ordination or dimension reduction methods), to point out homogeneous subsets samples or descriptors (variance analysis, discriminant analysis, clustering) and to characterise the data structure (canonical correlation analysis, non parametric multiscaling).

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Here we present an innovative application of multivariate techniques (Cluster analysis and Principal Component Analysis) for the interpretation of the Business As Usual - BAU scenario results for 28 EU country models, obtained in the NEEDS project (VI Framework Programme, Priority 6.1: Sustainable Energy Systems). In this application, data matrices are made up by electric energy and heat production, fuels import and consumption, renewable use, CO<sub>2</sub> emissions by country and by time period (time horizon 2000-2050, subdivided into ten time periods). The aim of the analysis is to derive a general applicable procedure for characterizing information redundancy and data correlation structure, in order to identify sustainability indicators, to support decision making processes for complex energy systems.

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## **HEALTH AND ENVIRONMENT NETWORK (HENVINET) - PROJECT PRESENTATION**

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Human health is closely connected to the surrounding environment through interactions that are not necessarily well understood. The anthropogenic contamination of soil and water resources, the pollution of air, the presence of chemical compounds in food and other forms of environmental damage present in the human environment adds to the already existing uncertainty about the correlation of environment and human health.

To protect the health of populations and individuals, policies need to integrate environment and health issues. The aim of the HENVINET project is to support such informed policy making. HENVINET will review, exploit and disseminate knowledge on environmental health issues based on research and practices, for wider use by relevant stakeholders. Further, it will lead to validation of tools and results with emphasis on the four priority health diseases (asthma and allergies, cancer, neurodevelopmental disorders and endocrine disrupting effects) identified in the European Environment and Health Action Plan (EHAP) 2004-2010.

Building on previous research and policy initiatives, HENVINET will collect, structure and evaluate material and present it in a consistent manner, which will lend itself to transparency and identification of knowledge gaps.

HENVINET will establish an overview of results, activities, projects and tools existing in Europe and will promote international stakeholder networking through workshops and annual project meetings. Knowledge, best practices and decision support tools will be reviewed to allow wider exploitation by the relevant stakeholders such as policy makers. Recognizing that dissemination of knowledge, best practices and decision support tools is crucial in supporting the implementation of the EHAP, the project will define ways to disseminate information in collaboration with main stakeholders, with emphasis on the needs of users of information. To allow for efficient data gathering, information exchanges, and targeted dissemination, the project will utilise state-of-the-art Internet solutions and methodologies.

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## ON RECYCLING ENVIRONMENTAL EDUCATION e-MATERIAL TOWARDS BETTER COMMUNICATION OF ENVIRONMENTAL INFORMATION

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Communication of information concerning environmental issues may be transmitted through various channels in the area of the existing Information and Communication Technologies (ICTs). Examples towards such contribution of the latter include Internet-based applications that guarantee high distribution of the delivered information of interest to the end-users. However, this model, of one-way communication, leads to a passive receipt of the information with doubtful educational results. The evolution from one-way to two-way communication may be critical in cases where environmental education is the focus of the communication of interest. This model allows for a more participatory contribution of both the communication parties and provides a framework for their mutual understanding.

The use of ICT in the last decades has led to a large body of digital material (hereafter e-material, which includes components like text, photos, videos, animations) that supports environmental education and is delivered through varying means, e.g., CD-Roms, Internet. The focus of this paper is on the e-material that has been designed and developed on the basis of a specific educational aim and holds a static form of delivery of information. Since a lot of time, effort and cost have been invested for the development of this e-material, the effort is extended to its recycling towards better communication of the carried information. The steps of the recycling procedure of existing environmental education e-material include: a) realization of the existing e-material and its components, b) definition of the end-users and the aim of the communication of the new information that is to be produced, c) screening of the aforementioned components on the basis of the above definitions; production of a body of information, i.e., knowledge-base and checking for its possible enhancement, d) choice of an instruction theory to provide the theoretical background for the appropriate logging and the recombination of the knowledge-base components.

Within the above framework, two prototypes have been developed on the basis of existing e-material. The first refers to an attempt to contribute to the discrimination of a wetland functions and values and the second to the realization of the concept of the carrying capacity. An MS Access data-base has been developed and elements of the Learning Object Design and Sequencing Theory have been used. The interactive character of the prototypes, along with their ability to be delivered through the Internet, is expected to contribute to a two-way communication of information concerning environmental issues. Further justification is scheduled through the evaluation of the prototypes towards their further refinement.

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**ENVIRONMENT AND CHILDREN'S HEALTH: RESEARCH ACTIVITIES FUNDED  
BY THE EUROPEAN COMMISSION'S RESEARCH DIRECTORATE-GENERAL**

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Ninety-two international multidisciplinary research projects dealing with the environment and health issues were funded by the European Commission's Environment and Health 'key action' in the Fifth Framework Programme of Research (1998-2002) with total funding of around €160M. Most of these projects have ended recently and results are now becoming available. The projects dealt with many issues pertaining to children's health: impacts (reproduction, neurodevelopment, cancer...) of environmental chemicals (endocrine disrupters, heavy metals...), air pollutants, EMF, UV light, noise etc. While the Sixth Framework Programme of Research (2002-2006) has been ongoing, the EC adopted the Environment and Health Action Plan in 2004, one of the aims of which is to understand the links between exposure to environmental stressors and health outcomes such as neurodevelopmental disorders. Implementation of the research actions under this Action Plan have resulted in the funding of a number of both specific targeted research projects as well as a few large-scale integrated projects or networks of excellence, focusing on, e.g., long-term health impacts (including children) of exposure to low levels of heavy metals. EC contribution to these projects now exceeds €200M. Research efforts to implement the Action Plan will continue in the Seventh Framework Programme of Research (2006-2013), which will have a specific activity called 'Environment and Health' under the 'Environment' theme. First calls for proposals have been launched and several topics address issues related to children's health and environment.

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## FROM ECB TO ECHA, A NEW EU AGENCY IS BORN

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REACH (Registration, Evaluation and Authorisation of Chemicals), the new EU legislation regulating the management of Chemicals has been adopted on 18 December 2006, published in the Official Journal on 30 December 2006 and entered into force on 1 June 2007.

REACH will require a registration, over a period of 11 years, of some 30.000 chemical substances. The registration process requires the manufacturers and importers to generate data for all chemicals substances produced or imported into the EU above one tonne per year. The registrants must also identify appropriate risk management measures and communicate them to the users.

The implementation of this Regulation is under the responsibility of the European Chemicals Agency (ECHA), an independent body of the European Union established since 1st of June 2007 in Helsinki, Finland, and headed by an Executive Director to be controlled by a Management Board. ECHA's staff is expected to grow from about 100 by now, to over 400 persons by 2010.

This new Agency will coordinate the registration, evaluation, authorisation and restriction of chemicals manufactured or imported, and used in the EU by ensuring consistency in chemicals management across the EU. Its tasks include providing scientific/technical advice and developing guidance and tools for registrants and Member State competent authorities; checking the completeness of registration dossiers and their compliance with the requirements of the legislation; evaluating testing proposals; coordinating the evaluation of chemical substances; considering exemptions for research purposes; advising the Commission on substances to be authorised or restricted; coordinating two Scientific Committees (one on Risk Assessment, the other on Socio-Economic Analysis), a Member States Committee, an Enforcement Forum and a Board of Appeal.

In addition, the staff will provide helpdesk assistance to Member States, registrants and other stakeholders by managing IT based guidance documents, tools and databases via the Agency website. REACH-IT is ECHA's central IT-system that supports its regulatory management tasks.



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The Agency has to build up its personnel and internal structures with a view to becoming fully operational, i.e. able to execute all its functions and take over unfinished business from the European Chemical Bureau on the existing chemical legislation, from 1st of June 2008 onwards i.e. 12 months after entry into force of the REACH Regulation.

The first challenge of the Agency in the first 6 months of operation (1 June 2008 to 30 Nov 2008) will be to manage the preregistration of substances and intermediates. About 180.000 dossiers are expected to be submitted during the first 6 months of operation, relating to 30,000 substances and 20,000 intermediates.

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## DEVELOPMENT OF ENVIRONMENTAL GUIDELINES FOR THE REGION OF WESTERN BALKANS

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This paper will present the scope and objectives of the WEB-ENV project. The project's main objective is the development of general environmental guidelines concerning the region of Western Balkan Countries, with a particular focus on water resources, renewable energy and use of recycled materials. These guidelines could be useful for the formation of a generalized approach for the management of major environmental problems and natural resources as well. This will be reached by the following:

Extended mapping exercise to identify these problems

Development of evaluation criteria permitting the selection of the most significant problems in terms of water resources planning and policy, wastewater treatment and reuse technologies, use of recycled material, renewable energy and hybrid systems, taking into account the socio-economic and human health impacts

Assessment of innovative low-cost remediation technologies

Review of the existing legislation of each country in comparison with the EU Environmental legislation and EU environmental directives

A consortium composed by CERTH as the coordinator and 5 other partners from the academic community represented 4 from the five countries of the region assures an adequate regional participation.

An integrated dissemination plan foreseen activities like: the development of an environmental web portal providing reliable and up-to-date information, organization of local and general workshops, and participation in worldwide environmental events like congresses, conferences, expositions etc., will facilitate the dissemination of project results.

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The development of general environmental guidelines is expected to contribute to the formation of a common environmental policy and sustainable management of natural resources in the region, to arise peoples' sensitivity in crucial environmental problems, to contribute to the economic development of the region and to provide assistance to all the stakeholders involved with the enhancement of the political and social situation in Western Balkans.

The expected project results contribute to INCO general objectives since they encourage the trans-regional partnership and international cooperation and are linked to activities aimed at the prevention and re-mediation of environmental problems both in regional and global dimension of the area, to EU Water Initiative, to the Millennium Development Goals in terms of the assurance of environmental sustainability and to the Action Plan for S&T Cooperation between EU and the Balkan Countries.

The main objective of the project is the development of general environmental guidelines concerning the region of Western Balkans that could be useful for the formation of a generalised approach for the management of environmental problems of great significance and natural resources. To achieve this, an extended mapping exercise was carried out in each country, for the identification and evaluation of important environmental problems of the Western Balkan region, with particular focus on problems related to water resources planning and policy, wastewater treatment and reuse technologies, use of recycled material, renewable energy and hybrid systems. The development of a reliable environmental map of the region depicting the areas with significant environmental problems and recording the rehabilitation needs for each case was based on the mapping exercise. The identification and assessment of low cost innovative technologies to be implied for the remediation of the identified environmental problems, the review of the existing national legislations, and the preparation of 4 techno economical preliminary feasibility studies of cases of great significance (one for each participating country from the Western Balkan region) were undertaken. The preparation of the environmental guidelines will take place during the period during the last period of the project taking into account socio- and techno-economic parameters for each country and for the region of Western Balkans as well, encouraging the transnational research, technological and scientific collaboration.

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## ENVIRONMENTAL ATTITUDES AND VALUES IN A WILDERNESS CAMP

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Measuring adolescent environmental perception is a multifaceted task. This complex construct requires both the formulation of a theoretical basis thoroughly founded in the literature as well as the construction of an empirical, psychometrically sound measurement instrument, employing as a minimum requirement factor-analytic techniques, cross-sample testing and/or cross-validation by other studies. A questionnaire battery designed to measure the factors Utilization (U) and Preservation (P) in the field of adolescent environmental perception was administered to some thousand European secondary school pupils. Maximum likelihood factor analysis yielded the two hypothesized orthogonal factors U and P. Three cross-validation studies shed additional light on this measurement approach, two of the author together with other research groups, a third one of a New Zealand group which originally was undertaken in order to challenge the two-factor second-order structure as proposed by Bogner & Wiseman model (Milfont & Duckitt, 2004).

The presented paper will detail the direct measurement of both higher-order factors U and P and highlight the need to cross-examine an evaluation scale independently. Further on, it will show the instrument's introduction in a specific field course evaluation detailing the educators' background information and feed back of the programme quality.

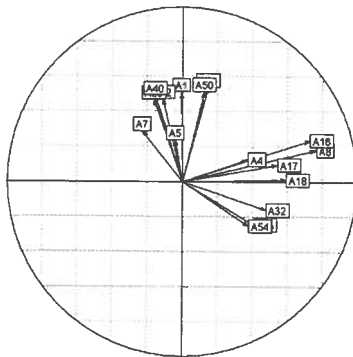


Figure: Factor analytic structure of the 2-MEV model portraying two distinct factors of Preservation and Utilisation.

## THE IMPACT OF SOCIAL DESIRABILITY ON ENVIRONMENTAL ATTITUDE AND BEHAVIOUR

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To control the success of environmental education programmes, valid measurement of environmental attitude and behaviour is essential, though in many studies not guaranteed. Especially the validity of self-reported behaviour, but also of attitudes has been suspected to be biased e.g. by social desirability because ecological awareness can be considered a social norm. Only few studies yielded high effects of social desirability however, and especially for children there research yielded conflictive results about actual impact of this bias.

In our study we applied a lie scale in the context of environmental attitudes, Preservation and Utilisation<sup>1)</sup>, and self-reported general ecological behaviour<sup>2)</sup>. We surveyed 198 Bavarian pupils (grade 5 and 6). Forming subgroups based on lie scores (low, medium and high) we found a significant moderate impact of lie scores on the Preservation attitude measure and a smaller impact on the self-reported behaviour score, but not on the Utilisation attitude measure (figure 1).

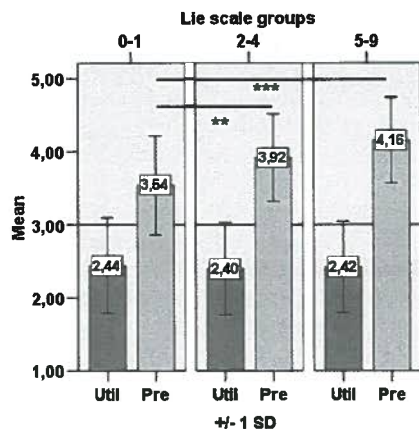
<sup>1)</sup> Bogner, F. X., & Wiseman, M. (2002). Environmental perception: Factor profiles of extreme groups. *European Psychologist*, 7(3), 225-237.

<sup>2)</sup> Kaiser, F. G., Oerke, B., & Bogner, F. X. (2006). Behavior-Based Environmental Attitude: Development of an Instrument for Adolescents. submitted for publication.

Figure 1: Preservation and Utilisation means for subgroups with low (0-1), medium (2-4) and high (5-9) Lie scores.

However, if in multiple regression analysis behaviour was predicted by means of attitude, the inclusion of lie score did not significantly change the amount of variance explained by attitude.

Implications are discussed.



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## CONTRIBUTIONS OF BIRD WATCHING AND RINGING EXCURSIONS IN ANTALYA REGION TO ENVIRONMENTAL EDUCATION

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In this study contribution of bird watching and ringing excursions in Antalya between 1999-2006 to awareness and consciousness of nature (Campus of Akdeniz University, Yamansaz, Termessos National Park, Bogazkent-Kocagöl, Kovada Lake, Burdur Lake, Egridir Lake). Bird watching and ringing are important activities for nature. After excursions, an improvement in understanding of environmental protection was observed among native people and students from different disciplines. After excursions, some of the participants (who claimed to be good hunters) showed more sympathy for nature after observing and understanding the relationships and diversity of birds. Afterwards their interest for hunting is mostly replaced with observation and photography. Also inviting press members to excursions has resulted in higher number of articles in media, and contributed to public awareness for environment, nature, and birds.

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## STRATEGIC ENVIRONMENTAL ASSESSMENT. THE GREEK CORRESPONDENCE

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During the past few decades there appeared to be an important increase in the interest about the environmental issues, the sustainability and the better management of development, respecting the environmental resources. New legislations, national and international (i.e. the European Union) influence, nowadays, the relationship between the development and the environment. Strategic Environmental Assessment (SEA) of policies, plans and programmes, introduced by the European Commission and incorporated to the national legislation of the member states, is trying to achieve sustainable development always respecting the environment.

It is widely believed that SEA have the ability to influence the environmental and sustainable nature of strategic decisions and to provide efficient, integrated and sustainable policies and planning frameworks in order to support and help the development process of projects.

Sustainability has been developed as a very popular term for planners, politicians, experts, businesses, local authorities, non governmental organisations and the public. The role of SEA is closely connected to the idea of sustainability since it was recognized as a mechanism for the success of sustainable development. The added value that is attributed to the environment through the SEA process is the ability to assess the economic and social impacts of plans or programmes, so that the plans or programmes could become sustainable. In order to apply the principles of sustainable development into plans and programmes someone should not target only to the natural and ecological issues but also should extend to the sectors of social prosperity and economic development.

Strategic Environmental Assessment constitutes a motive and at the same time a challenge for all the EU member states in order to promote a more sustainable way of assessing the impacts of plans and programmes. Greece has incorporated the SEA Directive into the national law in September 2007. Applying SEA to Greek programmes and plans, as well as to all the other countries of the EU the sustainability of the countries could be strengthened and confirmed.

Greece had never before experienced the process of assessing plans and programmes which both a challenge and a new potential for the county's planning. SEA allows the country to be able to assess plans and programmes such as regional, spatial and urban plans and programmes. This will help the developers, the planners, the authorities and the public to be able to recognize the probable direct or indirect impacts on the environment and on the sustainability. After all, SEA is a tool of integrated assessment, an on-going process which will empower the sustainability in Greece.

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## ENVIRONMENTAL EVALUATION OF CONTRA FLOW BUS LANES

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It is well known that public transport play an important role in sustainable urban mobility worldwide. This is the reason why local authorities have designed and implemented various priority measures in order to improve the performance of the public transport system and to promote its use in their areas. An efficient public transport system means less use of private passenger cars and it lead to the overall improvement of the traffic and environmental conditions.

Transport Demand Measures (TDM) are widely used as an attempt to control the demand due to private cars and at the same time to protect the environment. One of the TDM measures are the bus priority measures which include, among others, with flow and contra flow bus lanes. A contra flow bus lane runs in the opposite direction to traffic. It must be mentioned at this point that bus lanes are one of the most widespread measures worldwide.

Within the framework of this paper the environmental impacts of contra flow bus lanes based on the international experience are presented. In addition, the environmental impacts of a contra flow bus lane are evaluated through the use of modelling techniques having as a study area the city of Thessaloniki. The Thessaloniki city centre and its surrounding area serve high traffic volumes, especially during peak hours, and this fact has a direct impact on the environment. The authorities promote the use of public transport by constructing a quite extensive network of bus lanes in the city (there are now four with flow bus lanes and this network will be extended) but many drivers of passenger cars continue to use their vehicles for their trips to and from the city centre. Therefore, this fact imposes an external cost (environmental cost) to the residents and employees in the area.

The simulation model used in order to perform the evaluation of the contra flow bus lane is the SATURN (Simulation and Assignment of Traffic to Urban Road Networks), which is a suite of flexible network analysis program developed at the Institution for Transport Studies, University of Leeds.

The results from the examination of various environmental parameters such as energy consumption and pollutants emitted (CO, CO<sub>2</sub>, NO<sub>x</sub>, HC, and Pb) through the use of SATURN are presented and discussed. Although the decision whether to proceed with the implementation of a contra flow bus lane in a congested is based on a number of parameters, it is considered that the environmental evaluation will substantially assist this decision.



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## THREAT OF URBANIZATION AND SELECTION OF ENVIRONMENTAL CONSERVATION AREAS

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In this study, the change detection process has been applied by using LANDSAT-5-1989 and LANDSAT-7-2001 to determining the environmental conservation area at Terkos basin in Istanbul which are Istanbul and surrounded area is threatened of urbanization.

Images were classified by using topographic maps, forestry maps and auxiliary data for example GPS measurements. The results of classification were presented that was lost forestry area was approximately 10 000 hect.

The GIS model was implemented to determine the environmental conservation area with the fauna and flora information and other data. The results of model were proposed to governmental units.

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## THE VALUE OF MARINE SPATIAL DATA INFRASTRUCTURE FOR INTEGRATED COASTAL ZONE MANAGEMENT

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In any case where right decisions are critical and a number of stakeholders are involved, Spatial Data Infrastructures (SDI) become indispensable. Environmental resources management involves numerous cases where decisions are even crucial concerning sustainable development. Integrated Coastal Zone Management (ICZM) is one such case. The word “integrated” in the term “ICM” is for an interdisciplinary analysis of the major social, institutional and environmental issues and options affecting a selected coastal area. The analysis should take into account the interactions and interdependencies among natural resources and different economic sectors. On the other hand, politics and science have to work together for a successful ICZM program. Unfortunately some ICM programs have focused too much on science and too little on governance process; others have done the reverse. There are many related cases in Turkey which verify this diagnosis. One of the highlighting examples has been the illegal uses of the coastal areas. Another would be the dispute between the authorities of tourism and aquaculture on the fish cage site selection. There is no science at all in the former while its use has been rather insufficient in the latter cases.

Spatial Data Infrastructures (SDI)s including Marine SDIs can provide the data and services needed for the sufficient scientific involvement in the ICM programs. Being an “interoperability infrastructure”, SDI functions on top of a technical and organizational framework and enables cooperation among its participating partners. The “participating partners” refers to any provider or requestor of data and services within an SDI. Traditionally, however, Geographical Information Systems (GIS) have been employed for the scientific involvement of ICZM projects. As in many on going projects, there is generally a GIS software sitting somewhere at the project office, and the data is collected somehow in the system and various analyses are performed. The problem with this practice is the fact that it is isolated from the “everyday practice” or from the “real world”. The everyday practice has to be incorporated either technically or legally into the ICZM programs during the project level. Otherwise, let alone requiring extra time, this incorporation may be very difficult during the “real-life- application” of the project. This is especially true if the politicians are to be convinced for some legal arrangements. Philosophically, this view refers to the virtue of SDIs indeed; given the current “business models”, isolated systems can not promise any real life success. In this work some of the procedures which might be involved in a ICZM process will be taken into consideration. How these procedures may be effected with the support of SDIs, including Marine SDI, will be highlighted. Envisioned SDI implementation is based on the Services Oriented Architecture (SOA) and specificall

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## THE VALUE OF SPATIAL DATA INFRASTRUCTURES FOR ENVIRONMENTAL DECISION MAKING

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Today, the needs of spatial data applications have made cooperation among different organizations indispensable. In other words, information needs of Today's applications are far behind the capabilities of any single organization. Imagine the cases of environmental planning and Environmental Impact Assessment (EAI); in either of the cases a great variety of data from many different sources have to be combined. Otherwise, let alone being economical and rapid, the sound decisions or plans could not be reached. The needed is a Spatial Data Infrastructure (SDI) which would enable rapid and economical access to data and services of "others". A university, for instance, will be able to provide data from the SDI for doing research, under certain responsibilities and perhaps some limitations. Local governments will get cadastral and Land registry data. A real estate office will provide the requested data for her customers via the SDI. As the term, "SDI" is meant for the framework which defines and arranges the technologies, policies, and all the related activities to enable interoperability among its participants. Interoperability can be defined as the ability by which different applications can "talk" and cooperate with each other. Therefore, an interoperability infrastructure is at the heart of an SDI. And the key issue is how to implement this interoperability infrastructure. Emerging as the next generation of Web technologies, Web services (WS) seem to offer a great potential there.

Environmental decision making requires data from various sources. Two particular examples to environmental decision making would be zoning and Environmental Impact Assessment (EAI). The term "zoning" here may refer to any scale planning including coastal zone planning. Achieving these goals by traditional means may take long time and yield either erroneous or unhealthy results. There have been many examples to this even recently in Turkey. In many cases, prepared EAI's do not seem good enough either by their

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**MODELLING NATIONAL ENERGY SYSTEMS:  
A COMPREHENSIVE ASSESSMENT USING THE  
NEEDS-TIMES MODEL**

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The close relationships between anthropogenic activities and the environment require a careful analysis of economic and technological implication of energy-climate policies, to redirect the energy systems towards a configuration that harmonizes resources use, economic development and environmental protection. This implies the implementation of innovative decisional tools for policy assessment, to support the policy makers in the definition of sustainable energy-environmental strategies, assuring their consistency at different spatial scales. Important advances have been made in the ability to analyse global, national and local issues and to support the formulation of policies using comprehensive partial equilibrium models as the TIMES models generator, developed under the IEA-ETSAP Programme. This tool is being utilized in the framework of the Integrated Project "New Energy Externalities Developments for Sustainability" NEEDS financed by the EU Commission in the VI Framework Programme (Priority 6.1: Sustainable Energy Systems, Sub-priority 6.1.3.2.5: Socio-economic tools and concepts for energy strategy). Its main objective is to develop the energy system models of 29 EU countries, which are linked by energy and emissions trades in a multiregional approach implementing them into a unique modeling platform, the EU NEEDS TIMES model. These models include the techno-economic and environmental information necessary to characterize the long term development of energy systems, as well as data coming from LCA and ExternE. The aim is to implement an integrated modeling platform for the assessment of energy and environmental policies both at the level of individual countries and for the enlarged EU as a whole, allowing the evaluation of the full costs and benefits of the European energy system under different system's boundaries. We are presenting some results obtained at country level (equilibrium quantities of energy vectors, energy technologies and emissions) concerning the Business As Usual – BAU scenario that provides the optimised development of the energy system, considering the demand projections trends obtained by the GEM-E3 Europe (using the DGTREN 2005 data as key drivers) and the main national energy and environmental policies.

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## **TURKEY'S HEALTH, SAFETY AND ENVIRONMENTAL POLICY STATEMENT**

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Turkey policy is to minimize the negative impact of small scale instruction projects on the environment, to deliver projects that meet people's highest expectations and to ensure the safety and health of our most valuable resource. Training is important to improve person's understanding of the law and give them the authority to act responsibly. Turkey targets a "Zero Accident" work place by eliminating risks and expects all employees to participate in the process. The government takes environmental protection and pollution minimization into consideration at every stage of work. Turkey Government can proceed with its professions, knowing that all appropriate health, safety and environmental measures have been taken.

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## ENVIRONMENT POLICIES IN TURKEY

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In this study, development, involvement, targets and principles of the Environmental Policy of EU were investigated and Environmental Policy of the Union and the adaptation situation of Turkey to it were compared and progressions in environmental policy were evaluated. In this study, it was emphasized that although the environmental laws of both EU and Turkey own the same targets, there are differences between them. As a consequence of the study, it was stated that an institutional improvement in the implementation of environmental policy can be achieved by many regulations in Turkey and with these regulations, existent system may be enforced.

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## PBTs SCREENING BY MULTIVARIATE ANALYSIS AND QSAR MODELLING

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The limited availability of experimental data, necessary for risk assessment of chemicals, and the derived general lack of knowledge of the properties and activities of existing substances has led the European Commission to adopt the REACH (Registration, Evaluation and Authorization of CHemicals) legislation. The high expected cost of REACH has increased the interest on development and validation of alternative methods, such as the Quantitative Structure-Activity Relationships (QSARs), able to predict data and to provide priority lists.

Persistent Bioaccumulative and Toxic (PBT) chemicals are among those of higher concern requiring authorization, thus methods for early identification of these behaviour are needed. A structurally-based multivariate approach is proposed here for the screening of potential Persistent Bioaccumulative Toxic (PBT) chemicals into the environment.

Overall half lives data in air, soil, water and sediment, as well as BCF and fish acute toxicity data, were collected for a structurally heterogeneous set of more than 200 compounds, and combined by Principal Component Analysis in order to rank the chemicals according to their potential PBT behaviour. The PC1 score, able to identify PBT-like compounds, is modelled by QSAR approach by Multiple Linear Regression (MLR) and molecular descriptors. The here proposed QSAR model of this PBT index, also externally validated for its predictivity, is applicable to chemicals even without a priori knowledge of the toxicological and environmental behaviour, being it based on easily calculable theoretical molecular descriptors. This model, which results are comparable with the US EPA PBT-profiler screening tool, could be successfully applied as screening tool for the identification of new potential PBTs, also before their synthesis.

Finally, the here proposed model was applied to predict the PBT-potential of different classes of compounds also included in the ORATs and in The Water Framework Directive priority lists.

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## **DEVELOPMENT AND OPERATION ISSUES OF A DECISION SUPPORT SYSTEM FOR WATER MANAGEMENT IN AREAS WITH LIMITED WATER RESOURCES**

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Water is a constrained natural resource and in many areas of the planet water shortage is considered to be the one of the most important issues to be resolved. More than 25% of the world population lives in dry or semi-arid areas and the water supply chain management is evolving as one of the most difficult and urgent problems, since the water's demand and availability vary significantly with time. Furthermore, the environmental dimension of the water resources management should be taken into account in order to assess and avoid any unsustainable water supplies and allocations.

The problem of the optimal water system planning is created mainly in cases where water is supplied from various different sources and is distributed to various users with possibly conflicting requirements. The unit cost of water is different for each supply method, and its value varies for each specific allocation.

The present paper deals with the development and the operation issues of a Decision Support System for the optimal allocation of water resources to various users with conflicting demands. More specifically, the developed system calculates and suggests the water quantities that should be allocated to the users, taking into account that not all the demands are satisfied; however, the existing resources are optimally allocated.

The system's core is an optimisation model that maximises the total value of the water use, assigning a time-varying priority to each user and taking into account the resources capacity, and the possibility (cost) of not satisfying the demand. Technical and environmental parameters are taken into account in the optimisation problem. Special emphasis is given to the implementation of the method in specific Aegean islands with water shortage.

Furthermore, the present work analyses the various technical and operating issues of the decision support system and investigates the circumstances under which such a system can be a valuable tool for the solution of water management problems in areas with water scarcity.

The paper refers to the research work that is carried out in the Optimisation of Production Systems Lab., with the collaboration of Soft Energy Applications Lab. in the Technological Educational Institute of Piraeus and is funded by the ARCHIMEDES II – Environment Programme of the EPEAEK funding scheme.



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## THE USE OF ANCILLARY METOCEAN DATA FOR THE OIL SPILL PROBABILITY ASSESSMENT IN SAR IMAGES

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Accidental pollution at sea can be reduced but never completely eliminated, on the other side, deliberate illegal discharges from ships can indeed be reduced by the strict enforcement of existing regulations and the control, monitoring and surveillance of maritime traffic. Anyhow, operational oil discharges is a common practice and represents the main source of marine pollution from ships. Because of this situation the demand for efficient detection and mapping of oil pollution in the sea is growing. One of the key instruments to monitor and detect oil spills at sea are Synthetic Aperture Radar (SAR) systems.

SAR systems are able to detect spills on the sea surface indirectly, because of the effect on the wind generated short gravity – capillary waves. The oil film damps these waves which are the primary backscatter agents of the radar signals. Unfortunately, oil slicks are not the only phenomena which can appear as a dark feature in a SAR image. The contrast between the spill and its surroundings depends on a number parameters like wind speed, wave height, and the amount and type of oil released. Under certain air/sea boundary layer conditions, other sea surface manifestations of natural origin may result to SAR expressions or false targets, similar to those due to an oil spill. They are usually referred to as look-alikes objects.

The largest challenge in detection of oil spills in SAR images remains in the accurate discrimination between oil spills and look-alikes. Dark patches in SAR images can result from different sources like reduced wind speed or from reduced wind stress due to colder sea surface temperatures and other features. The knowledge of environmental conditions like wind, currents, precipitation and other concomitant marine and atmospheric phenomena like internal waves, upwelling, grease ice, algae blooms etc. as well as contextual information about slick position relative to surrounding objects (ships, maritime routes, rigs, platforms, natural seeps) of the past and at the time of the SAR acquisition is in many cases essential for the definition of the reliability of oil spill detections. The compilation of probability maps of occurrence of look-alike oil phenomena which are derived from ancillary metocean data and contextual information is to be used in the process of categorising the oil spill detections in SAR images.

This paper describes a new approach in categorising the detected oil spills from the SAR image analysis in different levels of probability based on metocean and contextual background information.

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## THE ISHTAR SUITE: A DECISION SUPPORT TOOL FOR ENVIRONMENT AND HEALTH POLICIES

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The FP5 ISHTAR Project (Integrated Software for Health, Transport efficiency and Artistic heritage Recovery) has produced a prototype software suite that is an innovative decision support tool for advanced urban and regional planning that performs the analysis of the effects of short-term actions and long-term policies to improve the quality of the environment, citizens health, conservation of monuments. Air quality modelling is one fundamental pillar of the integrated software. The suite includes both existing and newly developed models, covering the areas of citizens behaviour, transport, vehicles safety and emissions of pollutants and noise, pollutants dispersion and noise propagation, exposure to pollutants, noise and accident, and related risk assessment, monuments degradation and a tool for the overall comparison of the alternative policy scenarios. These modules are integrated by a software Manager, a Suite Data Base, a commercial GIS and a user-friendly interface software. This system represents an attractive alternative to the usual separated analysis of the effects of different measures on the various elements of the urban environment. With such a tool the future planner will be able to analyse in an integrated and 'coherent' way the various aspects of 'global' urban policies, in particular those based on the improvement of air quality. The high spatial and temporal flexibility of the Suite maximizes the possibility of application from local short-term actions to widespread long-term policies. The ISHTAR Suite has been tested in the seven cities involved in the FP5 EESD ISHTAR Project: Athens, Bologna, Brussels, Graz, Grenoble, Paris and Rome. At present the tool is being optimised in view of its commercialisation. The suite can be regarded as an example of tool 'from sources to health effects' and be used for planning and assessing E&H policies.

Topics involved :

air pollution modelling, transport emissions, population exposure, health effects, noise, accidents

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## URBAN AND SUBURBAN GREEN IMPROVEMENT PLANNING IN THE CITY OF VERIA, GREECE

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Green areas, green area accessibility, green area availability ( $m^2$  of green areas/inhabitant), urban area renewal, protected area as percent of total urban coverage, consist indicators that fall under the physical environment category and are part of a larger group of indicators that have been organized by the United Nations (UNEP/GRID Arendal) in conjunction with the Cities Environment Reports on the Internet program, for monitoring sustainability of the urban environment.

The object of the present paper is the study of the level of the urban and suburban green in the Municipality of Veria as far as the forestry urban green in the greater area and a proposal for upgrade and improvement of green, so much in the city as much in the suburban areas and the forests that are included in the Development Plan. The aim is, by the proposals that are suggested, to reduce the environmental problems of Veria, the aesthetic upgrade of the urban areas, the reduction of the geographic and social inequalities with regard to the distribution of areas of green in the city and finally, the optimization of the green quality indicator ( $m^2/resident$ ).

For the achievement of these objectives, the environmental standards of planning are incorporated in the urban planning of the studying area. This planning leads to standards and conclusions which will help the institutions, but also the citizens to comprehend the importance – environmental, social but also economic – of the clear sites and the areas of green.

The basic requirement is the configuration of fundamental standards and parameters for the planning of a complete system of clear cities and areas of green and the specification of actions for the materialization of this system.

In achieving the study goal, primary (field data collection) and secondary (bibliographical reviews, office work) sources of information are being used. Quantitative measurements, analysis and evaluation of the above indicator are being finalized in a summary fashion.

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Aiming the upgrade of quality of life and the improvement of the ecological components of the quality both of the urban and suburban environment, via the improvement of microclimate and the restriction of pollution in the wider region, issues that are related to individual objectives are looked into, such as protection or even an increase of, possible existing public sites of areas of green, enhancement of their isomeric territorial and social distribution, their qualitative upgrade, guarantee of accessibility and interconnection between them.

Methodologically the project is formed into three axes: a) Land planning and urban dimension of planning of green area network, b) Techniques and requirements of the growth of urban and suburban green and also of the forestry urban green and c) Synthetic proposal.

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## AN APPROACH FOR THE ESTIMATION OF TRAFFIC NOISE COST IN THESSALONIKI

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The basic parameter of urban noise is traffic noise. Traffic noise is one of the most important impacts from transport and it affects people's health and also property values. The constant increase of passenger car ownership and trips daily made by these cars affect traffic noise levels in urban areas. It is well known that traffic noise imposes social costs and the economic valuation of these costs is needed, more than ever, in order to justify the noise reducing measures.

In the framework of this paper the economic valuation of traffic noise in different countries is examined and presented. Traffic noise valuation methods include, among others, stated preference and revealed preference methods. The stated preference method introduces a large degree of uncertainty and therefore other methods should also be used so to estimate the health effects of traffic noise.

Based on the above methods, an attempt is made in order to estimate the cost of traffic noise in the city of Thessaloniki by using the available data of the Organization for the Master Plan and Environmental Protection of Thessaloniki (OMPEPT).

The first systematic measurements of traffic noise in Thessaloniki have been carried out by OMPEPT during the period 1988-89. Since that period, OMPEPT continues to monitor traffic noise levels in the city.

The butterfly-shaped city area of Thessaloniki is densely built and most of the basic road network is characterised by heavy traffic volumes and the associated environmental impacts, one of which is traffic noise. Recent traffic noise data for part of the basic city road network are presented in this paper together with the associated cost produced.

Although the involvement of the public in the design process of traffic management schemes is not at desirable level in the country, quite often questionnaire based surveys were carried out in order to identify the opinion of the people about the priorities need to be set in the framework of an integrated traffic management scheme. From the results of such surveys in Thessaloniki arises that environment plays an important role in people's priorities. Therefore, the need for appropriate measures for the confrontation of these problems is inevitable. It is believed that knowledge of the cost associated with these problems will assist the efforts of the authorities towards the decisions needed and the allocated budget.

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## CRITICAL REVIEW OF THE STATE OF THE ART ON CHEMICAL MIXTURE HEALTH RISK ASSESSMENT

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Most toxicological studies to date are performed on single chemicals even though human exposure is rarely limited to individual compounds. Most examples of environmental pollution involve concurrent or sequential exposures to a mixture of chemicals that may induce similar or dissimilar effects. In addition, people voluntarily expose themselves to a variety of chemicals such in food, drugs, alcohol and tobacco and are involuntarily exposed to other compounds from vehicle exhausts, in the workplace, or at home. In some cases, the mixtures are highly complex, consisting of a lot of chemicals that are generated simultaneously as by-products from a single source or process (e.g. coke oven emissions and diesel exhausts), in other instances complex mixtures of related compounds are produced as commercial products (e.g. PCBs, gasoline and pesticide formulations) and then released into the environment. Another category of chemical mixtures includes often unrelated chemically or commercially compounds that are placed in the same area for disposal or storage.

The current knowledge on the interaction mechanisms among chemicals is rather limited and there are several examples in which previous exposure to a compound increases greatly the toxicity of another chemical. Changes in the toxicokinetics and toxicodynamics of a substance induced by another chemical can modify the effective toxicity of the mixture. This work aimed at reviewing the current theoretical and practical approaches to the mixtures toxicity, through an in-depth analysis of regulatory guidance documents (EPA, ATSDR etc.) and of the key scientific literature concerning the mixtures risk assessment, and at discussing the most important limits and the major roadblocks of the current mixtures risk assessment methodologies. The review showed that only limited toxicological data exist for most chemical mixtures, that the majority of the available data take into account only the binary interactions between chemicals, and that only a few studies exist on chronic exposure to low doses of most mixture components. Most available experiments have tested only high doses of a few constituents, while most real world human and environmental exposures are pertaining to low doses and to a complex range of chemicals. Hence, uncertainties occur when extrapolating from high concentrations to lower environmental concentrations.

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In order to improve the state of the art in mixtures risk assessment methodologies it is important to address the following key issues:

development of a widely accepted classification scheme for either modes/mechanisms of toxic action or mechanisms of toxicity interactions need for more thorough studies on the action mechanism of the mixtures components using new approaches and techniques, including proteomics and genomics, along with computer modelling and application of biology-based modelling the issue of dose – dependence of both the mode/mechanism of toxic action and the mode/mechanism of toxicity interactions the problem of external versus internal dose metrics the influence of temporal dose factors.

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## HAZARDS AND CONTINGENCY PLANNING FOR OIL SPILLS IN THE ADRIATIC (ADRIATIC PIPELINE SYSTEM-JANAF)

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Getting oil from the well to the refinery and from there to the service station requires a complex transportation and storage system. Millions of barrels of oil are transported every day in tankers, pipelines and trucks. More oil is released into seas by illegal discharges than by shipping accidents. Oil spills from shipping – illegal discharges or from accidents - are an important source of pollution in sea areas.

JANAF system was constructed as an international oil transport system from the Port and Terminal of Omisalj to local and foreign refineries in Eastern and Central Europe. The design capacity of the pipeline is 34 million tonnes per year, and the installed capacity is 20 million tonnes. Located on the northern side of the island of Krk, the Port of Omisalj is an ideal port for oil receipt and discharge. The Terminal has tanks to store crude oil at the 12 tanks with total volume 760 000 m<sup>3</sup>. In the case of an oil spill, Omisalj Bay is protected by floating boom and bubble barrier prevents the spilled oil from spreading out of the bay. JANAF Project is planned for the export of crude oil from the Russian Federation through the Omisalj Port, with quantities of 15 million tonnes per year. The recently adopted European Water Framework Directive provides a strong instrument for the control of pollutants and monitoring in the catchments and coastal areas and improvement of water quality for all EU States and incoming accession States. A recent example of a non-binding agreement at the global level is collaboration between governments, organizations and institutions concerned with marine and coastal areas at all levels-national, regional and global. Although still in its early stages, the interest and commitment shown by governments in Europe are encouraging.



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## HUMAN EXPOSURE TO ENDOCRINE DISRUPTERS

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Two decades ago, reports of alterations in the reproductive function of some wild animal species and the demonstration of human and animal exposure to chemical substances with hormonal activity—agonist and antagonist—generated what is now known as the hypothesis of endocrine disruption. This is an emerging environmental health problem that has challenged some of the paradigms on which the control and regulation of the use of chemical compounds is based. The need to include in routine toxicology tests new research objectives that specifically refer to the development and growth of species and to the homeostasis and functionality of hormonal systems, has served to complicate the evaluation of new compounds and the re-evaluation of existing ones. The repercussions on regulation and international trade have not taken long to be felt. On both sides of the Atlantic, screening systems for endocrine disrupters (EDs) have been designed and established, and research programmes have been launched to characterise and quantify adverse effects on human and animal health and to develop preventive measures.

Although frequent exposure to some EDs has been documented in humans, evidence of human vulnerability to EDs is weak. Our understanding of the risks that EDs pose to human health is limited by our inadequate knowledge of the effects of chronic exposure to low levels and mixtures of chemicals, and of the relationship between early-life exposure and its impact on adult life. Concerns about this relationship have been heightened by indications from laboratory animal studies that early life stages may be especially sensitive to the effects of EDs and by observations of non-monotonic dose–response curves. There may be a long latency period between exposure and observed response. Thus, in utero exposure may have developmental effects that become manifest only when the offspring reaches sexual maturity. Human maternal–infant exposure during pregnancy is of special importance as a likely window of high susceptibility associated with severe and irreversible effects during critical developmental periods.

Ongoing European research focuses on building up databases on reproductive effects in males and exploring the mechanistic basis of male disorders, with a view to developing improved biomarkers and screening tools. Human epidemiological studies have only recently been conducted with sufficient rigour to adequately address cause-and-effect relationships between exposure to EDs and disease—that is, by using well-designed biomarkers of the combined effect of oestrogenic chemicals.

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## PERINATAL HEALTH RISK ASSESSMENT USING PHYSIOLOGY-BASED MODELS: THE CASE OF DIOXINS

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Pharmacokinetics of toxic chemicals during pregnancy is particularly difficult to study, for obvious reasons of risks to the fetus. A solution to this problem is to use a physiology-based pharmacokinetic (PBPK) model. PBPK models propose a realistic even if simplified description of the mechanisms of absorption, distribution, metabolism and elimination (ADME) of chemicals in the body. In these models, the body is subdivided into various compartments representing specific organs or homogeneous groups of tissues linked and irrigated by blood vessels. Compartments are characterized by a set of parameters of physiological relevance (e.g., volume or blood perfusion rate) which play a crucial role in explaining the behavior of chemical substances in the body, and represent invariants across substances.

To understand the role of chemical characteristics on the ADME behavior in the pregnant women and her fetus we propose herein an age-dependent mother-fetus model. Indeed, on a lifetime scale parameter values may change, due to growth or senescence of organs and tissues. However, a human lifespan is a long period compared to the typical residence time of chemicals in the body, and parameters are therefore usually assumed to be constant. Notable exceptions arise for persisting substances, such as 2,3,7,8-tetrachlorodibenzodioxin or lead, for which the elimination half-life may span years or decades. Another exception is pregnancy and gestation, during which the pace of organogenesis and remodeling can be measured in days and becomes commensurable with the scale of persistence of many chemicals in the body. It is, however, possible to mathematically describe the evolution of physiological parameters with gestational time.

The model presented in this paper subdivides the maternal body into 22 compartments. During pregnancy another 20 compartments describe the placenta, amniotic fluid and the fetal tissues and organs. Compartments have been included because they are sites of action for toxicity or because they have a major role in distribution, elimination of metabolism of substances. One of the compartments, labeled "other tissues" regroups all non-perfuse tissues (such as bone or teeth). This compartment plays a role only for the computation of total mass. The time-dependent model allows the consideration of different perinatal exposure scenarios, facilitating thus

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the better representation of real-life accidents. This enhances the mechanistic understanding of the clinically observed health effects of persistent and biocumulative substances. Time-dependent transfer functions are derived, enabling the use of surrogate dose metrics (e.g. concentration of dioxin in maternal blood) as biomarkers of internal exposure at sensitive target tissues (e.g. at the fetus brain). The above support the articulation of mechanistic hypotheses on the most plausible mode of action and the respective health risk to the fetus or the newborn for different perinatal exposure conditions. Coupling this modeling tool with epidemiological data in existing cohorts will improve our capacity to understand the toxicity mechanism and, thus, predict the health risks of biocumulative chemicals.

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## **DEVELOPMENTAL EXPOSURE TO ORGANOPHOSPHOROUS PESTICIDES AS A RISK FACTOR FOR NEUROBEHAVIOURAL DISORDERS IN CHILDREN**

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Prolonged exposure to environmental contaminants at apparently non-toxic doses might represent a major risk factor for children's health. Recent epidemiological data collected in US and European countries show increased prevalence of neurodevelopmental disorders such as learning disabilities, attention deficit disorder and autism. A role of environmental chemicals in the aetiology of these disorder has been hypothesized.

In this respect, chlorpyrifos (CPF), one of the most widely used organophosphorous pesticide, represents a paradigmatic example, as it elicits developmental neurotoxicity at exposure levels below the threshold for systemic toxicity, exerting subtle but disruptive effects on neural cell development, and possibly targeting the neuroendocrine axis. Recent human data reported delay in the maturation of sensorimotor reflexes and increased occurrence of attention problems, attention-deficit/hyperactivity disorder problems and pervasive developmental disorders at 3 years of age in children exposed prenatally to CPF (Rauh et al., *Pediatrics*, 118, 2006). In the past years we have studied extensively the neurobehavioural effects of developmental exposure to CPF in the mouse, focusing on end points related to social competencies in adolescence and adulthood. Early (postnatal days 1-4) or late (days 11-14) neonatal exposure to sub-toxic CPF doses enhanced reactivity to novel environmental cues and had pro-aggressive effects in adolescent male mice in a social interaction test (Ricceri et al., *Toxicology and Applied Pharmacology*, 191, 2003).

A subsequent study was designed as to compare the effects of either prenatal (pregnancy days 15-18), postnatal or prenatal+postnatal CPF exposure, in the attempt to model the human exposure scenario (Ricceri et al., *Toxicological Sciences*, 93, 2006). In adult male mice, gestational and postnatal CPF exposure affected motor activity and enhanced agonistic behaviour. In adult females, prenatal CPF increased social responsiveness, while postnatal CPF enhanced maternal responding towards foster pups. Mice of both sexes showed reduced anxiety levels in the elevated plus-maze after postnatal CPF. Finally, we found that neonatal exposure to CPF altered maternal behaviour profile and reduced aggressive response towards a male intruder in female mice.

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Altogether, CPF at doses that do not cause brain acetylcholinesterase inhibition induces long-term alterations in social responses and in sex-specific behaviour patterns of the mouse species. The behavioural disturbances observed in rodents developmentally exposed to sub-toxic doses of CPF might have some in common with neurodevelopmental disorder affecting the social domain and the emotional/affective responses to environmental challenges. Furthermore, the behavioural end point mostly affected by developmental CPF exposure are sex dimorphic patterns whose performance depends on the maturation of brain functional pathways subjected to hormonal regulation. The results of in progress experiments investigating CPF effects on thyroid hormones and oxytocin brain levels will be also presented, in support of the potential endocrine-disrupting activity of organophosphorous pesticides.

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## DETERMINATION OF THE EPIDEMIOLOGICAL ASPECTS OF AIR POLLUTION BY USING GIS IN ISTANBUL

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Air pollution is one of the most important and widespread environmental problems occurring at urban areas. Since it generally affects the people equally and frequently, it is a common environmental health problem. Effects of the air pollution over humans depend on geographical characteristics of the urban, type of fuels used, density of the traffic and land use characteristics. Besides, these effects cause different results, as acute respiratory diseases, reversible decreases on respiratory functions of the children, increase on cardiovascular diseases and mortality, over various groups of people such as the children, the aged, the people suffering from heart and lung diseases, and etc. It is proved by the epidemiological studies that the air pollution at low levels or under the accepted values causes increases on morbidity and mortality. Therefore, air pollution should be considered as a factor affecting the life quality and life span negatively and further epidemiological studies should be done on this subject.

GIS provides not only a medium for combining spatial data but it is also a powerful technology for the quantitative analysis of spatial data. Additionally, presentation tools add another dimension to this technology for being so popular. Assessment of the epidemiological data by using GIS is one of the application areas of this technology. Its capabilities on manipulation and analysis of spatial information make GIS an indispensable technique for these kind of studies. Additionally, GIS provides a better understanding on epidemiological problems by presenting statistical data in a spatially referenced way by using maps.

The aim of this study is to evaluate the Istanbul in terms of air pollution. For this purpose, Sodium Dioxide (SO<sub>2</sub>) and Total Suspended Particles (TSP) values were measured at 17 different regions of Istanbul for five years period from 1994 to 1998 when the air pollution measurement results started to improve from the lowest levels. Six of these regions are selected from Asian part while

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11 of them are from European part of the Istanbul based on geographical distribution of these regions and land use characteristics. Collected data were organized and various statistical results just as standard deviation, mean, median, minimum and maximum values were obtained seasonally, annually as well as the generally. Additionally, one way analysis of variance was executed to SO<sub>2</sub> and TSP values to determine annual change of air pollution. Finally, these data stored in a relational data base and it is geographically referenced in a GIS environment by providing relations between statistical and geometric data. Geo-spatial analyses were executed to introduce the regions under risk and thematic maps were produced to present the results of the study to the user according to epidemiological criteria. Use of GIS on epidemiological studies is recent development in Turkey. Turkish epidemiologists generally study by conventional methods. Therefore this study is an original example since it gathers epidemiologists and GIS specialists in a interdisciplinary work.

**Keywords:** Epidemiology, air pollution, environmental health, GIS, thematic maps.

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## RECENT CHANGES OF CHILDREN'S MORBIDITY IN ONE INDUSTRIAL REGION

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The aim of the work was to analyze children's morbidity in Kolpino (an industrial region of St.-Petersburg). We compared the morbidity in 2000-2004 and in 1990-1994 (morbidity during that period was studied by the authors). Children's morbidity was studied with the use of rank and cluster analysis; correlation of environmental factors and children's morbidity was also evaluated.

We found out the tendency of some non-infection diseases to growth in 1994, but on the whole, the level of morbidity in Kolpino was lower than in St.-Petersburg. Later, total morbidity in Kolpino continued to grow and in 2004 it exceeded the level of morbidity in St.-Petersburg regarding many diseases (the level of children's morbidity in St.-Petersburg in its turn was 29% higher than in Russia). The amount of diseases of blood and haemopoietic organs in Kolpino from 1994 till 2004 increased in 3.5 times and significantly exceeded the morbidity in St.-Petersburg (16.5 and 8.54 to 1000 persons). The amount of anemia (14.52 and 7.68 respectively) and diseases of nervous system (114.464 and 57.219 respectively) approximately redoubled during that period. The number of diseases of the organs of digestive and urogenital systems was also extended in same proportions.

Important tendency was the essential increasing of the number of oncology diseases in Kolpino (11.05 among 1000 persons in 2004). It also exceeded the morbidity in St.-Petersburg (5.45 among 1000 persons). Diseases of organs of respiratory system constituted the main part of children's morbidity (1227.92 per 1000 children); it was lower than in 1990-1994, but higher than in St.-Petersburg.

The investigation confirmed the presence of correlation between morbidity and ecological factors. Thirty percent of water samples in St.-Petersburg were not satisfactory because of the large amount of chemical elements and bacteria. The water contaminations by heavy metals (Mn, Al, Hg, Pb, Cd), phenols, oil and hydrocarbons were mostly significant. Maximal admissible contents were equal to 0.001 mg for Mn and 0.0006 mg for phenol per cubic meter of air and 0.06 mg Al and 0.164 mg Fe per cubic decimeter of water.



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## THE IMPACT OF CHEMICALS ON CHILDREN WITH FOCUS ON ENDOCRINE DISRUPTORS AND CARCINOGENS

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It is widely recognized that action is needed to protect children against potential toxic agents and allow them to grow, develop, and reach maturity without incurring neurobehavioral impairment, immune dysfunction, reproductive damage, or increased risks of cancer as a consequence of environmental exposures in early life. Children, from the prenatal period through adolescence often react differently to chemicals than do their adult counterparts because, they have different and enhanced exposures and behavior patterns, metabolism, physiology and special vulnerabilities determined also by critical time windows of development. Of particular concern are the potential effects of carcinogens, endocrine disrupters (EDCs) and cell signaling chemicals when exposure occurs during those "critical windows of development". Does present Risk Assessment consider children's special sensitivity, enhanced exposures and windows of vulnerability adequately? Information about the mechanism of action of EDCs, together with information concerning mechanisms of hormone action, predict that current risk assessment assumptions may lead to a dramatic underestimation of responses associated with exposure to low doses of EDCs. This in particular relates to exposures, during development when the effects of very small changes in hormonal activity are permanent. Our understanding of the nature and the amount of health effects produced on developing organisms, from the prenatal period to adolescence, by exposure to environmental agents is still incomplete. However, the evidence we already have of the role played by several environmental factors in determining disease and injury in children, and in inducing effects that may become manifest only in adult life, makes it necessary to act now in order to protect children's health, today and for the future. Thus in relation to children in particular, the Risk Assessment has to be further developed into a more integrated concept, an Inclusive Risk Governance, encompassing the application of PP to cope with uncertain but unacceptable risks. In the presentation an overview on children's vulnerability, exposure and related enhanced risks will be presented and the state of the art on the risk assessment of Endocrine Disruptors will be discussed.

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**PRACTICAL TOOLS TO CREATE CAPACITY ON CHILDREN'S ENVIRONMENTAL HEALTH "EXPERIENCES BUILDING PROFESSIONAL PEDIATRIC ENVIRONMENT AND HEALTH CAPACITY: LESSONS FROM LATIN AMERICA"**

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International Network on Children's Health Environment and Safety, INCHEs

The strategy of ISDE/INCHEs in Latin America for Children's Environment and Health (CEH) is to work with Pediatricians as our main partners in order to gain the attention of doctors, the community and government. Due to the lack of professional educational programs, resources, information, and materials on CEH in the Spanish language, and due to a low interest in the region on environmental problems impacting health, ISDE/INCHEs implemented regional alliances with various Professional Societies of Pediatricians.

This strategy followed the goal of "Action in Partnership" to build inter-sectoral alliances that could be easily replicated. Our tools include: education, information, development and dissemination of materials in Spanish. Further, we participate in epidemiological environmental research projects and develop appropriate interventions for local communities.

We choose Health Care Providers, Pediatricians and others, as our primary partner because they naturally focus upon and are committed to Children's Health.

Pediatricians:

worry about children's health and know about children's special vulnerabilities; understand the effects of exposure to toxics during developmental stages; are a trusted reference point in society and have important influence for advocacy; are credible professionals to society and government; are adept at explaining complex matters in simple language; are in close contact with families and the community; are one of the main partners for action and change; are responsible to promote actions for better knowledge, understanding and protection of the environments where children are born, grow, play and learn.

In our first meeting on CEH, we brought together the Presidents of seven National Societies of Pediatrics, all of whom agreed and expressed their willingness collaboration under the Mar del Plata Declaration of the Presidents of the Pediatric Societies of the Southern Cone and Peru on Children's Environmental Health<sup>1</sup> (Mar del Plata, Argentina – October 1st, 2003) "Children are the future of our Nations and protecting their health is our commitment".

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The analysis of environmental risks and children's health in Argentina, Bolivia, Brazil, Chile, Paraguay, Peru and Uruguay has shown that we share environmental problems that threaten the current health and future of our children and communities. This led to these Pediatric Societies to work together in the following areas:

education and training of their members; research of the major problems; advocate Children's Environmental Health in governments, national and international organizations; work towards the permanent control of Children's Environmental Health's quality in each country; promote actions for better knowledge and protection of community environments where children are born, grow, play and learn.

The presentation will also show the outcomes of our strategy: our programs, meetings taking place in the region and our projects; particularly, the successful project "Measuring the Environmental Impact on Children's Health in the Southern Cone" in cooperation with The Canadian Institute of Child Health (CICH), the Argentine Ministry of Health and Environment, Health Canada, the University of Ottawa and the Argentine Society of Pediatrics (SAP). The Project has been developed with support from the Canadian government through the Canadian International Development Agency (CIDA-ACDI).

1 Mar del Plata Declaration of the Presidents of the Pediatric Societies of the Southern Cone and Peru on Children's Environmental ([www.aamma.org/english/index.html](http://www.aamma.org/english/index.html))

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## **COLLATING THE HEAVY METAL LEVELS WITH REGULAR CONTROLS IN CHILDREN'S BLOOD HAVING REPEATED WHEEZING DISEASE**

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Atmosphere is polluted because of the wastes formed during production and consumption activities at the result of various activities of people and this pollution affects alive life on earth in an extremely negative way. One of the main problems especially in the last century is the health problems and dangers caused by air pollution reaching to increasing concentrations. According to World Health Association (WHO), 800 thousand people die because for the respiratory tract diseases due to air pollution and heart and lung diseases. Children make up the largest risk group against health effects caused by air pollution and children are effected more by the negative effects of the air pollution more than matures do. The reason for that is that the 80% of the alveolus is formed as post-natal and development of the lungs continues until the age of 6-8. Metals making up a part of the air pollution spread in the environment when fossil fuels are burned, during industrial activities and metal-containing products are burned in insinuator. Lead, cadmium, nickel, mercury, arsenic metals and asbestos, which are some of the metals affecting human health negatively and are commonly existing in the atmosphere, carry huge importance.

Epidemiologic studies performed in recent years show that asthma and other atop diseases have been increasing, especially in well-developed countries, on whole earth. This increase in asthma is very dramatic and it is thought that there is a current asthma pandemic on earth. That is a diagnosis describing the grunt that is seen in patients with wheezing asthma disease and that is showing stifling in respiratory tracts. Wheezing is one of the most seen symptoms in children and the studies performed in recent years show that air polluters increase the diseases relating to asthma and wheezing.

In this research, the effects of nickel, lead, mercury, aluminum and arsenic levels, which can be taken into consideration with air pollution in wheezing occasions showing a serious increase in children, have been studied. For this reason, 100 patients going to a children allergy clinic with repeated wheezing complain has been included in this research as the study group whilst 100 healthy children are included in the study as the control group. Blood samples have been taken from both patient and control group and blood levels of nickel, lead, mercury, aluminum and arsenic have been measured (ICPMS). In this way, it is tried to detect if there is any difference between the levels of nickel, lead, mercury, aluminum and arsenic in the blood samples of healthy children and children with repeated wheezing diseases.

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## PARTICULATE MATTER PM<sub>10</sub> AND CHILDHOOD ASTHMA IN ATHENS, GREECE

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The particulate matter (microscopic solids or liquid droplets) that are less than 10 micrometers in diameter (PM<sub>10</sub>) can get deep into the lungs causing serious health problems. It is one of the new pollutants, which began to be measured recently in the European Union, and constitute an important problem for the majority of the countries, especially the southern ones of the European Union. The purpose of this study was to evaluate the impact of suspended aerosol particulates with respect to PM<sub>10</sub> on childhood asthma admissions (CAA) in the greater Athens area (GAA).

Daily counts of CAA (2274 males, 1328 females) of the three main Children's Hospitals in Athens, recorded by the hospital registries during a 4-year period (2001-2004), were obtained. All children admitted with the diagnosis of "asthma", "asthmatic bronchitis" or "wheezy bronchitis", aged 0-14 years, living in the metropolitan area of Athens were included. The concentrations of PM<sub>10</sub> concern daily values recorded by the air pollution-monitoring network of 7 stations of the Greek Ministry of the Environment, Physical Planning and Public Works (Directorate of Air and Noise pollution Control). The mean daily value of PM<sub>10</sub> was calculated within all the stations of the network, and this is the representative value for GAA.

The national threshold is 50 µg/m<sup>3</sup> averaged over 24 hours and for 35 days within the year. Moreover, the Environmental Protection Agency (EPA) uses its Air Quality Index (EPA 2006) to provide general information to the public about air quality and associated health effects. An Air Quality Index (AQI) of 100 for PM<sub>10</sub> corresponds to a PM<sub>10</sub> level of 150 µg/m<sup>3</sup> averaged over 24 hours, and people with respiratory disease, such as asthma, should limit outdoor exertion. The analyses used in order to find out the possible relationship between CAA and PM<sub>10</sub> concentrations were the Logistic Analysis and the Generalized Linear Models with Poisson distribution, because the medical dataset presents large divergence from a Gaussian distribution. The results did not show any statistically significant ( $p < 0.01$ ) relationship between mean daily

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PM10 concentrations averaged within all the stations and CAA on the same day. Nevertheless, there was a statistically significant lag effect of 5 days between the increase in CAA and the peak in the concentrations of  $10 \mu\text{gr}/\text{m}^3$ , was associated with an increase of 3% for CAA. Furthermore, the control of the appropriate thresholds for PM10 ( $150 \mu\text{g}/\text{m}^3$ ) did not reveal any statistically significant impact on CAA, probably because there were only three violations during the examined 4-year period. In conclusion our results indicate that a  $10 \mu\text{g}/\text{m}^3$  increase in PM10 (5-day lag) is associated with increase in hospitalizations for childhood asthma in Athens, Greece.

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## EFFECT OF THE ENVIRONMENTAL CIGARETTE SMOKE (ECM) ON SERUM VITAMIN (A, E, C) LEVELS OF BABIES

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Environmental Cigarette Smoke (ECS) is the mixture of the smokes coming out of the cigarette smoked and breathed out by the smoker. ECS causes the formation of passive smoking of the individuals that do not smoke but stay in an environment in which other individuals do smoke. There are more than 4000 chemical materials within ECS and it is known that at least 43 of these materials are causing to cancer. Even though the ECS is dangerous for everyone, its negative effects on fetus, babies and kids are much larger. Respiratory system diseases and prevalence of respiratory system are seen more often on the kids whom parents smoke than the kids who are not exposed to cigarette smoke. And again there, even though just a little, are measurable changes in lung functions. This incident is realized when ECS is damaging the developing organs such as lung and brain.

This study is planned to detect the effect of the toxic materials, passed by environmental cigarette smoke which means passive smoking, to the serum antioxidant levels in babies fed and not fed by breast-milk, and if the breast-milk is protective against the harmful effects of the cigarettes. For this reason, sectional studies have been performed on 254 babies born just 6-7 months ago. Stories of feeding the babies, exposing to cigarette smoke and infection have been asked to the mothers. Serum vitamin A, E, C and urine coti levels in the bloods taken from the babies were tested. Researchers later tried to interpret the obtained experimental data on statistical models.

At the results of the studies performed, it is seen that the smoker mothers likely started using infant foods instead of breast milking their babies whilst non-smoker mothers kept providing their babies with only breast milk. It is found out that the babies of smoker mothers, rather than non-smokers, had oddities media, upper respiratory tract infection (URTI) and lower respiratory tract infection. Serum vitamin A, E and C levels of the babies, whose mothers are smokers, are found at low level than of the ones whose mothers do not smoke. The more the number of the cigarettes smoked in the house increase, the more the levels of serum A, E and C of the babies are tended to decrease. Obtained experimental results show that the breast milk increases the serum levels of the babies exposed to the cigarette smoke and protects the babies against infections.

Keywords: Environmental cigarette smoke (ECS), passive smoking, vitamin A, E, C

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## **ANALYSIS OF TOXIC ELEMENTS IN CHILDCARE PRODUCTS BY ICP-BASED TECHNIQUES**

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Several additives (i.e. inorganic and organic salts from heavy metal elements) are added to plastic materials in order to modify their physical and chemical properties. Nonetheless, some of these reagents, even at low concentration, are extremely toxic for human health.

The European Standard EN 71/3 and the Directive 88/378/CEE limit the migration of some heavy metals (As, Ba, Cr, Cd, Hg, Pb, Sb and Se) and their daily bioavailability in plastics used in toy industry. Other Draft Standard Projects, also based in the later directive, limit the same parameters in plastics used for childcare articles. Previous interlaboratory studies have shown that the migration analyses of heavy metals using European Standard lack of accuracy and reproducibility. In addition, analyte concentration in these materials is too close to the detection limits of the analytical techniques recommended (i.e. Flame, Hydride Generation and Cold Vapour Atomic Absorption Spectrometry).

The aim of this work is to evaluate and improve current methodologies for the analysis of toxic elements in childcare products. For this purpose, a careful optimization of digestion and extraction methodologies in different polymers (polycarbonate, PET, ...) were performed. Heavy metal analysis were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) since both techniques afford good reproducibility and accuracy, selectivity, multielemental capabilities and low limits of detection. Different sample introduction systems (e.g. concentric pneumatic nebulizer coupled to a cyclonic spray chamber and ultrasonic nebulization) were evaluated for elemental analysis in plastic materials.



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## NEUROPSYCHOLOGICAL ASSESSMENT OF COGNITIVE DEVELOPMENT IN CHILDREN FROM ENVIRONMENTALLY POLLUTED REGION IN SLOVAKIA

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Organic pollutants, particularly Polychlorinated biphenyls (PCBs) are neurodevelopmental toxicants and associations with neurobehavioral changes are found in some but not all epidemiological studies. Results suggests that the prenatal and perinatal development is the most sensitive for exposure to low doses of pollutants and is able to manifest as behavioral and learning disturbance of maturation.

The aim of study was to assess relations between PCB serum concentrations and other relevant factors of neuropsychological development in babies aged 16 months in region environmentally polluted by PCBs.

Methods: The examinations of babies (N=809) included: Bayley Developmental Scale (Mental, Motor), Home questionnaire (emotional and social background of development), PCB sampling and Pediatric examination and Pediatric report.

Results: The study was longitudinal continuation of project which included examinations of mothers at delivery and cord blood of the same babies (NIH project: I.Hertz-Picciotto, et al: PCBs and early childhood in Slovakia). The significant correlations were found between  $\Sigma$ PCBs serum concentrations (ng/g lipids) in 16 months of age (Mean:1024), at delivery (Mean: 953), and cord blood (Mean:732.2). Regression analysis included evaluation of independent variables: gender, maternal age at delivery, birth order of examined child, maternal BMI at delivery, smoking and alcohol drinking during the pregnancy, breast feeding, maternal education and intelligence score, and dependent variables: Bayley scores (Mental, Motor), Home score and health symptoms. Results showed tendency of associations between PCBs level (quartiles), and motor performances in babies, maternal intelligence scores and lower social background.

Conclusion: Preliminary evaluation of neuropsychological development in babies aged 16 months showed influence of environmental exposure to PCBs, with strong connection of social background of development.

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## MATHEMATICAL EVALUATION OF THE RISK OF DISEASES ARISING UNDER THE ENVIRONMENT CONTAMINATION

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The method of randomized integral indexes for multicriteria evaluation of diseases risk under the action of environment contamination is suggested in the form:

EMBED Equation.3

where EMBED Equation.3 – partial characteristics describing the ecological conditions, EMBED Equation.3 – randomized weighted coefficients indicating the significance of individual characteristics in summary risk evaluation.

The randomization of weighted coefficients is stipulated by the fact that investigator often has no possibility to ascribe distinct numerical values to the coefficients and has to be satisfied with its randomized character. We can get the probabilistic characteristics (mathematical expectation, dispersion et al.) for EMBED Equation.3 choosing the uniform distribution with maximal entropy as probabilistic distribution EMBED Equation.3 . We have to reduce entropy by introducing the limitations on the range of possible values of weight coefficients EMBED Equation.3 , if the exactness of the estimation is not enough.

The method was applied for risk estimation of diseases for one of industrial regions of St.-Petersburg. We constructed the summary index of the joint action of heavy metals complex using the data of contents of Zn in drink water, and Ni, Pb, Cd and Hg in air. The influence of heavy metals complex on children health was estimated by using the summary index of the complex of medical and ecological data (urine and blood analyses etc). As a result of calculations, the generalized estimations of the risk of health breakdown (the probability of diseases origin depending on heavy metals accumulation in children bodies) were obtained. Thus, the method made possible to ascribe to each child the concrete significance of probability of disease appearance under action of the heavy metals complex.

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## URBAN AIR POLLUTION, BY LICHENS BIOMONITORING, AND SCHOOL ABSENTEEISM, LUCCA, ITALY

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### Background

School absenteeism has been used in various studies as a proxy of health status among young children (Ransom and Pope, *Env Res*1992, Romieau et al *AJE*-1992 ), with the hypothesis that absences may reflect the health effects of short-term increases in levels of pollutants. Most (though not all) published studies appear to indicate that the ambient level of certain pollutants may have a small but discernible association with school absenteeism

A previous study on two years school absences conducted, in 1995-97, in a small Tuscany's village crossed by roads with intense trucks traffic, showed higher levels of absences among children in the school located in the most polluted area (Pieve S.Paolo). Starting from those results this study compares absenteeism, 1996-2003, with another school chosen in a less polluted same area (Marlia) adding more pollution measures.

### Materials

Students absences have been collected for the years 1996-2003 for each class of two elementary school. The local Agency for Environmental Protection has updated in 2004 the lichens biomonitoring ( previous was in 1997) and has conducted a three weeks monitoring campaign with a mobile station, near by the schools, registering the levels of PM<sub>10</sub>, NO<sub>2</sub>, CO, SO<sub>2</sub>. Moreover a study on chemical composition of suspended fine particles is on going.

### Results

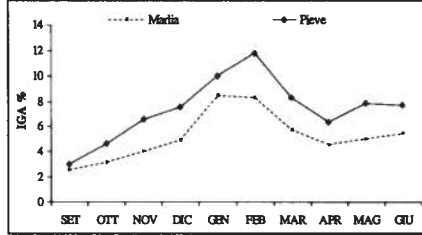
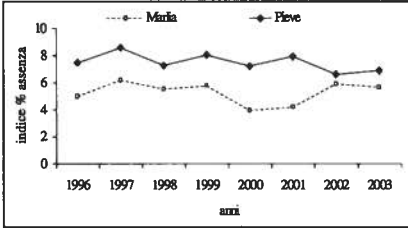
The school located in the more polluted area of Pieve S.Paolo, shows a higher levels of absenteeism than the one in Marlia along all the years and along all the winter months.

The socio-economic background of the two places is very similar, while the Pieve S.Paolo school is located quite near the high-way, the local paper-mills, and has worst micro-climate conditions. The new analyses on air pollution characteristic are on going and new lichen biomonitoring maps are on process.

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## Conclusions

School absences and lichens biomonitoring are two methods simple and cheap to implement for obtaining quite good indicators of air pollution and of health disorders among young children, which are a population group very sensible to environmental insult.



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## MEASURE OF THE EXPOSITION TO VOLATILE ORGANIC COMPOUNDS (VOC'S) AND NO<sub>2</sub> IN VALENCIA (SPAIN)

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According to the Environment and Health Action Plan which was launched by the European Commission in 2004 and the declaration of the Fourth Ministerial Conference on Environment and Health, which was held in June 2004 in Budapest, a network for childhood and environment (INMA) was developed in 2003 in Spain to establish the environmental effects on children's health. The main objective of this work was to assess outdoor, indoor and personal exposure to air pollutants (VOC's and NO<sub>2</sub>) in the Valencia area, in three sampling campaigns of two and seven days, distributed throughout 2004.

Measurements were performed using a radial diffusive sampler in ninety representative sites in the study area. For the personal exposure measurements, twenty volunteers were selected and the samplers were exposed for two days outside and inside their houses, and one of them was carried by each volunteer. Analysis of the diffusive samplers was done by thermal desorption and gas chromatography with FID for VOC's and spectrophotometry of UV-VIS for NO<sub>2</sub>.

Ambient mean concentration levels varied from 1,32 ug/m<sup>3</sup> to 4,52 ug/m<sup>3</sup> for benzene, 7,24 ug/m<sup>3</sup> to 26,37 ug/m<sup>3</sup> for toluene, 1,54 ug/m<sup>3</sup> to 6,89 ug/m<sup>3</sup> for ethylbenzene, 4,05 ug/m<sup>3</sup> to 37,1 ug/m<sup>3</sup> for the m+p xylenes, 1,11 ug/m<sup>3</sup> to 4,31 ug/m<sup>3</sup> for o-xylene and 23 ug/m<sup>3</sup> to 47 ug/m<sup>3</sup> for NO<sub>2</sub>. Indoor/outdoor ratios were higher than 1 for all compounds, in some cases reaching a value of 2 or 3, and the indoor/personal ratios were lower than 1. These ratios give an approximation of the indoor air pollution and the exposure of people living in these houses.

The results obtained show that pollution inside the houses is greater than that in the air outside the houses and greater than the air in the city. It has also been found that personal exposure levels are higher than those existing in the indoor air, suggesting the existence of other sources of emission of the study compounds, especially VOC's, like those related to lifestyle, such as tobacco smoke.

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## EXPOSURE OF CHILDREN TO PARTICULATE MATTER IN URBAN AREAS – MODEL CALCULATIONS

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The aim of this paper is to investigate children's exposure to particulate matter in urban environments using a novel tool for calculation of total human exposure, developed as part of the Urban Exposure project. The tool calculates the quantitative contribution to the personal exposure from various indoor and outdoor sources in various micro environments. Results from Oslo are presented as an example of child exposure estimates in urban areas.

The effect of air pollution exposure differs between children and grown-ups due to differences in physiological characteristics such as body weight and metabolism, as well as behavioural differences such as activity level and the amount of time spent in the various micro environments in the course of a day.

A numerical tool for calculations of personal exposure to particulate matter has been developed and integrated into an existing Air Quality Management System, AirQUIS. Based on defined daily routes, the hourly concentration of particulate matter is calculated for various micro environments. The outdoor concentrations are calculated using an Eulerian dispersion model. The indoor concentrations are calculated on the basis of both outdoor concentrations and contributions from selected indoor sources. Based on the concentrations, activity level, gender and age, the respiratory deposition for various particle sizes is calculated as hourly values. The accumulated dose for a given period can be calculated from the hourly values.

Calculations have been performed for Oslo, which is the largest city in Norway. The main emission sources for air pollution are traffic and resuspension of particulate matter as well as wood burning for domestic heating.

Typical scenarios describing children's daily routes in terms of location of home and kindergartens or schools, the manner in which the children travel to and from their home and time spent indoors and outdoors, respectively, have been defined. The activity level, which is generally higher for children than for grown-ups, is also taken into account. For a typical winter and summer case, the corresponding indoor and outdoor concentration levels and resulting respiratory depositions have been calculated. In addition, the results are compared to those obtained for grown-ups.

The results show that the home environment makes a substantial contribution to the accumulated dose, mostly because a significant part of a day is spent there. In addition, choices of travel route and activity level are of importance. Finally, some indoor sources can enhance the indoor concentrations and thus the exposure significantly.

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## PREDICTION OF POLYCYCLIC AROMATIC COMPOUNDS' MUTAGENICITY AND GENOTOXICITY BY QSAR CLASSIFICATION MODELS

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Polycyclic aromatic hydrocarbons (PAHs), absorbed mainly on urban aerosol, are ubiquitous pollutants of high environmental concern. The experimental data of a mutagenicity test on human B-lymphoblastoid cells (alternative to the Ames bacterial test) for a set of 70 oxo-, nitro- and unsubstituted PAHs, detected in particulate matter (PM), were modeled by Quantitative Structure-Activity Relationships (QSAR) classification methods (k-NN, k-Nearest Neighbour, and CART, Classification and Regression Tree) based on different theoretical molecular descriptors selected by Genetic Algorithms. The best models were validated for predictivity both externally and internally. For external validation, Self Organizing Maps (SOM) were applied to split the original data set. The best models, developed only on reduced training sets, show good predictive performance also on the prediction set chemicals (sensitivity: 76.9-92.3%, specificity: 55.6-87.5%). The classification of PAHs according to their mutagenicity, using only few theoretical molecular descriptors, allows a preliminary assessment of the human health risk, and the prioritization, of these compounds.

Analogously, the genotoxicity of 276 heterogeneous Polycyclic Aromatic Compounds (PACs) was modeled by QSAR classification methods. The studied response consisted of a priori defined classes of genotoxicity obtained on the basis of SOS Chromotest values. In order to propose only externally validated models, three different splitting approaches, D-optimal Experimental Design, SOM and Random Selection, were applied to the original data set for methodology comparison and selection of the best predictive model, independently of the splitting. QSAR models were developed applying CART and k-NN methods on a training set of 174 compounds. The best models, based on two 1D- and 2D-descriptors, have high sensitivity and specificity also for chemicals of an external prediction set of 102 chemicals, not participating to model development.

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## SPATIAL DISTRIBUTION OF PM1 AND HEALTH IMPACTS IN ATHENS, GREECE.

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The study of particulate matter PM1 in Athens' atmosphere and their impacts on health is the goal of this study. Seven thousands sporadic samples of PM1 were collected by two detectors (light scattering method), from nine vital points in high traffic peak roads, during the cold period of the year 2006 (October to March). The collected PM1 samples concern the same hours of the day, in absence of wind and minimal peaks of humidity as possible. As we know, systematic mapping studies of PM1 have never been carried out in our city. Using the Kriging method, we constructed relevant maps with respect to the seasonal spatial distribution of PM1.

In order to find out the impacts on health, we analyzed epidemiological data collected by the physicians, (Oculists, Cardiologists, and Internists) of the Social Security Institute and a Regional Hospital of Athens at the daily time external (normal and emergency) ambulatories. Results demonstrate a significant correlation of PM1, especially with arrhythmias, eyes irritation and general fatigue. It is already known that PM1 represent the main hazard in cardio respiratory syndromes in the most polluted cities of Europe, which confront high traffic problems, due to the enormous number of exhausts emissions the last trentenium.

Our multi-specialists team proceeds in continuous epidemiological investigation, concerning multiplied symptoms, as eye irritations and nasopharyngeal inflammations, upper respiratory infections associated with headache, dizziness and generalized symptoms as cataptosis and malessere of the organism. In conclusion we wonder whether the European Health organizations should set new safety standards and restrictions for the PM1, as they have already done for other PM for the correct promotion rule of public health in European continent.



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## MUTAGENETIC EFFECTS ON MICE EXPOSED TO RADON-222 EMISSIONS IN LAZIO (ITALY)

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Comprehensive studies on Radon as a mutagenic and carcinogenic agent have been performed in buildings, caves and underground mines in cases of increased concentration.

The aim of this work is to investigate the mutagenetic effects of the exposure to Radon-222 and its progeny in laboratory mice, and to analyze the possible correlation between data obtained from radiometric measurements of Radon and induced genetic damage. In order to realize this objective, a study was carried out in parallel in two small towns, where Radon pollution is notoriously present.

Six week old CD1 females mice (N=50), were used as bioindicators. Four groups of animals, placed in cages, were located in a basement flat (Ciampino-Rome) and three groups in a cellar (Vetralla-Viterbo) and exposed for 30 days to Radon emissions. Radon-222 activity measures were carried out both on a continuous basis using AWARE Corporation (U.S.A.) electronic detectors and every 10 days using CR-39 closed detectors (U-series Srl., Italy) sensitive from 10 to 14000 Bq/m<sup>3</sup>. In order to evaluate the effective dose, the potential alpha energy concentration (PAEC) has been continuously measured with Analogous Progeny Sensor (Sarad GmbH, Germany)

The micronucleus test, a sensitive mutagenicity test in vivo widely used to detect cytogenetic damage induced by chemical and physical mutagens, was applied to the peripheral blood of mice before the exposure, and 10, 20, and 30 days after. Micronucleated erythrocyte (MNE) frequencies were determined counting 2000 erythrocytes per animal. Smears carried out before the exposure were used as controls.

Results showed that in mice groups exposed to Radon-222 (2200-5300 Bq/m<sup>3</sup>), the micronucleated erythrocyte frequency (MNE/1000E) was significantly higher than that observed before exposure. In particular, a significant increase of MN frequency was observed in mice exposed for both 20 and 30 days in comparison with controls ( $p=0,0075$  and  $p=0,019107$ , respectively). A significant correlation between increase of MNE/1000E and increase of Radon concentration, was observed. Therefore, the levels of MN in peripheral blood of mice might be due to the chronic Radon exposure. These preliminary results suggest an investigation of the mutagenic properties (aneugenic and/or clastogenic) of Radon and its progeny in order to establish a possible relationship between these and carcinogenesis.

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## **EFFECT OF COASTAL TOURISM ON ENVIRONMENT, SEAWATER QUALITY AND PUBLIC HEALTH**

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All the countries are supporting tourism activities to meet their expectations by increasing the number of tourists visiting their countries. Most of the tourists in the world prefer coastal areas to spend their vacations. Sea, sun and sand are the most important characteristics of the coastal tourism. Increase in the number of tourists have both negative and positive impacts on the environment. If the coastal area is opened to tourism without the necessary infrastructure was established and the carrying capacity of the area was considered some of the impacts may be unrecoverable.

The increase in population during peak season results to an increase in the amount of wastewater generated. Most of the time these wastes are discharged into marine environment without being treated. They cause deterioration of the seawater quality which has negative impacts on the public health.

In order to determine the relation between coastal tourism, seawater quality and the public health, a survey was conducted at the most popular beaches of Turkey. A questionnaire about the health problems which local and foreign tourists suffer as well as their demographic information, swimming habits, etc. were prepared in different languages and distributed to randomly selected Test Groups and Control Groups of different sex and ages. In parallel to the survey with questionnaire, seawater quality at the beaches where people swam was determined. The results of the research proved that there is a direct relation between the sea pollution and public health. Those swam at the polluted waters had more health problems than the ones swam in the clean beaches. Also foreign tourists, children and elderly people were more affected by the polluted seawater than the others.

The results of the research will be presented in detail in graphics and tables in the final manuscript.

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**RECOMMENDATIONS OF IFCS:  
“PROTECTING CHILDREN FROM HARMFUL CHEMICAL EXPOSURE”**

Ing. Verónica Monti, Dr. Lilian Corra

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“In 2000, more than 4.7 million children under the age of five died from illnesses aggravated by unhealthy environments. Most of the 13,000 child deaths each day due to the dangers present in the environments in which they live, learn, play and grow. Contamination by persistent organic pollutants and chemicals that disrupt endocrine functions may adversely affect the health and development of children who are most vulnerable to emerging environmental threats. These threats may cause up to one third of the global burden of disease. Over 40% of this burden falls on children under the age of five who make up only about 10% of the world's population” (World Health Organization, WHO, 2002).

In relation to this, the Intergovernmental Forum on Chemical Safety (IFCS), a broad-based alliance of all stakeholders concerned with environmentally sound management of chemicals, started to operate on the basis of full and open participation, offering representatives the opportunity to meet and build partnerships, provide advice and guidance, make recommendations and monitor progress. Significant recommendations were agreed by representatives of over 125 governments and other stakeholders on actions that can be undertaken by governments, organizations and communities. The recommendations recognize the important and valuable role organizations such as the Asociación Argentina de Médicos por el Medio Ambiente (AAMMA) together with the International Society of Doctors for the Environment (ISDE) have in promoting protective measures to protect children from harmful exposures to chemicals.

Children and Chemical Safety was a special focus of discussion at the Fourth Session of the IFCS (Forum IV) held in Bangkok, Thailand 1-7 November 2003. The Forum IV recommended actions to protect children. Specifically, the recommendations state: “...Government, with support from all stakeholders,... should promote education and training on children's chemical safety...” Governments and stakeholders should commit to sharing information on options for taking effective action to protect children from established chemical threats and from chemical risks where there is a degree of uncertainty...”. Under these statements, the IFCS Recommendations promote actions providing background information and scientific rationale

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from the Decision and the Informative Paper “Protecting Children from Harmful Chemical Exposures (Chemical Safety and Children’s Health)” presented at the Forum.

The most effective means of protecting children from chemical risks is by preventing hazardous exposures. This can best be achieved by identifying risks and implementing preventive measures that will reduce unsafe exposure, minimize risks, and promote transparent science-based assessment procedures, clearly expressed on the IFCS Recommendations.

Governments from around the world have agreed that addressing chemical threats to children’s health should be an integral component of every country’s public health and environmental agenda. Individuals, organizations, and agencies responsible for protecting children need to become more aware of the threats and take actions to prevent them. The achievement of the Millennium Development Goals (MDGs)<sup>1</sup>, especially those that aim at reducing child mortality (MDG 4) and ensuring environmental sustainability (MDG 7) requires the safe and sound management of chemicals.

The publication “A global guide to resources” prepared by the Intergovernmental Forum on Chemical Safety (IFCS) Children and Chemical Safety Working Group is intended to:

- Alert a variety of potential stakeholders to the problem of hazardous chemicals in the global environment and the reasons that children are particularly vulnerable;
- Describe recent international recommendations intended to guide efforts to protect children from harmful chemical exposures; and
- Suggest strategies and available resources that can help government officials and other stakeholders to prevent harm to children.

Fourth Session of the Intergovernmental Forum of Chemical Safety, IFCS FIV – December 1st to 7th 2003, ([www.ifcs.ch](http://www.ifcs.ch))

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**CHILD AND TEENAGER LABOR:  
EXPOSURE TO PESTICIDES AT RURAL FAMILY WORK**

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This work is produced based on the Report of "Workshops of Experts on Impacts on Health and Possible Preventive Actions in Rural Child Labor" organized by AAMMA, 2003-2004.

Reviewed by the "Working-Group on Mobilization and Detection of Pesticides", under coordination of Dr. Argelia Lenardon, Litoral National University

Co-author: Ing. Diana Carrero, Expert on Hygiene and Agrarian Security, Professor of the Technological National University.-AAMMA Consultant.

The situation of many children involved in "rural family work" needs to be specially addressed as it creates the opportunity of exposure of children and adolescents to pesticides.

It is an undeniable reality the participation of children in rural labor and certainly it's impossible not to relate these tasks with pesticides exposure.

When we talk about child labor eradication, it is obvious that in our daily life there are limitations to take it forward in the rural area, almost in short term. Reality indicates that while searching child labor eradication, tough urgent situations that expose children to danger are denied.

This presentation will give a view on the real current situation valued by experts of different professional areas on lessons learned within child labor and the exposure to pesticides at rural family work in Argentina

Based on 182 ILO Convention (Eradication of the Worst Forms of Child Labor), that includes toxic exposure (also pesticides) in child labor, the recommendation for these tasks is "ZERO Tolerance" for children and teenagers (0-18 years old). The incorporation of teenagers to rural work may start at the age of 14 (or 15 depending on the country, in Argentina under Law 20.744: "Work Contract Law"). Is important to consider that in Argentina, under the Agrarian Work Law (Law 22.248) also children and adolescent may collaborate in family rural work (this situation exist also in many other countries of develop and developing world). If the child is a member of a rural family, legal owner of the land, all the family including children may participate at the exploitation with the condition that children assists to school. This legal situa-

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tion creates a framework of high danger that increases enormously the possibilities of exposure to pesticides of children and adolescents.

Neither in rural school's curricula are included topics to educate and inform pupils, family and community adequately on preventive measures; media is not used as expected to spread information or recommendations on preventive measures to rural population. Radio is, for rural people, the most important and principal way of communication, information and education.

In relation to medical assistance and preventive actions: detection of situations of exposure, data assessment on acute and chronic poisoning and/or incorporation of information of the participation of children or teenagers in rural labor in contact with pesticides usually are not registered in the clinical history.

Regulation, education and dissemination of information on children and teenagers exposure to pesticides at family rural work for many people still is "a problem of conscience". Sometimes inaction in these areas is justified by pointing only to the display of eradication campaigns. But "total" eradication is difficult when applied to children that participates in family rural work and to teenagers older than fourteen or fifteen that are starts to be part of the working force.

If we look at the results of bibliography and publications searches on these topics we can find that recommendations, preventive actions and medical epidemiological studies or reports are limited or null. Do we suppose that these situations are not taking place? That the facts do not happen?

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## MODELLING THE TRANSFER OF METALS IN THE ATMOSPHERE AND IN AGROSYSTEMS FOR ASSESSING EXPOSURE OF HUMANS – APPLICATION TO INDUSTRIAL RELEASES IN A MEDITERRANEAN REGION

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Atmospheric inputs of heavy metals to agriculture systems can be a significant contributor to metal contamination in soil and plants. Because potential health effects of heavy metals on human health are well recognized and because the intake of contaminated foodstuffs (e.g. vegetables) can be the main exposure pathway for humans, a better understanding of the full-chain exposure system (point source(s)-atmosphere-soil-plant) is essential for future health risk assessments. However, the coupling of atmospheric dispersion models and food-chain multimedia models was scarcely conducted in the past and, often, only for point sources.

The originality of our study lies in coupling two sophisticated models that respectively simulate the transport of heavy metals in the atmosphere at the regional and/or European scale (POLAIR3D model) and the transfer of contaminants in the air-soil-plant system (OURSON model).

As a case study, a region situated in the South-East of France (around the Martigues city) was selected. It is characterized by strong industrialization, with industries potentially releasing cadmium and lead, but also by intensive agricultural activity.

Lead and cadmium concentrations were calculated in several environmental compartments involved in the human food chain (soil, leafy vegetables, fruit vegetables) and compared to critical concentration values (e.g. CODEX). An uncertainty analysis was also conducted to determine the probability to exceed critical values.

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**DISTRIBUTION ASPECTS OF TOXIC TRACE ELEMENTS  
S IN SOME OF NORTH AFRICA WILD MEDICINAL HERBS**

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A rather broad survey of some toxic trace elements was carried out in a number of wild medicinal herbs from LAMIACEAE family known to grow widely in North Africa open wilderness and widely consumed by locals as a remedy to cure many diseases.

Since these plants are prone to possible environmental pollution therefore representative samples of three selected herbs from the family were carefully collected from Libyan wilderness, stored then analyzed specifically for their toxic elements contents.

Among the studied elements Aluminium was found to be significantly and noticeably higher than any of the other toxic elements.

The concentration pattern of the determined elements were carefully studied regarding to the possible interaction of the different chemical elements in the herbs, giving special attention to the environmental aspects such as location, climatic conditions and the possibility of using some selected members of this family as biomonitors.



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## BIOLOGY-BASED DOSE-RESPONSE MODELS FOR HEALTH RISK ASSESSMENT OF CHEMICAL MIXTURES

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The current orientation in chemicals risk assessment is to tackle them as single substances affecting individual health endpoints while, in reality, human exposure occurs to mixtures of chemicals as they are present in the environment and consumer products. This can result in lower toxicity (antagonism) or greater toxicity (synergism) of mixtures than would be expected from the individual chemicals. The extent of the change in tissue dose depends on the concentrations of all components and the mechanism(s) of interaction. Physiologically based pharmacokinetic models (PBPK) are modeling tools which describe the mechanisms of absorption, distribution, metabolism and elimination of chemicals in the body resulting from acute and/or chronic exposure. The organism is represented as a network of tissue compartments (e.g., liver, fat, poorly and richly perfused tissues) interconnected by systemic circulation. Transfer of chemicals between compartments is described by a set of differential equations. Each compartment (tissue) is described by a mass balance differential equation, which reckons the time-dependent concentrations of the chemical and its metabolites.

In this work we present a quaternary chemical PBPK/PD model for benzene, toluene, ethylbenzene and xylenes developed as a combination of "single chemical" models in which four sets of identical equations are used, one for each chemical, along with an equation that specifically accounts for the interactions at the site of metabolism. Following this approach the resulting change in the metabolic rate of one chemical in the mixture can be expressed as a function of the following variables: its maximal velocity of metabolism, its Michaelis affinity constant, the venous blood concentrations of the chemical leaving the site of metabolism, the venous blood concentrations of the competing chemicals at the site of metabolism and the inhibition constant. The metabolic chain of benzene was modeled starting from previously developed PBPK/PD models for benzene metabolism in mice and its extrapolation to humans. This was necessary due to the carcinogenic potency of the benzene metabolites, which has been associated to increased risk of leukemia. We have further elaborated a pathology model for associating the probability of cancer risk to the total concentration of benzene metabolites in the urine across the dose-response space. Extensive validation of the PBPK/PD model against a series of human cohorts corroborated its usability.

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Our results show that combined exposure modifies risk estimates even at low (environmentally relevant) doses, when individuals are exposed to the mixture of VOCs after lifelong periods. Risk modification, however, is dose-dependent. More important change is found when the VOCs are inhaled at doses that characterize specific working environments (e.g. in refineries or in the paint industry). Even if all four chemicals are at concentrations that respect the limits set by occupational health protection regulations, the biologically effective dose of each chemical can be as high as twice the respective dose when it is inhaled individually. Estimation of cancer risk due to benzene requires a detailed calculation of the biologically effective concentrations of its metabolites at the bone marrow. These can be reduced if benzene metabolism is significantly inhibited by the presence of the other three components of the quaternary VOC mix, resulting in lower cancer risk.

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## CHARACTERISATION OF HUMAN EXPOSURE TO CHEMICALS RELEASED FROM CONSUMER PRODUCTS/ARTICLES

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The EIS-ChemRisks project (European Information System on "Risks from chemicals released from consumer products/articles") is carried out by the Joint Research Centre (JRC) on behalf of Directorate General for Health and Consumer Protection (DG SANCO) with the aim to develop methodology and tools for consumer exposure assessment to support the implementation of the General Product Safety Directive (GPSD, 2001/95/EC) and Registration, Evaluation and Authorization of Chemicals (REACH, 1907/2006/EC). A key deliverable of EIS-ChemRisks is the "EU Exposure Assessment Toolbox" (in the following named EU Toolbox), which provides exposure data, tools and scenarios to facilitate harmonised and up-to-date exposure assessments for consumer products.

Valuable exposure information has been compiled for the EU Toolbox in the frame of the ChemTest-Phase I-Project (2006-2007), whose objectives were the analysis and evaluation of data and methodologies to qualitatively and quantitatively characterise human exposure to chemicals released from the following types of consumer products and articles: apparel/clothing and home textiles, carpets, automotive textiles, toys and non-woven personal care products.

These goals were achieved by an extensive literature search, by a Europe-wide questionnaire survey, by developing evaluation criteria for data quality, and by conceptual contributions to the further development of the EU Toolbox, especially of two modules: ExpoData (a reference data base for chemical specific exposure data related to consumer products) and ChemTest database (a reference data base for exposure testing methods).

The identification of any major missing data and needs for the measurement of emissions or migration of chemicals from consumer products, and development of novel testing concepts were other important milestones in this project.

The realisation of these objectives was achieved in close cooperation with different stakeholders from industry and research institutions.

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## STUDY OF POLYCHLORINATED BIPHENYLS AS POTENTIAL MODIFIERS OF DEVELOPMENTAL NEUROTOXICITY OF METHYLMERCURY

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A number of clinical and experimental studies have demonstrated that the developing brain is highly susceptible to methylmercury (MeHg) toxicity even at low exposure levels that have no obvious consequences in adults. Typical features of MeHg toxicity to the immature organism include the delayed onset of symptoms, the persistency of central nervous system injury/dysfunction and variations in response caused by diet, nutrition, and by external modifiers such as co-exposure to other neurotoxic pollutants. All these factors are important in real world exposure and represent an area of concern as they can influence the effect threshold and, consequently, the margin of safety of MeHg-contaminated products.

Polychlorinated biphenyls (PCBs) are often detected as contaminants of fish and seafood in combination with MeHg. Certain PCBs have been shown to induce subtle nervous system changes in the developing organism suggesting that co-exposure to PCBs may have contributed to the neurotoxic outcomes seen in epidemiological studies of MeHg in fish-eating populations. Recently, we observed that both MeHg and PCB congeners such as 2,2',4,4',5',5'-hexachlorobiphenyl (PCB 153) can affect neurotransmission parameters in the developing rat brain following perinatal exposure. The changes induced by these agents involve neurochemical systems, in particular cholinergic, dopaminergic and glutamatergic systems that play a critical role in the regulation of brain development. Imbalance in cerebral neurotransmission has been shown to occur as a mechanism associated with the behavioural deficits observed in laboratory animals exposed in utero to low levels of MeHg or PCBs (Johansson et al., 2007; European Commission DevnerTox Project, final Report, 2007).

Our data showed that the neurodevelopmental effects of MeHg and PCB 153 given alone were not exacerbated by combined exposure. For example, the individual treatment with MeHg (1 mg/kg/day, GD7-PD7) or PCB 153 (20 mg/kg, GD10-GD16) caused changes in the density of muscarinic receptors in the cerebral cortex of weanling rats that were similar in extent to those seen after combined MeHg-PCB 153 exposure. In some instances, the effects induced by MeHg were even attenuated by PCB 153 co-exposure. These effects were confirmed at transcriptional level analysing by Total Genome micro-arrays the modulation of gene expression. At

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1, 21 and 36 days PD we did not find major commonalities in profiling the gene expression in the cerebellum following in uterus exposure to MeHg or PCB153 compared to co-exposure to MeHg plus PcB153. The concordance of in vivo observations and gene expression findings demonstrate the importance of integrating experimental data from laboratory animals and new molecular approaches in relation to the human risk assessment process for environmental pollutants.

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## METAL CONTENT IN FINO WINES FROM ANDALUCIA (SPAIN)

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Apart from the occupational exposure, drinks and food constitute the main exposition source of metals for the general population. Therefore, knowledge of the metal content in food and beverages may serve as an indicator of possible toxic exposure in general and high consumers.

The objective of this study was to investigate the content of several metals in different commercial fino wines, all of them from Andalusia region (south of Spain). Three kind of these wines were studied with DO trademark: Jerez-Xérès-Sherry & Manzanilla-Sanlúcar, Montilla-Moriles and Condado de Huelva, in order to characterise them and to evaluate human exposure through their consumption.

Twelve metals (Ca, Mg, Sr, Ba, K, Na, P, Fe, Al, Mn, Cu and Zn) were determined in 50 samples of fino wines by Inductively Coupled Plasma Optical Emission Spectrometry (IPC-OES). The procedure involved H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub> treatment and heating in an oven. As was quantified following the standard addition method to avoid undesirable matrix effects.

All samples accomplished the limit values established by the European legislation and an average intake of each element/person/week was evaluated from our results by considering the estimated wine consumption in Spain and the mean content of the corresponding element.

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## **δ-AMINOLEVULINIC ACID DEHYDRATASE IN BLOOD AS A BIOMARKER FOR LOW-LEVEL LEAD EXPOSURE**

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**Introduction.** Lead (Pb) poisoning at both low and high concentrations adversely affects haematopoietic, vascular, nervous, renal, and reproductive systems. Recent research has indicated that even blood Pb concentrations below 10 µg/dL (0.48 µmol/L) may be associated with negative health outcomes especially those in children.

Determination of lead in blood, serum/plasma, urine, hair, bone, teeth, nail, milk etc., is used in epidemiological studies. Therefore, not all mentioned indicators equally reflect exposure – dose and internal dose – effects relationship.

The aim of our research was to review recent literature related with studies of δ-aminolevulinic acid dehydratase, and to evaluate whether it could be used as a biomarker of low-level lead exposure.

**Materials and methods.** We searched PubMed/MEDLINE and Google Scholar for relevant publications using the headings “aminolevulinic acid dehydratase”, “ALAD AND lead”. The headings matched 5330 hits for “ALAD”, and 2270 hits - “ALAD AND lead”, dated from the year 1986. We selected 70 articles to be included based on the selection criterions and keywords presented below.

**Results and discussion.** One of the primary detectable parameters of lead exposure is inhibition of haeme synthesis and the decrease of the δ-aminolevulinic acid dehydratase (ALAD) activity in erythrocytes. Lead inhibits three enzymes in the haeme biosynthesis pathway - ALAD, coproporphyrinogen oxidase, and ferrochelatase - but its effects on ALAD are most profound.

At the molecular level, lead displaces a zinc ion at the metal binding site, producing inhibition through a change in the enzyme’s quaternary structure. The ALAD inhibition results at blood lead levels less than 10 µg/dL while there are indications that ALAD activity is not proper measure of lead exposure at high (>50 µg/dL) blood lead levels.

The differences in susceptibility to lead toxicity could be explained by ALAD G177C polymorphism, which yields two co-dominant alleles, ALAD-1 and ALAD-2. The rarer ALAD-2 allele, predominant among Caucasians as compared to other races, has been associated with high blood

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lead levels and has been thought to increase the risk of lead toxicity by generating a protein that binds lead more tightly than the ALAD-1 protein. Studies also imply that carriers of the ALAD-2 allele who are exposed to lead might then retain it in their blood and tissues longer, increasing the chance of an adverse effect due to inhibition of ALAD and consequent build-up of  $\delta$ -aminolevulinic acid (ALA) or perhaps due to lead itself, which can initiate oxidative damage and change the structure of cellular components.

**Conclusions.** It is suggested that the critical dose of blood lead, causing the increased levels of ALA in plasma and urine is below 10  $\mu\text{g}/\text{dl}$ . The degree of erythrocyte ALAD inhibition has been used clinically to gauge the degree of lead poisoning. Thus, the ALAD activity may be used as one of the earliest and sensitive diagnostic biomarkers of low-level lead exposure. Moreover, it is essential to take into account an ALAD genotype when studying lead kinetics and adverse health effects.

**Keywords:**  $\delta$ -aminolevulinic acid dehydratase, polymorphism, lead, biomarker, blood, low-level, exposure, effects



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## **EXPOSURE OF HAZARDOUS POLLUTANTS ON SHIPYARD WORKERS IN TUZLA BAY, ISTANBUL**

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There is a major manpower requirement to process production in shipyard industry under hard working conditions with hazardous material. Most of the processes such as welding, painting, blasting, fibreglass production has direct effect on workers health, i.e. exposure to VOC's, fumes resulting from burning through base metal and from burning the interior and exterior coatings that are often left in place can cause acute and chronic health problems.

Both acute and chronic human exposure around dry-docks facilities are studied previously; therefore, short term and long-term effects are reported as valid results. Previous studies results show dysfunction of the central nervous system (dizziness, nausea, confusion...) and eye, nose, throat irritations are the major effects of acute exposure. The main systemic chronic effects of toluene are also effects on the central nervous system leading to hearing troubles and memory dysfunction. Minimal effects on the liver and kidney have been reported.

With over 40 shipyards, Tuzla Bay is one of the areas with the highest density of industrial establishments in Istanbul. During production processes in this industrial area, these pollutants are being released to air, soil and water, such as volatile organic compounds (VOCs) which belong to a special category of air pollutants that can adversely affect our health and yet receive little attention in Turkey.

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## ANALYSIS OF TOXIC ELEMENTS IN WINE SAMPLES USING ATOMIC SPECTROMETRY TECHNIQUES

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The elemental composition of wines is very influenced by several factors such as climate, soil and anthropogenic contamination sources (i.e. mining, industries, wine storage). To prevent toxic effects on human health, analysis of elemental composition in wine samples along whole the winemaking process is required.

Atomic spectrometry techniques are widely employed for elemental analysis in the analytical laboratories mainly because of their selectivity, sensitivity, high precision, low limits of detection and multielemental capabilities. Among them, flame and graphite furnace atomic absorption spectrometry (FAAS and GF-AAS, respectively), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) have been used for elemental wine analysis. Nevertheless, direct wine analysis by these techniques is very troublesome due to the high organic (ethanol 10%) and salt content of wine samples. To overcome these matrix effects, several methodologies have been proposed: (i) sample digestion; (ii) wine dilution; and, (iii) use of alternative sample introduction systems such as desolvation or electrothermal vaporization (ETV) devices.

The purpose of this work is to evaluate the analytical performance of GF-AAS, ICP-AES and ICP-MS for the analysis of several toxic elements (i.e. As, Cd, Pb) in wine samples. Several methodologies (i.e. sample dilution, sample digestion, standard addition) and sample introduction systems in ICP-based techniques (i.e. desolvation system and ETV) were tested. The results show that the matrix effects can be reduced by digesting or diluting wine samples. However, the throughput is reduced. When a desolvation system or an ETV device is coupled to ICP techniques, limits of detection are improved respect to those shown by the conventional sample introduction system. In addition, organic matrix effects are reduced. Nonetheless, matrix effects due to inorganic species (i.e. K, Na, Ca, Mg) are sometimes enhanced.

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## RISK ASSESSMENT OF DIETARY EXPOSURE TO ORGANOPHOSPHORUS RESIDUES VIA OLIVE OIL AND MILK CONSUMPTION IN GREECE

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Dietary ingestion is a significant pathway of human exposure to organophosphorus (OPs) pesticides. These pesticides are among the most extensively applied pesticides in agriculture and for animal ectoparasite control. With their use, the risk of residues remaining on the food consumed is present. For this reason, governments and international organizations have published a list of pesticides and their maximum residues limits (MRLs). Olive oil and milk consumption is an important route of human exposure to organophosphorus (OPs) residues in Greece. In order to assess the potential health risks associated with these compounds, olive oil and milk samples were collected from different prefectures of Greece during 2004-2005. Nine organophosphorus insecticides and four of their major metabolites were screened by Headspace Solid Phase Microextraction (HS-SPME) combined with Gas Chromatography- Flame Thermionic Detection (GC-FTD). Fenthion, fenthion sulfoxide and fenthion sulfone residues were detected at concentrations ranging from 0.0356 to 0.6118 mg/Kg. Dimethoate and omethoate were detected at concentrations ranging from 0.0220 to 0.0573 mg/Kg.

An exposure assessment, based on organophosphorus levels detected in the samples analyzed in this study, was evaluated for Greek adults. The chronic dietary risk assessment was conducted by comparing the National Theoretical Maximum Daily Intake (NTMDI) of the studied organophosphorus insecticides with the Acceptable Daily Intake (ADI) given by the Food and Agriculture Organization (FAO). This percent ratio for the detected pesticides was mostly below 16.3%. As a more realistic estimation, the National Estimated Daily Intake (NEDI) of organophosphorus pesticide residues was calculated based on mean food consumption data and mean pesticide residues' data from the monitoring program and ranged between  $2.74 \cdot 10^{-6}$  mgkg<sup>-1</sup>/b.w./day and  $5.72 \cdot 10^{-6}$  mgkg<sup>-1</sup>/b.w./day. Additionally, the acute dietary risk assessment was evaluated by comparing the National Estimated Short-Term intake (NESTI) of the OPs with the Acute Reference Dose (ARfD) given by the Food and Agriculture Organization (FAO) and this percent ratio was below 6,70% of the ARfDs of the detected pesticides. Furthermore, a cumulative risk assessment approach was estimated by the calculation of Hazard Index (HI) taking into account that organophosphorus insecticides share the same mechanism of toxicological action.

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The resulting intake levels estimated in this study confirm that the intake of OPs through food consumption in Greece does not represent a health risk to consumers.

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## BIOMONITORING AND HEALTH RISK IN INCINERATOR WORKERS

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**Background:** The literature produced in the last decade highlights consistently that best prevention of negative health effects cannot adequately be obtained without measuring the concentration of toxic chemicals responsible for the observed health effects. To this end and to better define individual exposure in the ecological study a basic requirement is the availability either of environmental measures of the concentration of toxic substances or of internal levels of biomarkers of exposure.

**Objective:** The present review on health effects and waste incineration collects 26 studies published from 2003 up to now and provides an update of occupational exposure and risk on the base of environmental and biological monitoring data. Selected papers have a study design addressed to evaluate outcomes defined as early biological effects. A schematic table is available to make a qualitative comparison between studies results and to have a cumulative outlook of main health effects on exposure biomarkers caused by the incinerator pollutants.

**Methods & Results:** Twelve studies (71%), out of 17 relating about the effects of exposure on biomarkers, evaluate dioxins effects, only in 4 (23%) cases data on personal and ambient exposure are obtained and in 2 (12%) cases only on ambient exposure. Personal monitoring was used to determine the exposure to PAH, metals, particles, aldehyde, VOC. In many cases biomonitoring measures point out significative differences of exposure between groups of workers with different tasks(i.e. it is possible to identify jobs and tasks that suffer the highest increase in urinary and plasmatic metabolites).

**Number of recent studies on incinerator workers with statistically significant effect on biomarkers of exposure**

	in urine	in plasma	genetic damage (comet)
p<0.5	4	4	3
n.s.	3	5	-

However in a short lag of time from exposure it is possible that differences of biomarkers levels cannot be observed depending on the mechanisms repairing genetic damage and cellular balance. Results might be influenced also by bias on job contents and time-activity profile used to define exposure groups. A low characterization of the health effects observed in exposed workers is a cue of a lack in research activity.

**Conclusions:** Recent findings based on biomarkers measures emphasize the relevance of mechanisms and dynamics of dispersion, absorption and degradation occurring either in the environment or in the human body, in determining the observed health outcomes. Consequently the epidemiological studies are required to better elucidate and state description and characterization of biological dynamics of markers used as to make possible useful and valid comparisons between studies.

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## GROUNDWATER RISK ASSESSMENT OF PCE AT A CONTAMINATED SITE

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Tetrachloroethylene (PCE) is widely used as solvent for dry-cleaning and in industrial activities such as degreasing, metal stripping, chemical manufacturing, pesticide production, coal gasification plants and creosote operation. Under favourable groundwater microbial and hydro-geochemical conditions, it has been observed to be naturally attenuated in the form of its transformation products: trichloroethylene (TCE), dichloroethylene (DCE) and vinylchloride (VC).

High PCE concentrations are toxic to both human and animal, while the human health effect of low level exposure is not well established. PCE has been shown to cause liver and kidney tumours in mice and rats and it is therefore considered a carcinogen. However, some of its breakdown products like 1,1-DCE and VC are more toxic and cancerogenic than PCE, thus, though human health risk related with PCE presence is attenuated by degradation, it is further increased by the subsequent formation of toxics substances.

Risk assessment of a former industrial plant situated in South of Italy is analyzed in this work. Risk is estimated by simulating PCE degradation and formation of breakdown products. Transport of PCE, TCE, 1,1-DCE and VC in groundwater is simulated accounting for sorption, dispersion and kinetics degradation within a time horizon of 90 years. Since reliable value of sorption partitioning coefficients and degradation kinetics are rarely available at contaminated site, risk is evaluated in several scenarios in which the physical-chemical parameters values are varied according to literature values. The risk results to be really influenced by different but feasible scenarios, emphasising that reliable site specific field data are necessary to accurately assess the risk. Moreover, the naturally occurring PCE degradation does not always result in a decreasing risk with time. The human health risk can increase because of the formation of the more toxic substances and, only at really large time, attenuated by further degradation.

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**ZEA MAYS (L.) IN AREAS WITH DIFFERENT ANTHROPIC POLLUTION  
SOURCES: RELATIONS BETWEEN TOXIC ELEMENT CONTENT  
S IN SOILS AND IN VEGETABLE TISSUES**

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The aim of this work is to evaluate the pollution level of different *Zea Mays* (L.) cropped agricultural soils in the area surrounding Rome and the effects on toxic elements content in vegetable tissues. Therefore we have studied ten farms exposed to different anthropic pollution sources, considering both areas near various environmental pollution sources (as industries, thermoelectric power plants and wasteyarde) and areas that are away from these pollution sources. Sampling is carried out specifically for studying element bioavailability in the soil and their translocation from the roots to the epigeal part and for directly evaluating the relations between each plant and its rizosphere. Therefore in each site we have collected three whole maize plants and the soil volumes matching with their rizospheres. Thus we have obtained a set of thirty plant/rizosphere specimens. The soils have been characterized for the main physical-chemical properties and submitted to selective extraction procedures with EDTA and simulated rainwater for obtaining information about the mobile (or mobilizable) fractions. Both the total content and the extractable fractions of elements were determined. Concerning the maize plants, we have determined the element content for each vegetable tissue apart: roots, epigeal and grains (edible). Measurement of the element contents was carried out by ICP-AES and ET-AAS, after acid digestion by microwave system.

This work gives a conspicuous experimental data set that can be used to evaluate the element translocation into the different vegetable tissues. The results let especially estimate the element mobility and bioavailability considering each single plant/rizosphere specimen. Thus we could split the individual variability and/or the inhomogeneity into the field and we could easier detect the parameters that influence the elemental mobility and the interelemental relations. Concerning the element content and distribution in the different vegetable tissues, we had always the following order: roots > epigeal part > grain. While Pb, Cd, Mn and Cu contents were not so different between roots and epigeal part, Cr, Fe, Ni and V have shown changes also higher than an order. In any case the results don't show the overcome of the limit values set by the EC Directives 1881/2007 and 32/2002 (and amendments) respectively for foodstuffs and feed. On the whole the results don't arouse any concerns for consumption both as food and as feed. Some interesting interelemental relations and some observations on vegetable/soil extractable contents ratio are pointed out with considerations about the effectiveness of the two extractants employed.

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**MONITORING PRIORITY POLLUTANTS AND EMERGING  
CONTAMINANTS IN THE WATER- SEDIMENT SYSTEM OF THE  
EBRO RIVER BASIN (AQUATERRA PROJECT)**

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In this presentation the most recent results on the monitoring contaminants relevant to soil-water-sediment system at the Ebro river basin will be reported.. These data is part of the EU IP funded project AQUATERRA (2004-2009).

The Ebro is typical Mediterranean river characterised by seasonal low flows and extreme flush effects, with an important agricultural and industrial activity that caused heavy contamination problems: historical Hg pollution coming from different plants for the production of solvents, chlorinated pesticides) and widespread contamination by pesticides.

Up till now six monitoring campaigns of the surveillance monitoring were completed at 24 sampling points including the 18 monitoring control points of the Confederación Hidrográfica del Ebro (CHE) where surface water sediment samples will be collected along the already established facilities of the CHE. In addition 18 groundwater and soil samples wells will be motioned. Priority compounds measured are the ones included in the Directives 2006/11/CE (follow up of the recently abolished directive 76/464/CE) and 2455/2001/EC and comprised 20 organochlorine compounds, 8 polycyclic aromatic hydrocarbons (PAHs), 2 alkylphenols (APs) and 40 polybrominated diphenyl ethers congeners (PBDEs) and various pesticides and metabolites.

Investigative monitoring at 3 risk zones (Flix, Cinca and Estuary) has also been carried out using already established facilities for sampling in order to determine the levels of organic and inorganic compounds in surface waters, corresponding sediment and biota samples. Sampling campaigns in the estuary (Delta) area were performed in periods which cover harvesting/post-harvesting activities.

Risk zones (Flix, Cinca) – industrial impact. The following two main areas are being studied: 1) Spatial and temporal distribution of POPs in risk zones and 2) Measurement campaigns conducted to address the most important subjects related with the Hg contamination Floodplain and Estuary – agricultural impact. Surveillance monitoring has been carried out to estimate the distribution of pesticides (carbendazim, atrazine, terbutylazine, alachlor) within soil/sediment/river water. Monitoring of groundwater to determine quality parameters and trends in relation to an extensive agricultural activity.



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**DETECTION OF MICROCYSTINS IN FISH INTESTINE:  
VALIDATION OF ELISA ANTI-ADDA AS SCREENING TECHNIQUE**

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Toxic blooms of cyanobacteria in freshwaters have been reported in many water bodies throughout the world, being a clear sign of eutrophication, which has become more intensive during the last century. Anthropogenic inputs by domestic, industrial, agricultural, and urban discharges have been identified as the primary cause for this enrichment. Surveys in different parts of the world have revealed that between 25 and 75% of cyanobacterial blooms are toxic. Cyanobacterial toxins fall into four classes: hepatotoxins, neurotoxins, non-specific toxins and lipopolisaccharides, being hepatotoxins the most commonly encountered. These toxins, microcystins (MCs), have been shown to be a hazard to human health. MCs accumulate in aquatic organisms probably as a result of irreversible binding to liver protein phosphatases. The aim of this work is to calculate the uncertainty to a binary response, of the type yes/no, originated from an instrumental screening system. The validation was performed with standard commercial MCs (MC-LR, MC-RR and MC-YR). It was applied to a competitive indirect ELISA anti-ADDA screening system to analyse MCs in intestine homogenates from exposed fish. A cut off value from the responses of the calibration samples is calculated and compared with the responses obtained for unknown samples. From this comparison, we will be able to take a compliance yes/no decision, with an alpha probability of committing a type I error.

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**SUBCHRONIC DIETARY EXPOSURE TO VIRGIN OLIVE  
OIL SUBJECTED TO DIFFERENT FRYING INTENSITIES  
INDUCE OXIDATIVE STRESS IN LIVER OF RATS**

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Virgin olive oil is a typical ingredient of the Mediterranean diet and its benefits are recognized worldwide. However, high temperatures associated with the repeated use of the same oil lead to the breakdown of some fatty acids, forming numerous toxic polymer compounds and peroxides. The level of polar compounds (PC) is the parameter that indicates the frying intensity. Spanish regulations state that oil with a % PC > 25% is not permitted for human consumption.

The alterations on the antioxidant status induced by the subchronic dietary exposure to virgin olive oil (VOO) and VOO subjected to different degrees of frying were investigated in rats. The rats were divided into five groups: one control, which received 2% of ordinary oil (OO) in the diet for three months, one group that received 12% VOO, and three groups that received 12% of VOO subjected to different degrees of frying containing 12.5, 26.5, and 33.6 % PC, respectively. The effects on lipid peroxidation (LPO) and antioxidant enzymes such as superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPx) and glutathione reductase (GR) were investigated.

Results show an increase in the LPO levels and alterations in the antioxidant enzymes activities. These effects on the oxidative biomarkers studied were dependent on the level of polar compounds of the oil samples.

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## A NESTED ASSESSMENT OF POLLUTANT FATE AND ECOSYSTEM RISKS AT PAN- EUROPEAN SCALE

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Assessing the existence of trends in the discharge of pollutants in the European environment and evaluating how climate change, land use, life-style and management actions will influence these inputs are challenges to be faced if we want to determine impacts of a variety of environmental policies. A retrospective (ex-post) analysis based on monitoring records will tell us how good or bad we have been so far. The only accessible instrument to test if we will be able to keep under control economic, social and environmental drivers to prevent further damage or recover good quality conditions is forecast (ex-ante) analysis based on scenario building.

This paper will report on results of the FATE methodological approach, which brings together emission sources, ecosystem properties, landscape parameters and other pan-European datasets in a modelling context, for an assessment of pollutant loads and average concentrations in different environmental compartments at European scale, which is the central information for exposure assessments of ecosystems to potential pollutant risks.

The FATE project for Europe and beyond addresses the fate and impacts of pollutants in terrestrial and aquatic ecosystems across a range of temporal and spatial scales. Results are pollution risk and vulnerability maps, which are very useful to assess the impact of EU policies, raise public awareness and facilitate planning of management scenarios. At the scale of continental Europe the focus is on identifying hot spots, spatial trends and general pathways of pollutants; at the scale of catchments and associated coastal zone the interest is on the apportionment of mass inventories and aggregated in and out fluxes.

FATE is integrated into HORIZON 2020, the Commission initiative that, in collaboration with the Mediterranean Conventions, intends to tackle sources of Mediterranean pollution by the year 2020, with industrial emissions, municipal waste and urban wastewater as priority areas. The extension of FATE to the Mediterranean region will support the monitoring of impacts of HORIZON 2020 by providing spatially and temporally resolved insights of trends in concentrations of pollutants such as nutrients, pesticides, pharmaceuticals and industrial chemicals.

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## MERCURY AND OTHER TRACE ELEMENTS IN SOILS AFFECTED BY THE MINE TAILING SPILL IN AZNALCÓLLAR (SW SPAIN)

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The Aznalcóllar accident (28th April 1998) occurred because the collapse of the tailing-dam dike of the Aznalcóllar-Los Frailes mines. Soils affected by a slurry composed of acidic water loaded with trace elements, finely divided metal sulphides, and materials used in the refining /floating process. Studies carried out before and after the soil restoration activities (sludge removal, amending, tilling, and afforestation) showed severe trace element contamination (mainly As, Cd, Cu, Pb, Tl and Zn) in the superficial layer of the sludge-affected soils. Despite Hg is an important component of the Los Frailes ore and therefore of the contaminant sludge, data of the Hg content in sludge affected soils was scarce and sometime controversial. The aim of this study was to determine the effect of the spill and of restoration measures on the Hg content of soils and its relationship with other elements. Concentration of Hg immediately after the spill was 8-fold the background ( $0.061 \pm 0.012$  mg kg<sup>-1</sup>; Mean  $\pm$  SD) at the surface (0-5 cm) and 3-4-fold at deeper layers (0-20; 0-50 cm). After the remediation measures mean values of Hg and other elements (As, Cd, Cu, Pb and Zn) remained still higher than the corresponding background values, occasionally higher than mean values before restoration, having high variation coefficients. These anomalies are accounted by the remains of sludge left on the soils surface and buried during restoration operations that resulted in an irregular distribution of trace elements on the surface of soils. The highest values for the less mobile elements (up to 176 mg kg<sup>-1</sup>As, 2.36 mg kg<sup>-1</sup> Hg and 1556 mg kg<sup>-1</sup> Pb) were observed in the first kilometres close to the tailing dam, the more contaminated section after the spill, which had to be cleaned twice.

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## DETERMINATION OF TRIHALOMETHANES IN DRINKING WATER DISTRIBUTION NETWORK

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Chlorine is used widely in disinfection of drinking water in treatment plants. As a result of reactions between free chlorine and natural organic matters disinfection by products such as trihalomethanes (THMs), haloacetic acids (HAAs), are formed. THMs in disinfection by products are especially important because of their potential carcinogenicity. In this work, analyses methods namely US EPA 551 microextraction method and German DIN 38407 standard method were compared for suitability of the analyses of THMs (Chloroform, Bromodichloromethane, Dibromochloromethane, Bromoform). Consequently USEPA method 551 microextraction method was used in the analyses of water samples for THMs since recovery ratios were better for this method in the fortifications experiments. Water samples were collected from various points of drinking water distribution network and analyzed for THMs. THMs concentrations were found to be near to the limit values at same sampling points. The order of THM compounds in abundance in the distribution network could be given as chloroform>bromodichloromethane>dibromochloromethane>bromoform.

Key words: THMs, microextraction, GC/ECD, distribution network

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## DETERMINATION OF BENZENE COMPOUNDS IN DRINKING WATER DISTRIBUTION NETWORK

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Chlorinated benzenes are carcinogenic, toxic and flammable compounds which are by products of gas and coke coal production or produced from petroleum. These compounds are brought through precipitation or industrial wastes to the water sources. Chlorinated benzenes are not soluble in water easily neither they could be broken down by microorganisms in soil. However, chlorinated benzenes are easily evaporates from waters and soils into Atmosphere. Production, use, transportation and discharge of chlorinated benzenes cause environmental pollution. In this work EPA micro extraction method (EPA method 504) was adapted and compared with German micro extraction method (DIN 38407) for the analyses of 1,3- Dichlorobenzene; 1,4-Diklorobenzene; 1,2-Diklorobenzene; 1,2,4-Triklorobenzene; 1,2,3-Triklorobenzene in water samples by GC/ECD. Adaptation of the micro extraction method was carried out using MTBE (metilttertbutileter) instead of n-hexane. Higher recovery ratios were obtained with comparing German standard method (DIN 38407). Although in the city water distribution network chlorinated benzene values were not exceed limit values given by EPA, WHO and EU, 1,3-Diklorobenzene results were observed to be near the limit values. Therefore it is important to monitor drinking water distribution systems for such compounds.

Key words: Chlorinated benzenes, micro extraction, GC/ECD, distribution network

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## THE IMPACT OF POLLUTION ON TRACE ELEMENTS CONTENTS OF WILD MEDICINAL PLANTS

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To contribute to the study of the possible impact of environmental pollution on the wild life and therefore the possible human exposure to some toxic trace elements through consumption of the raw natural herbs as a remedy in a wide area of Southern Mediterranean region, therefore several plants from ASTERACEAE family known to grow widely in northern Africa coastal area were collected from locations which more prone to environmental pollution due to industrial activities, then analyzed for their trace elements contents.

The results were contrasted with the data obtained from the analysis of the analogous plants collected from mountain and semi-desert areas which are located away from industrial and other notorious human activities.

The concentration levels of the studied major, minor and the toxic elements specially lead were investigated in relation to environmental quality, location, the possible source of the pollution and possible environmental health effects on the natives in this part of Mediterranean region.

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## DETERMINATION OF DYING-OFF RATES OF SALMONELLA TYPHIMURIUM IN CRYSTAL SUGAR

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Food-borne illnesses have become a major public health focus and considered emerging problem worldwide. Outbreaks of salmonellosis have been reported for decades, but within the past 25 years the disease has increased in incidence on many continents. Salmonella species are not able to survive under the normal process conditions of sugar manufacturing and reproduction and metabolism of this microorganism is not possible due to the low water activity in sugar. However, these organisms might be introduced to the sugar after the production process by humans, animals like rodents, birds or insects if good manufacturing or warehouse practices are not applied.

In this study, the dying-off rate of Salmonella typhimurium in crystal sugar was determined. Crystal sugar obtained from the process was contaminated with the pure culture of *S. typhimurium* ATCC 14028 by using microbank rings to get reproducible infection. Contaminated sugar was stored at room temperature and samples were taken periodically up to 90 days. Standard I nutrient agar and Xylose-Lysine-Desoxycholate (XLD) agar were used as an universal medium for the recovery and selective medium for the quantify of *S. typhimurium*, respectively. The population of *S. typhimurium* decreased from  $2.1 \times 10^3$  cfu/g to non detectable levels after 36 days of storage in standard I nutrient agar while the counts on XLD dropped less than 1cfu/g at day 25.

Sugar has been considered intrinsically safe because of its nature. However, our results provide additional evidence supporting the public health risk that *S. typhimurium* could be a problem when cross contamination occurs in sugar; therefore, all possible hygienic measures should be taken to reduce the risk of microbial contamination.

Key words: Dying-off rate, Salmonella, sugar, storage



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Results from the three monitoring programmes (November 2004, November 2005 and 2006) showed two principal types of BFR contamination at the Cinca risk area. The first one corresponded to deca-BDE-209, and the second one, to HBCD. Next studies will be focused to the determination of potential sources of contamination, including a textile industry, a tannery, a factory of EPS production and a factory of PVC production. Different sediments and industrial effluents will be analysed for this purpose.

A comprehensive survey of pharmaceutical residues in the Ebro river basin has been completed together with the monitoring of several possible point sources (wastewater treatment plants in Zaragoza, Logroño, Pamplona, Lleida, Vitoria, Miranda, Tudela) and water/sediment quality downstream of the discharge points. In receiving surface water most ubiquitous compounds were the analgesics and anti-inflammatories ibuprofen, diclofenac, naproxen, the lipid regulators bezafibrate and gemfibrozil, the antibiotics erythromycin, azythromycin, sulfamethoxazole and trimethoprim, and less frequently ofloxacin, the antiepileptic carbamazepine, the antihistaminic ranitidine and the  $\beta$ -blockers atenolol and sotalol. Although levels found in WWTP effluents ranged from low  $\mu\text{g/L}$  to high  $\text{ng/L}$ , pharmaceuticals in river waters occurred at least at one order of magnitude lower, at low  $\text{ng/L}$  range due to dilution effect. From the results obtained it was proved that WWTP are "hot-spots" of aquatic contamination concerning with pharmaceuticals of human consumption.

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## EFFECTS OF WATERSHED DELINEATION FROM GRID DEMS IN GIS TO NON-POINT SOURCE WATER POLLUTION MODELLING

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A watershed is a region in which all the rainfall coming from the land drains to a particular body of water or common point. Watersheds allow us to evaluate the quality and quantity of our water resources geographically. Watershed assessment is the measurement and use of chemical, physical, and biological properties to determine the current health of streams.

The requirement to digitally delineate accurate watershed boundaries is a routine task necessary in numerous natural science disciplines. The base topographic data necessary for watershed analysis in many jurisdictions is typically contained within two primary photogrammetrically interpreted base topographic layers: the hydrology (streams, rivers, wetlands, lakes, etc.), and the elevation (contours, spots, digital terrain model points, etc.). From these two data sources, a flow direction corrected, single line, vector hydrology network and a raster digital elevation model can be developed. There are numerous approaches to watershed delineation, but the most accurate implementations employ both these enhanced data sets in extracting watershed divides.

Pollutants and sediments found in surface waters can often be traced to specific point sources where management actions can be focused to improve water quality. In many other instances, however, pollutants and sediments cannot be traced to distinct points of origin. In these cases, water quality can be examined in a larger spatial context to relate landscape patterns (both natural and anthropogenic) with downstream pollutant and sediment loads. Similarly, predicting the impacts of land use changes on water quality requires an understanding of the physical processes related to non-point source pollution. Delineation of the watersheds is one of the most important stages of this process since it will provide information in the determination of the total potential of the hydrologic parameters such as suspended sediment and flow within a certain watershed. Commercial GIS softwares usually offer solutions using digital elevation models (DEMs) based on grid approach. For this purpose, water flow direction and flow accumulation grids are derived from drainage network. Selection of flow accumulation threshold value is a critical issue in delineating watersheds (especially for sub-watersheds). However, there is not a reliable method to define this value at different DEM resolutions. A proposal is made for determining appropriate flow accumulation threshold value to extract drainage network by comparing different proposals on this subject. Its effects to the watershed delineation and hence to the non-point source pollution modelling are shown in a case study, using 5-metre and 30-metre DEMs in ArcGIS software.

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**DETERMINATION OF PESTICIDE TRACES IN SOME FRUIT AND VEGETABLE  
SAMPLES COLLECTED FROM SUPERMARKETS OF KONYA CITY CENTRE**

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**Abstract:** In this study; the existence of organochlorine pesticide residues have been investigated in 18 kind fruits and 24 kind vegetables specimens collected from markets of Konya city, Turkey. A Gas Chromatography was used for investigation of food organochlorine pesticide residues in this study.

The names of the 24 vegetables and 18 fruits specimens examined were as follows: marrow, aubergine, potato, tomato, cucumber, radish, red radish, bean, cauliflower, red cabbage, parsley, green pepper, spinach, bell pepper, lettuce, onion, spring onion, broccoli, leek, cabbage, lemon, sugar beet, rocket, dill, celery, apple, pear, black grape, plum, quince, carrot, white grape, persimmon, orange, pomegranate, banana, tangerine, pumpkin, grapefruit, strawberry, kiwi, Jerusalem artichoke, medlar. As a result, it was found that, the levels of organochlorine pesticides in the all investigated fruit and vegetable specimens except  $\alpha$ -endosulphan,  $\delta$ -HCH,  $\epsilon$ -HCH, hexachlorobenzene in celery and oxy-chlordane in leek were lower than those of the MRL of European Legislations.

**Key Words:** Organochlorine pesticides, Fruit, Vegetable, Konya, Turkey

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## **XTRAFOOD: A MODEL FOR THE IMPACT ANALYSIS OF CONTAMINANTS IN PRIMARY FOOD PRODUCTION**

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In view of recent food crises, quality control and risk assessment of the food chain from the farm to primary food products is an important issue and food safety is one of the major issues on the Agenda of the European Commission. There is a need for integrated models calculating transfer and impacts of contaminants in primary food production. Currently, no generic modelling tools are available that predict the impact of contaminants in the environment to the primary food chain.

We present the development and demonstration of an integrated model, called XtraFOOD (Xenobiotics transfer in the FOOD chain), that calculates transfer of contaminants in the agroecosystem and associated impacts on human health. The transfer model consists of modules calculating transfer to the farm (e.g., atmospheric deposition, import of manure, fodder, incidental transfers...), transfer in and from soil (i.e., leaching, plant uptake, volatilization, degradation), and transfer to cattle (intake, transfer to organs, fat, milk, muscular tissue, ...). Model outputs are contaminant levels in various primary food products such as crops, grains, milk, meat, and eggs. Calculated concentrations were evaluated by comparison with measured concentrations in food products. The transfer model was coupled to food consumption data. The XtraFOOD model provides as output the food intake data and resulting contaminant intake, segregated into age and gender categories. Exposure can be calculated as being representative for a population (group) or separately for local and background intake. All these intakes are linked to the output of the farm model. Additional inputs are provided to allow for concentration data in non-farm related foods (e.g. fruit juice, fish, ...). Human exposure is calculated and compared to the available toxicological levels to estimate impacts on human health.

The model is applied to persistent contaminants accumulating in the food chain and causing residues in food products (i.e., dioxins, PCBs and cadmium). The model is generic in that sense that data used in the model like food consumption, environmental concentrations etc. are specific for Belgium but can be replaced with data for other regions.

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## POSSIBILITIES AND CONSTRAINTS OF THE PHYTOSTABILIZATION OF METAL POLLUTED MINE TAILINGS IN THE CARTAGENA-LA UNIÓN AREA, SOUTHEAST SPAIN

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For more than 200 years, mining activities were the most important economic activity in the Cartagena-La Union Mining District, Southeast Spain. Many environmental problems developed in the areas surrounding the mine wastes. These areas included crop lands, beaches, streams, ground water and fisheries. Approximately 20% of the 50 km<sup>2</sup> of the mining area is affected by the former mining activities. Mine tailings cover 160 ha, most of which are bare and thus unprotected against erosion. In addition, they contain high concentrations of toxic heavy metals, especially lead, copper, zinc, arsenic and cadmium. The growing population in these zones has encroached into areas that are highly exposed to pollutants from the nearby tailings.

The removal of the mine tailings is complicated by the difficult orography and their large volumes. Therefore, the remediation of these sites requires in situ low-cost technologies. Revegetation may decrease the environmental risks associated with the tailings, by stabilizing their surfaces and thus reducing erosion. There are some native plant species that have colonized the tailings of this zone despite their high metal concentrations (e.g. 12000 mg kg<sup>-1</sup> Zn, 8000 mg kg<sup>-1</sup> Pb, 1800 mg kg<sup>-1</sup> As) and high electrical conductivity (6-18 dS m<sup>-1</sup>). The different pHs (3-7) of the tailings affects metal solubility. Up to 14% of the total Zn is extractable in water in tailings with pH 3. This in turn has influence in the establishment of vegetation: *L. spartum* survived in tailings with pH below 4 and had relatively low metal concentrations in the shoots (175 mg kg<sup>-1</sup> Zn; 55 mg kg<sup>-1</sup> Pb); in contrast, *Z. fabago*, grew in situ at neutral pH tailings with elevated leaf metal concentrations (770 mg kg<sup>-1</sup> Zn; 100 mg kg<sup>-1</sup> Pb). Under controlled conditions in growth chambers, these plant species took up more metals (up to 4500 mg kg<sup>-1</sup> Zn in *L. spartum*) compared to those in field conditions. Lime amendments improved the growth of *L. spartum* in acid substrates by increasing the pH from 3 to 5.5 and simultaneously decreasing plant metal uptake. However, this pH still was too low for the growth of *Z. fabago*. The addition of fertilizer in early stages may improve the growth of *L. spartum*, *P. miliaceum* and *Z. fabago* in neutral tailings. Images taken with neutron radiography revealed different patterns of root growth in plants in mine tailings compared to those in non-polluted soil.

Here, we present a review of the environmental impacts of mining activities in the Cartagena-La Unión area and outline a selection of plant species and soil amendments that may enhance phytostabilization. We discuss the advantages and limitations of this approach.

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## INVESTIGATION OF HALOACETIC ACID FORMATION IN KONYA-TURKEY DRINKING WATER DISTRIBUTION NETWORK

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Chlorine has been used in disinfection of waters and wastewaters for about 100 years. Haloacetic acids are formed due to the reactions between hypochlorous acid or hypochlorite and dissolved organic matters and bromide.

In this work, for determination of 7 haloacetic acid (HAAs) compounds in drinking water distribution network, acidic methanol esterification GC/ $\mu$ ECD method was applied. Advantage of this method is toxic diazomethane was substituted by acidic methanol in the derivatization step. Recovery ratios for 7 haloacetic acids were determined between 67 % and 103 %. Only recovery ratio of monochloroacetic acid was determined as low (67-100 %) however the recovery ratios of the rest of the haloacetic acid compounds were quite high. Recovery ratio of monochloroacetic acid was also reported as low in other researches that the derivatization was carried out by diazomethane. Detection limits for haloacetic acid compounds were determined as 10.714, 0.814, 0.0771, 0.051, 0.0285, 0.074, 0.0428  $\mu$ g/L for monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid, dibromoacetic acid, 2,4,6 trichlorophenol respectively.

Keywords: DBPSs, HAAs, Chlorination, GC, Konya.

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## ACCUMULATION AND DISTRIBUTION OF HEAVY METALS IN SEDIMENTS OF SEMI-ENCLOSED BASIN SOUTHEASTERN MEDITERRANEAN SEA, EGYPT

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The distribution, enrichment and accumulation of heavy metals and texture characteristics in the surficial sediments of the Eastern Harbour (Mediterranean coast of Egypt) were investigated. Surface sediments in the <63mm fraction collected from 12 sites representing all area of the Harbour, were analyzed by Atomic Absorption Spectrophotometry for Cd, Cu, Zn, Cr, Pb and Al. Metal concentrations were compared with literature data to assess the pollution status of sediments, Enrichment factors (Efs) and the geoaccumulation Index (Igeo) has been calculated as a criterion to assess if their concentrations present contamination levels. All heavy metals studied, except Cr had moderate or high enrichment factors. Analytical results have been elaborated by using a Geographical Information System (GIS) software to show metals accumulation area.

The Mediterranean Sea is an area where sediments have different geochemical composition. Eastern Harbour (EH) is located in southeastern Mediterranean Sea, latitudes 31° 12' - 31° 13' N, longitudes 29° 53' - 29° 54' E, it is an important semi-enclosed basin (mean depth 6m), and has been strongly affected by growing population and industrialization The Harbour is sheltered from the sea by an artificial breakwater leaving two openings (left and right). The left opening is the main navigation entrance to the Harbour, 300 m width, through these openings the exchange of water between the harbour and Mediterranean water takes place. Sources of pollution include untreated domestic discharges through many submersible minor outfalls distributed along the harbour marginal coast. Also the harbour water receives extra waste effluents from fishing ships and shipyard at its western side. The importance of this Harbour happened when the excavations has led to the discovery of the location of ancient buildings on the peninsula of the Timonium and Antirrhodos Island, the artificial dikes constructed by the Ptolemies by Marcus Antonius. Also this basin consider as one of the main fishing sources in the Alexandria City and its adjacent areas. The main objectives of the present study are to: assess the trace metal status of sediment samples from the harbour area in the context of the specific impact of the minor sewers using the enrichment factor (EF). Prepare distribution maps of concentrations of the trace metals (Al, Zn, Cr, Cu and Cd) using GIS approach. Geoaccumulation index (Igeo) has been calculated to assess sediments concentration and establish if metals concentrations represent background levels for the Mediterranean Sea.

Surficial sediment samples were carried out in June 2006 and collected by Van Veen Grab from twelve stations covering the all area of the harbour. Samples were digested according to US

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EPA method 3050B, then analyzed on a flame AAS (Varian Techtron-Model 1250) for Cd, Cu, Cr, Zn, Pb and Al.

Surface sediment samples collected from twelve stations, representing the all area of the Eastern Harbour, were analyzed using AAS. Examining the general properties of sediment data from the Eastern Harbour, it was found that Zn represents the highest median concentration, followed by Pb. According to calculations of enrichment factors, Pb and Cd are of moderately sever enrichment, while Zn has the highest level of enrichment (sever enrichment). Other elements, Cr, is at background concentrations and Cu is of minor enrichment. The distribution of metals concentration gives information about sources of pollution in the area, Al display a distribution differing from pollution-derived elements. Furthermore, similar pattern of distribution shared by Cr and Cu indicates that mixed sewage wastes affect the area. Finally, similar distribution patterns for Cd, Zn and Pb with high EF point to the operation of numerous shipyards (construction and paint) in the same area.



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## VOLATILE ORGANIC COMPOUNDS IN THE AIR OF STREETS AND INSIDE OF CARS IN THESSALONIKI

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Two series of measuring campaigns were carried out during 2005-06 in order to determine the levels of volatile organic compounds (VOCs) in the air of Thessaloniki greater area. The first series of measurements include VOCs sampling in the air of city centre and near the industrial region. The second series of measurements include VOCs sampling in various streets of the city and inside of cars.

The concentrations of the following organic compounds have been determined: benzene, toluene, octane, p,m-xylene, o-xylene, a-pinene, b-pinene, 1,3,5-trimethylbenzene, b-myrcene, 3-carene and d-limonene.

There is an important seasonal variation of VOC concentrations between winter and summer periods. The values of toluene, octane and p,m-xylene are higher during the summer period, but there is not important seasonal variation of the o-xylene values.

The toluene concentrations are the highest of all VOC values in all periods and in all sampling sites.

Benzene concentrations measured in various streets range from 2 – 10.3  $\mu\text{g}/\text{m}^3$  (June 2005 and June 2006). In November 2005 concentrations vary from 4.2 to 12.3  $\mu\text{g}/\text{m}^3$ . In many locations the levels of benzene exceed the established limit value (5  $\mu\text{g}/\text{m}^3$  annual mean) set by the European Commission to be met by 2010. The lowest levels of benzene were measured near the industrial area of Thessaloniki. The ratio toluene/benzene is very similar in all locations (between 3 and 3.9), which indicates traffic emissions as the main source.

Inside of almost all cars examined very high concentrations of air pollutants were measured. In particular fuel originated compounds (aromatic, aliphatic compounds) are present in high concentrations. This fact deserves particular attention, even if the time spent inside the cars is limited. Exposure to multiple air pollutants in concentrations as they have been measured in some cars might constitute a health risk for the car owners.

The VOC concentrations during 2005-06 are relatively higher from those observed during previous measuring campaign carried out ten years ago (1995-96).

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**METAL SPECIATION IN COASTAL MARINE SEDIMENTS  
FROM MALIAKOS GULF USING A MODIFIED BCR-SEQUENTIAL  
EXTRACTION PROCEDURE, CENTRAL GREECE.**

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Sediments constitute an important deposition tank for metals and other pollutants entering the marine environment from various sources; however under changing environmental conditions, they can act as a secondary non-point source by releasing the labile fractions of metals to the overlying water column, with adversely effects on aquatic organisms.

Although total metal analysis may provide information concerning possible enrichment of heavy metals in sediment, additional studies or more detailed analytical protocols are required in order to assess the potential environmental impacts of contaminated sediments on biota, as it is generally regarded that the bioavailability and biological toxicity of heavy metals strongly depends on their chemical forms.

The objective of this study was to determine the concentration, distribution and fractionation of heavy metals in surface sediments of Maliakos Gulf. Maliakos Gulf is a semi-closed gulf located in the eastern part of central Greece; it is an area of ecological significance included in the Natura 2000 network.

The modified BCR (European Communities Bureau of Reference) three-step sequential extraction procedure was applied in order to fractionate heavy metals in the sediments. For the determination of the residual metal concentration of the sediments, complete sample dissolution was achieved by using HF/HClO<sub>4</sub>/HNO<sub>3</sub> acid mixture in closed vessel system. The metal concentrations were measured by FAAS and GFAAS. A reference material was also analyzed.

The results obtained from the measurements of the BCR sequential extraction procedure indicated relatively high mobility of Pb, Cd and Mn in the sediments, while Fe, Cr, Zn and Cu were mainly found in the residual fractions and therefore are regarded as relatively inert. The highly toxic metals Cd and Pb were mainly found in the first three fractions at percentages of up to 80%, indicating that their highest proportion is bioavailable, although total concentrations were not detected to be high.

Fe and Cr were in the residual fraction at 90% which indicates the geological origin of elements. Zn and Cu were also found in this fraction at percentages up to 80%, implying that these metals were strongly bound to the sediments and will not be released under natural conditions. Similar distribution patterns of Zn and Cu between the individual fractions suggest a common source or common fixation, transport and deposition mechanisms of these elements.

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## CATEGORIZING THE WATER QUALITY OF DAM LAKES FROM THE ANGLE OF EMPLOYABILITY OF THE WATER SOURCES

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Dams, built due to various reasons such as electrical energy, irrigation water or drinking water assurance, and their water storage tanks cause many changes in many characteristics of their environment. Every change that can occur in shapes and sizes of surface waters will cause the formation of the organism groups adapted to the living conditions of new special conditions and also formation of the microorganisms that are creating these groups. Furthermore, with the formation of dam lakes, natural structure will go into changes and this will cause disruptions in limnological and ecological structures of the lakes and in the water quality while quality water demand and consumption will continuously increase because of population increase, developments in hydrous-agriculture and industry and urbanization. For this reason, both the changes made by dam lakes in their environments and the environmental pollution problems that they are subject to require that the employability of the water sources in these fields should be determined with detailed examinations for water quality.

In this study, Gökçekaya Dam Lake located on Sakarya river is examined for physical, chemical, biological parameters. Chosen field has a characteristic showing differences from previously performed studies. This dam lake is located between two dam lakes on Sakarya river. In other words, the main stream feeding the lake comes from Sarıyar dam lake. With this study, In Gökçekaya Dam having a different input water characteristic from the other dam lakes, the change in natural systems is evaluated with many parameters (physical, chemical, biological, toxicological). Water quality change in the lake is performed within a two-year period (2005-2007) and in seasonal periods (spring, summer, autumn, winter). Water quality change is measured in 5 different stations determined in the lake and with the samples taken through the depth. The measured quality of the lake was compared with the Turkish Water Pollution Control Regulation (TWPCR) and according to the classification given in the TWPCR. The trophic state of the lake was evaluated by using German Technical Standard Method.

Key words: Dam lake, lake water quality, trophic state

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## PM2.5 AND PM10 MASS CONCENTRATION IN ZONGULDAK-COAL MINING AREA- TURKEY

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In this work, the effect of meteorological parameters and local topography on mass concentration of fine (PM2.5) and coarse (PM2.5-10) during December 2004 to October 2005 has been investigated. A total of 236 samplers were collected during this study period using Anderson Dichotomous sampler. The average mass concentration of PM2.5 and PM2.5-10 and PM10 was found as 29.38 mg/m<sup>3</sup>, 23.85 mg/m<sup>3</sup> and 53.72 mg/m<sup>3</sup> respectively. The concentration of PM2.5, and PM10 were higher in heating seasons than in summer time. The increase of relative humidity and cloudiness is concurred with an increase of PM episodic events. During non-rainy days, the episodic events for PM2.5 and PM10 have been increased by 30% and %10.7 respectively. As expected, the low temperature is associated with an increase in the number of episodic events. This is a result of the extensive use of fuel during winter-time for heating purposes and also due to stagnant air masses formed because of low temperature and low wind speed over the study area. Back-trajectory studies show that atmospheric transport over Mediterranean region, Europe and Africa has reached the study region frequently.

Key words: PM2.5 and PM10 distribution, elemental composition, factor analysis, Zonguldak.

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## SPATIAL AND TEMPORAL DISTRIBUTION OF PESTICIDE RESIDUES IN SURFACE WATERS IN AN AGRICULTURAL BASIN IN NORTH-EASTERN GREECE

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One of the objectives of the Water Framework Directive (WFD) is to obtain a good status for rivers by 2015 in European countries and to develop water management regimes based on river basin districts. The aim of this study was to assess both temporal and spatial distribution of pesticide residues in the river Erithropotamos located in Evros region, in north-eastern Greece, as well as the ecological risk. The study has been focused on agricultural area with known large-scale pesticide use. Main crops in the area are cereals, corn, sugarbeets and sunflower.

River water samples have been collected seasonally (May 2006 –December 2006) from three sampling points covering the distance from the Greek-Bulgarian borders down to the river's discharge in the Greek territory. Analysis of the water samples after solid phase extraction by GC-MS revealed the dominance of soil applied pesticides in most samples. From the 147 pesticides that were included in the analytical method, 12 were constantly detected in the river water samples. Generally, low levels of residues were found in the first sampling point (Greek-Bulgarian borders) however, o'p' DDT, and o'p' DDE were only detected in this sampling point regarded as transboundary pollution. The most commonly encountered pesticides in the river waters were trifluralin, carbofuran, alachlor, prometryne and metolachlor. Pesticide residues ranged from 0.003 – 0.064 ppb; 0.076-0.256 ppb; 0.013-0.26; 0.018-0.423 ppb and 0.002-0.039 ppb for trifluralin, carbofuran, alachlor, prometryne and metolachlor respectively. Peak concentrations were observed during the application period in the second and third sampling point. Increased loading (primary as well as secondary peaks) seemed to be a consequence of application (timing, rate, frequency) and intense rainfall during the application period.

Aquatic risk for the detected pesticides was assessed on the basis of LC50 (incorporating an AF factor of 103) and/or NOEC values by using the risk quotients PNEC/PEC. PEG (predicted environmental concentration) is the highest level of each pesticide that the ecosystem is exposed to (highest detected concentration). PNEC (predicted no effect concentration) is the concentration below which no adverse effect is likely to occur. Three trophic levels (Daphnia, fish and algae) were considered. Data, concerning the most sensitive species were derived from the ECOTOX data base. Aquatic risk assessment revealed that certain residue levels (carbofuran, alachlor) may pose a threat to either of the considered trophic aquatic levels, while others (e.g. trifluralin) are not likely to cause any adverse effects to the ecosystem. Possible implications of DDT residues to the aquatic ecosystem are discussed.

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## CHELATE ASSISTED PHYTOREMEDIATION OF BORON FROM SOILS

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Boron is a naturally-occurring element found combined with other elements throughout the environment. It is neither transformed nor degraded in the environment, although changes in the specific form of boron and its transport may occur, depending on environmental conditions. No quantitative data were located regarding man-made releases of boron compounds to soil. However, it is reported that the boron concentration in sewage sludges from 23 U.S. cities ranged from 7.1 to 53.3 mg/kg.

Most boron compounds are transformed to borates in soil due to the presence of moisture. Borates themselves are not further degraded in soil. However, borates can exist in a variety of forms in soil. Borates are removed from soils by water leaching and by assimilation by plants.

The quantity of boron released varies widely with the geographic variations in boron-rich deposits. Background boron levels in U.S. soils were reported at a geometric mean concentration of 26 mg/kg with a maximum concentration of 300 mg/kg. In Turkey having the highest amount of boron in the world, many agricultural sites have similar high level of boron contents.

Boron is normally an essential nutrient for plants. However in high concentration, boron may have toxic effects on plants. Boron is assimilated by plants from soil and is therefore a natural constituent of many foods, mainly fruits and vegetables. The amount of boron absorbed varies considerably among different plant species. The U.S. Food and Drug Administration (FDA) has set a tolerance limit of 8 ppm boron for citrus fruit.

Since the removal of boron from soils by physical and chemical techniques requires expensive and difficult methods both in economical and technological sense, agronomic techniques may be used as an ecological and economical solution alternative. In order to clean contaminated soils, Phytoremediation technique is one of the commonly used alternative methods.

In this study, phytoremediation of boron from soils by using corn, sunflower and canola plants were studied. Additionally, effect of chelate addition to soils for increasing the removal efficiency was investigated. Boron was uptaken by three plants in high level. Especially sunflower and corn absorbed highest amount of boron both in their roots and leaves. Although canola is known as of the hyperaccumulator plants in phytoremediation technology its efficiency was lower when compared with the other plants.

The detailed results and calculations will be explained in full paper.

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**PHYSICAL, CHEMICAL AND BIOLOGICAL PROPERTIES OF WATER COLUMN  
AND SEDIMENT AT THE SEA BASS / SEA BREAM FARM IN THE MIDDLE  
ADRIATIC, CASE STUDY – MASLINOVA BAY**

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This paper presents results of impacts from one sea bass / sea bream breeding farm on physical, chemical and biological properties of the water column and sediment. The farm is located in semi enclosed bay on the middle Adriatic island Brac. Measurements and samplings were performed during December 2001, May 2002 and March 2003, at three stations inside the breeding area and one reference station approximately 500 meters distanced from the cages.

Parameters investigated in the water column were: temperature, salinity, density of the seawater, transparency, suspended matter concentration, pH, oxygen saturation, dissolved silicate concentration, inorganic and organic nitrogen and phosphorus concentrations as well as phytoplankton biomass. Parameters measured in the sediment were: granulometric and organic matter content, organic carbon and total nitrogen content, sediment redox-potential, inorganic phosphorus species concentration (biogenic apatite P, authigenic apatite P, detrital apatite P and P bound on to iron oxides and hydroxides) and organic phosphorus.

There were no significant changes in nutrient concentrations and oxygen saturation in the water column during investigated periods and concentrations remained in the range usual for middle Adriatic, while phytoplankton biomass showed enhanced chl a concentration at cage station in relation to referential station (0.352 and 0.194 mg dm<sup>-3</sup>), respectively.

Significant enhancement was determined for sediment inorganic P concentrations which ranged from 3.9 to 38.2, while organic P ranged between 0 and 6.7 mmol g<sup>-1</sup>. SEDEX method showed enhancement of all P species, except detrital P, from 1.6 to 4.1 times higher in sediment of cage station in relation to referential station. Total nitrogen and organic carbon content ranges were between 0.01–0.26% and 0.339–1.291%, respectively. These values are in range of middle Adriatic values, but lower than ranges reported for some tuna farms at this area.



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## INFLUENCE OF DIFFERENT KINDS OF ORGANIC MATTER ON SOIL REDUCING CONDITIONS AND ON THE DEGRADATION OF PHENANTHRENE.

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Soil redox potential is a key parameter in environmental soil chemistry as it strongly influences the speciation and solubility of inorganic pollutants and the degradation of organic contaminants.

Soil organic matter is an important factor in determining the onset of reducing conditions, as it represents the main electron donor in soils. Different kinds of organic matter may have a diverse influence on soil redox potential, according to their molecular weight, electron-transfer capacity, and availability to microorganisms.

Microorganisms can use organic contaminants as substrate for energy and growth, converting them into harmless products. The organic pollutants can be used by the microorganisms as energy and carbon source and in anaerobic conditions as electron donors.

Among organic pollutants, polycyclic aromatic hydrocarbons (PAHs) are of particular concern due to their persistence in soils and their recalcitrance to microbial degradation. While the processes of aerobic degradation of organic pollutants are relatively well described in the literature, only a few studies are available on the dynamics of PAHs in reduced soil systems.

Aim of this study was to evaluate the influence of different kinds of organic matter (humic acids, dissolved organic matter, sewage sludge, glucose and native soil organic matter) on soil redox potential and on the degradation of phenanthrene.

Four soils (urban, agricultural and natural) were selected for this experiment. A portion of these samples was pre-treated with H<sub>2</sub>O<sub>2</sub> to remove the organic matter. The first round of experiments was conducted both with oxidized and untreated soil. Samples were submerged by a CaCl<sub>2</sub> solution in dark-glass bottles, under an oxygen-free atmosphere. An inoculum, obtained from a submerged paddy-soil, was added to all samples. Different electron donors were also added to each bottle (humic acid, dissolved organic matter, glucose, sewage sludge). The progress of the reducing conditions was monitored measuring Eh, pH, Fe(II) after 4h, 24h, 48, 72h, 168h, 264h and 312h from the beginning of the experiment. The second round of experiments was conducted using the same methodological approach, but with the addition of phenanthrene to the samples. The degradation of phenanthrene was monitored by measuring its concentration in solution at different time intervals.

Results show that different kinds of organic matter influence the redox potential of soils in different ways. The time needed to reach a threshold value of Eh is different as well as the final potential value. The pH varies accordingly. Phenanthrene degradation appears to be highly dependent on the microcosm characteristics.



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## GENERATION OF AN EMISSION INVENTORY FOR TURKEY

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Emission Inventories are important tools in order to set environmental policies on air quality and control. There are several international conventions that oblige the parties to submit emission inventories to the executive boards. Turkey is also a party to Long Range Air Pollution Convention, and United Nations Framework Convention on Climate Change which oblige Turkey to submit emission inventories to the executive boards of the conventions.

Objective of this study is to generate an emission inventory for Turkey based on the pollutants which cause eutrophication, acidification, and ground level ozone pollution. These pollutants are SO<sub>2</sub>, NO<sub>x</sub>, VOCs and NH<sub>3</sub>. Since PM10 is an important conventional pollutant that significantly impact human health, it is also included in this study. Data of mobile sources, small combustion processes, large combustion plants, and important industrial processes which affect environment significantly have been collected where available. So that emission inventory is only based on anthropogenic sources. Available data has been assessed and this data has been used as the base of the study.

Collection and assessment of the data was an important step of the study. Many different references and methodologies have been used to calculate the activities and finally the emissions. Fuel consumption data is the base of the study although production capacities have been considered for industrial processes. So that, top down approach and bottom up approach combined together in this study. Emission factors which were necessary to estimate emissions are provided by COPERT III for mobile sources and IIASA Rains Online Model for other sources.

This study shows the relevant sectors for different pollutants which can be an important indicator to realize the most important sector causing air pollution and to define the abatement technologies for this sector. Also fuel quality which consumed in Turkey has been assessed and can be evaluated as an important beginning point for emission abatement.

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Results show that the highest pollution in share occurs in the major metropolitan provinces in Turkey which are Istanbul, Ankara, Izmir. Also cities which have a thermal power plant have high SO<sub>2</sub> emissions. As a result of this study 630 kt/a NO<sub>x</sub>, 1050 kt/a PM<sub>10</sub>, 750 kt/a VOC, 110 kt/a NH<sub>3</sub>, 2400 kt/a SO<sub>2</sub> emissions have been estimated for year 2003. Mobile sources are the most important reason of NO<sub>x</sub> pollution where PM<sub>10</sub> emissions are mainly caused by industrial processes, SO<sub>2</sub> emissions are mainly caused by thermal power plants, NH<sub>3</sub> emissions are caused by agriculture and VOC emissions by solvent use. The calculations will be updated as new data become available and the study is going to be revised according to the new results.

Keywords: Emission Inventory, Air Quality

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Mn was found in the acid-soluble fraction at percentages of 40-50%. The high proportion of Mn in that fraction implies that Mn is bound to carbonates. Pb is the element showing the highest proportion (up to 60%) in the reducible fraction, especially in samples from the central part of the gulf indicating that lead is mainly bound to oxides.

The metals studied can be ranked as follows according to the percentage of each in the first three fractions (more mobile and bioavailable): Pb > Cd > Mn > Cu > Zn > Fe > Cr.

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## ANALYSIS OF AN AIR POLLUTION EVENT OVER THE ALGERIEN COAST WITH THE AID OF THE SKIRON-CAMx MODELS

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Air pollution and photochemistry in the atmosphere are complicated processes that define air quality standards in urban and remote locations. This is especially true in areas with complicated physiographic characteristics (rough terrain, coastal areas, vegetation variability etc). Mediterranean Region is characterized for its topographic variability and distinct climatic characteristics. These regional and local climatic characteristics are favour of photochemical processes and smog formation. The location of sources (anthropogenic and/or natural) is in favour of multi-scale transport that is responsible for air quality problems in several locations. Most of the anthropogenic sources are located in Europe while the natural ones have their origin in North Africa (desert dust) and Mediterranean waters (sea salt, dimethyl sulphate). Ozone and aerosol formation in the Mediterranean Region is a major problem for many places not only urban. The large increase in background of tropospheric Ozone concentration is mainly due to transport of long-range and anthropogenic emission of gases leading to ozone formation, the so-called ozone precursors (NO<sub>x</sub>, CO, CH<sub>4</sub> and VOCs ). Meteorological and air pollution modelling are useful tools to study such complicated phenomena and develop scenarios for improvement.

The main objective of this study is the combined use of the SKIRON meteorological model together the CAMx photochemical one in order to study transport and transformation phenomena in West Mediterranean and the Northern coast of Africa. The modeling exercise is focusing on the analysis of the air pollution episode of 28/7 – 1/8/06 occurred along the Algerian coast.

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## SOLID-PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION FOR MULTIRESIDUE DETERMINATION OF PESTICIDES IN WATERS

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Pesticide contamination of surface and ground water from agricultural use has been well documented around the world. The widespread use of pesticides in agricultural and non-agricultural purposes has resulted in the presence of their residues in various environmental matrices. Thus, their residue analysis in environmental samples has received increasing attention in the last few decades, resulting in many environmental monitoring programs on a broad range of pesticides. Studies involving the determination of pesticides in environmental matrices often deal with samples with low analyte concentrations containing high number of interfering compounds. Thus, simple and highly sensitive analytical techniques are required to detect and quantify pollutants in water at trace levels.

As it is already known, the determination of pesticides by chromatographic techniques requires an extensive and time-consuming step of sample preparation, previous to final concentration. This step usually includes an extraction step (liquid-liquid extraction (LLE), supercritical fluid extraction (SFE) or solid-phase extraction (SPE)) as well as cleanup procedure in order to obtain a final extract fully compatible with the chromatographic determination.

The last years, several authors point out the need for a major simplification in the sample preparation accounting for a miniaturization in scale, which will also result in a reduction of time and solvent consumption. Solid phase microextraction (SPME) developed by Pawliszyn and co-workers is a recent sample preparation technique that is proving increasingly useful in analytical chemistry and presents some of the characteristics outlined before as primordial in new sample preparation strategy. The method eliminates the use of organic solvents, has the advantage of simplicity and integrates sampling, extraction, concentration and sample introduction into a single solvent-free step. SPME technique has been successfully employed to analyze a wide range of pollutants, such as BTEX (benzene, toluene, ethylbenzene and xylene), polycyclic aromatic hydrocarbons (PAHs) and polycyclic biphenyls. Pesticides have also been determined by SPME in different matrices like wine fruits, soils, honey, biological fluids and aqueous samples.

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In the present work, a solid-phase microextraction (SPME) method for the simultaneous determination of a large number of pesticides ( $\alpha$ -endosulfan,  $\beta$ -endosulfan, esfenvalerate, bromopropylate, tetradifon, bifethrin, dicofol, fluvalinate, trifluralin, ofurace, quinoxifen,  $\lambda$ -cyhalothrine,  $\gamma$ -chlordane, chlozolinate, heptachlor, acrinathrine,  $\delta$ -HBC) with a wide range of polarities and chemical structures (organochlorine, pyrethroids, acetamides, quinoline, trifluoromethyl and others) in water samples by GC-ECD has been developed. To perform the SPME, five types of fibre have been assayed and compared: Polyacrylate (PA 85  $\mu\text{m}$ ), and polydimethylsiloxane (PDMS 100  $\mu\text{m}$ ), polydimethylsiloxane/divinylbenzene (PDMS-DVB 65  $\mu\text{m}$ ), carboxen/polydimethylsiloxane (CAR/PDMS 75  $\mu\text{m}$  and 85  $\mu\text{m}$ ). The main parameters affecting the SPME process such as extraction time, salt additives, memory effect, stirring rate and desorption conditions were studied. The selected conditions were: a 100  $\mu\text{m}$  polydimethylsiloxane (PDMS) fibre, 60 min of extraction time, sample agitation (960 rpm), pH (4) and ionic strength (15% w/v). Good detection limits, linearity and repeatability were obtained with this method for all the pesticides studied. The method was validated for all the pesticides following the recommendations of the international norm ISO/IEC 17025 including the calculation of the uncertainties. The detection limits were below 0.1  $\mu\text{g/L}$  which is the maximum limit set by the European Union for each pesticide. Furthermore, repeatability (<14%) and intermediate precision (<17%) were shown to be satisfactory. To validate matrix effects for drinking and surface water (river water, sea water and lake water) analytical recoveries were calculated for these matrices. The results demonstrate the suitability of the SPME method for routine screening multiresidue analysis in natural waters.

**Keywords:** Pesticides, Solid-phase microextraction (SPME); Gas chromatography–electron capture detection (GC–ECD); Method validation; Uncertainty; Water analysis.

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## PASSIVE SAMPLING TECHNIQUES FOR MONITORING VETERINARY PHARMACEUTICALS IN AQUACULTURE ENVIRONMENTS

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Environmental monitoring programs for water quality control is one of the most important issues in marine aquaculture. Commonly used monitoring systems usually record only pollutant concentrations at a specific point in time by collecting spot or bottle samples. Passive sampling, widely used to monitor air pollutants, has been gaining acceptance for monitoring organic contaminants in water. Contrary to grab sampling, passive sampling is less sensitive to accidental extreme variations of the organic pollutant concentration in natural waters and is suited to the determination of time-weighted average concentrations of the pollutants. Passive sampling is based on free flow of analyte molecules from the sampled medium to a collecting medium (liquid or solid) as a result of a difference in chemical potentials. Over the past 10 years passive sampling devices have been developed that accumulate organic micropollutants and allow detection at ambient sub ng/l concentrations.

This work deals on the use of passive sampling devices for screening fish farming chemotherapeutics in seawater. A validation study of passive sampling devices as effective tools in environmental monitoring programs for fish farm cage systems is addressed by determining the capability to detect trace levels of veterinary pharmaceuticals and sampling rates. The "pharmaceutical" configuration of Polar organic chemical integrative samplers (POCIS) consisting of a hydrophilic microporous membrane enveloping a single solid-phase sorbent (Oasis HLB) were tested in the present study. Liquid chromatography coupled with diode array (DAD) and mass spectra (MS) detection is used for the determination of medicinal compounds. Despite the wide application of passive samplers, calibration data that relate sampling rates of chemicals to their aqueous concentrations are rare. Finally, the application of passive sampling in a field study was conducted by monitoring of veterinary pharmaceuticals concentrations in two different fish farms situated in Northwestern Greece near Igoumenitsa.

Keywords: seawater quality control, veterinary pharmaceuticals, passive sampling devices, aquaculture

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## TiO<sub>2</sub> PHOTO CATALYTIC DECOMPOSITION OF BIOCIDES

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The use of semiconductor photocatalyzed degradation of organic and inorganic substrates as a method of treatment of wastewater pollutants is currently attracting considerable attention. Earlier studies have shown that a wide range of organic substrates can be completely photomineralized in the presence of TiO<sub>2</sub>. A wide variety of pesticides are nowadays introduced into the water system from various sources, such as industrial effluents, agricultural runoff and chemical spills [1]. Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to societies and regulating authorities around the world.

Most aromatic molecules undergo photocatalytic degradation when irradiated in the presence of suitable semiconductors. The most commonly used catalyst is TiO<sub>2</sub> (cheap, non toxic and abundant product). The initial step of the transformation is the formation of electron-hole pairs in the semi-conductor particles when irradiated with light or energy higher than the band-gap. Photocatalytic degradation occurs through a multi-step process involving the attack of the substrate by radical species, among which the OH radical is recognized to be the most powerful oxidant [3]. In most cases the final stoichiometric oxidation of organic carbon to CO<sub>2</sub> is achieved. However, the evaluation of the mineralization degree achieved for the organic pollutants after treatment is necessary. If only partial degradation is envisaged, toxicity assessment of treated water becomes necessary. Several rapid and established methods for direct acute toxicity assessment are available. Among them Microtox is especially rapid and reliable. Chlorothalonil and dichlofluanid are fungicides with protective action that are widely used in order to control many fungal diseases of plants worldwide. In the last few years both compounds have been also used as alternative to tributyltin (TBT) active ingredients in antifouling products. The continued input of the above pesticides has led to reports of elevated concentrations in natural waters (fresh and marine) and sediments posing a risk to aquatic life. Therefore the protection of water resources requires effective micropollutants degradation technologies that allow their removal in a fast and low-cost manner. The objectives of the present study were: i) to evaluate the kinetics of chlorothalonil and dichlofluanid disappearance, ii) to monitor the evolution of CO<sub>2</sub> and of the main inorganic ions produced during the process, iii) to measure the toxicity of the long-lived transformation products and iv) to determine the main transformation products formed.



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The photocatalyzed degradation of the biocides chlorothalonil and dichlofluanid has been investigated in aqueous suspensions of titanium dioxide under simulated solar irradiation. The primary degradation of the micropollutants follows a pseudo-first-order kinetics following the Langmuir-Hinshelwood model. In our conditions total disappearance of chlorothalonil and dichlofluanid was achieved in 90 and 20 min respectively whereas the mineralization of organic carbon to carbon dioxide after 240 min of irradiation was found to be 100% for chlorothalonil and 78% for dichlofluanid. The evolution of heteroatoms (Cl, N, S, F) followed by ion chromatography showed a mineralization into chloride, nitrate, sulfate and fluoride anions respectively. In addition Microtox bioassay (*Vibrio fischeri*) was employed in evaluating the ecotoxicity of solutions treated by photocatalysis. Photocatalytic intermediates detected during the degradation of biocides were identified by GC-MS techniques. Based on this byproduct identification a simple degradation scheme was proposed for both biocides including dechlorination, hydroxylation, dealkylation and decarboxylation leading to the mineralization of the starting molecules.

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## THE CONTAMINATION OF AMVRAKIKOS GULF COASTAL LAGOONS BY ORGANIC MICROPOLLUTANTS

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The contamination of transitional ecosystems by modern pesticides and persistent organic pollutants (such as organochlorine pesticides (OCPs) and PCBs) is of great concern. Thirty-five modern pesticides from various chemical groups were analyzed in water and surface sediment samples from three coastal lagoons (Logarou, Tsopeli, Rodia) of Amvrakikos Gulf. Additionally, twenty-one OCPs and seven target PCBs were analyzed in sediment samples. Analysis of water samples was performed by solid phase extraction SDB-RPS disks while sediments were extracted by ultrasonication followed by clean-up in alumina-activated copper columns.

Analysis of water samples indicates contamination mainly with organophosphorus compounds such as dimethoate (up to 182 ng/l), dichlorvos (up to 156 ng/l), mevinphos (up to 138 ng/l) and malathion (180 ng/l) while herbicide residues were found lower (e.g. up to 76 ng/l for metolachlor and 45 ng/L for propachlor). Low levels of pesticides (up to 6.7 ng/g for parathion methyl) were monitored in sediments. Total maximum concentrations of OCPs in Logarou, Tsopeli and Rodia sediment samples were 28.3, 20.4, and 26.7 (ng/g dry weight), respectively. Finally, PCB levels in sediments never exceeded 1.4 ng/g dw for the sum of seven target congeners. Surface run-off is the main transport pathway for modern pesticides residues and for past applications of OCPs while atmospheric deposition are considered as additional and main pathway for the introduction of OCPs and PCBs respectively, into the lagoons.

A preliminary assessment was performed to examine the water and sediment quality and potential risk to the aquatic species of Amvrakikos lagoons. Existing sediment quality guidelines and water quality criteria were used for this reason. The results showed that maximum concentration of certain OCP residues are above the recommended threshold values for the protection of aquatic life and might pose a threat to the health of the most sensitive marine inhabitants. Finally, all the sediment samples were below the prescribed ecotoxicological assessment criteria level for the sum of PCBs.

Keywords: Pesticides, Persistent organic pollutants, Amvrakikos Gulf lagoons, Greece

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## DETERMINATION OF THE TOTAL CONCENTRATION AND SPECIATION OF METAL IONS IN RIVER, ESTUARINE AND SEA WATER SAMPLES

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The geochemical cycling, the distribution in the environment and the bioavailability of trace metal ions depend on their chemical speciation. Metal species formed by inorganic and organic ligands, at relatively high concentration and with weak complexing properties, determine an important fraction, very reactive, with high mobility and usually high toxicity. Other ligands, present at low concentration, even at nM level, may be also important when they are very strong. In fact, although present at the concentration similar to that of the trace metal ion, they drastically decrease the free metal concentration, by several magnitude orders.

The Resin Titration is a method developed in our laboratory<sup>1,2</sup> to investigate the speciation of metal ions at trace level in complex matrices. It is a competition method, in which the competing agent is a solid, i.e. a complexing resin. It was proved to be particularly useful in the detection and characterization of strong ligands in natural samples at low concentration<sup>2</sup> because of the very high competition strength of the complexing resins used. Ligands of this kind are of particular relevance for trace metal ions in the environment and they have been detected in high and low salinity natural waters. The RT method can be used for the speciation of many metal ions simultaneously, since it does not require the addition of the titrant metal. A positive feature of the RT method is that it is based on the sorption of the metal ion on the resin, and determination of the concentration of sorbed metal ion after elution. In this way, many of the interferences of the final detection method are eliminated.

In the present investigation the RT method is proposed for the determination of total concentration and speciation of Cu(II), Pb(II), Al(III), U(IV) in river, estuarine and sea waters. These samples are collected during a cruise in Adriatic sea, in a transect between the mouth of Po River (locality Po di Goro) and the Central Adriatic, along the plume, direction East-South East. For each sample two RT were performed, on board immediately after sampling and using different complexing resins: the iminodiacetic Chelex 100 and the carboxylic Amberlite CG50. This allow to examine different competition strength, and to better detect different ligands. The results obtained are treated by Principal Component Analysis (PCA), considering the variables: pH, temperature, salinity, conductivity, the total metal ion content, measured directly and the total metal ion obtained from RT with Chelex100, the concentration of the weakly complexed metal, the concentration of the strong complexes for all the considered metal ions.

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## STUDY OF ATMOSPHERIC NITRATED AND OXYGENATED POLYCYCLIC AROMATIC HYDROCARBONS IN THE MARSEILLES AREA (FRANCE)

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The objective of this study was to characterize the nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons (NPAHs and OPAHs) in the Marseilles area (South of France), and to identify the main primary and/or secondary sources of these contaminants. Atmospheric concentrations of these classes of compounds are great of interest because of their high potential mutagenicity and carcinogenicity.

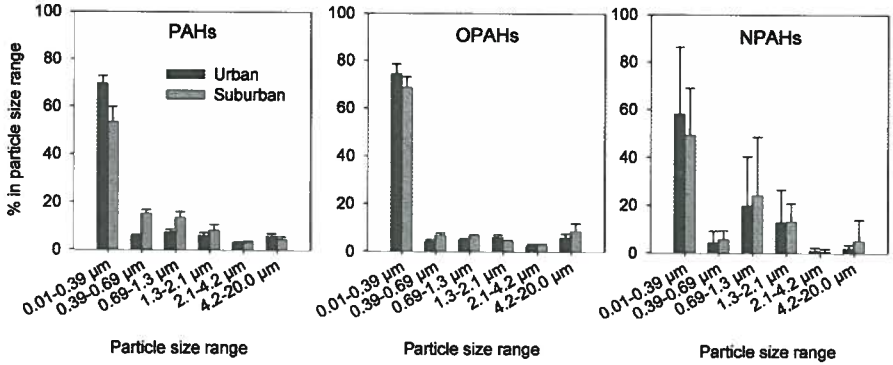
Samplings were performed during July 2004 on three different sites (urban, sub-urban and rural). Both, ambient air particulate and gas phases were collected and particle size distribution was also studied.

Results show that total PAH and OPAH concentrations (gas + particulate phases) were in the same order of magnitude (0.7 to 30.1 ng m<sup>-3</sup>) whereas NPAH concentrations were one to two orders of magnitude lower (10 to 1260 pg m<sup>-3</sup>).

At both urban and sub-urban sites, PAHs and NPAHs were mainly associated with fine particles (D<sub>p</sub><2.1 μm) (Figure 1). OPAHs with molecular weights between 156 and 208 g mol<sup>-1</sup> were distributed between the fine and coarse particles. OPAHs with molecular weight >230 g mol<sup>-1</sup> were associated primarily with the fine aerosol fraction (>90%). The fact that these toxic compounds were mainly associated to the fine particles is an important information regarding to risk assessment.

Study of source specific ratios (2-nitrofluoranthene/1-nitropyrene) clearly showed those primary NPAH sources influence the urban and sub-urban sites whereas production of secondary NPAHs by gas phase reactions was prevalent at the rural site. The study of NPAH and OPAH sources suggested that gasoline engines were an important source of such compounds whereas the dominant source of 1-nitropyrene, 2-nitrofluorene, 6-nitrochrysene and benz[a]anthracene-7,12-dione seems to be diesel vehicles. Finally, 9,10-anthraquinone presents a double origin: primary diesel emission and photochemical processes.

Figure 1: Average PAH, OPAH and NPAH concentration fractions in the different particle size ranges for the urban and suburban sites.



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## EMISSION INVENTORY FOR THE EVALUATION OF URBAN AIR POLLUTION IN ESKISEHIR, TURKEY

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Urban air pollution, which becomes a serious public health and environmental problem especially in mega-cities of developing countries, is an issue of common concern. Many people living in big cities are exposed to high levels of air pollution during their daily activities. Rapid urbanization and industrialization are the most important causes of this problem. Assessing the quality of ambient air in a region by studies such as emission inventories, monitoring and modelling studies is important for fully understanding the present situation and formulating policies to control the pollution.

Estimation of air pollutant emissions from various sources in a given area by preparing emission inventories is a widely used technique and a valuable tool when sufficient and reliable data are available. Emission inventory studies have been carried out in Eskisehir, which is a rapidly developing intermediate size (approximately 570,000 inhabitants) Turkish city, since 1989.

In this study, an emission inventory for the 123 k m<sup>2</sup> area region which covers 65 districts (101 k m<sup>2</sup>) in the centre town and an industrial region (22 k m<sup>2</sup>) in Eskisehir was prepared for fossil fuel combustion related emissions for 2006. This inventory includes five common air pollutants which are particulate matter (PM), sulphur dioxide (SO<sub>2</sub>), carbon monoxide (CO), volatile organic compounds (VOC) and nitrogen oxides (NO<sub>x</sub>). Data about population, residential fuel consumption, heating system characteristics for every district and data about registered counts of vehicles and industrial fuel consumption rates for the study area were acquired. By using these data together with the suitable emission factors, the annual emission mass flow rates (ton/year) of each pollutant were calculated for the selected area, line and point sources. Also pollution maps indicating spatial distribution of the emissions (in tons/ k m<sup>2</sup>-year) in the study area were generated by using Geographic Information Systems.

The inventory results being interpreted in terms of per capita basis were 1.3 kg/capita-year, 3.8 kg/capita-year, 13.1 kg/capita-year, 0.7 kg/capita-year and 4.9 kg/capita-year for PM, SO<sub>2</sub>, CO, VOCs and NO<sub>x</sub>, respectively. As compared to the data of some cities in Turkey and in the world having similar populations, the air quality in Eskisehir may be considered moderate and the differences in rates of pollutant emissions may be caused by the differences in their climatic and topographical conditions. Residential heating appeared to be the most important source for the formation of PM, SO<sub>2</sub> and CO emissions with the contribution of 84%, 68% and 79%, respectively. Consumption of hard coal and lignite with high sulphur and ash content for residential heating played an important role in the formation of these three pollutants emissions. Traffic is the major source of the VOC and NO<sub>x</sub> emissions with the contribution of 56% and 51%, respectively. Share of industrial combustion related emissions is less than 10% for all pollutants except NO<sub>x</sub> as only natural gas is used in the industrial region. When compared to the emission inventory and monitoring results of the previous years, it is observed that the use of natural gas for heating and industrial activities starting from 1994 instead of coal provided considerable improvement in air quality of the city.

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## LEACHING BEHAVIOUR OF SINTERED CONTAMINATED MARINE SEDIMENTS

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The incorporation of waste materials into the production cycles is an interesting alternative in the modern industry, which leads to an economical profit and considerable reduction in environmental impact. The incorporation of waste materials in brick manufacturing has become more and more established. Marine sediments can be used as clay replacement in ceramic processes to obtain building materials. During the sintering process, organic contaminants are oxidized and metal contaminants are either converted to stable immobile compounds or volatilized.

Sediments from Santander and Suances Cantabrian estuaries (Northern Spain) have been previously characterised by different chemical and ecotoxicological parameters in order to study the pollution of these coastal areas. Sediments from both estuaries contain significant concentrations of heavy metals and organic pollutants derived from intensive industrial, agricultural and urban activities, making necessary treatment and confined disposal to manage them properly. Previous works have shown that it is possible to obtain dense sintered compacts from highly contaminated marine sediments dredged from Cantabrian estuaries. Composition, thermal and technological behaviour of sintered ceramic bodies from contaminated sediments were evaluated. It can be concluded that studied marine sediments can be used as secondary raw materials from ceramic brick by powder technology. The aim of this work is to assess the environmental risk of produced ceramic bodies by means of the equilibrium leaching tests proposed in European Directive on the landfill of waste at end-life step as granular material (disposal scenario). The fired samples were subjected to the Compliance Leaching Standard Tests EN 12457 1-2 using different liquid to solid ratios ( $L/S=2$  and  $10$ ). The leachates were analyzed in order to determine the requested chemical parameters. The results showed a low mobility of pollutants in relation to proposed limits for disposal in inert waste landfills. Therefore, the environmental risk of the analyzed fired samples can be considered very low.

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## SUSTAINABLE MANAGEMENT OPTIONS FOR CONTAMINATED SEDIMENTS AND DREDGED MATERIAL

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Sediment quality assessment should be carried out through the application of tiered decision-making frameworks which involve measurement of multiple lines of evidence (e.g. chemistry, acute or chronic toxicity, in situ benthic community alteration, biomagnification) in sequential steps. When the decision reached after the application of these frameworks is that the sediments could pose an environmental risk, the need to remediate the contaminated sediments in a sustainable way arises.

Remediation and management of contaminated sediments and dredged material is often difficult due to the complex mixtures of chemical pollutants that usually impact the sediments. The selection of the best option that leads to the sustainable management of the sediments of a site is not an easy task, and it should be based on the integration of technical, economic, social and environmental criteria. The involvement of stakeholders is of crucial importance to achieve successful results in the decision-making process of management and treatment alternatives.

In this work, the main alternatives for the management of contaminated sediments and dredged material are analysed, including no action (i.e. natural remediation), capping, in situ treatments, ex situ treatments or confined disposal. The principal characteristics, applicability and limitations of these methodologies have been compiled and compared. A hierarchical sequence of preferred management and destination options for sediments and dredged material, summarising the recommendations of international organizations and relevant experts in the field, is also proposed.

Special emphasis has been given in this study to the presentation of possible beneficial uses of dredged material. Although beneficial use of products of dredged material is not common currently, several examples of the utilisation of techniques for sediment treatment that finally allows the beneficial use of the material (e.g. as construction material, in bricks or ceramic products, or as manufactured soil products) can promote this management option. A summary of the results obtained by our research group about the use of contaminated sediments as substitute of raw materials in the ceramics production is also presented.

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## DISTRIBUTION AND SOURCE OF TRACE METALS IN COASTAL WATER OF THE BAY OF TANGIER (NORTH WEST MOROCCO)

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The bay of Tangier is located in North West Morocco, on the southern of the Strait of Gibraltar. This bay is rimmed by a beach of about 5 km in length, being a very important tourist and bathing site. This beach is affected by the discharges of Grand Canal water that receives many inputs from industrial estate of Tangier, causing deterioration of water quality.

In this paper, the results of monitoring of contamination originated by effluents of industries from Tangier are presented. Sediment and water samples from Grand Canal were collected at twenty stations, characterized and several metals were analysed (Fe, Mn, Cu, Cd, Zn, Pb, Ni, Co, Hg, Ba and As). The concentration of the metals in labile sediment fractions was determined as a means of assessing bioavailability, using ammonia acetate as leaching extractant.

As consequence of the obtained results, water samples of eight stations were collected along the bay of Tangier in order to evaluate the influence of the discharges in the coast. Dissolved and particulate metals were determined in order to evaluate the adsorption capacity of the suspended matter and the incorporation of metals to the solid phase of the ecosystems.

Metals from water were determined by differential pulse anodic or cathodic stripping voltammetry (DPASV or DPCSV) and metal from sediments were determined by atomic spectroscopy (ICP-AES, GF-AAS and cold vapour-AAS).

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## EFFECT OF THE ORGANIC AND MINERAL FERTILIZATION ON THE PERSISTENCE OF CHLORTAL-DIMETHYL IN SOIL UNDER LABORATORY CONDITIONS

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It is studied the behaviour of the herbicide chlortal-dimethyl in a characteristic soil of the region of Murcia (Southeast Spain) with low organic content and lime, located in Cehegín (Murcia). And also, the effect of the sterilization and the organic and mineral fertilization could have on its degradation. The determination of the herbicide was carried out by gas chromatography, electron capture detector, non-polar capillary column and programmed temperature. The extraction was carried out by an online micromethod using acetonitrile as extractant. The analytical methodology was validated according to SANCO recommendations reaching a limit of quantification of 0.005 mg/kg.

The study was carried out in soil under four different conditions: without fertilization (WF), sterilized (SE), with liquid organic fertilization (SOF) and fertilized by a fertilizing mixture of organic and mineral matter (SMF). The tests were carried out at two concentrations in order to determine if the initial level influenced the eliminated percentage of the herbicide 66 days after the test.

The mineral and organic fertilization provokes a higher dissipation of the herbicide. Tables I and II show the results of the evolution of the herbicide at the conditions mentioned. The half-life times corroborate the influence of the fertilization on its dissipation.

**Table I.- Evolution of the residual content of chlortal-dimethyl in the four soils (initial concentration 0.5 mg/kg).**

Days	SE	WF	SOF	SMF
0	0.496	0.499	0.491	0.479
2	0.467	0.459	0.459	0.451
4	0.475	0.486	0.418	0.420
7	0.469	0.462	0.378	0.396
15	0.454	0.459	0.350	0.342
24	0.443	0.424	0.279	0.261
36	0.429	0.409	0.237	0.213
51	0.407	0.402	0.210	0.161
66	0.348	0.341	0.100	0.062

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**Table II.- Evolution of the residual content of chlortal-dimethyl in the four soils (initial concentration 2 mg/kg).**

<b>Days</b>	<b>SE</b>	<b>WF</b>	<b>SOF</b>	<b>SMF</b>
0	1.966	1.971	1.902	1.975
2	1.978	1.940	1.405	1.425
4	2.068	1.913	1.174	1.204
7	1.834	1.860	0.994	0.836
15	1.737	1.700	0.785	0.638
24	1.673	1.635	0.633	0.598
36	1.556	1.483	0.625	0.536
51	1.516	1.377	0.575	0.481
66	1.500	1.271	0.553	0.314

Concentrations expressed in mg/kg.

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## PERSISTENCE OF CHLORTAL-DIMETHYL IN DIFFERENT AQUATIC SYSTEMS

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It is studied the degradation of the residual and non-systemic herbicide chlortal-dimethyl in four types of water properly characterized: Milli-Q water; depurated water from an EDAR (Waste Water Treatment Plant) located in Murcia; water from the Mediterranean Sea, collected in La Llana beach (San Pedro del Pinatar, Murcia) and drinking water from the tap (Murcia). The determination of the herbicide was carried out by gas chromatography, electron capture detector, non-polar capillary column and programmed temperature. The extraction was carried out by an online micromethod using dichloromethane/acetonitrile as extractant. The analytical methodology was validated according to SANCO recommendations, reaching a limit of quantification of 0.0025 mg/l.

The study was carried out in two series of water samples spiked at two concentrations (0.5 and 2 mg/l), one of them exposed to solar radiation and the other one stored at dark. In both cases samples were periodically analysed to 44 days.

According to the statistical parameters obtained by linear regression, it can be inferred that the first-order kinetic model used is valid to describe the dissipation and persistence of the herbicide chlortal-dimethyl in the different types of water studied.

In relation to the dissipation of the herbicide in the proposed conditions (presence or absence of solar radiation and initial concentration), the highest dissipation of chlortal-dimethyl residues takes place in the sea water. Besides that, the higher concentration of dissolved solids in the types of water, the higher elimination of the pesticide.

In all the types of water studied, it is observed an important effect of solar radiation on the pesticide dissipation. This effect increases with the presence of dissolved solids, since some of these compounds induce an indirect photolysis because they act as photocatalyzers. The higher initial concentration of the pesticide, the higher disappearance.

A relevant part of the herbicide dissipation studied is produced by a direct photolysis (capture of luminic energy by the herbicide) as it is showed in the Milli-Q test, where a higher degradation is produced in presence of solar radiation, even without photocatalyzers (indirect photolysis) which can influence the photodegradation.

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## PRELIMINARY RESULTS ON PM1 AND PARTICLE - BOUND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN KOZANI, GREECE.

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During the last decade there is an increased concern on atmospheric pollution in areas suffering from major air quality problems, such as Kozani, Greece, due to the operating lignite- fire power station and their mining activities<sup>(1)</sup>. Recent epidemiological studies and research on the mutagenic effects of airborne particulate matter focused on the adverse health effects of fine and ultra fine particles (PM1) as they could enter deep into lungs and they are carriers of various toxic substances<sup>(2)</sup>. As a consequence of the growing interest in PM1 and the insufficient data, more and more studies paid attention on this mass fraction.

This study was therefore conducted to provide information for PM1 concentrations as well as the chemical composition of the above mentioned fraction regarding polycyclic aromatic hydrocarbons (PAHs). The sampling site was located in the campus of University of West Macedonia (UOWM) which is approximately 0.5 Km far from city centre. The sampling platform was placed at the roof of the building (at a height of approximately 10 m). PM1 was collected during January 2007 for one week, using low volume pumps and Teflon Filters of 47 mm. The analysis of the filters for PAHs concentration was conducted at the Environmental Technology Laboratory, UOWM using Gas Chromatography Mass Spectrometry (GC- MS). Meteorological parameters (temperature, pressure, relative humidity and wind speed and direction) were available from the meteorological station located at the University.

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## REMOVAL OF LINDANE AND DIELDRIN FROM AQUEOUS SOLUTIONS BY MONTMORILLONITE AND BENTONITE AND OPTIMIZATION OF PARAMETERS

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In Turkey, different pesticides are widely applied in agricultural activities. The need to remove these toxic compounds from the environment and to reduce the dispersion of pollutants, different clays can be effectively used as an alternative adsorbant to activated carbon which is used commonly. In this study montmorillonite and bentonite clays were used to adsorb lindane (g-BHC) and dieldrin, by a batch equilibration technique from different water medias. The study was carried out as functions of contact time, pH, initial lindane and dieldrin concentrations, amount of monmorillonite and bentonite and adsorption isotherms were obtained as Freundlich and Langmuir Isotherms. Besides, clays were modified to increase their adsorption capacity.

Determination of lindane and dieldrin, in water samples were carried out according to EPA Method 3510C liquid-liquid extraction (LLE). The adsorption was followed by GC equipped with  $\mu$ -electron capture detector ( $\mu$ -ECD). The features and operating conditions of GC-  $\mu$ -ECD system was as follows: GC Agilent 6890 N, HP-5 % phenylmethyl siloxane fused silica capillary column (30 m length, 0.32 mm i.d. and 0.25  $\mu$ m film thickness). The split/splitless injector was set at 250 oC and operated in the splitless mode (purge delay 1 min, purge flow 30.1 mL/min). Detector temperatures was 320 0C. Splitless injection was performed by an Agilent 7683 B Series automatic injector. The detector response was linear in the range of concentration 0.01-10 ng  $\mu$ L<sup>-1</sup> for OCPs, and the correlation coefficients for the studied compounds were found 0.999. LODs of lindane and dieldrin were found 0.22 pg/ $\mu$ L and 0.83 pg/ $\mu$ L, respectively and relative standard deviation lower than 4.2% was found for  $\mu$ -ECD. The experiments demonstrated that adsorption capacities of clays are decreasing with higher pH values and montmorillonite clay is a better adsorbant than bentonite clay.

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## ASSESSING URBAN AIR POLLUTION VARIATION IN TURKEY BY GIS

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Turkey is undergoing rapid industrialization, urbanization, and population growth as a developing country and has high atmospheric emissions due to excessive use of fossil fuels, low quality coal and fuel-oil consumption and exhaust gases emitted by transportation vehicles. Air pollution is becoming a great environmental concern in the country and it is essential to monitor air pollutants in large areas and take strict measures.

The aim of this study is to determine the air quality variation in Turkey in terms of SO<sub>2</sub> and PM (particulate matter) concentrations. The study was carried out for some selected industrialized and densely populated city centers from different regions in the country. Spatial map of average PM and SO<sub>2</sub> concentrations were prepared by using Geographic Information Systems (GIS) with ESRI Arc View GIS. Spatial data was evaluated with Turkish and European Union limit values. The average yearly SO<sub>2</sub> and PM concentrations revealed that some cities face serious air pollution problems in some industrialized parts of the country, especially in the hard climate conditions.

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## A RELIABLE METHOD TO SAMPLE VOLATILE ORGANIC COMPOUNDS IN HUMID CONDITIONS

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Volatile organic compounds (VOCs) represent one of the most frequent categories of air pollutants found in the atmosphere along with sulphur oxides, nitrogen oxides and small dust particles. VOCs are emitted by solvents, road transports and the biomass. They have negative impacts on environment and on human health; they are also ozone precursors. However, not all the VOCs have the same properties and effects, for that reason it is necessary to separate, quantify and identify them properly. In order to separate and quantify the VOCs, a gas chromatographer (GC) is needed and its reliability is seriously affected by water presence. Indeed, the humidity trapped during the sampling of ambient air, can cause retention time shifts, damage chromatography columns and some detectors, it can break the filament of mass spectrometer, for instance. All these problems lead to unreliable analytical results for low concentration of VOCs. Many methods have been tested to remove humidity from air samples such as the use of drying agents, ion exchange membranes and the dry purge of adsorbent cartridges, among others. These methods were successful for the analysis of specific VOCs but they can cause loss of VOC families.

A common and economic VOC sampling method consists in using sampling bags on site and analysing the samples in the laboratory by GC, with or without a pre-concentration step, depending on VOC concentration.

In this study, different types of commercial sampling bag films were investigated: Tedlar, Teflon, Flexfoil and Nalophan. These sampling bags were filled with humid air and placed into a chamber flushed with a dry air stream. Tedlar and Nalophan sampling bags have shown considerable water vapour diffusion through their film, after a few hours the bag samples were dry (relative humidity < 5 %). Flexfoil has not shown any significant internal humidity variation. The influence of this sample water removal method on VOC stability was examined. Nalophan and Tedlar bags were filled with humid air containing 8 VOCs at 10  $\mu\text{g}/\text{m}^3/\text{VOC}$ . Sample bags were dried for 15 hours the same manner as described above. These experiments have shown no significant VOC losses.



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## PAH's IN NEEDLES AND HUMUS OF ALPINE ECOSYSTEMS (MONARPOP)

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PAH's (Polycyclic Aromatic Hydrocarbons) are a large group of chemical compounds comprising two or more aromatic rings. These semivolatile substances, mainly deriving from combustion processes, are transported by air masses and, as other persistent compounds, are susceptible to deposition in environments like the Alps with low temperatures and high precipitations. PAH's are of toxicological and ecotoxicological concern since some of them are considered probable or possible carcinogens.

Concentrations of 20 PAH's (including 16 EPA PAH's) in Norway spruce needles and forest humus were measured in samples collected in 56 alpine sites including 7 vertical profiles. PAH's were analysed using an isotope dilution method combined to HRMS (high resolution mass spectrometry).

Benzo(b)fluoranthene, Chrysene and Fluoranthene are the most abundant PAH's in the humus layer with means between 30 and 37 ng/g dw. On the other hand, the most abundant PAH in needles are Naphtalene and Phenantrene with means between 5 and 7 ng/g dw.

In humus samples the highest total PAH's concentrations are observed in the northern slope of the Alps while the lowest concentrations are observed in the south-eastern Alps. Most of the needle samples with high PAH's total concentration come from the western zone of the study area while the lowest concentrations are observed in the middle Alps

In the central and northern Alps the vertical profiles of total PAH's in humus present two maxima, the first of which in the lowermost altitudes and a second one in general between 400 and 700 m above the valley floor.

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PAH's concentrations in needles are higher in the lowermost altitudes in sites located in the central and northern Alps while those in the southern Alps present one peak at intermediate or high altitudes.

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## PARTICULATE MATTER TRENDS AND CHEMICAL COMPOSITION IN THE ALPINE CITY OF SONDRIO (NORTHERN ITALY)

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The city of Sondrio (awarded Alpine city 2007) is located in the Valtellina valley floor, an scarcely industrialized area in northern Lombardy. The area (300 m a.s.l.; 46°11'N; 9°53'E) is protected by the prealpine orobic barrier from polluted air masses arriving from the Po plain. Mean annual temperature and precipitation in the period are 12 °C and 1200 mm respectively. In this city, the concentration of air pollutants are monitored in a urban background permanent monitoring station since 1993. In the last decade, mean annual concentration of SO<sub>2</sub>, NO<sub>2</sub> and CO were 16 µg/m<sup>3</sup>, 34 µg/m<sup>3</sup> and 1,0 mg/m<sup>3</sup> respectively. As expected, considering the city size and its location, the concentration of gaseous air pollutants comply with the standards established by the European Directives 1999/30/CE and 2000/69/CE. On the contrary, concentrations of particulate matter (PM10) overrun the European thresholds for daily and annual mean concentrations. Since 1999 the number of PM10 daily means above the 50 µg/m<sup>3</sup> always overshoot the allowance while annual means exceeded the limit value of 40 µg/m<sup>3</sup> 4 times.

In order to characterize the chemical composition of the aerosol, its toxicity and to evaluate the contribution of the different sources to this pollutant, a three years survey (2004 – 2007) in a urban site, and in a background site was carried out within the framework of the project PAR-FIL funded by the Lombardy Region. The particulate matter has been characterized from the chemical point of view by measuring: NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>++</sup>, NH<sub>4</sub><sup>+</sup>, Pb, Cl<sup>-</sup>, As, Cd, Ni, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Fe, Mn, Cu, Zn, Br, PAHs, organic carbon (OC), and elementary carbon (EC).

The concentration of PM and its chemical composition in Sondrio present a strong seasonal pattern. In addition, temporal trends of particulate matter in this area differs from those observed in other cities in the sub-alpine belt and in the Po plain. The main component of PM10 is Organic Matter (40%), followed by nitrates (12%), EC (10%) and sulphates (9%). Pb, As, Cd. And Ni meet the European standards while annual mean of Benzo(a)Pyrene exceeds the threshold of 1 ng/m<sup>3</sup> for the annual mean. The source apportionment indicates biomass burning as an important contributor to the total PM.

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## INFLUENCE OF COPPER ON PHOSPHOMONOESTERASE IN GALICIAN SOILS

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Currently, heavy metal contamination of soils derived of industrial activity, urban wastes and by-products of agriculture deposition constitutes an important environmental problem. Copper, an essential element for biota, is able to be toxic for organisms in case of concentrations exceeded certain levels. In soils, copper affects deeply microorganisms, changing their growth, morphology and metabolism and finally, it affects the proper ecosystem's behaviour. So, it is important to evaluate properly the disturbed contaminated soils using tools such as biochemical parameters to monitor such harmful effects.

The aim of the present study was to evaluate the activity of phosphomonoesterase enzyme as an indicator of copper soil contamination. To attain this, a laboratory experience was carried out. Samples from 21 Galician topsoils (different use and physicochemical properties), were contaminated with increasing doses of copper (120, 360, 1080, 3240 mg kg<sup>-1</sup>) and incubated for 7 days at 25 °C and a moisture content corresponding to the water holding capacity. Copper affected phosphomonoesterase activity by reducing it when comparing with uncontaminated soil. However, by the same level of copper, studied soils showed percentages of inhibition very different. Lowest dose caused only small changes (22% inhibition) being no significant ( $p < 0.05$ , Duncan's test) in some soils. The highest dose caused an important inhibition (up to 79%) and its significant in the most of soils tested.

The enzymatic activity negatively correlated with copper doses, in a negative way (phosphomonoesterase activity =  $92.652 - 0.008 * Cu$ ;  $r = -0.883$ ,  $p = 0.0471$ ). On the other hand, at intermediate contamination levels, phosphomonoesterase was positively correlated with soil properties as total N, total C, CIC, Fe and Al oxides and silt percentage, and negatively with P content. The ED<sub>20</sub> values (i.e. the amount of metal necessary to reduce a 20% the activity referred to uncontaminated soil) were calculated by adjusting data to a sigmoid model equation of three parameters. The obtained values were very variable (ranging from 115 to 6529 mg kg<sup>-1</sup>) being positively correlated with total N, total C and CIC, but in a negative way with soil pH.

Phosphomonoesterase activity was a sensitive parameter to evaluate copper contamination on Galician soils. Soil properties such as organic matter and Fe and Al oxides affected the copper toxicity to soil microbes. Conversely, ED<sub>20</sub> values were very variable, thus limiting their applicability to monitoring purposes.

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## EFFECT OF TIME OF CONTACT BETWEEN 2,4,5-TRICHLOROPHENOL AND A FOREST SOIL ON DIFFERENT PROPERTIES USED IN THE DIAGNOSIS OF EDAPHIC CONTAMINATION

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Royal Decree 9/2005 defines the criteria for considering soils as contaminated, establishes the generic reference levels (GRL) for different organic products and indicates that the methods that should be used for diagnosis of contaminated soils are some of ecotoxicity tests proposed by the OECD. Problems associated with the decree as regards the criteria chosen for defining the GRL or the lack of detailed methodologies for the analytical techniques have already been discussed (Moscoso et al., 2007). However, another problem is that many of the products included in the list of contaminants outlined in the Royal Decree are volatile or are readily degraded by edaphic microorganisms, and thus the effect that they have on soils depends on the time of contact between soil and potential contaminant, which makes evaluation of the degree of contamination even more difficult. In the present study, we investigated the behaviour of a soil contaminated with two different doses of 2,4,5-trichlorophenol (2,4,5-TCP), throughout a period of contact of 24 days, with the aim of determining the response to various OECD tests over time. For this, samples of the Ah horizon of an Umbrisol under climax vegetation of Atlantic oak (pHKCl: 4.22, %C total: 10.13, % N total: 0.882; texture: loam) were artificially contaminated in the laboratory with doses of 2,4,5-TCP of 100 or 500  $\mu\text{g g}^{-1}$  (respectively 10 and 50 times the GRL). At 3, 10, 17 and 24 days after application of the contaminant, analyses were carried out to determine soil respiration and mineralization of nitrogen compounds. The microbial biomass was determined in the non contaminated control soil at the start of the experiment and in the control and artificially contaminated soils after 24 days. The responses in terms of the properties studied were variable. Thus in the first few days, respiration was much higher in the contaminated soils than in the control soil; this effect was buffered over time, and at the end of the experiment the highest values of respiration were obtained in the soil contaminated with the lowest dose of the contaminant. Nitrogen mineralization was much higher in the contaminated soil than in the control soils in the first days after contamination, and from day 10 onwards, was much higher in the control soil. The presence of the product also caused inhibition of nitrification, which tended to increase with time of contact. The microbial biomass scarcely changed in the soil to which the lowest dose of contaminant was added (93% of the control), and in the soil to which the highest dose was applied, it only decreased to 72% of that in the control soil.

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These highly variable results demonstrate the complexity of the biochemical processes in soils contaminated with organic compounds and demonstrate the need for in-depth studies to enable selection of appropriate analytical techniques for the diagnosis of contaminated soils.

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## IMPACT OF MUSSEL FARMING IN SEAWATER QUALITY IN MALIAKOS GULF (AEGEAN SEA, GREECE)

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The impact of the mussel farming on the seawater quality was studied in Maliakos Gulf, Greece, a shallow semi-enclosed embayment located in the north western part of North Evoikos. In order to achieve our target we carried out measurements of temperature, dissolved oxygen, pH, salinity, chlorophyll a (chl- $\alpha$ ), inorganic nutrients concentrations (ammonia, nitrate, nitrite and phosphate) in the water column.

Sea water samples were collected from four sampling points at varying distances from an area of commercial mussel farms. Sampling took place every month from September 2005 to October 2006. Seawater samples were collected from 4 sampling sites at surface and at bottom using sampling bottles. Temperature, dissolved oxygen, pH and salinity were measured in situ using portable multi parameter YSI field equipment. Concentrations of inorganic nutrients N-NO<sub>3</sub><sup>-</sup>, N-NO<sub>2</sub><sup>-</sup>, N-NH<sub>3</sub>, P-PO<sub>4</sub><sup>3-</sup> were measured with standard spectrophotometric methods. Concentrations of Chl- $\alpha$  were measured with trichromatic spectrophotometric method.

Our findings suggest the classification of Maliakos gulf as a eutrophic system without significant differences between the sampling stations. Chlorophyll- $\alpha$  values of Maliakos Gulf are comparable to those reported in other Aegean and Mediterranean systems affected by anthropogenic influences. The temporal and the spatial dynamics of the examined parameters were also discussed. Our data should aim at the estimation of the carrying capacity of Maliakos gulf.

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## ENVIRONMENTAL QUALITY OF THE COASTAL WATERS IN THE GULF OF IGOUMENITSA, IONIAN SEA

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Igoumenitsa is a coastal city in northwestern Greece. In Igoumenitsa Gulf treated domestic and raw domestic wastewaters are discharged, intense marine activities are developed (harbour of Igoumenitsa) and a lot of fish farming is currently operated.

The objective of this work was an assessment of seawater quality in the gulf, and anthropogenic impact. The seasonal variations of temperature, dissolved oxygen (D.O), salinity, pH, inorganic nutrients and chlorophyll- $\alpha$ , were investigated in a Mediterranean embayment (Igoumenitsa, North Western Greece).

Seawater samples were collected from 5 sampling sites at surface and at depth of 5 and 10 m using sampling bottles. The corresponded sampling sites were characterized by various anthropogenic activities, increasing distance from the shore and are covering the whole area of the gulf. Temperature, dissolved oxygen, pH and salinity were measured in situ using portable multi parameter YSI field equipment. Concentrations of inorganic nutrients  $N-NO_3^-$ ,  $N-NO_2^-$ ,  $N-NH_3$ ,  $P-PO_4^{3-}$  were measured with standard spectrophotometric methods. Concentrations of Chl- $\alpha$  were measured with trichromatic spectrophotometric method.



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## SPATIAL AND SEASONAL BIOAVAILABILITY OF SEDIMENT-ASSOCIATED METALS ALONG THE ESTUARY OF GUADALETE RIVER (SW SPAIN)

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Within the framework of setting environmental quality criteria for certain metals in sediments (Cu, Pb, Zn, Cd, Ni), SEM/AVS (simultaneously extracted metals/ acid volatile sulfides) ratio has been proposed as the primary standardization method in order to predict quite well the availability of various metals for different organisms. Because the anthropogenic contamination of estuaries frequently resulting in changes in the predominating biogeochemical conditions and increases the importance of anaerobic processes influencing trace metal behavior, such as the AVS production and preservation within the sediments, this study was realized to investigate spatial and seasonal distribution of both AVS and SEM in anoxic sediments of estuary of Guadalete river (SW Spain).

For this study ten representative sampling stations were selected along the estuary and surficial sediments SEM and AVS concentrations were sampled in winter and summer and analyzed. Mean total SEM concentration was not significantly different among time series however it showed seasonal significant difference between sampling stations. Acid volatile sulfides had been detected in all of investigated sediment samples and the concentrations showed spatial and temporal variations. The corresponding SEM/AVS ratio was found to be smaller than one in all except one station located near the mouth of the estuary during summer. In winter, the decrease of AVS concentration, probably due to colder temperature of sediment and water that reduce the activity of sulfate-reducing bacteria hence decreasing AVS production, affected another one station, apart from that above mentioned, which SEM/AVS ratio was larger than one. According to the application of AVS concept, toxic effects of certain metals are expected under this condition. This study highlighted that seasonal variations in the sediments of Guadalete estuary can affect AVS production, exceeding metal binding capacity of this sedimentary phase and increasing metal availability for organisms. Moreover the results provided information on potential pollution source near the mouth of the estuary where sediments displayed a SEM/AVS ratio larger than one during the year. The pollution probably depended on the vessel related activities, such as antifouling paint hull coatings, realized in a local harbor area located near the station.

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**METAL CONTAMINATION IN THE COASTAL AND ESTUARINE  
ECOSYSTEM FROM THE SOUTHWEST OF IBERIAN PENINSULA,  
IS THERE A RISK SITUATION?**

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Metals are introduced in coastal and estuarine ecosystems as result of natural erosion, metal transport for the air and water and anthropogenic activities (mining, industrial and urban sewage). The southwest coast from Iberian Peninsula has been subjected to the impact of mine activities from many centuries. In consequence, metal levels are quite high in several coastal ecosystems from this area. Nevertheless, in this zone, there are several relevant ecological ecosystems which are protected from different administrative regulations, also.

In order to know, the situation of these coastal areas from environmental risk assessment point of view, a review of metals levels (Cd, Cu and Zn) in sediment and biota has been carried out. The hot spots areas have been identified. These allowed to use biomarker approach to evaluate the effect of this contamination and the inclusion of quality guidelines. The comparison of metal levels with quality guidelines allowed establishing and improving the risk assessment from this coastal area. A proteomic approach will be developing to complement and improve the tools for environmental risk assessment.

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## ADRIATIC SEA SEDIMENT CHARACTERISTICS

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During national project PELMON (Pelagic monitoring of the Adriatic) in August and September 2005 surface sediments from 39 stations ( $z = 29 - 268\text{m}$ ) were sampled at eastern part of the Adriatic Sea. Granulometric composition, organic matter, carbonate and phosphorus content of the sediment samples were determined in purpose of classification of middle Adriatic Sea sediment.

Sand and silt were predominant grain size fraction in sediments. Organic matter and carbonate contents ranged from 0.6 to 8.2 % and 27 to 75 %, respectively, while total phosphorus concentrations were in the range from 6.45 to 24.79 mmol g<sup>-1</sup>. Elevated total phosphorus concentrations (>17 mmol g<sup>-1</sup>) were determined mostly at "off shore" stations located in north and west part of investigated area with prevailing sandy sediments. Phosphorus increase in this part of the Adriatic was probably generated by summer circulation of the Po River. These results are not in accordance with previous investigations which indicated maximum phosphorus accumulation in fine sized sediments at "near shore" stations. SEDEX analyses of phosphorus species were used to determine which phosphorus species was responsible for enhancement of total phosphorus.

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**BREATHABLE PARTICULATE (PM5) AND PAHS EXPOSURE  
DURING THE OLIMPIC WINTER GAMES OF "TORINO 2006"  
IN A COHORT OF TRAFFIC POLICEMEN**

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The XX Winter Olympic Games of "Torino 2006", occurred from 10 to 26 of February 2006, were studied under several aspects. Some of these regarded the impact of this event on health of people living and working in the Olympic venues. In this work forty voluntary traffic policemen, explicitly selected because workers in Torino traffic or close to road or building sites, were enrolled. Each subject, wore two active personal samplers to collect the total suspended particulate (PTS) and particulate having a diameter up to 5  $\mu\text{m}$  (PM5). Furthermore, after grouping both the two type of filters (PTS and PM5) in three "temporal" sub groups: filters collected before (December 2005 and January 2006), during (February 2006), and after (March-May 2006) the Olympic Games, chemical analysis of Polynuclear Aromatic Hydrocarbons (PAHs) were carried out on each of the six groups of filters.

Total means for all the 6 months were 115,1  $\mu\text{g}/\text{m}^3$  for PM5 and 275,2 for TSP. If compared to the A.C.G.I.H. limit (3.000  $\mu\text{g}/\text{m}^3$ ) the recorded level of PM5 results 30 times lower, showing a very low level of health risk, similar to that of "normal" town dwellers.

The means concerning PM5 and PTS before, during and after Olympics show a general similarity for PTS but a higher level of personal contamination for PM5 before the games (154,6  $\mu\text{g}/\text{m}^3$  vs. 64,4  $\mu\text{g}/\text{m}^3$  and 81,9  $\mu\text{g}/\text{m}^3$ ), during a period of high traffic and preparative works, until January 30 when a very long period of meteorological drought stopped and an abundant snowfall started. Probably, activities who preceded Olympics diffused in air higher amount of finer particulate.

The levels of PAHs, carried on PTS and PM5, show a similar behaviour, if compared to particulates (TSP and PM5). Nevertheless, decrease from before to after Olympics was continuous (from 72,7 to 7,9  $\text{ng}/\text{m}^3$  for PAHs on PM5 and from 27,7 to 8,1  $\text{ng}/\text{m}^3$  for PAHs on TSP) .

In conclusion, considering ultra fine particulate and PAHs, impact on human health of XX Winter Olympic Winter Games of Torino 2006 was low, even if during the Olympics preparation in the months before February 2006 levels were higher. Traffic policemen were chosen aiming to represent the worst conditions of air pollution due to the Olympic Games and aiming to consider winter, the season in which the meteorological conditions induce the higher level of primary pollution and, therefore, the higher health risk due to this type of risk factors.

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## BENZENE AND FORMALDEHYDE IN AIR OF TWO OLYMPIC VENUES OF "TORINO 2006"

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Several chemicals are present in automotive exhausts. Benzene (B) and formaldehyde (FA) also arising from other sources, are two micro pollutants typically detectable in urban air and in general close to areas with high traffic. Furthermore, these chemicals are of interest for public health also considering the well known carcinogenic properties of benzene and the carcinogenic properties of formaldehyde, still under complete definition.

The aim of this study was to determine the atmospheric levels of benzene and formaldehyde in two Olympic venues of "Torino 2006": Torino (the capital of Piedmont Region having almost 900.000 inhabitants) and Pragelato (a little mountain village of 500 inhabitants, 1518 m. above the sea level) both hosting several sport competitions. Samplings took place each month from May 2005 to April 2006, 24 hours a day for 10 consecutive days each month, except February 2006 (the Olympic month) when air sampling lasted for all the 16 competition days. Each "sampling line" worked at 1 litre/minute and the solid supports were specific for the two different chemicals; all the analysis were performed by means of a GC/MS specifically prepared.

Personal air was also measured in 2 groups of volunteers, chosen to represent the two sites. During the entire day of February 22, 2006 (concomitantly with several competitions) B and FA were collected by 10 volunteers who wore two passive personal samplers working with radial symmetry (Radiello®). Data obtained in Torino were compared to those obtained in Pragelato.

Annual geometric means for B were higher in Torino ( $2,9 \pm 1,9 \mu\text{g}/\text{m}^3$ ), if compared to results arising from Pragelato ( $1,5 \pm 1,7 \mu\text{g}/\text{m}^3$ ) but always lower than the legal limits ( $10 \mu\text{g}/\text{m}^3$ );

Significantly higher levels of B were found during winter (October - March) in both sites (Torino =  $3,9 \pm 2,3 \mu\text{g}/\text{m}^3$ ; Pragelato =  $2,2 \pm 1,2 \mu\text{g}/\text{m}^3$ ) in according to the atmospheric behaviour of this primary pollutant during the coldest months. Probably this was also due to the lack of precipitations until January 30, 2006 when a very long period of meteorological drought stopped and an abundant snowfall started.

Annual geometric means for FA were approximately similar in Torino ( $1,6 \pm 0,7 \mu\text{g}/\text{m}^3$ ) and Pragelato ( $1,25 \pm 0,4 \mu\text{g}/\text{m}^3$ ) and no statistical differences were observed comparing winter and summer concentrations (Torino winter vs. summer:  $1,5 \mu\text{g}/\text{m}^3$  vs.  $1,7 \mu\text{g}/\text{m}^3$ ; Pragelato winter, vs. summer:  $1,28 \mu\text{g}/\text{m}^3$  vs.  $1,23 \mu\text{g}/\text{m}^3$ ).

Personal air data pointed out, either for benzene and formaldehyde, higher values than those obtained in air fixed sampling; this was probably due to the highest proximity to the more intense output. Finally, any particular risk was recorded during the Winter Olympic Games with respect to these two chemicals, also during the month just before the officials competition.

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## ADSORPTION OF HERBICIDE MCPA ON LAYERED DOUBLE HYDROXIDES (systems Mg-Al, Mg-Fe and Mg-Al-Fe)

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The pesticide residue levels in surface and ground waters are continuously increasing due to the widespread use of these chemicals in agricultural and other activities. Layered double hydroxides (LDHs) are receiving increasing attention as potential adsorbents of pesticides from contaminated water. LDHs are layered materials with a general formula  $[M1-xIIxIII(OH)2]x+[Xx/mm-nH2O]x-$ , where  $II= Mg^{2+}, Mn^{2+}, \dots$ ,  $III= Al^{3+}, Fe^{3+}, \dots$ , and  $X= CO_3^{2-}, Cl^-, NO_3^- \dots$ . The possibility of anion exchange and recovering of the original layered structure by rehydration of their calcined product (500°C) make LDHs good adsorbents of anionic contaminants, including anionic pesticides. The aim of this work was to assess the potential usefulness of different LDHs (varying trivalent layer cations) and calcined LDH as adsorbents of the herbicide MCPA [(4-chloro-2-methylphenoxy)-acetic acid], which is a widely used acidic herbicide. The adsorbents and adsorption products were characterized by X-ray diffraction and Fourier-transform infrared spectroscopy.

LDH compounds with theoretical formula:  $[Mg_3Al(OH)_8]_2Cl \cdot 4H_2O$ ,  $[Mg_3Fe(OH)_8]_2Cl \cdot 4H_2O$ ,  $[Mg_3Al_{0.5}Fe_{0.5}(OH)_8]_2Cl \cdot 4H_2O$  ( $Mg_3Al$ ,  $Mg_3Fe$  and  $Mg_3AlFe$ , respectively), and  $Mg_3Al$  calcined at 500°C (HT500) were prepared with the aim to obtain different adsorbents for MCPA from aqueous solution. Adsorption experiments were carried out at pH= 6 for different contact-times (kinetics) and herbicide concentrations (isotherms). The amount of MCPA uptaken by the samples was monitored by the batch equilibration technique using high performance liquid chromatography. The results indicated the great affinity between the adsorbate and the adsorbents. The greatest adsorption of MCPA was obtained through reconstruction mechanism of HT500, while the adsorption by anionic exchange was lower and similar for the three LDHs tested. Namely, at an initial MCPA concentration 1 mM the amounts of herbicide adsorbed were  $C_s = 300 \mu\text{mol/g}$  for HT500 and  $C_s = 100 \mu\text{mol/g}$  for  $Mg_3Al$ ,  $Mg_3Fe$  and  $Mg_3AlFe$ . Thus, the variation of the trivalent cation did not affect greatly the adsorption of MCPA by the studied systems.

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## TRACE ELEMENTS AND SALINITY IN SOILS AND PLANTS OF THE DOMINGO RUBIO TIDAL CHANNEL (LEFT BANK OF THE TINTO RIVER, HUELVA, SPAIN)

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The Domingo Rubio tidal channel is a small estuary (6 km long, 1 km of maximum width, 480 ha) located in the left bank of the mouth of the Tinto river (37° 12' N, 6° 54' W, Palos de la Frontera, Huelva). Domingo Rubio estuary is a typical marsh system with a semidiurnal tidal regime. Nowadays, because of the infilling process, the tidal only affects the low course of the tidal channel, while the middle and high course become a like lake environment. The estuary is affected by the water of the Tinto river, contaminated with trace elements, and by the rain and drainage waters from the land in which different chemical and agricultural industries are located.

Soil samples were collected in spring of 2004 and 2006 at six different point of the area for soil chemical analysis: electrical conductivity, pH, organic matter and nitrogen content, total and 0.05 M EDTA-extractable trace element concentrations. In the same points and at the same date, the most frequents plant species (*Halimione*, *Astrhocnemun*, *Tamarix*, *Juncus* and *Paspalum*) were also collected for chemical analysis of the aboveground organs. Washed and unwashed vegetal samples were analysed.

We found that in both samplings soil contamination by trace elements was highly correlated with soil salinity. Trace element content in soils increases seaward and is very high in the tidal stretch of the estuary (up to 1000 mg kg<sup>-1</sup> As, 6.00 mg kg<sup>-1</sup> Cd, 2500 mg kg<sup>-1</sup> Cu, 1900 mg kg<sup>-1</sup> Pb and 1300 mg kg<sup>-1</sup> Zn). The origin of the contamination seems to be related with the Tinto River waters. Moreover soils in points with higher salinity and trace element pollution presented also the higher nitrogen and organic matter content.

Despite the high values of trace element extracted with EDTA from soils (up to 35 mg kg<sup>-1</sup> As, 0.60 mg kg<sup>-1</sup> Cd, 0.50 mg kg<sup>-1</sup> Cr, 900 mg kg<sup>-1</sup> Cu, mg kg<sup>-1</sup>, 400 Pb, 350 mg kg<sup>-1</sup> Zn), we only found in washed plants some values of Cu and Cr higher than those considered normal in plant tissue (especially in *Halimione* and *Astrhocnemun*). Samples of leaves of *Cistus* and *Salix* – the latest is a typical accumulator of Cd and Zn in its tissues - growing on areas of low contamination, showed accumulation of Cd, Mn and Zn in their leaves.

In general unwashed samples of *Halimione*, *Astrhocnemun* and *Paspalum* presented higher concentration of trace elements than washed samples. These species are smaller than the others and are exposed to higher contamination cause by the deposition of soil particles.



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## POLYCHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS (PCDD/Fs) OVER THE MEDITERRANEAN SEA

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The marine environment is subjected to contamination by a wide spectrum of chemicals mainly due to anthropogenic activities. Among these chemicals, persistent organic pollutants (POPs) have gained a lot of attention in the last decades due to their ubiquity in many environmental compartments, and their adverse health effects in biota and humans. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are a family of POPs formed by 209 congeners. Seventeen of these congener have been described as the most toxic ones (2,3,7,8-substituted congeners) being able to bioaccumulate and enter the foodwebs. Although certain amount of information on environmental levels and processes of PCDD/Fs is available for coastal areas, very little is known about their levels and behaviour far from the shore line (open seas).

In this work environmental air concentrations and spatial distribution on PCDD/Fs across the Mediterranean Sea are presented. Data were collected during a sampling cruise (from Barcelona to Istanbul on board of the B/O Garcia del Cid, CSIC) performed within the framework of the IP THRESHOLDS of Environmental Sustainability. A distance of 3850 nautical miles (~ 7100km) was covered and a total of 5 transects were sampled along the Mediterranean and Marmara and Black seas. Air samples (particulate + gas phase) were collected by using two high volume samplers installed on the upper deck of the boat (around 6-7 m above the sea level) close to the bow. The samplers, operating in parallel, were equipped with a wind direction interface that stopped the sampling when wind was blowing from the poop of the vessel in order to avoid possible contaminations from the ship exhausts. Quartz fibre filters (QFFs) were used for air particle phase collection whereas compounds in the gas phase were trapped by using polyurethane foam (PUF) plugs. Samples were Soxhlet extracted with n-hexane/acetone after being spiked with internal standards, cleaned-up and analysed by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS). Isotopic dilution technique was used for quantification of target compounds according to 1613 U.S. EPA method.

PCDD/F ( $\Sigma$ 17 toxic congeners) ambient air concentrations (particulate + gas phase) in the 4 transects along the Mediterranean Sea ranged from 114 to 813 fg m<sup>-3</sup> (3-7 WHO98-TEQ fg m<sup>-3</sup>). The one sample transect collected at Marmara and Black Seas exhibited a higher PCDD/F concentration of 1555 fg m<sup>-3</sup> (15 WHO98-TEQ fg m<sup>-3</sup>). Congener patterns obtained were in general typical from distant sources with a predominance of the higher chlorinated dioxins (HpCDD and OCDD). The results from this campaign constitute a unique data set since no data on PCDD/Fs ambient air concentration across the Mediterranean Sea has been reported to date. Analyses of water samples, also collected during the campaign, are undergoing and will help to complete the picture and better understand the current status of contamination of this marine environment by PCDD/Fs.



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## ORGANOCLAY-BASED FORMULATIONS OF THE HERBICIDE DIURON TO REDUCE HERBICIDE LEACHING IN SOIL

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Extensive ground and surface water contamination by herbicides used in olive groves in Spain and other Mediterranean countries is demanding the development of strategies directed to reduce offsite movement of the applied herbicides. Organoclays, i.e. natural clay minerals with their inorganic exchange cations replaced with organic cations, have been proved to be efficient adsorbents for the removal of pesticides from contaminated water and as supports for the development of slow release formulations of pesticides, to attenuate their environmental impact once applied to soil.

In this work, two montmorillonites (SWy-2 and SAz-1) were modified with different organic cations, and the resultant organoclays were characterized and tested as adsorbents of a herbicide commonly applied to olive groves: diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]. Among the different organic cations used to modify the clay minerals, the polyamine spermine (SPERM) and the surfactant hexadecyltrimethylammonium (HDTMA) produced the greatest enhancement in the affinity of SWy-2 and SAz-1 for the herbicide diuron. Organoclay-based formulations of diuron were prepared by supporting the herbicide on SWy-2 and SAz-1 exchanged with SPERM and HDTMA cations, and the release and leaching behaviour of these formulations was determined through batch release and column leaching tests.

The assayed organoclay-based formulations of diuron retarded the release of the herbicide into water and reduced the herbicide leaching compared to a conventional diuron formulation containing the herbicide in an immediately available form, thus indicating reduced mobility of the herbicide and consequently reduced risk of ground and surface water contamination.

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## UPTAKE AND ACCUMULATION OF LEAD BY BROCCOLI PLANTS GROWN IN CONTAMINATED SOILS

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Lead (Pb) is a major anthropogenic pollutant and has been accumulated in different terrestrial and aquatic ecosystems. Since Pb accumulation in plants has been implicated as the cause of several health problems, reduction of plant uptake of this element in food crops is desirable. The aim of this work was to study lead (Pb) uptake and accumulation by broccoli plants grown on polluted soils. The plant species studied during the present investigation were two varieties of *Brassica oleracea* L. var. *italica* Plenck (broccoli), namely Chevalier and Romanesco. For studying the uptake and accumulation of Pb in broccoli plants, two experiments were realized in pots. In the first experiment, plants were grown in polluted soil (mean content of 224 mg. Pb kg<sup>-1</sup>) from the experimental area "El Vicario" close to the pyrite mine of Aznalc llar (Seville, Spain). The second experiment was performed by adding Pb as PbNO<sub>3</sub> (lead nitrate) at 400 mg Pb kg<sup>-1</sup> to the surface of standard soil.

Results of this work show that lead toxicity reduced broccoli plant growth and produced chlorosis along the margins of young leaves. Broccoli roots had the highest Pb concentration among all examined plant parts. Pb content in plants of Broccoli Romanesco was higher than Broccoli Chevalier plants. The human health implications of Pb accumulated in the edible part of broccoli plants are discussed.

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## INTEGRATION OF IN-SITU AND REMOTE SENSING TECHNIQUES FOR STUDYING SALINIZATION PHENOMENA IN COASTAL AREAS

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"The coastal zone is of great environmental, economic, social, cultural and recreational importance to Europe" as underlined by the EU initiative Integrated Coastal Zone Management (ICZM). Among the different problems affecting the coastal areas, saltwater intrusion is one of the major environmental threats due to the contamination of freshwaters and soil salinization that reduce the availability of freshwaters for potable and agricultural uses and cause a reduction of biomass productivity in both natural and man-managed environment. In this study, a multidisciplinary approach based on chemical-physical, geochemical, geophysical and satellite observations was carried out to evaluate the extension and severity of the salinity phenomenon in a coastal forest reserve of Southern Italy. The study area (Forest Natural Reserve of Metapontum, Basilicata Region), is a part of a broad area of about 250 ha of pine forest that was planted in the first decade of 50's along the Ionic coast (about 50 km) in order to preserve the coast and the inland cultivated areas.

To characterize the effects of salinization processes in the study area, several field campaigns were performed by integrating soil and groundwater samplings, electrical resistivity tomographies (ERT) and resistivity measurements (SEV). From laboratory analyses, electrical conductivity, chemical and agronomical parameters were determined on soil and groundwater samples. Satellite data from Landsat-TM and NOAA-AVHRR sensors were analyzed to evaluate the spatio-temporal characteristics of vegetation activity. In particular, classification methods were applied to estimate patterns of forested areas and NDVI (Normalized Difference Vegetation Index) was adopted to evaluate the evolution of photosynthetic activity.

The maps obtained from geophysical measurements show that the salt infiltration phenomenon has not only a horizontal distribution, but also a vertical diffusion interesting the layer active for plant roots. Laboratory analyses on the soil and ground water samples confirm geophysical investigations, in fact, even if a sub-alkaline pH (7.60-8.0) is not limiting for plant survival, the high concentration of dissolved salts is the main limiting factor. Satellite data classifications were used to delimit the areas involved in vegetation decline, then the time-dependent changes of vegetation canopy were analyzed. We found that after a first period of vegetation recovery diffused all over the area, in the second stage vegetation approached a steady state in areas

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affected by salty water, whereas in the neighboring areas vegetation was involved in a further increase. First results show that the decline in vegetation activity of the forest reserve is mainly a consequence of the saline contamination that inhibited the complete vegetation recovery.

The obtained results show that the proposed multidisciplinary approach can be useful for its management implication for both planning (e.g., the delineation of the critical areas for restoration policies) and assessment phase (e.g., the evaluation of the effectiveness of the applied restoration activities).

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**ELECTRIC AND MAGNETIC PARAMETERS  
FOR STUDYING EROSION PROCESSES:  
"CALANCHI" OF ALIANO (SOUTHERN ITALY)**

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Southern Italy is one of the Mediterranean areas where climatic, geopolitical and anthropogenic factors are likely driving land degradation processes enhancing desertification risk. In this framework, we focus on a form of accelerated erosion producing landforms characterized by steep, scarp slopes with knife-edge ridges, known as calanchi. The investigated area is located in Southern Italy (Basilicata Region) in the territory of the municipality of Aliano, where the main land uses are agriculture and pasture. Here, erosion processes produce dissection of poorly consolidated or poorly cemented materials; moreover, vegetation cover is very sparse. Within such an area we selected two calanchi forms, with the same alignment and slope, but characterized by contiguous scarps with different degree of erosion. Our goal was to evaluate the ability of some physical parameters to discriminate areas with different degree of erosion. In particular, we selected a pair of eroded-vegetated contiguous sides for each one of the two calanchi. We collected 50 samples of soil and we measured soil magnetic susceptibility (in laboratory and in situ), electrical conductivity, and pH on each sample.

The magnetic susceptibility measurements were performed using a Bartington MS2 meter with a field survey probe (MS2F) with a diameter of 15mm for high resolution surface measurements and a laboratory sensor (MS2B), that is able to work at two different frequencies for obtaining information about the magnetic grain size of soil.

The measurements of electrical conductivity and pH were performed following the protocols indicated in D.M. 13.09.1999 (G.U. n. 248 del 21.10.1999).

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According to our preliminary results, electrical conductivity seems to be able to discriminate calanchi characterized by different erosion degrees whereas magnetic susceptibility values seem to discriminate soils with different geological characteristics.

In addition, the superficial soil magnetic susceptibility measured along the eroded side of one of the two calanchi (sampling grid:  $120 \times 60 \text{ c m}^2$  with a cell of  $10 \times 10 \text{ c m}^2$ ), show a spatial distribution with clear directionality that is probably ascribable to the water motion in the subsurface of the calanchi form.

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## BIOINDICATION OF ELECTROMAGNETIC POLLUTION OF SOILS

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The term «global electromagnetic environmental contamination» is officially entered in 1995 by the World Health Organization which has included this problem in the list priority for mankind (Grigoriev et al., 2003). From the beginning of 90th years of XX century there were changes in structure of sources of the electromagnetic fields (EMF), connected with occurrence their new communications, development of new frequency ranges a body and broadcastings, development of means of remote supervision and the control, etc. Feature of these sources is creation of a uniform zone of «radiocovering» that is increase in an electromagnetic background in an environment.

Among bioindicators of electromagnetic pollution enzyme activity of soils is steadier against electromagnetic influence, than microflora. Microwave radiation (duration of influence 30 sek., 1, 10 and 60 minutes) rendered overwhelming influence on catalase, invertase and dehydrogenase activity of chernozem ordinary. In most cases variable magnetic field (VMF) by induction of 1500 and 6000 mkTl (frequency of 50 Hz) does not render influence on enzymes investigated soils, behind exception of dehydrogenase of grey forest soils and brown forest soils where VMF rendered overwhelming influence.

Microbiological parameters (number of the basic groups of soil microorganisms of bacteria and micromycetes) of investigated soils are sensitive to electromagnetic influence. For gamma-radiation and microwave radiation amplification of overwhelming influence with increase in a doze and duration of influence accordingly was marked. To VMF the soil microflora is steadier, in some cases number of microbes authentically does not differ from the control, over weak levels of influence (100 and 500 mkTl 1 hour) was observed by duration stimulating effect.

It is possible to construct the following lines of stability of soils and microorganisms to electromagnetic influence. The degree of overwhelming influence EMF decreases in a line: gamma-radiation > microwave radiation > VMF.

On stability to soil EMF form the following lines.

Microwave radiation: chestnut soil > grey forest soil > brown forest soil.

VMF: brown forest soil > chernozem ordinary chestnut soil > brown forest soil.

On stability of microbiological parameters to influence of EMF:

Microwave radiation: Azotobacter > sporous bacteria > ammonyfying bacteria > micromycetes

VMF: micromycetes >= Azotobacter > ammonyfying bacteria

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## FIRST RESULTS OF THE EVALUATION OF BIOLOGICAL SOIL PROPERTIES AS INDICATORS OF AIR PARTICLES POLLUTION

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In the Kozani –Florina basin (Northern Greece) 6 power plants are functioning using as fuel lignite resulting in a considerable air pollution mainly by ash particles. In this presentation it is examined the indicator value of the following soil biological parameters: Soil microbial biomass, soil respiration, soil microbial diversity assessed by the biolog method and the nematode content.

At present soil samples are coming from the fields in the area and not the depositions.

First results show that although soil content in heavy metal, appears slightly increased compared to purely agricultural soils from other areas, the above mentioned parameters do not show a clear tendency.

The data set is going to be enlarged and the method of neural networks to be tested in order to detect if a parameter is showing better indicator capacity.



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## SEASONAL – SPATIAL FLUCTUATION AND PHASE DISTRIBUTION OF HEAVY METALS IN A SHALLOW MEDITERRANEAN LAGOON

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The geo-environment of the wetland area of Korissia lagoon in the southwest of Corfu Island, Greece, is being studied during the last three years. The Korissia lagoon is a shallow coastal ecosystem of great aesthetic and ecological importance. This is the reason for its inclusion in the EU catalogue of Sites of Community Importance and in the Natura 2000 network of protected areas.

The lagoon is connected to the sea by an artificial channel and its depth varies between 0.5 and 1.2 m. By the end of summer the salinity exceeds 50 P.S.U. and surface temperature is 23.6-26.1 °C, while D.O. values are 75-100 %. In spring salinity falls to about 19 P.S.U., surface temperature is 13.5-16.2 °C and D.O. varies between 91 and 115 %.

The present paper focuses on the study of seasonal fluctuations and spatial and phase distribution of heavy metals in the wetland area. In particular heavy metals such as zinc and copper have been measured in water samples collected from the lagoon and subsurface water samples from wells adjacent to the lagoon in two sampling periods, on September 2005 (dry period) and on March 2006 (wet period). Moreover, during the first period sediment samples were collected from the lagoon's bottom surface. Heavy metals were also measured in the suspended material of water samples after their filtration through 8 µm and 0.45 µm Millipore filters.

On September 2005 Zn values in the lagoon showed a decrease with direction from southeast to northwest and were of the same order of magnitude with sea value (0.2 ppb). On the other hand, on March 2006 dissolved zinc was, on average, half the value of September, while sea value had been doubled (0.4 ppb). Moreover, dissolved Zn in the wells varied between 1.2-46 ppb on the first sampling period and between 0.5-21 ppb on the second sampling period and was 1-2 orders of magnitude higher than lagoon values. The wells at the southeast side of the wetland area exhibit higher zinc concentrations than the wells at the northwest.

The lagoon was relatively homogenous in dissolved copper (0.2 ppb) on September 2005 with sea value slightly higher at that time. In late winter copper values had doubled in the lagoon (0.3-0.6 ppb) and exhibited spatial differences. In summer most wells had copper values ten times higher than the lagoon but in winter the differences were smaller.

Heavy metals' values in suspended material and in the sediments exhibited interesting trends and relations with the according dissolved ones.

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## FIELD METHOD COMPARISON BETWEEN PASSIVE SAMPLERS, SODIUM IODIDE METHOD AND CONTINUOUS MONITOR FOR NO<sub>2</sub> IN ESKISEHIR, TURKEY

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Nitrogen dioxide (NO<sub>2</sub>) is one of the main gaseous pollutants with the important effects on both indoor and outdoor air quality. The main outdoor sources include transportation, combustion processes and industrial activities. The monitoring of NO<sub>2</sub> for regulatory purposes requires methods suitable measuring concentrations in the range relevant for Europe, i.e. 0-500 mg/m<sup>3</sup>, with a sufficiently high accuracy. There are several well-established monitoring methods for NO<sub>2</sub> in this concentration range, some of which can only measure NO<sub>2</sub>, while others can also measure NO and/or NO<sub>x</sub>.

Active and passive discontinuous methods are normally used for daily to monthly sampling. The manual discontinuous methods are relatively cheap and simple, but have several disadvantages including the need for manpower for sampling and analysis, the limited time resolution and the time delay until results are available.

Passive sampling of NO<sub>2</sub> has recently become an attractive monitoring method for longer sampling periods, on weekly or monthly basis. The sampling technique is based on molecular diffusion of the gas molecules into the sampler, where they are quantitatively collected on an impregnated filter. No electricity, pump or other equipment is needed. The NO<sub>2</sub> collected on the impregnated filter is extracted from the filter with water and determined by chemical analysis. When calculating the concentration, the ambient air temperature must be taken into consideration, since the diffusion velocity is temperature dependent.

Sodium iodide method is also one of the most common active methods. This method is based on the absorption of NO<sub>2</sub> on a sodium iodide impregnated sintered glass filters. NO<sub>2</sub> is absorbed and reduced to nitrite by the iodide on the filter. The nitrite formed is extracted with deionised water and determined spectrophotometrically with the Griess Saltzman method.

In this study, field performance of the new tailor-made plastic passive sampler is tested parallel with sodium iodide technique and continuous NO<sub>x</sub> analyzer for the determination of ambient air NO<sub>2</sub>. Passive sampler results have a good agreement (error level is less than 20 %) with chemiluminescence measurements, as well as with the potassium iodide method. Also, highly precise results (<5% relative standard deviation, RSD) were found for NO<sub>2</sub> measurements from collocated passive samplers.

**Key Words:** Air pollution, Monitoring, Nitrogen dioxide, Passive samplers, Sodium iodide method, Continuous monitors.

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## THE INTERACTION OF TIN-CATALYSTS WITH SOILS

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The ability of pollution prediction by environmental hazardous and toxic metals via modelling experiment is necessarily for environmental modelling. Due to a wide industrial utilization of tin and its compounds, mainly organotin compounds are widely used in PVC stabilization, production of catalysts, wood preservatives, antifouling paint, and biocides, the catalyst stannous-2-ethylhexanoate was selected for this study. The stannous-2-ethylhexanoate ( $\text{Sn}(\text{Oct})_2$ ) is the most commonly used catalysts/initiators for preparing biodegradable and biocompatible polymers. The first part of this contribution deals with influence of the purification by various solvent after preparation of the "crude" PLGA/PEG//PLGA and ITA-PLGA/PEG/PLGA-ITA polymers. The processes of purification have a strong affect on the total content of tin in different matrices. The existence of modified matrices (ITA-PLGA/PEG/PLGA-ITA) and purification with organic solvent caused the increase of the total amount of tin catalyst in polymer matrices. It leads to a higher concentration of tin catalyst in waste after preparing polymers.

The next part of this work includes the sorption study of tin-catalysts owing to presence of the tin in the waste after preparation of polymers. The different montmorillonites with known chemical and structural properties were used for the sorption study as model soil matrices. It is generally known that the sorption mechanism is not well understood because  $\text{Sn}(\text{II})$  could be easily oxidised into  $\text{Sn}(\text{IV})$  and the tin(II) form is influenced by hydrolysis reactions, too. The adsorbing amount can be expressed as total adsorbing amount of tin at the exactly defined conditions. The "Batch" method was used for the adsorption study. The adsorption data confirmed strong influence of pH factor, concentration of chlorides, type of sorbents and form of tin (inorganic and organic forms). The total adsorbing amount of  $\text{Sn}(\text{Oct})_2$  into montmorillonite was determine at 0,44 mmol/g. The tin concentrations were determined by means of instrumental method ICP - OES and a spectrophotometric method.

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## THE SORPTION STUDY OF CU, ZN FUNGICIDES ONTO MINERAL COMPONENTS OF SOILS

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The quantitative prediction of contaminants transport in environments is important for evaluation of the risks associated with their migration. The sorption study of Cu and Zn cations into montmorillonite and calcite with known chemical composition was studied. The study fungicides Champion, Cupricol and Dithane contained Cu and Zn cations in the active substance. Model experiments of these substances contained exactly defined matrices were used for this research. The montmorillonite type OCMA with structural formula  $(Ca_{0,175} Na_{0,114} K_{0,058})(Al_{1,330} Mg_{0,334} Fe_{3+0,317} Ti_{0,033})(Si_{3,932} O_{10})(OH)_2$  which belongs to the group of clay minerals was used as a model soil matrix. The calcite  $CaCO_3$  with different in structure and chemical composition was used as another model of a soil matrix.

Two methods - "Batch" method and "Flow-Through" column system method - were used for the adsorption and desorption study. The sorption equilibrium and kinetics of compounds were examined at various conditions. Two types of mineral samples were examined as a function of pH, time, and starting aqueous Cu, Zn fungicides concentrations. The sorption data were correlated with the Langmuir, Freundlich models. The sorption capacity of used materials was calculated and other thermodynamic parameters were calculated, too. The Cu, Zn concentrations were determined by means of instrumental method F-AAS.

The montmorillonite belongs to very effective sorbents for various types of fungicides mainly of Cu type fungicides as Champion and Cupricol, which was confirmed. The results showed that the Cu fungicides could be strongly adsorbed into soils. All results point out that those fungicides could be adsorbed onto soils and could be desorbed in various concentrations from soils. This study confirmed that utilization of these fungicides measurably could contribute to soil and water pollutions.

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## CONTROLLED RELEASE OF CHLORSULFURON FROM ETHYLCELLULOSE COATED FORMULATIONS

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In the agrochemical industry the use of controlled release (CR) systems could be a potential solution to improve low efficacy and prevent environmental pollution derived from the use of conventional pesticide formulations. The aims of CR formulations are to protect the supply of the agent, to allow the release of the agent to the target at a controlled rate, and to maintain its concentration in the system within the optimum limits, over a specified period of time, thereby providing great specificity and persistence. Thus, it reduces the loss by evaporation and leaching and minimises pesticide pollution that is also a risk for animals and humans' health.

In this research the herbicide chlorsulfuron [1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea] was coated with ethylcellulose (EC) to obtain granules that show CR properties. A commercial formulation (Glean, a.i. 75 %) was coated in a Wurster-type fluidised-bed equipment using two different amounts of ethylcellulose. That of the highest one was modified by the addition of a plasticizer, dibutyl sebacate (DBS). The effect on chlorsulfuron release rate caused by the incorporation of ethylcellulose and DBS in commercial formulation was studied by immersion of the granules in water under static conditions.

Using an empirical equation, the time taken for 50% of the active ingredient to be released into water (T50) was calculated. From the analysis of the T50 values, the influence of ethylcellulose appears clearly defined. A delay in release rate of chlorsulfuron from EC coated granules respect to the commercial formulation was observed. The release of chlorsulfuron into water was controlled by diffusion mechanism being the thickness and the permeability of the coating film the most important factors that affect chlorsulfuron release.

The mobility of chlorsulfuron from commercial and CR formulations were compared using soil columns. The use of EC coated formulations retards the release and reduces the presence of chlorsulfuron in the leachate compared to the commercial product. This way a 100% recovery in the case of commercial formulation, whether meanwhile just a 63% for the CR formulation containing EC plus DBS were obtained respectively.

This study might be useful to design and select the most appropriate CR formulation, depending on the environmental factors as well as to reduce the possibility of chlorsulfuron to reach and pollute the groundwater resources.

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## ASSESSMENT OF ATMOSPHERIC INPUTS TO THE GUADALQUIVIR RIVER IN SEVILLE. RELATIONSHIPS BETWEEN INORGANIC POLLUTANT LEVELS IN THE AMBIENT AIR AND IN RAINWATER

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The main objectives of the project are to monitor the concentrations of selected contaminants in precipitation (rainwater) and air (atmospheric particles) and their depositions in order:

- to assess the atmospheric input of the selected contaminants to the maritime area and regions to determine long-term trends in atmospheric inputs; for their use in relation to modelling activities, specifically
- to validate atmospheric transport models used for assessments of atmospheric inputs to maritime area.

The selected area was the marine zone of the Guadalquivir River, from Alcalá del Río (North of Seville) to the mouth (Sanlúcar de Barrameda). In the preliminary part of the project five sampling stations were studied: Alcalá del Río, the city of Seville, Palomares del Río, Lebrija and Trebujena. The results presented in this work correspond to the zone where the major atmospheric emissions were observed (city of Seville).

Rainwater samples (wet deposition) were collected with an automatic wet-only deposition sampler MCV CLA-001. The sampling covered the deposition from autumn 2006 to summer 2007. The sampler collects rainwater classifying the total precipitation in volumes of 10 ml. This way the concentration of pollutants can be time distributed from the beginning to the end of each rain episode. Total suspended particles (TSP) were collected using high-volume samplers MCV CAV/HV. Sedimentable particles (dry deposition) were collected with a standards sampler. TSP samples were collected just before and after each rain event. Sedimentable particles were collected each 28 days (one per month).

Inorganic pollutants were selected according the OSPAR convention and the RID and CEMP programs (Riverine Inputs and Direct Discharges, Coordinated Environmental Monitoring Programme). Heavy metals, nutrients (N and P), cations (Ca, Mg, Na, K,  $\text{NH}_4^+$ ) and anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{=}$ ) and specific parameters (pH, EC, Ered) were measured in all samples. Relationships were studied between concentrations in atmospheric samples and rainwater samples.

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### LEAD IN SOILS FROM NW SPAIN: 3,000 YEARS OF ATMOSPHERIC POLLUTION

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Since the beginning of mining and metallurgy Pb has been incorporated to soils by atmospheric deposition. In podzols a self cleaning mechanism has been identified which sequesters Pb from the surface and stores it in the subsuperficial horizons (i.e. spodic). This decreases toxicity risks and the transfer of Pb to superficial and subterranean waters.

Here we described the results for two podzols from NW Spain, sampled at regular intervals of 5 cm. Total Pb, Al, Si, Fe and Ti were measured by XRF. The fractionation of Fe and Al was evaluated using selective dissolution techniques (extractions with in LaCl<sub>3</sub> 0.33M, CuCl<sub>2</sub> 0.5M, Na-pyrophosphate 0.1M, acid NH<sub>4</sub>-oxalate 0.2M and NaOH 0.5M), and the exchangeable fraction using KCl 1M. All extracts were measured by AAS. Stable lead isotopes were also analyzed using ICP-MS.

The highest Pb concentrations were found in the spodic horizon (Bhs), and the lowest in the eluvial (E) horizon. Lead is highly correlated to exchangeable Al and to Al extracted with CuCl<sub>2</sub> 0.5M, suggesting that Pb in these podzols may be mostly as exchangeable Pb and as low/moderate metal-humus complexes. The latter seem to be responsible of the transport of Pb to the spodic horizon, where it accumulates. <sup>206</sup>Pb/<sup>207</sup>Pb isotope ratios are highest (1.22-1.23) and almost constant below 35 cm (Bs and C horizons), indicative of geogenic Pb. In the upper 35 cm of the soils the ratios decrease to minimum values of 1.14-1.15, similar to those found in leaded gasolines. For this soil compartment (O, A and E horizons) the isotope ratio is highly correlated to total Pb, indicating a mixing with Pb from a source with higher Pb concentration and a lower <sup>206</sup>Pb/<sup>207</sup>Pb isotope ratio. Thus our results suggest that pollution lead deposited in the soil surface has been transported by podzolisation processes (probably as metal-humus complexes) up to a depth of 35 cm into the soil column. Since atmospheric Pb pollution in NW Spain has been shown to have began some 3,000 years ago, the average transport rate is of 1 cm per century -similar to that found in other soil studies in Sweden. Consequently, Pb deposited since the beginning of the Industrial Revolution (last 300 years), including Pb from gasolines, is still stored in the upper few centimetres of the soils.

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## DETERMINATION OF N-METHYL CARBAMATES PESTICIDES AT THE OUTLET OF AN AGROFORESTRY CATCHMENT BY ELECTROSPRAY IONIZATION TANDEM MASS SPECTROMETRY (LC-ESI-MS).

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There is clearly a need to reduce agricultural use of pesticides in modern society, because of environmental implications. In particular, there is overwhelming evidence that agricultural use of pesticides has a major impact on water quality and may lead to serious consequences. The impact of pesticides on water quality depends not only on the active ingredient in the formulation and its degradation rate but also on environmental factors such as for example climate, soil type and soil use and management and agricultural practices. Carbamates are known for their reversible cholinesterase effects. N-methylcarbamates are a class of carbamates with insecticide action. The aim of this work was to develop a method using liquid chromatography electrospray ionization-tandem mass spectrometry to analyze ten N-methyl carbamates (aldicarb, carbaryl, carbofuran, ethiofencarb, methiocarb, methomyl, pirimicarb, promecarb, propoxur and oxamyl). Water samples were taken at the outlet of an agroforestry catchment of 36.3 km<sup>2</sup> surface in the Valiñas River, near A Coruña, Spain, under Atlantic climatic conditions. Samples were collected at five different stations in October 2005.

The extraction and clean-up procedures used in this work were as described in US EPA 8318 and the determination method was flow-injection electrospray ionization (ESI-MS/MS). The average recoveries from water fortified at the level of 25 µg/l ranged from 71.1 to 123.4 % with coefficients of variation between 4.6 and 17.5 %. The chromatographic separations were performed on a Zorbax Eclipse XDB C18 column (Agilent Technologies) at 35 °C using gradient elution with water : acetonitrile. The MS/MS system was operated in the positive ionization MRM mode. The ESI conditions and the MS/MS parameters were optimized for each individual selected precursor/product ion transition. The two most abundant product ions were chosen for each carbamate, so that the most abundant were used for quantification and the other as confirmation transition. The calibration curves obtained for all quantification transitions were linear over the range 3 - 300 µg/ml for the ten studied pesticides with correlation coefficients, R<sup>2</sup>, higher than 0.99. The [M+NH<sub>4</sub>]<sup>+</sup> and the [M+Na]<sup>+</sup> ion were used as precursors for oxamyl and aldicarb respectively. Molecular ions were used as precursors for the remaining carbamates. According to this method, the reported instrumental limits of detection (LOD) were from 1.4 to 30 µg/l (S/N=3) whereas the limit of quantification, determined as the lowest calibration curve standard, were from 0.06 µg/l.



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The method presented an excellent sensibility for all carbamates analyzed. In three out of five analyzed water samples carbaryl contents were above 0.1  $\mu\text{g/l}$  threshold, with values 0.17; 0.17 and 0.13  $\mu\text{g/l}$ . Although these concentrations are above the maximum permissible concentration for individual pesticides of 0.1  $\mu\text{g/l}$  established by European Union directive on drinking water quality (98/83/CE), the results indicated a low risk of contamination for the carbamates studied.

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**BIOMONITORING OF HISTORIC PARKS USING EPIPHYTIC LICHENS:  
VILLA DORIA PAMPHILJ (ROME, ITALY)**

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The aim of this work was to evaluate the air quality in Villa Doria Pamphilj, one of the older historic Park in the city of Rome, through the determination of lichens diversity (LB) on *Quercus ilex*. The reference sampling method, used on national scale, has been modified because of the small size of the area. The proposed system consists in a set of cells - Campionary Units (CU)- of 200x200 mt., where the tree nearest to the CU's centre has been selected. Twenty-eight cells have been used. The LB values, included between 0 and 80, have been used to compute a naturality/alteration Map. This Map points out two main areas characterized by poor air quality: the eastern and western boundary lines of the area and the middle of the park. These two areas are close to the streets with high traffic. The florula found in the Park has been analysed with an ecological method. The acidophilous and non-nitrophilous species were more frequent, according to the characteristic of the tree bark sub-acid quality. The most xerophilous and eliophilous lichens have been found in open and flat areas. Furthermore, the hydrophilous lichens have been found in the trees near the border of wood live-oak strips. Our results seems to be in agreement with other studies performed in urban open fields of Rome. This study suggests that the proposed approach could be adopted to evaluate the alteration of air quality even in small areas, like urban parks and historic gardens.

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## A WINTERTIME STUDY OF PAHs IN TWO URBAN CITIES OF TURKEY

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Polycyclic Aromatic Hydrocarbons (PAHs) are major components of toxic air pollutants. In this work, PAHs were measured in the winter of 2006 in Eski ehir and Kocaeli cities of Turkey. Eski ehir is a typical urban city having limited industrial activity with a population of 650.000 and it is 233 km far from Ankara. Kocaeli is an industrialized city with a population of 1200.000 and it is 111 km far from Istanbul. Sampling instrument was placed near a busy road in the center of Eski ehir while sampling was performed on the roof of a building, 20 m above the street level in Kocaeli city center.

Twenty four hours ambient air samples were collected by PUF samplers to determine gas and particle phase PAHs in both cities. Filters were weighed prior to use and after sampling to determine total suspended particulate (TSP). Samples were Soxhlet extracted and analyzed by Gas Chromatography-Mass Spectrometry. Recovery of PAHs was determined by adding labeled standards prior to extraction and satisfactory recoveries were obtained.

Wintertime mean TSP levels were found as 193.87 and 176.38 mg/m<sup>3</sup> for Kocaeli and Eski ehir. The most abundant PAHs as a total of gas and particulate phase was found as phenanthrene (21%), fluoranthene (13%), pyrene (12%) and fluorene (11%) in Kocaeli. Distribution of PAHs in Eski ehir was found to be different than Kocaeli as phenanthrene (21%), fluorene (14%), fluoranthene (10%) and acenaphthylene (9%) and pyrene (9%). For both sites, lower molecular weight PAHs was found to be in the gas phase and higher molecular weight PAHs in the particulate phase.

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## TRANSFERENCE DYNAMICS OF TERBUTHYLAZINE AND DIURON TO RUNOFF FLOW IN NON-TILLAGE SYSTEMS WITH GROUND COVER STRIP

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Despite the fact that relatively small amounts of herbicide are carried away by surface runoff water in relation to the amount applied, they do constitute a potential environmental risk due to their toxicity and persistence, especially if you consider that this is mainly how these substances are spread towards surface waters.

Terbuthylazine and diuron are pre-emergence herbicides used in olive grove management. In order to reduce the residual effects of these herbicides in surface water, both are subject to a series of usage restrictions. One of these restrictions refers to the total application surface permitted, and this is limited to the area surrounding the trees. In accordance with Andalusian legislation implementing the current Common Agriculture Policy Reform, when herbicides are applied below the olive tree canopy, ground cover strips must be established between the tree rows. This soil management technique has been shown to be an alternative to the use of non-tillage with totally bare soil, generating less erosion and a smaller amount of runoff water. The aim of this article is to evaluate the transference dynamics of pre-emergence herbicides from the soil surface to the runoff flow in olive groves with ground cover strips with the required conditions of application. For this, three erosion plots were established: one with bare soil and two with ground cover strips. A commercial product was applied (terbuthylazine 28.5% and diuron 28.5%) with a 1 kg/ha application rate and simulated rainfalls of 20mm/h and 30mm/h. Runoff and sediments generated during the simulated rainfalls were sampled and terbuthylazine and diuron concentrations were determined.

In the evolution of runoff flow and sediment concentration during trials in the plots with ground cover strips, there were a series of oscillations due to the effect of the strips. The evolution of herbicide concentration in water and sediments, however, was more stable in all the cases. Similarly, the differences between bare and covered ground and between rainfall intensities were not pronounced. This suggests that in herbicide transference to the runoff flow, the control exerted by the soil-water interface in the surface mixing area is dominant compared to the control exerted by the physical variables in runoff generation.

In view of the temporary evolution results for herbicide concentration in water and sediments, an exponential function was proposed with adjustment parameters which seem to be related to the initial point of runoff.

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## INFLUENCE OF LIMING ON THE SPECIATION AND TOXICITY OF LIXIVIATES FROM SOILS CONTAMINATED BY PYRITE SLUDGE

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The present work studies the interaction of a contaminant solution (CS) from the oxidation of pyrite sludge with soil and the influence of liming on the composition of the lixiviate. To this end, the horizon Ah of a eutric Cambisol, located in Soberbina (Seville, Spain), SB0, to which increasing amounts of CaCO<sub>3</sub> were added (2, 4, 6, 8 and 10%), obtaining the samples SB0, SB2, SB4, SB6, SB8, SB10. A total of four doses of 50 ml of CS were added to each sample, analysing the effect of liming on the composition and speciation of the different lixiviates. The pH of the soil lixiviates decreased with the addition of the doses of CS. The sharpest decrease was observed after the first addition of CS. It was most notable in the case of SB0, which varied from 7.62 to 2.6, while the variation of sample SB10 was from 8.10 to 6.14, due to its greater potential to absorb.

The speciation calculation was carried out using the SOLMINEQ 88 programme. In these solutions the most important metal complexes/compounds were established with sulphates (over 40% of the total aluminium, over 70% of total Fe, Ca and Mg; 80% of total Pb total and 60% of Zn). Potassium appears mainly as a free ion, this form representing over 70%, and its value decreases in the lixiviates of soils which have no carbonates, particularly on adding four doses of CS to the original soil, representing approximately 40% of the total. Nevertheless the percentage of the different complexes/compounds which the sulphate forms with the metals varies according to the doses of CS added.

As regards aluminium, the predominant kind depends on the pH. Al-SO<sub>4</sub> predominates between 1.89 and 5.55, with a greater presence of the compounds Al (SO<sub>4</sub>)<sub>2</sub><sup>-</sup> when the amount of CS added and the content in carbonates are smaller. At higher pH, the predominant type of aluminium is Al-OH, although the total activity of aluminium is very low. In no case does Al +3 account for more than 4% of the total forms.

Of the main elements analysed, aluminium is the most toxic since it has an adverse effect on plant development due to its interference in the absorption of certain cations such as Ca<sup>+2</sup> or Mg<sup>+2</sup> (A. Haug, 1984). When the Ca/Al molar ratio of the soil solution is between 0.2 and 2.5, there exists the risk of toxicity (Yang and Chen, 2001). This is also true when the toxicity index of aluminium is higher than 2 (Boudot, 1994). Taking the molar ratio and the toxicity index as reference, only sample SB10 shows no evidence of Al toxicity in any of the percolates.

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## USE OF RECEIVER-OPERATING CHARACTERISTIC (ROC) TO VALIDATE ANALYTICAL METHODS FOR POLLUTANT IDENTIFICATION IN ENVIRONMENTAL MATRICES

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Screening and qualitative methods are often used to provide binary responses of type "yes/no" or "1/0", thus, indicating whether an analyte concentration is above or below a specified limit. The rapid instrumental responses provided by these systems are often used for taking immediate decisions: For instance whether or not submit a tested sample to a more elaborate quantitative analysis.

A procedure to estimate the unreliability associated to a binary response (yes/no) originated from an instrumental screening system is outlined according to the use of Receiver-Operating Characteristic (ROC) curves.

ROC curves were developed during World War II military radar operations as a means to characterize the operator's ability to correctly identify friendly or hostile aircraft based on a radar signal. The ROC curve was devised as a graphical means to explore the trade-offs between these competing losses at various decision thresholds when a particular quantitative variable is used to guide the decision.

ROC curves are excellent at representing the sensitivity and specificity of dichotomous decision process. They are extensively used in the fields of medical science and clinical chemistry to evaluate and compare diagnostic systems for their ability to reliably determine whether or not an individual has given illness or condition. ROC curves are also used in machine learning, computational science and environmental science, and very recently also in analytical chemistry as a tool for the validation of qualitative procedures.

ROC curves can be used to predict the unreliability for an instrumental screening system, the limit of detection, the number of false positive, false negative and global accuracy (ROC curve area). To suitably perform a ROC analysis, the candidate method should be compared against a gold standard one, by using two well defined groups: a control group (samples without pollutant contamination) and a group of samples over a given tolerance level.

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## ON THE USE OF SUPPORT VECTOR MACHINES FOR CLASSIFICATION OF PESTICIDES ACCORDING TO THEIR TOXICITY AGAINST FISH

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SVMs (Support Vector Machines) are a relatively young classification technique originally proposed by V. N. Vapnik that become increasingly popular after their introduction in the late 1990s, especially within the Machine Learning community. SVM applications have been successfully developed in several areas, including bioinformatics, econometrics and biometrics. More recently, SVMs have been proposed for the analysis of chemical data and have attracted the attention of the pattern recognition forum, as a classification technique especially devoted to intrinsic non-linear boundaries.

SVMs derive from the principles of the Statistical Learning theory, and it attempts to produce boundaries between classes by both minimising the empirical error from the training set and also controlling the complexity of the decision boundary, which can be non-linear. SVMs use a kernel matrix to transform a non-linear separation problem in the called input space to a linear separation problem in a dimensionality enhanced feature space. Typical kernels include the Radial Basis Function, polynomial and sigmoidal functions. In many simulated studies and real applications, SVMs show superior generalisation performance compared to traditional classification methods, including Artificial Neural Networks (ANN). The main advantages of SVMs against ANN trained by back-propagation are the avoiding of use an extra verification set to control overfitting as well as the deterministic consistency of classification results (in ANN, each time the initial weights are taken at random and leads to slightly but different final weights).

In this contribution, we compare the classification of a series of pesticides (carbamates, organophosphorous and chlorinated) according to their toxicity against fishes when using classical linear methods (LDA, SIMCA, PLS-DA) and non-linear ones (ANN, SVMs).

Traditional linear methods are very effective under certain circumstances, especially in traditional analytical chemistry where the problems are essentially linear and well understood, and SVMs may well be unnecessary. However with a new generation of problems emerging, especially in the interface of biology and analytical chemistry, SVMs could be an excellent approach to tackle complex non-linear problems.

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**NON-SPECTROSCOPIC MATRIX EFFECTS DUE TO EASY IONIZABLES  
ELEMENTS IN ICP-AES. APPLICATION TO THE ANALYSIS  
OF ENVIRONMENTAL SAMPLES.**

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Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) technique is widely employed in environmental analysis due to its analytical performance: high sensitivity and analysis throughput and low limits of detection. Matrix effects due to the presence of concomitants in the sample is one of the most important error sources in ICP-AES. Nonetheless, the origin of these interferences is not well known.

The goal of the present work is to perform a systematic study about the origin of the matrix effects in ICP-AES due to the presence of several elements commonly found in environmental samples. The effect of sample uptake rate, matrix composition (Li, Na, K, Ca, Mg...) and concentration are evaluated in terms of aerosol drop size distribution, aerosol transport rate and analytical figures of merit. Preliminary results indicate that matrix effects: (i) are not additives; (ii) strongly depends on the sample uptake rate; and (iii) seems to be related with the atomic radius of the concomitant. These findings have been applied for the elemental analysis of several environmental samples containing high salt concentrations (rocks, soils and foods).



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## ATMOSPHERIC POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN AIR: A STUDY IN A HIGH TRAFFIC AREA, FOR WINTER PERIOD, IN ISTANBUL

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Atmospheric aerosols are ubiquitous in the troposphere and play an important role in atmospheric chemistry. They include inorganic and organic chemical species which can have harmful effects on human health. Polycyclic aromatic hydrocarbons (PAHs) are one of the several hundred organic compounds that have been identified in the particulate matter in air. PAHs are semi-volatile organic pollutants consisting of two or more fused aromatic rings. Most of the PAHs were analyzed by International Agency for Research on Cancer. According to these analysis results, some of them were classified as probable or possible carcinogens to humans (such as; benzo(ghi)perylene, dibenz(ah)anthracene, benzo(a)pyren etc.). At the high concentrations PAHs are the respirable size range of airborne particulate matter. Because of the ubiquitous nature of atmospheric PAHs and their high levels in urban environment, the risk to human exposure is high for the inhabitants of the cities. Atmospheric PAHs are partitioned between the particulate and the gaseous phases. This gas-particle partition has strong dependence on molecular weight of PAHs. Low molecular weight of PAHs have higher concentrations in the vapor phase while high molecular weight ones are often associated with particles. The recognized carcinogenic PAHs are mostly associated with particulate matter. PAHs are produced by high-temperature reactions such as incomplete combustion and pyrolysis of fossil fuels. Road traffic is one of the most important sources of PAHs in urban air, along with residential heating systems and various industrial activities involving combustion.

The aim of this study is to identify and quantify 16 USEPA atmospheric PAHs which have not been determined for Istanbul Metropolis. In this study, the daily atmospheric PAH concentration present in the high traffic area were determined and this concentration values were compared TSP values and meteorological factors. Comparative evaluation was also carried out for the limit values and literature.

In this study atmospheric concentration of PAHs and total suspended particles (TSPs) were measured in a selected traffic area in Istanbul from October 2006 to March 2007 for characterize winter periods. The sampling site is located in Yildiz Technical University (YTU) campus which is mainly influenced by the local traffic. The sampling platform was positioned 4 m from a large road and 1,5 m above ground level to simulate breathing zone. Samples were collected on working days within the period. Airborne samples were collected using PS-1 high-volume samplers. GFF filter collected airborne particle-bound PAH and TSP, PUF+XAD2 plug collected gas phase-PAH separately for 24 hour period. The samples were extracted and cleaned up according to EPA Method TO 13A and 3630C. All extracts were analyzed using HPLC with both UV and fluorescence detector.

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Totally 55 airborne samples were analyzed for 16 US EPA Priority PAHs at the site and 14 of 16 PAH could be determined in samples. Total PAHs concentration at sampling site were measured as  $89.9 \pm 52.1$  ng/m<sup>3</sup> and TSP concentration were  $100.9 \pm 44.6$  µg/m<sup>3</sup> for the time interval studied. Maximum PAH concentration was observed during December 2006 with average  $139.5 \pm 74.9$  ng/m<sup>3</sup> for nine samples. Heavy PAHs with 5 or more rings, being mainly associated with particulate, are benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene. Total of these heavy PAHs in samples were in the range of  $15 \pm 11.3$  ng/m<sup>3</sup> and correlation of these with TSP values were higher than 60%.

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## **PREDICTION OF VEHICLE TRAFFIC EMISSIONS THROUGH ISTANBUL BOSPHORUS BRIDGES BY COPERT III MODEL**

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Istanbul is the most populated city of Turkey with 12 millions populations. In this city, there are totally 2,400,000 vehicles based on 2006 year data. Because of its location spread out between both Asia and Europe continents, transportation is the most serious problem in this city. Current daily traffic flow is provided with two intercontinental bridges of Bosphorus (BB) and Fatih Sultan Mehmet (FSM). Bridges and connection roads especially are congested with traffic in morning and evening rush hours, and these situations are resulted in most highly air pollution. The transportation passing modes of these two bridges is different in terms of vehicle types. In BB, just only small cars are allowed to pass, while, in FSM Bridge, all types of vehicles can use this bridge route. On the other hand, in the past, passing these bridges was allowed by only paying cash, while currently, alternative paying methods is available such as Automated Passing System (OGS) and Card Passing System (KGS) for preventing traffic accumulation. After April 2006, BB has been allocated for just OGS and KGS passing, while, FMS also has been assigned for all vehicles and all paying types. These kinds of implementations play an important role in the air pollution caused by bridge vehicle traffics.

In this study, prediction of air pollution caused by vehicle traffics using Istanbul Bosphorus Bridges has been performed with COPERT III Model. In this scope, vehicles were evaluated in detail based on their fuel usages and model years. On the other hand, monthly, daily and hourly variation of vehicle numbers and vehicle types used these two bridges was carried out based on 2005 and 2006 year's data. Vehicle fuel consumption rates were assumed to similar to all Istanbul vehicle data. Based on day times, vehicle speeds were evaluated in the bridges and road of approach. Further, the length of vehicle tails between 7 and 9 in the morning and 17 and 20 in the evening were determined. COPERT III Model was used for Istanbul vehicles using Bosphorus Bridges based on different vehicle speeds. Moreover, average emission factors were developed in Istanbul based on vehicle usage characteristics. The model was applied to bridges with 4 different scenarios, and the modeling results indicated that there was 30-45 % increase in carbon monoxide (CO) and hydrocarbon (HC) emissions in BB in 2006. However, the results showed a decreasing trend with 10-30 % in CO and HC emissions for FSM Bridge. Because of these adverse aspects in BB, this bridge has been just assigned for small cars since 2005.

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On the other hand, NO<sub>x</sub> emissions was not showed any changes in BB, while there was an 50-140 % increase in NO<sub>x</sub> emissions for FSM. This high level of NO<sub>x</sub> rising was contributed to heavy duty vehicles. Further, study results showed that increasing current vehicle speed from 15 to 50 km/h resulted in 30-75 % reduction in vehicle emissions. Traffic is the most important problem in terms of air pollution sources in Istanbul. Therefore, modeling studies has gained more attention for preventing traffic originated air pollution. Besides, in order to perform some emission inventory studies and comprehensive modeling approaches, there is an urgent data requirement in this area.

Keywords: Vehicle emissions, air pollution, Copert III, Istanbul

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## HYDROCARBON LEVELS AND DISTRIBUTION IN SURFACE SEDIMENTS FROM KORINTHIAKOS GULF, GREECE

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The aim of this work was to study the aliphatic and polycyclic aromatic hydrocarbon (PAH) levels and distribution in surface sediments collected from Korinthiakos gulf in Greece and to investigate their sources and impact. Aliphatic hydrocarbons are major components of petroleum and all fossil fuels but many of them have also biogenic and/or terrestrial origin. PAH are widespread hydrophobic organic pollutants with high persistence and most of them have strong carcinogenic and/or toxic properties. Their origin could be either pyrolytic or petrogenic and they usually enter the marine environment through the various municipal or industrial discharges, terrestrial runoff or by atmospheric deposition. Korinthiakos gulf coastal zone is influenced by various anthropogenic activities. Along its north coasts, a big industry is located, processing local bauxite mines to produce alumina and aluminium.

Surface sediment samples were collected from 6 stations in December 2005 and the analysis was performed by gas chromatography-mass spectrometry. The compounds determined were: total aliphatic hydrocarbons, resolved aliphatics and UCM, n-alkanes from n-C14 to n-C35 and in total 24 PAH including parent compounds with 2 to 6 aromatic rings, dibenzothiophene and the methylated derivatives of naphthalene, phenanthrene and dibenzothiophene. Aliphatic hydrocarbon concentrations were low in the whole area (8.8 – 39.8 µg/g dw) indicating limited petroleum related pollution. The study of the ratios of unresolved to resolved compounds (U/R) suggested that petroleum residues existed in only two locations. The high molecular n-alkanes predominated in all samples showing an important odd/even preference (CPI values: 4.1-9.3). These values indicated an important allochthonous contribution from terrestrial plants

Extremely high total PAH concentrations (> 10.000 ng/g dw) were measured at the station located relatively close to the industry. These sediments present a strong probability to cause adverse effects in marine biota as many individual PAH concentrations exceeded the limits set by various sediment quality guidelines. In all the other stations PAH values were significantly lower, but still higher than those found in uncontaminated sediments, and ranged between 236 and 979 ng/g. This pattern indicates the presence of a very strong point source supplying the marine environment with high quantities of PAHs, but the serious pollution caused from this source seems to be restricted only to a small marine area.

PAH compounds with four or more aromatic rings, which are known to be of pyrolytic origin, were dominant in all cases and especially in the highly contaminated sample. Various diagnostic criteria based on specific isomeric PAH ratios (MW: 178, 202, 228, 276) were applied, confirming the strong pyrolytic PAH origin and indicating wood or coal combustion as the most probable sources for the PAH mixtures found in the area.

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## THE CONTRIBUTION OF RENEWABLE ENERGY SOURCES ON REDUCING THE AIR POLLUTION OF GREEK ELECTRICITY GENERATION SECTOR

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The Greek electricity generation sector is based -as far back as the early 60's- on the usage of local lignite and imported heavy-oil. Therefore the electricity production process is assumed responsible for more than one half of CO<sub>2</sub>, for almost 80% of SO<sub>2</sub> and for approximately one third of NO<sub>x</sub> national emissions. Taking also into consideration that during the last 25 years considerable energy consumption increase has taken place in view of the local economy development and standard of living improvement, Greece faces serious difficulties on fulfilling the EU Directives concerning the reduction of the greenhouse gas emissions and the protection of the local population from the dangerous toxic effects of various harmful gases and particles release, like nitrogen oxides, sulphur dioxide etc.

On the other hand, renewable energy resources -like hydro, wind and solar energy- used extensively for electricity production throughout the world, are practically air-pollution free on a life cycle base analysis. In this context, the present work investigates first the specific air pollution emission factors related with the electricity production from fossil fuels in Greece. Next, the air pollution avoided due to the exploitation of the available hydro and wind potential is predicted on an annual basis for the last decade. Finally, the potential contribution of the renewable energy sources on significantly reducing the above mentioned pollutants is estimated on the basis of the corresponding EU targets included in the relative EU-Directives (e.g. 2001/77/EC).

According to the results obtained, despite the up to now fair participation of the existing hydro power stations and wind parks on reducing the air pollutants, the renewable energy sources may, in the near future, contribute significantly on minimizing the environmental impacts of the electricity generation sector, including the emissions of carbon dioxide and other various harmful gases, at rational investment cost.

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## DISINFECTION BY- PRODUCTS OF KONYA (TURKEY) DRINKING WATER

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In order to eliminate waterborne diseases various chemicals are used for water disinfection. Widely used chemical for water disinfection chlorine. Free chlorine and dissolved organic matters in waters are reacting to form disinfection by products.

In this work haloacetonitriles (Trichloroacetonitrile, Dichloroacetonitrile, Bromochloroacetonitrile, Dibromoacetonitrile), haloketones (1, 1 Dichloro-2-propanone, 1,2-Dibromo-3-chloropropanone), chloropicrine (Chloropicrin) and some other disinfection by products (1,1,1-Trichloroethane, Carbon tetrachloride, trichloroethene, 1,2-Dibromoethane) are investigated in Konya drinking water treatment plant and water distribution networks. The disinfection by products were analysed adopting the EPA GC/ECD Method 551. The recovery ratios of adapted method were determined as between 97.6%-104% in fortified samples. Widely found disinfection by products in water treatment plant and water distribution network are carbon tetrachlorid, trichloroethene, 1,1,1-Trichloroethane, Dichloroacetonitrile and Bromochloroacetonitrile

Key words: chlorination, DBPs, HANs, CP, HKs, network, GC, Konya.

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## ESTIMATION OF EMISSIONS AND LOCAL EMISSION FACTORS IN THE REGION OF WESTERN MACEDONIA, GREECE

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The Region of Western Macedonia in Greece is one of the most polluted areas in Europe due to large lignite – fired power plants with total installed capacity of approx. 4500 MW. The determination of emissions and emission factors for the region is an essential part of an EU-supported project (SMAQ), aimed at developing methods for optimizing pollution abatement plans and for early warning of extreme pollution incidents. Using the Corinair methodology developed by the European Environment Agency, emissions and local emission factors have been estimated for the main industrial and nonindustrial activities in that region. Biogenic sources such as animal husbandry and agricultural activities have been examined as well. The particular source sectors examined are power stations, lignite mining, road transport, central heating systems and agriculture. Calculated emission factors are based on data from the local pollution sources, while default values from Corinair or other sources were used to fill existing information gaps. Results are summarized in the following, according to the main source categories.

**Power Stations.** Data have been treated from five major Power Stations (Agios Dimitrios, Amyntaio, Ptolemais, Kardias and Meliti), regarding PM emissions, energy production, lignite ultimate analysis and consumption, for the years 2001 to 2004. The primary data have been provided by the Public Power Corporation (PPC), the owner and operator of the power plant facilities. PM emission factors have been calculated for the above emissions. NO<sub>x</sub> and SO<sub>2</sub> average emission factors based on annual emission data and annual flue gas flow rates have been employed for calculating monthly emissions. These power plants are the main pollution sources contributing to air quality degradation in the region.

**Lignite mining.** PM<sub>10</sub>, NO<sub>x</sub> and SO<sub>2</sub> emissions for the period 2000-2005 have been estimated by taking into account emission factors for lignite transportation retrieved from literature sources and the annual production of lignite excavated from the local mines.



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Road transport. Estimated and literature emission factors are obtained for transportation in 2001 (reference year), concerning urban and rural roads and highways, for each vehicle category. Estimates are based on relationships developed following the Corinair methodology. Hot and cold emissions for urban and rural roads and highways in the region have been computed by using the above emission factors and by taking into consideration the age distribution, the capacity, the weight and the mileage of the local vehicles.

Central heating systems. Emissions for a variety of pollutants (SO<sub>2</sub>, PM<sub>10</sub>, CO etc.) from domestic central heating systems (period 2000-2005) have been estimated based on default emission factors from fuel oil combustion.

Agriculture. Ammonia and methane emissions for the period 2003-2005 have been estimated for the region examined, based on default Corinair emission factors, the area cultivated and the numbers of animals. CH<sub>4</sub>, NH<sub>3</sub>, PM, NO<sub>x</sub>, CO, N<sub>2</sub>O emissions from agricultural tractors and other related machinery have been estimated as well.

The information obtained is considered fairly complete and it is currently being used in conjunction with other data (e.g. epidemiological) and model results, as well as satellite images, to develop a novel methodology (in the context of SMAQ project) for air pollution predictions.

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## CHROMIUM (VI) AND CADMIUM(II) IONS BIOSORPTION FROM AQUEOUS SOLUTIONS BY IMMOBILIZED BIOMASS OF OSCILLATORIA SP. H1 ISOLATED FROM FRESHWATER (MOGAN LAKE)

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The *Oscillatoria* sp. H1 (Cyanobacteria) isolated from Mogan Lake was researched for the removal of chromium (VI) and cadmium (II) ions from aqueous solutions and were used immobilized (in Ca-alginate) live and immobilized heat-inactivated biomass as a biosorbents. Particularly, the effects of physico-chemical parameters like pH, the temperature change, initial concentration, biosorption time and biosorbent dosages on the biosorption of Cr(VI) and Cd(II) ions were investigated. The biosorption of Cr(VI) ions for all biosorbents was determined a highest value at pH 6.0. The temperatures changed between 20 and 40 °C did not affect the biosorption capacity. The biosorption of Cr(VI) ions on immobilized (live and heat-inactivated) *Oscillatoria* sp. H1 biomass (mg/g) was increased as the initial concentration of Cr(VI) ions increased in the medium. Biosorption equilibrium was established in about 60 min. The retention of Cr(VI) increased with increasing the amount of the adsorbent up to 0.04g and 30 bead. The results were showed that immobilized inactive cells (13.83 mg/g) had less biosorption capacity than that of the immobilized live form (20.82 mg/g).

The sorption of Cd(II) ions by on the sorbent used was examined for the cadmium concentrations in the range of 25 - 250 mg/L. Maximum biosorption capacities for plain alginate beads, immobilized live and heat-inactivated *Oscillatoria* sp.H1 were 32.16 and 27.46 mg/g, respectively. Biosorption equilibrium was established in about 1 h for the biosorption processes. Maximum adsorption was observed at pH 6.0. It was also represented with Langmuir and Freundlich adsorption isotherms. The biosorbent systems could be regenerated by washing with a solution of 10 mM HCl. The percent desorption achieved were as high as 98% (Cr VI) and 85% (Cd II). The biosorbents were reused in three biosorption-desorption cycles without significant loss of their initial biosorption capacity.

The results indicated that the immobilized live of *Oscillatoria* sp. H1 may be suitable for development of efficient biosorbent for the removal of chromium (VI) and cadmium (II) from wastewater of chemical and allied process industries.

**Keywords:** Cadmium(II), Chromium (VI) removal; biosorption; bioaccumulation; microalgae; Ca-alginate; *Oscillatoria* sp.

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## STUDIES ON THE SENSITIVITY OF FRESHWATER MICROALGAL ISOLATES TO CHROMIUM (VI) AND CADMIUM (II)

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The toxicity of the heavy metals, chromium (VI) and cadmium (II) in a common filamentous cyanobacteria (or blue-green algae), *Oscillatoria* sp., were studied. The *Oscillatoria* sp. H1 and H2 were isolated from Mogan Lake in Turkey. *Oscillatoria* sp. were cultured in a BG11 medium, which was supplemented with 5, 15, 25, 35, 45, 50, 100, 250 mg/L of Cr (VI) and Cd (II), and were separately harvested after 24, 48, 72 and 96 hours. The toxicity symptoms of Cr (VI) and Cd (II) to *Oscillatoria* sp. showed damage and disintegrated cell wall and death. There were significant decreases in the relative growth when the exposure time and concentration were increased. The sensitivity of two freshwater microalgae isolates to the two heavy metals was studied by using algal probit analysis. 48-hour EC50 values of Cr (VI) and Cd (II) (at 95% confidence limits) used in our study were found 50,4 mg/L (Cd II) and 25,7 mg/L (Cr IV) for *Oscillatoria* sp. by probit analysis. No cell deformation or cell death was observed in the control group throughout this period. According to this, it may be stated that *Oscillatoria* sp. H1 is a more tolerant alga to cadmium and chromium when compared to *Oscillatoria* sp. H2.

**Keywords:** Cadmium(II), Chromium (VI), toxicity, microalgae, *Oscillatoria* sp.

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**PARAMETERS AFFECTING As(III) OXIDATION BY ZERO  
VALENT IRON AND HYDROGEN PEROXIDE AT  
CIRCUMNEUTRAL pH IN AERATED AQUATIC SOLUTIONS**

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The worldwide occurrence of arsenic contamination of groundwaters is recognized as one of the major drinking water problems and the removal of arsenic from groundwaters is essential and often challenging. In the present work, we have investigated the use of zero valent iron to oxidize and remove As(III) from aerated aquatic solutions at circumneutral pH.

The mechanism of As(III) removal by zero valent iron in aerated solutions includes both oxidation of As(III) and adsorption on iron oxides of As(V), which are formed from the oxidation of Fe(0) to Fe(III). The oxidative power of zero valent iron in contact with air is strongly dependent on the corrosion of zero valent iron, with release of Fe(II), accompanied by the generation of hydrogen peroxide and on the oxidation of Fe(II) to Fe(III), which leads to the formation of intermediate oxidants.

In the present work, we have examined the parameters, which affect the As(III) oxidation at pH 7: the concentration of zero valent iron, the ionic strength and the phosphate concentration. It was found that the rate of As(III) oxidation increased with increasing the concentration of zero valent iron and the ionic strength, and decreased with increasing the phosphate concentrations.

In an advanced oxidation treatment, we have combined the use of zero valent iron with different concentrations of hydrogen peroxide. The oxidation of As(III) did not take place when only hydrogen peroxide was used, but it drastically increased in the presence of both zero valent iron and hydrogen peroxide. It was found that complete and very fast oxidation of 6.7  $\mu\text{M}$  As(III) was achieved with 10  $\mu\text{M}$  of  $\text{H}_2\text{O}_2$ , while the residual  $\text{H}_2\text{O}_2$  was roughly 3  $\mu\text{M}$ .

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**EXPERIMENTAL MEASUREMENTS OF C2-C5 AND C6-C10  
IN URBAN AREA OF THESSALONIKI, GREECE**

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The present study refers to experimental ambient air hydrocarbon measurements in the city of Thessaloniki, Greece, from May to July 2006. The measurements are performed at two sites of the Municipal Air Quality Network of Thessaloniki, at the commercial city center (11.4 m asl) and at an urban peripheral site (174.0 m asl). The two locations, city center and peripheral site, have been selected because they represent the maximum and minimum levels of pollutants measured in Thessaloniki, respectively.

The measurements concern two hydrocarbon groups, C2-C5 and C6-C10 and were performed with three automatic gas-chromatographs, selected for their suitability to measure in the field, equipped with FID and PID detectors. The daily and hourly variations of these measurements are presented and a comparison between the two sites is performed.

An attempt is made to explain the differences, in relevance to the meteorological conditions and the emission characteristics. Moreover an additional comparison is made with the permanent measurements of BTEX and other relevant air pollutants performed at the urban area of Thessaloniki.

**Keywords:** urban air pollution, ambient hydrocarbon measurements, gaseous phase chromatography.

**Acknowledgements:** The project is also co-funded by the European Social Fund & National Resources – EPEAEK II, PITHAGORAS and ARCHIMIDIS II.

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## APPROXIMATE SOLUTIONS OF THE RADIATION BUDGET EQUATION IN COMPLEX TERRAIN

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A theoretical investigation is presented on the approximate solutions of the radiation budget equation in complex terrain. A method of calculating an exact solution to the net radiation balance is also developed and compared to the commonly used approximations.

The suggested procedure adopts the effects of multiple reflections of the longwave radiation by evaluating an infinite convergent geometric series in terms of the surface emissivity and sky view factor. The exact solution varies significantly from the approximate methods, and the need for a full solution of the radiation budget equation becomes more critical as the sky view factors or the surface emissivities decrease.

A simple semi-empirical scheme based on the exact solution of the radiation budget equation is also presented, which gives estimates of the net all-wave radiation avoiding the use of surface radiation temperature. Finally, the theoretical estimates were validated and compared with actual measurements.

**Keywords:** Radiation budget, complex terrain, multiple reflections, exact solution, longwave radiation.

**Acknowledgements:** The project is also co-funded by the European Social Fund & National Resources – EPEAEK II, ARCHIMIDIS II.

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## ACTUAL SITUATION OF AIR POLLUTION IN ALBANIAN CAPITAL CITY, TIRANA

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Car exhalation is just the top of the iceberg. Tons of rubbish; diesel, petrol burning near by the city roads, caoutchouc bottles, non organic rubbish, car tires, etc may be found every where in Tirana even there where it is mend to be a children playground.

At the moment the equipment placed at five meters from the surface of capital centre shows a level of 467 microgram dust for every meter cube air, level which is four times higher than the European Commission permitted rate. Owing to this rate, Tirana incumbencies the unbreakable record now from years as the city with the most polluted air in the whole Europe.

Alike ciphers the European record is discovered in Tirana even from the monitoring of cancerogenic smut in the air, part of Tirana respired air every day.

The firm mote deterrence in Tirana waves between 70-200 microgram/m<sup>3</sup> overfulfilmenting evidently the 24 hour and annual average. Kinetic composition of the dust and its aerosols it is not yet monitored. Quoad to the CO restraints, their values in all seasons do not exceed the WHO respective rates. Maxim CO content in air is less than 0.40 mg/m<sup>3</sup>, which is in shape with the respective national and international standards.

Respirated dust (PM 10) is the most problematic air contaminant viewpoint to health in all the checked points to monitorate. It exceeds everywhere the Albanian and WHO precept over 1.5 – 8 times (63-483 µg / m<sup>3</sup> determinated actually reconcile to 50-60 µg / m<sup>3</sup> accessible).

Problematic monitored checked points are Tirana 1 ( city centre), Tirana 2 ( New Bazaar zone), Tirana 4 ( quartier 21 Decembre), Tirana 5 (DHE).

$\mu\text{g} / \text{m}^3$	LGS	PM10	SO <sub>2</sub>	NO <sub>2</sub>	Ozone	Pb
Tirana 1	286	119	16	37	95	0,13
Tirana 2	226	105	14	30	100	0,155
Tirana 3	126	70	13	20	91	0,12
Tirana 4	995	483	20	48	110	0,195
Tirana 5	215	98	10	20	110	0,25
Albanian						
Norme 2006	140	60	60	60	120	1,0
WHO rates	90	50	50	40	120	0,5

**Keywords:**

Smog: A mixture of smoke and fog; air pollution: harmful contaminant air state; respiratory tract diseases: serious illnesses affecting one or both lungs, causing difficulty in breathing or worse; public health: service which concerns the people in general health; environment: natural conditions, eg land, air or water in which human live are affected by them.



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## DIFFUSION COEFFICIENTS OF NO<sub>2</sub> IN ARTIFICIAL SEA WATER AND PARTITION COEFFICIENTS IN WATER-AIR INTERFACE IN THE PRESENCE AND THE ABSENCE OF SURFACTANTS

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It is an undeniable fact that the increase of air pollutants is a plague in this day and age with detrimental effects on humanity and environment. The most important atmospheric pollutants are carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), and other hydrocarbons (C<sub>x</sub>H<sub>y</sub>), while the most important vapors come from some volatile organic toxic substances. The evaporation of organic volatile substances from water and the absorption (solution) of gases from (to) water are processes of utmost importance as far as the exchange of air pollutants between atmospheric and water environment is concerned [1-3]. The mass transfer coefficients of the aforementioned processes depend not only on temperature, pressure and diffusion coefficient of the transferred substance, but also on the presence of other pollutants on water surface and the strobilization in the air-liquid interface, which is controlled by air velocity and water stream. Surfactants (surface active agents) are molecules that, when added to a liquid at low concentration change its properties at a surface or interface. The presence of surfactants at a gasliquid interface affects the rate of transfer of a solute from the gas to the liquid. Surfactants alter the interfacial region and provide additional resistance to diffusion even when the liquid is quiescent. The presence of surfactants at an interfacial region can offer significant resistance to the transfer of a solute between a gas and a liquid phase. Surfactant films have long been through to be a factor in modulating physical transfer processes. The molecular organization of these films is an important factor governing interfacial process. Recent laboratory studies in wind-wave flumes have yielded new insights on the inhibiting effects of surfactants on gaseous exchange [4]. In the present work reversed – flow gas chromatography has been applied not only to study the adsorption mechanism of NO<sub>2</sub> into pure water as well as into artificial sea water and the influence of temperature and pH values on this mechanism but also to investigate the role of surfactant into this procedure. All the above can be carried out by the calculation of the diffusion coefficient of NO<sub>2</sub> into liquid phase, DL, the rate constant for the first order reaction between NO<sub>2</sub> and liquid, kR and the partition coefficient of NO<sub>2</sub> in the air-liquid interface, K.

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## FLUX DECLINE CHARACTERISTICS OF HUMIC ACID AND ALGINATE BY NANOFILTRATION MEMBRANE

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Membrane systems are very effective for surface water treatment and started to be used at high capacities to supply water to big cities. Natural organic matter can be removed by nanofiltration membrane successively. However, flux decline may occur and this may affect the membrane performance during operation.

In this study, dead end nanofiltration membrane studies were performed and alginate and humic acid solutions which have different molecular weights were studied. These solutions were also mixed with silica particles to investigate the effect of inorganics on flux decline. Experiments were performed until the recovery rate of 85 %. Membrane cleaning was performed after first fouling and then second membrane fouling experiment was done. At least, three fouling experiments were performed for each solution at long periods. According to experimental results, flux declines with alginate solution which represents the polysaccharides, were high according to humic acid solution. Addition of particles increased the flux decline for both alginate and humic acid solutions. While irreversible fouling was observed for alginate solution, addition of particles changed this situation to reversible. Reversible fouling was dominant if the particles are mixed. Results of all experiments will be given the full manuscript.

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## SCREENING ASSESSMENT OF PESTICIDES AND PERSISTENT ORGANIC POLLUTANTS IN WATERS AND SEDIMENTS OF AXIOS RIVER

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Axios (Vardar) river is the second - in length - river of Balkan area, with a total length of 380 km (306 km in FYR of Macedonia and 74 km in Greece). In its estuaries to Thermaikos Gulf (located in the greater area of Thessaloniki - Greece), Axios river formulates an extended delta together with Aliakmonas and Loudias rivers. This river delta is a very rich in flora and fauna wetland and is protected by Ramsar convention. Agricultural, industrial and urban activities are the main pollution sources of Axios river. Axios river is polluted by industrial chemical waste in Kostivar and Titovo areas, by urban waste from Scopje city and about 12 other smaller cities in FYR of Macedonia. Smaller rivers (Axios river tributaries) from Prilep and Bitola areas diffuse pollutants to Axios river with industrial and agricultural origin. In Veles area, there are lead, zinc and fertilizer factories, which lead to pollution reached sometimes the Thermaikos gulf. In Greek territory, Axios river is also polluted by industrial, urban and agricultural waste, while its river delta presents some other significant problems related to its protection status.

The present paper is a part of a greater research project aiming to determine the transboundary pollution of Axios river, its water and sediment quality and the direct and indirect impacts to human health and environment. In the framework of this project, it has been determined, the physical-chemical and microbiological quality parameters, the presence of toxic chemical compounds and elements such as metals, pesticides and other related organic pollutants in various sampling stations during the year 2006. Axios River was chosen because it has a typical Mediterranean hydrological regime and it is one of the most important aquatic systems of the northern Greece, entirely within Greek territory. Our initial efforts were to collect and evaluate all available chemical data regarding the load of dissolved inorganic nutrient and the presence of organic and inorganic contaminants in the river. Its spatial distribution, and the seasonal variations and trends of the contaminants concentrations were evaluated in order to assess the quality of waters and sediments, in the watershed and the coastal area. The protection and management of Axios waters are of great economic and ecological importance and should be based on an integrated environmental approach.

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## **INORGANIC AMENDMENTS TO DECREASE METAL AVAILABILITY IN SOILS OF RECREATIONAL URBAN AREAS: LIMITATIONS TO THEIR EFFICIENCY AND POSSIBLE DRAWBACKS**

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The effect of amendment with various inorganic materials on the availability of potentially toxic metals (PTM) in soils of recreational areas of the city of Sevilla was studied.

Three parks were chosen, and three inorganic materials that are supposed to cause a strong decrease of metal solubility or availability were added to the soils in a field experiment. In each park, a network of 1- m<sup>2</sup> plots were used, arranged in an incomplete block design. A zero treatment with no material added was included in each park. The materials were Y-type zeolite, calcium phosphate (apatite), and 'slovakite', a synthetic material manufactured by IPRES, Slovak Republic. Samples were taken from every plot during one year, and available PTM contents (either to plants or to humans through ingestion) were estimated in all samples by different methods. Total PTM contents and general characteristics of the soils were determined at the beginning of the experiment.

Some influence of the amendments on PTM availability was observed, although the results depended strongly upon the method used to estimate such availability. Moreover, often the magnitude or the sign of such influence did not agree with those expected from the literature for these materials. It was concluded that despite their accepted applicability in other instances, the materials tested here are not unequivocally applicable to neutral urban soils, probably due to the specific origin of some urban PTM.

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## EMISSION OF INORGANIC INTERMEDIATES DURING THE PHOTOCATALYTIC OXIDATION OF NO<sub>x</sub> OVER TiO<sub>2</sub>-CONTAINING PAINTS

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Heterogeneous Photocatalytic Oxidation (PCO) is considered one of the most promising technologies for the elimination of air pollutants. However, intermediates have been detected in some PCO processes. Intermediates can be totally degraded by the photocatalytic system despite the fact that their emission from the catalyst surface to the gas phase as pollutants, has also been reported.

It is the purpose of this study to detect the inorganic intermediates emitted in the gas phase from the surface of TiO<sub>2</sub>-containing paints, during the photocatalytic degradation of NO<sub>x</sub>. The study was conducted using commercial TiO<sub>2</sub>-containing paints which were spread over the surface of glass panels and placed into a stainless steel (30 m-3) walk-in type environmental chamber under controlled environmental conditions.

Three types of nanoparticle TiO<sub>2</sub>-containing paints were tested: a mineral silicate paint (P1), a siloxane paint (P3) and a water-based styrene acrylic paint (P4). Experimental results showed significant effect of TiO<sub>2</sub>-materials on reducing NO<sub>x</sub>. Photocatalytic rate and deposition velocity were calculated for each material indicating higher photocatalytic performance of the P4 paint. Additionally, the concentration levels of the emitted inorganic intermediates (NO/NO<sub>2</sub> and O<sub>3</sub>) were recorded during the photocatalytical processes. During the photodegradation of NO on the P1, P3 and P4 paints, the concentration of NO<sub>2</sub> in the gas phase was increased up to 34, 37 and 35 ppb respectively while on P4 the corresponding NO<sub>2</sub> values followed a decreasing performance reaching 25 ppb by the end of the experiment. The corresponding values of NO, during the NO<sub>2</sub> photodegradation experiment were 29, 18 and 7 ppb respectively, while on P4 NO totally eliminated by the end of the experiment. The intense photocatalytic properties of P4 lead to the photo degradation of the intermediates. O<sub>3</sub> formation was kept at very low levels during all the experiments (~5ppb). The formation of NO and O<sub>3</sub>, during NO<sub>2</sub> photocatalytic experiments, seemed to be independent concerning the photocatalytic procedure, presenting the same behavior on both TiO<sub>2</sub> and blank (without TiO<sub>2</sub>) samples. Their presences in the system were the result of NO<sub>2</sub> photolysis in the gas phase.

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## EFFICIENCY OF GLYPHOSATE IN THE CONTROL OF SPARTINA DENSIFLORA BRONGN IN A MARSHY SOIL FROM ODIEL NATURAL PARK

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*Spartina densiflora* Brong. (Poaceae) is a species native from South America that is invading salt marshes in SW Europe, NW Africa and SW North. The invasion of *S. densiflora* is one of the most important conservation problems affecting the estuarine environment in the SW of Spain, and the development of strategies for its control or eradication is necessary. The objective of this study was to investigate the effect of glyphosate on the photosynthetic apparatus and growth of *S. densiflora*. The bioavailability of the herbicide was also studied by means of dose-response and soil adsorption studies.

Adults clumps of *S. densiflora* were collected from a natural population (37°14'N-6°57'O), and transplanted in individual plastic pots, filled with previously sampled air-dried marshy soil from Odiel Natural Park. The herbicide doses used were 2, 4, 6, 10, 15 and 20 l ha<sup>-1</sup>. Chlorophyll fluorescence measurements were recorded 24 h after herbicide application and weekly during the time of the experiment. At the end of the experiment (after 2 months), percentages of surviving, dead and new tillers were recorded in all treatments. Adsorption studies were performed with the marshy soil and glyphosate with initial concentrations ranging from 0.5 to 50 mg l<sup>-1</sup>. The amount of herbicide present in the marshy soil was extracted after spraying the plants and at the end of the experiment.

Our results show that only the three highest concentration of glyphosate (10, 15 and 20 l ha<sup>-1</sup>) had a negative effect on chlorophyll parameters of *S. densiflora*, reducing the maximum quantum efficiency of PSII photochemistry (Fv/Fm) and quantum efficiency of PSII (ΦPSII). An increase in dead tillers respect to the control was observed with 10, 15 and 20 l ha<sup>-1</sup> herbicide doses (20, 50 and 70%, respectively). A reduction in the number of new tillers was also recorded with increasing concentration of glyphosate. Adsorption studies show that the marshy soil has a very high sorption capacity for glyphosate, due to its very high iron oxide content. Soil extraction at the beginning and at the end of the experiment revealed that glyphosate is either degraded or strongly sorbed to soil, which indicates a very low risk of surface or ground-water contamination in this protected site.

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## ROLE OF ORGANIC LIGANDS AS AFFECTING CHANGES OF METAL TOXICITY IN RIVER WATERS

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Environmental risk assessment and water Quality Criteria for metals are presently based on results from standard toxicity testing. However, metal-toxicity tests set-up in standard media may be poorly representative for the water-chemistry effect of natural surface waters since metal-toxicity largely depends on physical-chemical water properties, including hardness, pH and dissolved organic matter, which govern metal bioavailability to aquatic organisms.

While mathematical models have recently developed to predict site-specific metal-bioavailability, the direct biological approach, as developed by EPA to provide site-specific WERs (Water Effect Ratios), since based on the ecotoxicological evaluation of metal toxicity, can directly estimate the water-chemistry effect on metal bioavailability in site-waters.

With the aim to evaluate the role of DOC on Cu-bioavailability in river waters, an experimental framework combining sample-treatment, like in TIE-based procedures, with WER ecotoxicological-testing was adopted. In this study, the simultaneous testing of the original sample and the sample treated by SPE extraction was a strategy aimed to provide the experimental evidence for the increase of Cu-toxicity following the removal of organic-ligands in the postcolumn site-water.

The water-chemistry effect was experimentally measured by comparing values of Cu-toxicity in river-water and in standard medium. The green-alga *Selenastrum capricornutum* was used to measure the 72h % Inhibition values. Changes of Cu-bioavailability were evaluated both over time, during one-year sampling, and over the river-course, by comparing two Lambro river-sites located respectively up and downstream from a highly industrialized area around Milan, in Northern Italy.

As expected, the water-physicochemistry was deeply modified in the lower part of the river, most key-parameters which affect metal-toxicity being significantly different in the two river-sites all over the sampling period. The results from toxicity-testing showed parallel WER increase, Cu being up to three times less toxic in the down than in the up-site, the greatest differences being observed in the highest flow events recorded during the sampling.

The results obtained by the SPE treatment clearly showed the increase of Cu-toxicity following the removal of organic matter, the WERs being reduced to the upstream values in all the postcolumn downstream-samples.

The primary role of DOC, as strongly suggested by these experimental results, is also supported by the close relationship linking Cu-WER to DOC content, as observed in high river-flow conditions, which are expected to support the major enrichment of natural organic ligands in river waters.



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## GFAAS AS AN ANALYTICAL TOOL TO THE DETERMINATION OF ORGANOTIN COMPOUNDS IN ENVIRONMENTAL SAMPLES

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Organotin compounds have been the subject of environmental studies for two obvious reasons. Firstly is the increasing world wide use of inorganic and organotin compounds in many industrial, chemical and agricultural areas, very little being known about their environmental fate; secondly, there is a great difference in toxicity of various organotin compounds according to the variation of the organic moiety in the molecule. These compounds occur extensively in the ecosystem, being found in natural and marine waters, sea creatures and sediments. Organotin levels as low as 1 mg·L<sup>-1</sup> (as tin) in water can affect the population and mariculture of marine organisms, especially shellfish. Considerable effort has been made to improve the sensitivity and selectivity of the analytical methodology used to detect such species.

Most of the quantitative methods used include the use of a separation technique coupled to a sensitive and tin-selective detector. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is an adequate technique for these purposes due to its ease of operation and cost effectiveness. Nevertheless, differences between tin emission signals of different organotin and inorganic tin compounds in ICP-AES have been reported. These differences have been attributed to differences in volatility. To avoid these differences graphite furnace atomic absorption spectrometry (GFAAS) could be used.

The aim of this work is to study the behaviour of organotin compounds in GFAAS. To this end, different organotin compounds (BuSnCl<sub>3</sub>, n-Bu<sub>2</sub>SnCl<sub>2</sub>, t-Bu<sub>2</sub>SnCl<sub>2</sub>) and inorganic tin solutions (SnCl<sub>4</sub>) have been determined by employing different temperature programs and up to a total of twenty chemical modifiers and mixtures. Results showed a clear effect of the tin compound on the analytical signal for all the conditions tested. Moreover, the effect of the modifier depends on the chemical compound used.

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## PAHS IN URBAN SOILS OF FOUR EUROPEAN CITIES

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The purpose of this study was to determine the degree of contamination with polycyclic aromatic hydrocarbons (PAHs) in urban soil samples from four European cities: Seville (Spain), Glasgow (UK), Torino (Italy) and Ljubljana (Slovenia). Fifteen PAHs (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysenene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene) were measured in urban soil samples, using harmonised sampling, sample extraction and analyte quantification methods. Although the mean concentration of each PAH in urban soils of each city showed a wide range of values, high levels of contamination were only evident in Glasgow, where the sum of concentrations of 15 PAHs was in the range 1487-51822 mg kg<sup>-1</sup>. Ranges in the other three cities were about ten-fold lower (89.5-4488 mg kg<sup>-1</sup>). The three predominant PAHs were phenanthrene, fluoranthene and pyrene, being the sum of these compounds about 40% of the total PAH content. These data, together with some special molecular indices based on ratios of selected PAHs, suggest pyrogenic origins, especially motor vehicle exhausts, to be the major sources of PAHs in urban soils of the four cities.

The largest concentrations for PAHs were often found in sites close to the historic quarters of the cities. Overall, the different climatic conditions, the organic carbon contents of soil, and the source apportionment were the dominant factors affecting PAHs accumulation in soil.

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## OPTICAL CHARACTERISATION OF THE MIDDLE AND SOUTHERN ADRIATIC WATERS – DISCRIMINATING POLLUTION IMPACT

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The paper aims to demonstrate the differences in water optical properties between the regions of the Eastern Middle and Southern Adriatic. Investigated are particular locations in the channel and bay areas as well as the open sea.

The research is derived from the spectral measurements of daylight intensity, performed with the profiling radiometer PRR800 (Biospherical Instruments Inc.). High resolution measurements of downward irradiance and upward radiance were carried out at 14 wavelengths from UV to visible light (340; 380; 412; 443; 465; 490; 510; 532; 555; 589; 625; 665; 683 and 710 nm) together with the PAR (400-700 nm) and natural fluorescence measurements. Among the measurements performed through 2003-2006, selected were those that demonstrate high spatial variability of optical characteristics, pointing to the different exposure of the areas to the coastal pollution on one side or to the influence of clear open sea waters.

Optical water types were determined for the stations, based on comparison with the Jerlov optical water types, from PAR attenuation measurements and from irradiance spectra. The open sea stations and some channel stations show characteristics of unpolluted sea, like clear oceanic waters of optical types I, II or III. Stations located in semienclosed bays and the stations exposed to the river runoffs have characteristics of coastal optical water types, spanning over the full range of types 1 to 9. The optical water types were also related to thermohaline characteristics.

Attenuation coefficients define the light penetration and are therefore important for the propagation of solar energy through the water column. The same solar energy input warms stronger the surface layers of the more turbid waters, resulting with a different temperature and salinity structure and producing different stability and currents fields, shown through our numerical hydrodynamical experiments. Since the light penetration enables photosynthetic activity, the consequences of changed optical properties can influence the whole ecosystem. The highest attenuation coefficients point to the possible coastal/anthropogenic impact to the marine environment and to potentially threatened areas. Therefore, optical properties, among other environmental parameters can bring out helpful information about the water quality useful for the management of marine areas.

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## PHOTODEGRADATION OF MONURON HERBICIDE ADSORBED ON SELECTED CLAY SUPPORTS

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Photodegradation processes are involved in dissipation of pesticides in water, soils and plants. Therefore, the study of these abiotic transformations makes an appreciable contribution in the determination of the final fate of such chemicals in the environment.

Monuron (3-(4-chlorophenyl)-1, 1-dimethylurea) is widely applied for pre- and post-emergence weeds control in many crops and it acts as an inhibitor of photosynthesis because it is characterized by its long life time in the environment.

In order to understand the photodegradation of monuron adsorbed on clay surfaces, irradiation experiments were performed on monuron adsorbed clays at  $\lambda \geq 290$  nm using a suntest reactor. The disappearance and phototransformation of the parent compound were followed by HPLC. The kinetics of the photodegradation process follows the first order reaction with a half life time of 55H36min and 37H44min for clay extracted from two soils which differ by their amount of organic matter. These results were compared to those obtained with commercial clays: montmorillonite and kaolin.

Several photoproducts were identified using HPLC/MS and a degradation mechanism has been proposed.

Keywords: monuron, soil, clay, photodegradation

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**ANOMALOUS ARSENIC CONTENTS IN AGRICULTURAL SOILS  
AND CROPS IN AN AREA OF THE DUERO RIVER BASIN**

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The study was carried out in an intensively cultivated agricultural area of central Spain where were reported high As content in groundwater. Soils, plants (potato, sugar beet, and carrot), and irrigation water samples were analysed for As and other parameters. Irrigation water shows high As concentrations ranging between 10 and 136 mg l<sup>-1</sup>. Arsenic total concentration in the uppermost soil layers of the sugar beet field (36 mg kg<sup>-1</sup>) is high in relation to the soil of the less intensively watered wheat field (10 mg kg) and more than 3.5 times higher than in the soil irrigated with uncontaminated water (<10 mg kg<sup>-1</sup>). Water soluble As in the top soil layer range between 0.03-0.96 mg kg<sup>-1</sup> exceeding the limit 0.04 mg kg<sup>-1</sup> for agricultural use. In potato tuber the As concentrations are more than 15 times higher than value of 0.03 mg kg<sup>-1</sup> measured at the uncontaminated control site. A significant increase of As (0.9 mg kg<sup>-1</sup>, average value) was also found in samples of sugar beet, which exceeds the WHO limit for foodstuffs and could stand for a risk to the human health.

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**WET DEPOSITION IN TWO GREEK SITES:  
LARISSA AND ATHENS**

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The determination of the chemical composition of rainfall related to the origin of the air masses, in two urban sites in Greece during the year 2006, is investigated in this study. Two model automatic rain samplers were installed, the first in the city of Larissa and the second in Heraklio, a northern suburb of Athens. The concentrations (ppm) of the major cations (H<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> and Mg<sup>2+</sup>) and major anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>), as well as Zn<sup>2+</sup>, Mn<sup>2+</sup>, Fe, Pb, total hardness (ppm CaCO<sub>3</sub>), pH and electric conductivity in 25 °C (μS/cm) for 27 rainfall samples -11 samples in Larissa and 16 samples in Heraklio (Athens)- were determined.

In Larissa, the figures of pH range from 5.13 to 6.13 with mean ± SD value: 5.64 ± 0.30, while in Heraklio (Athens) the pH mean value ± SD (6.32 ± 0.54) within the range 5.62 to 7.88 indicates a shift of the rainfalls towards alkalinity. The electric conductivity in Larissa ranges from 16.30 μS/cm to 110.60 μS/cm with mean value ± SD: 35.38 ± 25.35 μS/cm and in Heraklio (Athens) from 7.00 μS/cm to 151.00 μS/cm with mean value ± SD: 42.81 ± 37.48 μS/cm. The analysis showed that Ca<sup>2+</sup> ions are abundant within all examined samples, while HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> present the highest concentrations within the anions. Moreover, in order to find out the origin of the air masses, the air mass back trajectories were calculated.

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## PHOTODEGRADATION OF FENITROTHION AND MALATHION IN DRINKING WATER BY PHOTO-FENTON REACTION UNDER SUNLIGHT IRRADIATION

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A wide variety of organic pollutants are introduced into the water system from various sources such as industrial effluents, agricultural runoff and chemical spills. The necessary use of pesticides in intensive agriculture has important effects on the quality of environmental water. The removal of these organic pollutants from water is a very important strategy from a health and hygienic point of view. The use of light-induced reactions in water treatments has drawn increasing attention recently. Many investigations have been carried out with the aim of understanding the fundamental processes and enhancing photocatalytic efficiencies especially for water, air, and soil pollution control. Fenton-type systems employing  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  are a source of hydroxyl radicals and therefore of interest for treatment of waters containing hazardous organic compounds like pesticides.

In this work, we have investigated the photodegradation of two organophosphorus insecticides, fenitrothion and malathion in drinking water by use of  $\text{FeSO}_4$  as photosensitizer and  $\text{H}_2\text{O}_2$  as oxidant. The experiment was carried out in a pilot plant placed in Murcia, SE Spain (latitude  $37^{\circ}59'N$ , longitude  $1^{\circ}08'W$ ) using natural sunlight irradiation and compound parabolic collectors during June 2006. Drinking water used had pH of 8.12, EC of  $0.85 \text{ dS m}^{-1}$  and DOC of  $1.32 \text{ mg l}^{-1}$ . The mean global and UV radiation were  $670 \text{ W m}^{-2}$  and  $19 \text{ W m}^{-2}$ , respectively, and water temperature was  $24 \pm 2 \text{ }^{\circ}\text{C}$  during the exposition time (90 and 480 min). Several samples were taken during the two photoperiods. A LL microextraction method was used for the isolation of the pesticides and their residues were analyzed by GC-ECD and confirmed by GC-MS.

The kinetic degradation followed a first order reaction. After 480 min of exposition in presence of  $\text{FeSO}_4$ , the remaining percentages for fenitrothion and malathion were 2% and 7%, respectively. These values were sensibly lower than those obtained in absence of photocatalyst (70-81%). In both cases a rapid degradation was observed during the first 30 min. For this reason, a second experiment with short exposition (90 min) time was carried out during the hours (14-15.30 h) of maximum luminous intensity ( $800\text{-}900 \text{ W m}^{-2}$ ). In this case the half lives were 38 and 40 min for malathion and fenitrothion, respectively. No significant differences on the decrease of the pesticide concentration were observed when  $50 \text{ mg l}^{-1}$  of catalyst were used. The necessary times to reach the MAC established by the EU ( $0.1 \text{ } \mu\text{g l}^{-1}$ ) were 7.6 h for malathion and 8.5 h for fenitrothion when photosensitizer was added to drinking water while these values were 403 and 194 h for the same compounds when the experiment was carried out without catalyst.

Accordingly, it can be concluded that the photolytic reactions carried out in the absence of photocatalyst exhibit very low efficiencies as compared to the reactions in the presence of a catalyst. Photo-Fenton reaction results as a very efficient process for the elimination of malathion and fenitrothion from drinking water.

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## PHOTOCATALYTIC DEGRADATION OF PROPANIL AND ALACHLOR IN DRINKING WATER EXPOSED TO SUNLIGHT BY EFFECT OF DIFFERENT PHOTSENSITIZERS

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Contamination of waters by xenobiotic compounds such as pesticides presents a serious environmental problem. Photocatalytic oxidation by semiconductors has environmental interest for the treatment of contaminated water. Titanium dioxide (TiO<sub>2</sub>) has been demonstrated to be an excellent catalyst and its behaviour is very well documented in the literature although the photocatalytic effect of other semiconductors is not well known. For this reason in this work we have studied the effect of WO<sub>3</sub>, MoS<sub>2</sub> and ZnO on the photolytic degradation of two herbicides, alachlor (chloroacetamide) and propanil (anilide) in drinking water under natural sunlight.

The experiment was carried out in a pilot plant placed in Murcia, SE Spain (latitude 37°59'N, longitude 1°08'W) using natural sunlight irradiation and compound parabolic collectors during July 2006. The mean global and UV radiation were 650 W m<sup>-2</sup> and 17 W m<sup>-2</sup>, respectively and the water temperature was 24±2 °C during the exposition time (480 min). Water samples (200 l, n=3) were spiked with the pesticides from 1-2 ppm level with commercial products. Finally, the photosensitizers and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were added at 10 mg l<sup>-1</sup> and 20 mg l<sup>-1</sup>, respectively. Several samples were taken during the photoperiod. A LL microextraction method was used for the isolation of the pesticides and their residues were analyzed by GC-ECD.

Both herbicides showed higher degradation rates in drinking water when they were exposed to natural sunlight irradiation for the exposition time in comparison with the same experiment carried out without sensitizers. ZnO was the most efficient photosensitizer in both cases. The remaining percentages at the end of the experiment (8 h) carried out with ZnO were 25% and 27% for both, alachlor and propanil, with half-lives of 272 and 329 min, respectively. The necessary times to reach the Maximum Admissible Concentration (0.1 µg l<sup>-1</sup>) established by the EU were 62 and 74 h for alachlor and propanil, respectively. The effectiveness of the photosensitizers was in the order: ZnO > WO<sub>3</sub> > MoS<sub>2</sub>.



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## DEVELOPMENT OF AN AIR QUALITY INFORMATION SYSTEM IN THESSALONIKI, GREECE

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The design, development, realization and operational support of an air quality online information system in Thessaloniki are presented in this paper. The system is based on modern information systems with emphasis on internet and mobile telephony applications.

It provides online visualisation of real-time air pollution, forecasts on the basis of computational intelligence methods and special features like discussion boards, end user tailored early warnings. Dissemination of information is based on high sophisticated communication lines like interactive internet maps and mobile telephone technologies.

The system can serve citizens as well as professionals, local and regional authorities across Thessaloniki Metropolitan Area and other relevant institutions.

The technology applied constitutes a further development of the methodology resulted from the European program APNEE-TU, which established a uniform and transposable portal on environmental information in different European regions, using air quality as the application domain. The APNEE-TU activities aim at increasing the knowledge of citizens on air quality while developing exchange of information both on local level in European cities and among European institutions.

New communication technologies were employed for enriching information content, for adapting to the needs of cities and providing more advanced environmental information for the citizens. APNEE-TU was a take-up action on the basis of the EU supported IST project APNEE, and included a considerable number of end user sites, institution and telecommunication/informatics companies in Europe.

The usage of collaborative exercises for system design is discussed, while usability principles are investigated, while the results of web site design analysis are also used for the development of the current system. The application of computational intelligence methods like Neural Networks and Classification algorithms are providing with a powerful, from the operational point of view, palette of early warning notifications. The work of the current paper is also linked to various scientific activities in the field of environmental informatics and operational systems analysis, that are going to be addressed in detail.

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## LEVELS AND SOURCES OF PM10 URBAN AEROSOL FRACTION IN ISTANBUL - TURKEY

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Today, the interest of particles is high mainly because of their effect on human health, including effects on the respiratory and cardiovascular systems, asthma and mortality. They have also determining effect on visibility and contribute to the soiling of monuments. Compared to trace gases, aerosols are relatively complex to characterize because of their multi-component chemical composition, and because of the large range of particle size, ranging from nanometers to several micrometers. These have led to considerable concern and the establishment of health-based air quality standards. This paper summarizes the results of series of measurements of particulate matter at ten monitoring stations in Istanbul in the period 1999-2004. Major PM10 sources in Istanbul were determined that a result of human actions, notably from vehicle and combustion for heat. High PM10 levels are occurred during cold days in winter period and dry days in summer period. The lowest PM10 levels are usually recorded during wet weather conditions and summer period. The residential sources are the major component of the total PM10 emission in winter and the mobile sources is the major PM10 emission source in summer. EU, EPA and Turkish air quality standards limits are commonly exceeded in urban area of Istanbul.

Keywords: PM10, Source apportionment, air quality standards.

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**ASSESSING MICROBIAL ACCESSIBILITY OF NATIVE  
PAHS IN SOILS AND SEDIMENTS: RELEVANCE FOR  
BIOREMEDIATION**

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The aim of this work was to develop the methodology to determine the accessibility to degrading microorganisms of native PAHs present soils and sediments. We developed an accelerated biodegradation assay, consisting in the incubation of the samples in the presence of a sufficient number of PAH-degrading microorganisms. The samples exhibited different levels of pollution, i.e., from background levels (mg/kg), originated by atmospheric deposition, to acute concentrations (g/kg) corresponding to industrial spills. The addition of  $^{14}\text{C}$ -labelled PAH to the samples allowed the measurement of mineralization (production of  $^{14}\text{CO}_2$ ) as a physiological indicator of the biodegradation process. After mineralization reached the plateau, the residual concentrations of the native compounds were determined by extraction and HPLC analysis in replicate samples that contained no  $^{14}\text{C}$  and that had been maintained under the same conditions. In this way, we could identify situations involving different degrees of bioaccessibility: from heavily polluted soils containing highly bioaccessible (>95 %) compounds, to soils previously treated with bioremediation or containing background levels of pollution, showing a reduced bioaccessible fraction (< 30 %). The results were highly consistent with separate studies on desorption kinetics with Tenax extraction. The methodology can be used during the management of PAH pollution, including assessment of bioremediation endpoints and prevention of remediation failure.

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## TOOLS FOR HEAVY METAL POLLUTED SEDIMENTS CHARACTERISATION: TOWARDS A SUSTAINABLE REMEDICATION

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The “quality” of coastal lagoon sediments, with reference to their heavy metal (HM) pollution level, has been investigated by an integrated approach with the aim to provide a useful tool for the evaluation of their disposal after dredging.

The studied area (Phlegraean lagoons, IT) shares with other Mediterranean lagoons environmental degrade problems due to pollution and to the indiscriminate abuse of their biological resources. The ecological relevance of the trace (toxic) elements in the water/sediment system is due to their mobility and bioavailability more than to their total content.

The study is based on the following steps:

- (1) Application of BCR standardised analytical procedure of sequential extraction (Rauret, 1998), providing information on the distribution of HM among the different “geochemical phases”;
- (2) Evaluation of the kinetic of release of pollutants by leaching tests, to consider also other methods for the estimation of potential metal mobility, taking into account the kinetic aspects of the metal-sediment association and release.
- (3) Use of compost (aerobic degradation product of selected domestic organic wastes) and “red mud” (by-product of the alumina production) to reduce the toxic element mobility and to enhance plant growing in the sediments, allowing phytostabilisation/remediation, is evaluated. Considering the total concentration, the surface sediments of lagoon appear to be slightly “polluted”, in the following order by  $Pb > Cu > Zn$ . Moreover, sediments show quite high levels of As that can be related to the natural geochemical background.

It is well known that the toxicological and environmental risk mainly depends on the possibility of the occurrence of redox variations, pH changing and organic matter decomposition. The combination of results obtained by BCR three-step sequential procedure and by kinetic fractionation approach, allowed to evaluate these features bringing to a better evaluation of elements mobility and therefore of the associated risks.

Finally, the behaviour of sediments added with amendants has been tested: “red mud” proved to be a valid scavenger of heavy metals and it appears to be a useful tool in the remediation of contaminated sediments.

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## CHARACTERIZATION OF THE SETTLEABLE AND SUSPENDED ATMOSPHERIC PARTICLES TO SOLVE AN AIR QUALITY PROBLEM.

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The main objective of this study is to characterize the settleable and suspended air particles of an industrialized area close to a population centre, due to the complaints carried out by a group of citizens to the town council of this locality situated in the province of Castellón.

An exhaustive control of the levels of particles has been carried out using a PS Standard Britannic captor and a model PS1 high precision Retsch cascade impactor which is a seven-stage cascade impactor mounted on a standard low-volume air sampler. Afterwards, air samples were analysed using a scanning electron microscopy (SEM) and X-ray diffraction (XRD) order to know the structure, morphology and composition of the particulate matter and identify its origin sources.

In connection with the aerosol collected by the cascade impactor, the greatest values are located in the range of fine particles (50% of particulate matter is distributed in the range of particles from 1 to 4  $\mu\text{m}$  and 70% in particles lower than 4  $\mu\text{m}$ ).

On the other hand, the main components identified in the samples are minerals particles coming from natural emission and ceramic industry, particles of glass and carbonaceous amorphous matter (mainly carbon) plus small quantities of S, Ca and Na coming from combustion processes (traffic, combustion of fossil fuels, industrial processes of high temperature).

According to mineralogical analysis, quartz, calcite and illite/mica are the most abundant compounds in the samples, but dolomite, K-feldspar, plagioclase and kaolinite/ chlorite are also common. The mineralogical composition of the atmospheric particulate samples obtained in the study area has been compared with two areas in order to evaluate the influence of industries based on mineral raw materials.

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**Key Words:** Settleable air particles, suspended air particles, SEM, XRD, mineral particles, glass particles, cascade impactor, industrialized area.

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## RECONSTRUCTING Pb ATMOSPHERIC POLLUTION IN NW SPAIN USING PEAT CORES: SPATIAL VARIABILITY

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The fluxes of many trace metals to the atmosphere have increased as a result of human activities, in some cases greatly exceeding the natural fluxes. For some elements, like Pb, the investigations have revealed a long history of anthropogenic pollution (dating back to 3,000 years ago). Reconstructions are based on analysis of different natural archives (lake sediments, polar ice, peat records). But most of these studies rely on single cores and do not evaluate the spatial variability of the archive. Here we present the results of a investigation carried out in the Chao de Lamoso bog formation (CHL, Xistral Mountains, NW Spain), where we sampled four short peat cores (30 cm deep). The cores were sliced into 1-2 cm slices and in the dried peat samples we analyzed Pb, Ti, Zr by XRF and Pb isotopes using ICP-MS. The chronology has been established based on <sup>210</sup>Pb inventories using the CRS model.

The highest Pb concentrations were found at a depth of 3-4 cm in all four cores (74-111  $\mu\text{g g}^{-1}$ ). Maximum enrichment factors, calculated using Ti and Zr as reference elements, showed differences among cores regarding the depth (between 2 cm and 4 cm) and actual value. Enrichment factors calculated to Ti range between 126 and 168, while those calculated using Zr are much lower (26 to 33). Net accumulation of anthropogenic lead varied between 14  $\text{mg. m}^{-2} \text{ y}^{-1}$  and 22  $\text{mg. m}^{-2} \text{ y}^{-1}$ . In terms of chronology, maximum Pb concentrations correspond to 1963-1973; maximum EF correspond to 1958 and up to 1973; while net accumulations showed several peaks from 1935 to 1985.

Lead isotope ratios (<sup>206</sup>Pb/<sup>207</sup>Pb) showed minimum values (~1,16) coincident with Pb maximum concentrations, suggesting most Pb at this depth is related to the introduction and use of leaded gasolines. Isotope ratios increase in the superficial peat sections, indicative of the decrease of gasoline Pb in atmospheric deposition in recent times.

Although concentrations and isotopic composition give a coherent picture, other common estimators used to reconstruct historical Pb pollution (like enrichment factors and net accumulation rates) do not. Our results indicate that there is moderate spatial variation in Pb concentrations and net accumulation for the same bog; but a great variability in enrichment factors. Both, EF and net accumulation rates showed no chronological coherence.

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## HYDROTALCITE INTERCALATED BY CHELATING AGENT DMSA: UPTAKE OF METAL CATIONS

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Layered double hydroxides consist of brucite-like layers, with a partial substitution of divalent cations by trivalent ones, leading to an excess of positive charge compensated with hydrated anions situated in the interlayer. The hydrotalcite-like compound  $[Zn_2Al(OH)_6]NO_3 \cdot nH_2O$  ( $ZnAl-NO_3$ ), was intercalated with the chelating agent dmsa (meso-2,3-dimercapto succinic acid) by the anion exchange method, with the aim of uptake  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  from the aqueous solutions by chelating process. The adsorbent was characterized by the elemental chemical analysis (Zn, Al, Cd, Cu, C and N), XRD and DTA-TG techniques and FT-IR spectroscopy.

The chemical analysis indicate that the molar ratio Zn:Al in LDH- $NO_3$  is very close to those in the starting solution, whereas in the ZnAl-dmsa it is lower. This is probably due to the partial dissolution of the hydroxyl layers during the anionic exchange, realized at pH 5.5. Results of XRD techniques and FT-IR spectroscopy confirm the presence of dmsa in the hydrotalcite interlayer.

The amount of heavy metals adsorbed was monitored by atomic absorption technique at different contact time, pH and metal concentrations. The kinetic study indicates that the uptake of the metals occur in two slopes, where the first of them is a very fast (into 2h), reaching the equilibrium in a few hours. At initial pH=3, maximum adsorption of metals taking place, being the final pH in all cases pH=4.8. The results indicate a very high adsorption of these metal cations. For the initial metal concentration of 10mM, the amounts of  $Cu^{2+}$  and  $Cd^{2+}$  uptaked from the solution were Cs~1000  $\mu\text{mol/g}$  while in the case of  $Pb^{2+}$  it was extremely high (Cs~1900 $\mu\text{mol/g}$ ). The shape of the adsorption isotherms suggests specific interaction and high host-guest affinity. Notwithstanding, for high metals concentration during the adsorption on ZnAl-dmsa precipitation of metal hydroxides and carbonates is observed in some cases.

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**A COMPARISON OF PHYTORREMEDICATION CAPABILITY OF  
SELECTED PLANTS FOR CADMIUM AND LEAD  
IN CONTAMINATED SOILS FROM MINING ACTIVITIES**

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Heavy metal contamination derived from mining activities is one of the main environmental problems. Heavy metals are difficult to remove from environment and they cannot be chemically or biologically degraded. Phytoremediation is one of the environmental friendly technologies that uses plants to clean up soil from trace element contamination. The use of plants species for in situ stabilization is an attractive option.

In this work, Pb and Cd remediation possibilities by use of vegetation in soil samples contaminated were investigated. The aim of this study was to compare trace element accumulation capacities of 5 selected plant species from the mining region of Lá Union (SE Spain).

In soil samples, total content, soluble content in groundwater and bioavailable content were determined. In plant samples, total content was determined.

The results for Pb and Cd in soil samples are shown in the next table:

<b>(mg kg<sup>-1</sup>)</b>	<b>Pb (n = 4)</b>	<b>Cd(n = 4)</b>
Total	2318	110.0
Soluble	0.4	3.0
DTPA	120.0	3.2

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The next table shows the heavy metal concentrations found in dry matter of the different plant species and the transfer factor, calculated as the relation between metal concentration in plant and in soil. *Dittrichia* showed the highest values for all plant species, the lowest was *Arthrocnemum* for Pb and *Glaucium* for Cd. The highest TF value was for *Dittrichia*.

	<b>Pb (mg kg<sup>-1</sup>)</b>	<b>Cd (mg kg<sup>-1</sup>)</b>	<b>Pb TF (%)</b>	<b>Cd TF (%)</b>
Limonium	416.4	19.8	17.94	18.00
Arthrocnemum	0.1	24.9	0.004	22.63
Dittrichia	910.0	67.5	38.25	61.36
Zygophyllum	154.9	25.0	6.68	22.72
Glaucium	91.9	0.7	3.96	0.63

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## METHOD DEVELOPMENT FOR THE DETERMINATION OF FLUOROTELOMER ALCOHOLS IN SEMIPERMEABLE MEMBRANE DEVICES

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Fluorotelomer alcohols (FTOH) are important raw materials that find use in many commercial and industrial applications including polymers, paints, and coatings. Due to their volatility, FTOH are detectable in the atmosphere in urban and remote regions. Recently, FTOH were found to be probable precursor substances of persistent and potential carcinogenic perfluorocarboxylates.

Semipermeable membrane devices (SPMD), consisting of a polyethylene membrane filled with triolein, are used as passive samplers for the determination of various hydrophobic organic compounds in water and air. In this study, we present an analytical method for the determination of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH in SPMD. Different procedures for extraction and clean-up were compared. Recoveries of FTOH were determined by gas chromatography - mass spectrometry (GC-MS) using positive chemical ionisation.

Extraction of SPMD was tested with methanol, ethylacetate, acetone, and acetonitrile by shaking for 24 hours. Additionally, extracts in methanol and acetonitrile were liquid-liquid extracted with n-hexane.

For purification of SPMD extracts by solid phase extraction (SPE), the adsorbents C18-E (500 mg and 1g), C18 (1g), SDB-L (200 mg), and C18-E (500 mg) + Carboxen 1016 (100 mg) were tested. Solvents tested for elution of SPE cartridges were ethylacetate, methanol, methanol/ethylacetate (1/1), and methanol/ethylacetate (2/1).

The method of choice with best triolein removal and acceptable FTOH recoveries was extraction with acetonitrile followed by liquid-liquid extraction with n-hexane. Extracts are further purified by SPE with C18-E (500 mg) and Carboxen 1016 (100 mg) cartridges and then measured by GC-MS. FTOH recoveries of this procedure were between 40% for 4:2 FTOH and 64% for 10:2 FTOH. Although these results are below of the optimum range between 70 and 110%, they are comparable to other analytical methods for FTOH.

To show that FTOH are able to penetrate through the polyethylene membrane and accumulate in triolein, SPMD were exposed to FTOH in a glass chamber having no direct contact. After one month, the chamber was opened. SPMD were rinsed with ethylacetate to remove FTOH adsorbed to the SPMD surface. Then FTOH were determined in SPMD using the method described above. FTOH were found in a high amount in exposed SPMD. Especially short chain FTOH showed a good ability to penetrate into the SPMD due to their higher volatility and lower molecular mass.

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## EVALUATION OF AEROSOL AND OZONE PHOTOCHEMICAL MODEL OVER ATHENS

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Up to now few modelling and measurement studies have been performed in the Eastern Mediterranean in relation to ambient particulate matter and ozone and therefore there is a need to study the physico-chemical processes which control the dynamics of aerosols and photo-oxidants in the Mediterranean area. The main objective of the present study is the implementation of an air quality forecast system that predicts near surface gaseous and particulate pollutants levels over the Greater Athens Area (GAA). The forecast system consists of the prognostic meteorological model MM5 and the photochemical air quality model Comprehensive Air Quality Model with Extensions (CAMx) and runs operationally on a daily basis to issue 72-hour forecasts. The modelling domain covers Athens with a grid of  $2 \times 2 \text{ km}^2$  and has fifteen vertical layers extending up to almost 10 km. The emission data used as CAMx input data are hourly values of biogenic NMVOCs and anthropogenic NO<sub>x</sub>, NMVOCs, CO and PM<sub>10</sub> emissions. Evaluation of the modelling system for the GAA is performed through a comparison of the modelling results with measured ground-based data for ozone and PM<sub>10</sub> concentrations. The final aim of the evaluation process will be to improve the accuracy of the forecast modelling system so that it could be used to accurately predict air pollution levels and thus, help regulatory agencies and decision makers to develop efficient emission control strategies to improve air quality over the GAA.

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## EXHAUST GAS EMISSIONS FROM PETROL CARS IN THE CITY OF THESSALONIKI

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Air pollution remains a serious environmental problem in Greek cities because of the combined effects of various pollutants upon the health and the everyday life of citizens. Urban traffic has been firmly identified as a main pollution source, in particular the car tailpipe gases. The emissions from spark ignition car engines have been evaluated with inter-seasonal measurements for the period 2003-2006 in the city of Thessaloniki by close monitoring of the following tailpipe gases, both at idle and at 2000 RPM: CO, CO<sub>2</sub>, O<sub>2</sub> and HC. Sensory observations, i.e. aural, visual and nasal, have been simultaneously acquired from vehicles under test for a quick qualitative characterization of the engine operation. Based on the latter, a novel emission control method for the detection of gross polluters has been examined. The presence of a small number of gross polluting cars (approximately among 10 moving petrol cars there is 1 polluting as much as the rest 9 of them!) consists the main finding of the present paper, reconfirming some similar findings, both in Greece and worldwide. Unfortunately, at present most of these vehicles are left in circulation, escaping the rather meagre control measures and, interestingly enough, being also equipped with the proper national Exhaust Gases Card! Thus, while new vehicles start from much lower emission levels due to tighter new standards, the considerable deterioration rates manifested in practice suggest that low emissions may not be sustained unless serious steps are taken to keep the cars in good operating condition.

**Key-words:** car pollution, tailpipe emissions, sensory observations

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## EFFECTS OF SURFACTANTS ON CHEMICAL CHARACTERISTICS OF SOIL SOLUTION IN A SOIL FROM THE MEDITERRANEAN AREA

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Surfactants may be introduced anthropogenically in soil due to sludge application and wastewater irrigation, particularly in arid and semiarid region where water is scarce and soil physico-chemical properties and fertility need to be improved. Additionally, surfactants are also present as adjuvants to improve the delivery and effectiveness of agrochemicals. Because of their ability to reduce surface tension and modify the solid–liquid contact angle, surfactants affect water transport and consequently modify the chemistry of the soil solution. For this purpose leaching experiments were conducted to characterize the soil solution in relation with parameters relevant in relation to soil productivity and protection of the environment such as pH, conductivity, salinity and dissolved organic matter.

Columns from samples of a Mediterranean soil were percolated with solutions of three kinds of surfactants: anionic (Aerosol 22), cationic (HDTMA) and non-ionic (Triton X100) under laboratory conditions. Furthermore, irrigation with wastewater which contains different kinds of surfactants was tested. Test solutions were applied uniformly at a controlled rate and the leachate was collected periodically. After infiltration the soil was divided into 4 segments and significant physico-chemical properties were analysed, i.e. pH, conductivity, CEC, OC, water extractable OC.

Infiltration of surfactant leaching tests was significantly lower than that of control and wastewater application.

Leaching with wastewater and solutions containing cationic surfactants slightly acidified the soil leachate and increased conductivity at the beginning.

Application of cationic surfactants decreased Soil CEC, leading to wash-out of soil cations.

Water extractable OC will also be characterized (i.e. quantity and quality by humification index) and differences between applied solution and OC leached from soil will be determined.

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## STUDY OF XAD-2 ADSORBENT FOR PESTICIDE SAMPLING IN ATMOSPHERE: APPLICATION TO REAL CASES

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The porous polymeric adsorbents are widely involved in the organic compound investigations in different environmental fields. Our laboratory tested one of these adsorbents, XAD-2, in the sampling of some pesticides in atmosphere.

XAD, or amberlite, is a polymer classified according its constituting and is characterized by maximum temperatures of 200-250°C. Commercially, different XAD polymers are present: XAD-7, -8, -9 and -12 are used for sampling of polar compounds whereas XAD-1, -2 and -4 of apolar species. In some cases, especially for organophosphorous pesticides, the sampling ratio can be reach 30 L/min.

In this evaluation we used XAD-2 which is formed by monomers of styrene and divinylbenzene and has the following characteristics: specific surface area of 300 m<sup>2</sup>/g, mesh 20-60, porous size of 90 Å. The study was performed on different pesticides (i.d., dimethoate, omethoate, mevinfos, dicrotofos, disulfoton, paration methyl, formothion, paraoxon ethyl, fenitrotion, malaoxon, paration ethyl, iodofenfos, triazofos, phosalone, pirazofos and tribulyl phosphate) sampled in atmosphere. The study was completed by the collecting samples of soil, leaves and water just around the site located in the Central Italy (Molise region).

The communication will show the evaluation of the whole analytical procedure (including the breakthrough volumes and the adsorption isotherms) set up for using XAD-2 for enriching the organic pollutants above reported and present at trace levels in atmosphere.

The GC analyses were carried out using both gas chromatograph equipped with nitrogen-phosphorus detector and electron capture detector and gas chromatograph equipped with mass-spectrometry. In the studied concentration range, a linearity response was obtained ( $r^2=0.9995$ ) both in GC-NPD and GC-MS, the limits of detection were 0.001 ng  $\mu\text{L}^{-1}$  in GC-NPD and 0.003 ng  $\mu\text{L}^{-1}$  in GC-MS (SIM), respectively, with a relative standard deviation below 9.5%. This approach has been successfully applied to real samples: the main result underlines how the dimethoate concentration decreases according to the distance from the sampling site but it is still persistent in atmosphere after few days from the pesticide irrigation.

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## ARTIFICIAL NEURAL NETWORK MODELS FOR PREDICTION OF THC DAILY LEVELS IN ISTANBUL, TURKEY.

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In this paper, we present the results obtained using Artificial Neural Network (ANN) and Multiple Linear Regression (MLP) models to forecast the daily average Total Hydrocarbone (THC) concentrations in Istanbul, Turkey. We considered the sequential daily concentrations time series of THC, which were measured in the European part of Istanbul, during a year-2003. The model utilized selected meteorological variables, which were measured in the same region as input data. The performances of these models were compared with the observed values using five statistical criteria: correlation coefficient ( $r$ ), index of agreement ( $d$ ), Bias, Mean Absolute Error (MAE) and Root Mean Square Error (RMSE). We preferred three-layer perceptron type of ANN which consists of 9, 20 and 1 neurons for input, hidden and output layers, respectively. To evaluate the performance of ANN model, our results are compared to classical linear regression methods. The index of agreement ( $d$ ) of ANN and MLP model results are 0.99 and 0.83 in training and 0.59 and 0.65 in testing, respectively. The presented results demonstrate that MLP and ANN models are capable of capturing THC concentrations trends. It is found that ANN model is not considered a dramatic improvement, however it can be appreciated as an useful alternative techniques in modeling the complex air pollution emissions.

Keyword: Air Pollution, Total Hydrocarbons, Neural Network, Prediction, Linear Model,



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## A POLLUTANT DISPERSION MODEL FOR THE PIRAEUS, LAVRIO AND RAFINA PORTS AND THE ELEFSIS GULF

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Piraeus port includes passenger, commercial and ship remaining/repairing zones. Lavrio, situated in an area with metalliferous deposits serves as a passenger, primarily and commercial, secondary, port. Rafina is a passenger port in the vicinity of tourist areas without industrial activity. Elefsis port (located in a closed gulf) helps in the transportation of raw material and products from nearby refineries, shipyards, iron and steel industries, etc.

Surface and subsurface sediment samples were collected and analyzed with atomic absorption spectro-photometry for the determination of heavy metal content (especially for the metals Fe, Mn, Ni, Cr, Al, Zn, Pb, Cu, Sn and Cd). Also, carbonates and total organic carbon content were measured too.

Based on the assumption that the deposition of any given sediment in harbour etc actually constitutes a sedimentation in action, we concluded that the principles and experience of the mining industry are applicable in studying environmental problems associated with sedimentation. Thus, suitably modified geostatistical analysis was applied, followed by the presentation of metal content in contouring maps. Bearing in mind that (a) there is only one polynomial of n degree joining all the n+1 points, (b) metal distribution trend is best presented by a straight line or a smooth curve, and (c) a simple methodology like the least squares one is preferred, for each area and metal, two models were created, correlating the total metal content with North-South and East-West direction, respectively. Their combination via weight factors allowed all available data to be considered, while a first approach to sea-bed element dispersion is achieved. With this procedure, for any given point A of the study area, the metal content is calculated by the formula:  $F_A = \{R_x^2 / (R_x^2 + R_y^2)\} X_A + \{R_y^2 / (R_x^2 + R_y^2)\} Y_A$ , where,  $X_A, Y_A$  : the metal content predicted by each model on the respective axis, and  $R_x, R_y$  : the correlation factor between the total metal content and the respective axis. In practice, for k sampling sites, a prediction model is made using data from the k-2 and the model is tested for the prediction of the (already measured) concentrations of the remaining two samples, having in mind rather to interpolate than extrapolate. Then, the model is used to estimate the values for any point in the study area.

It is concluded that raw and transformed arithmetic data, contouring maps and metal distribution trend analysis, lead to a better understanding of the study area. The model succeeds in providing with acceptable accuracy forecasting values in case of homogeneous marine environments with dense sampling; in heterogeneous environments with sparse sampling, the model identifies new sampling sites for a better understanding of the study area.

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## SIZE DISTRIBUTION OF NUMBER, MASS AND IONIC CONCENTRATIONS OF AEROSOLS AT A KERBSIDE SITE IN THESSALONIKI, GREECE

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Various epidemiological studies have demonstrated adverse health effects due to exposure to airborne particulate matter (PM), particularly to ultrafine PM (typically, <100 nm). Which characteristic of PM- mass, surface area or number of particles- may be responsible for aerosol toxicity remains unknown.

In the present study, the size distribution of PM<sub>10</sub> mass concentrations and associated ionic components (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl-NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) was investigated at a kerbside site in the centre of Thessaloniki, northern Greece, with an average traffic density of ~ 80000 vehicles/day. Samples were collected in November 2005. Size-resolved aerosol was collected from the breathing zone (~2m above ground level) on a 24-h basis employing a DGI air sampler with 4 inertial impactors providing cut-off point sizes at 268, 546, 1087, 2698 nm (aerodynamic diameter) at the actual flow rate. Teflon coated fiber glass filters (TX40HI20-WW) were used for aerosol collection. Particle mass concentrations were determined gravimetrically. Typical air pollution parameters (PM<sub>2.5</sub>, PM<sub>10</sub>, SO<sub>2</sub>, NO, NO<sub>2</sub>, O<sub>3</sub>, CO, BTEX) and meteorological conditions (wind direction/speed, ambient temperature, relative humidity) were recorded during aerosol sampling. Ionic components were determined using ion chromatography. Particle size distributions in the range 10-360 nm (electric mobility diameter) were recorded every 2-3 min by a Scanning Mobility Particle Sizer (SMPS). A Condensation Particle Counter (CPC) simultaneously recorded particle number concentrations above 10 nm.

The mass concentration of PM<sub>10</sub> was found to be  $92 \pm 7.7 \mu\text{g}/\text{m}^3$  exhibiting monomodal distribution with maximum occurring in the submicron size range (546 – 1087 nm). An important mass proportion (77.5 %) was found in particle sizes <1087 nm, which corresponds to the alveolar fraction. The measured distribution is believed to result from diesel vehicle emissions of particles in the accumulation range (>100 nm) that tend to coagulate to larger particles.

Almost all ionic species exhibited similar size distribution to that of the PM (monomodal distribution with maximum in the submicron size range, 546 – 1087 nm). A shift to slightly larger sizes (1087 – 2698 nm) was observed for Ca<sup>2+</sup> whereas the distribution of Mg<sup>2+</sup> was totally different with the maximum occurring in the large size fraction (2698-10000 nm).

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Total number concentration was approximately  $6.9 \times 10^4$  particles/cm<sup>3</sup> in working days slightly decreasing during weekends ( $6.3 \times 10^4$  particles/cm<sup>3</sup>). In working days, the diurnal arithmetic concentrations exhibited a peak at 30 nm at 09:00 am, probably due to increased traffic density and intensive homogenous condensation – nucleation processes. Two smaller peaks appeared at 40 - 45 nm at 21:00 and 01:00 pm suggesting aerosol growth probably due to vapor condensation at nocturnal temperature and relative humidity conditions. During the weekend, there was no peak appearing in the morning and there were two peaks around 35 nm at 19:00 and 21:00 pm. These distribution patterns follow the traffic density variations during the day.

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## PAH LEVELS IN PLANTS AND SOIL FROM SPANISH CEREAL FIELDS

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic pollutants that are released into the environment as a consequence of incomplete combustion originated from both natural and anthropogenic processes.

The objective of the present study was to investigate the content of 27 polycyclic aromatic hydrocarbons (PAHs) in soil, fertilized or not with sewage sludge, and in cereal plants (barley, wheat and oat). Soil samples (0-30 cm) were collected for analysis before sowing, during growth of plants, 6 months later, and after harvest, 12 months later. Samples of cereal plants were collected six months after sowing and the root and aerial parts analyzed separately.

PAHs were extracted from soil (10 g) with a low volume of ethyl acetate. Soil samples were placed in small glass columns and the extraction was carried out assisted by sonication (SAESC).

Plants, 2 g for aerial part and 1 g for roots, were extracted with ethyl acetate by matrix solid-phase dispersion (MSPD). Samples were homogenized with Florisil-anhydrous sodium sulfate, placed in small columns and the extraction was carried out assisted by sonication. Purification was done by solid-phase extraction with aluminium oxide and PAHs were eluted with a hexane-ethyl acetate mixture.

PAHs were determined by isotope dilution gas chromatography with electron impact mass spectrometric detection in the selected ion monitoring mode (GC-MS-SIM) using deuterated compounds as internal standards.

In general, the most abundant PAHs found in plants were naphthalene and phenanthrene, whereas in soil samples the main compounds were phenanthrene, benzo[a]anthracene and benzo[b]fluorene. The application of sewage sludge, at a dose of 12 t/ha, did not affect the PAHs levels in soil and these levels did not show a significant difference with respect to the sampling time.

The concentration of PAHs found in soil and plants were similar to those obtained by other authors in rural areas.

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## INFLUENCE OF SOIL PROPERTIES ON THE ADSORPTION OF TWO IONIZABLE HERBICIDES BY MOROCCAN SOILS

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Agriculture is a very important part of Morocco's economy. Herbicides accounted for 10-15% of the Moroccan market in 2002. Adsorption of herbicides by soil controls their fate in this system, its transport in soil and possible contamination of surface and ground water. However, studies of adsorption of herbicides by Moroccan soils are scant until now. Dicamba (3,6-dichloro-2-methoxybenzoic acid) is an acid herbicide ( $pK_a=1.97$ ) very soluble in water (6.1 g/L at 25°C) and with Kow variable depending on the pH (-0.55 at pH 5.0). Terbutryn (N-(1,1-dimethylethyl)-N'-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine) is a basic herbicide ( $pK_a=4.3$ ) with solubility in water of 22 mg/L and Kow of 3.65. These herbicides are used in cereals, sugar cane, maize and citrus fruit in Morocco.

The aim of this study was to evaluate the adsorption of these two ionisable herbicides, dicamba and terbutryn by soils from the North of Morocco with low organic matter content (0.87-2.18%). Adsorption isotherms were obtained using the batch equilibrium technique. Futhermore, a study of the adsorption of these herbicides by one of these Moroccan soils at five different pH from 2 to 11 for dicamba and 3 to 10 for terbutryn was also carried out. The influence of the soil properties on the adsorption of these herbicides was studied by a stadistical approach calculating simple correlations between adsorption coefficients and soil properties.

The adsorption isotherms fit the Freundlich adsorption equation for all the soils studied. The Kf values ranged between 0.0013 and 0.67 for dicamba and 3.40 and 11.8 for tertutryn, and the nf values were always higher than unity for dicamba and lower than unity for terbutryn, indicating non-linear isotherms. The Kf constants were correlated positively with the soil organic matter content ( $r=0.69$ ,  $p<0.1$ ) for dicamba and clay content ( $r=0.92$ ,  $p<0.01$ ) and clay plus silt content ( $r=0.73$ ,  $p<0.1$ ) for terbutryn. The results obtained indicate that adsorption of dicamba is lower than that of terbutryn. Dicamba may cause water pollution because of its low adsorption and leaching potential. The adsorption of dicamba by the soil 2 at different pH showed a higher adsorption of this herbicide at lower pH values. Similar results were found for terbutryn and a negative and significant correlation was found between Kf and pH values ( $r=0.91$ ,  $p<0.05$ ) for this herbicide, indicating that decreasing soil pH generally increased herbicide adsorption. These results obtained are important to predict the fate of these herbicides in Moroccan soils and prevent water contamination.

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## EFFECT OF DIFFERENT COSOLVENTS ON THE ADSORPTION OF ETHOFUMESATE BY SURFACTANT-MODIFIED CLAYS

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Clays modified with cationic surfactants are adsorbent materials which could be used as barriers to immobilize hydrophobic contaminants as pesticides. In the natural environment pesticide adsorption by soils, sediments or its constituents can occur in a mixture of water and organic solvents (e.g. under waste disposal sites where pesticide residues and cosolvents coexist), which could modify the adsorption of pesticides by modified clays. In this work we have studied the adsorption of ethofumesate by two natural and modified clays in aqueous medium and in mixtures of methanol-water, hexane-water and humic acid-water with the aim to evaluate the effect of organic solvents on the adsorption of this pesticide by these systems.

Clay minerals from the North of Morocco were used: B-clay with smectite and P-clay with illite, kaolinite and chlorite as major mineral components. Clays were modified with short, tetramethylammonium bromide (TMA), and long, octadecyltrimethylammonium bromide (ODTMA), alkyl chain cationic surfactants. Ethofumesate ((±)-2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofuranyl methanesulfonate) was used as a model of hydrophobic pesticides. It has a water solubility of 50 mg/L at 25°C and a Kow value of 2.7 at pH 6.5-7.6, and it is moderately adsorbed by soils (Koc=203). Adsorption isotherms were obtained using the batch equilibrium technique in aqueous medium and in mixtures of methanol-water or hexane-water, containing 30% organic solvent by volume, or humic acid (100 mg/L).

The adsorption isotherms fit the Freundlich adsorption equation for all sorbent/solvent systems studied. In aqueous solution, the adsorption coefficients of ethofumesate by clays modified with the long-chain surfactant, ODTMA-B and ODTMA-P, increased 1258 and 289-fold in relation to that by the natural clays. The increase in the adsorption of this herbicide by short-chain surfactant modified clays, TMA-B and TMA-P, was lower (9.76 and 1.72-fold, respectively) comparing with that by the natural clays. In general, these adsorption coefficients decrease for the adsorption of pesticide in the organic systems studied. They varied in the order: water >= humic acid-water > hexane-water > methanol-water. The Kf values ranged between 4.34 and 30.4 for TMA-B and 1625 and 3917 for ODTMA-B and between 2.56 and 13.6 for TMA-P and 592 and 1698 for ODTMA-P in presence of water and different solvent mixtures studied. The results obtained are of great interest to be considered when organoclays are used in presence of organic solvents as adsorbent materials in barrier technologies to increase the immobilization of hydrophobic pesticides.

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## REMOVAL OF C. YELLOW AND R. BLUE BY USING FILTER CAKE

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The discharges of dyes from several industries such as textile, leather, cosmetics, and paper are sources of dye pollution. Dyes are not easily degradable and are usually not removed from wastewater by conventional biological wastewater treatment systems. Low-cost adsorbents are cheap and efficient materials to remove color from wastewaters.

In this study, the adsorption of Cibabron Yellow (C.Yellow) and Reactive Blue (R. Blue) dyes on to filter cake was carried out in a batch system. The effects of initial pH (3-11), filter cake dosage (1-10g/L), contact time (5-1440 min), initial dye concentration (50-1000 mg/L) and temperature (25-45oC) were studied.

Optimum pH, adsorbent dosage and initial dye concentration for both dyes were found to be 7, 10g/L and 250 mg/L, respectively. Maximum adsorption capacity of C. Yellow and R. Blue was determined as 24.07mg/g and 24.78 mg/g, respectively at optimum experimental conditions. Effect of the temperature was not important for the adsorption of dyes by filter cake. The experimental equilibrium data fitted to Freundlich adsorption isotherm model for both dyes.

Waste sludge after belt filtration called filter cake can be used an adsorbent for dye removal from wastewater treatment systems.

Keywords: Adsorption, dye, waste sludge, adsorption isotherm

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## CHROMIUM (6) AND MERCURY LEVELS IN SOILS, SEDIMENTS AND AQUEOUS SAMPLES OF TWO HOT SPOTS OF ALBANIAN SEACOAST

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**Abstract:** Soil, sediments and seawater samples were analyzed for screening heavy metals, Cr (6) and Hg content in contaminated areas of Durres and Vlora Bay.

The most contaminated parts of these areas remain to be the soils inside Durres ex-Chemical Plant and Vlora ex-Chlorine-Alkali Plant, pointed as "Hot Spot Pollution" from UNEP/MAP (1992).

The content of Cr+6 in soil and surface water samples inside territory of polluted site ("Porto Romano", Durres) is very high (goes to some g/kg in soil samples and up to 180 mg/l in surface water samples). 87-89% of Cr<sub>tot</sub> belongs to its easy soluble form and 2-10% belongs to the form bounded with soils. The content of Cr+6 in seawater (0.04 -0.06 mg/l) and sediment (5-6 mg/kg as Cr<sub>tot</sub>) samples resulted within the normal levels. Only 11 to 13% of Cr<sub>tot</sub> belongs to its easy soluble form and most of it (87-89%) belongs to the form bounded with sediments.

The soils of territory of Electrolysis plant was the most contaminated one with mercury mean concentration of 311.8 mg/kg and maximum concentration of some gram Hg/kg. This area presents an unacceptable threat to the environment and to the health of the people living on and around the site. Drops of metallic mercury in the hall of the electrolysis plant and in all of its drainage canals were observed.

The mean concentration of mercury in marine sediments resulted 0.314 mg/kg and maximum content was found 0.920 mg/kg. These values are much higher than the levels reported for the sediments of Southern Adriatic Sea and other Albanian areas. The concentration of total mercury in seawater samples near Soda-PVC plant resulted 0.121 mg/L, about 30% higher than in two stations of Duress area. Due to metallic form of Hg in contaminated site, low mercury concentrations resulted in all marine sediment samples in both sides of the contaminated site.

**Keywords:** seawater, sediments, soils, ground waters, mercury, chromium (6), speciation



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**CHARACTERISATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)  
IN THE TOULOUSE AGGLOMERATION (FRANCE).**

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The air quality over the Toulouse urban area (France) is recorded daily by the regional “Midi-Pyrénées” atmospheric pollution measurements network (ORAMIP). Relevant data is collected from about 100 analysers spread over more than thirty stations. The regulations covering major indicators of atmospheric pollution (ozone, nitrogen dioxide, sulphur dioxide) have been updated in recent years to include additional compounds like Polycyclic Aromatic Hydrocarbons (PAHs). The ORAMIP, in partnership with the ENSIACET has undertaken background PAH average concentration measurements over the urban agglomeration of Toulouse during spring 2006 for various types of sites (traffic, urban, industrial). For the two urban sites, total atmospheric concentrations between 12 and 20 ng/m<sup>3</sup> have been obtained, whereas for the industrial site the values averaged 22 ng/m<sup>3</sup>. In addition, and regardless of site, the average concentrations of Benzo[a]pyrene, at present the only regulated PAH, were always less than the 1 ng/m<sup>3</sup> limit.

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## USE OF ETHYLCELLULOSE MICROENCAPSULATED FORMULATIONS TO REDUCE NORFLURAZON DISSIPATION IN SOIL

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Environmental contamination by herbicides has grown considerably in the last few years as a consequence of their high application in agricultural practices. Controlled-release technology, as microencapsulation technique is being used for environmental pollution due to their advantages over conventional formulations such as reducing pesticide losses from degradation, leaching, or volatilization.

Norflurazon is an herbicide used in cotton, soybean, tree fruit and nut crops, citrus and cranberries. Unfortunately, this herbicide suffers losses when it is applied to soil. Photodegradation contributes significantly to field dissipation when norflurazon remains on the soil surface. Leaching also plays an important role in norflurazon losses in agricultural applications. In this sense, this herbicide has been detected in groundwater monitoring studies. Whereas microencapsulation has been observed to increase the persistence of several pesticides however, there is currently no information on the influence of microencapsulation on the persistence of norflurazon.

The present study describes the preparation of different norflurazon microspheres obtained by changing the conditions in the solvent evaporation method used. The results of the *in vitro* release studies of norflurazon in water showed a prolonged release of norflurazon to soil solution was successfully achieved by using ethylcellulose microspheres.

Norflurazon dissipation from the commercial formulation and ethylcellulose microencapsulated formulations was studied using a loamy sand soil. For this purpose, quadruplicate soil samples (5 g) were taken at 0, 14, 28, 42, 56, 70 and 84 days after treatment and norflurazon residues were extracted with methanol from soil samples and analysed by HPLC. The ethylcellulose microencapsulated formulations of norflurazon protected against dissipation in soil more than the commercial formulation ( $T_{1/2}$  values were 7.72 and 30.83 weeks for commercial and microencapsulated norflurazon, respectively). Likewise, formulation parameters influenced not only on the norflurazon released in soil-water system, but also-influenced on its dissipation in soil. The use of these formulations can be advantageous, since they can minimise the risk of groundwater contamination and permit herbicide use at reduced rates, maintaining the desired concentrations of herbicide in the topsoil layer for longer weed control periods.

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## **REDUCTION OF PESTICIDE POLLUTION IN AGRICULTURAL SOILS BY USING CONTROLLED RELEASE FORMULATIONS: EFFICACY AND PERSISTENCE STUDIES**

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Pesticides are widely used in agriculture although their inadequate usage can create hazards to both humans and the environment. The application rates for conventional herbicide formulations are generally greater than recommended dosage, in order to overcome losses from degradation, leaching, volatilization, and sorption during the time needed for weed control. All these factors have encouraged the development of controlled release formulations, which can reduce herbicides levels in the environment since less active ingredient needs to be applied for maintaining biological efficacy.

The present study describes the preparation, characterization and application to soil of controlled release ethylcellulose formulations containing the herbicide norflurazon and alachlor. Ethylcellulose formulations were obtained by a microencapsulation technique and characterized by scanning electron microscopy (SEM). Several parameters such as rent of production, encapsulation efficiency and pesticide loading in the microsphere, have been also calculated

The persistence of both herbicides in soil is greatly influenced by environmental conditions such as temperature, moisture levels, sunlight exposition, rainfall, microbial activity, organic matter content, etc. Likewise, the residual weed control is dependent on herbicide persistence and availability in soil.

In order to compare the herbicidal activity of norflurazon and alachlor applied as microencapsulated formulations with the commercial formulation, bioassay experiments were carried out. The formulations were applied as preemergence herbicide at 0.8 and 1.6 mg kg<sup>-1</sup> for norflurazon and alachlor, respectively. The treated soils were transferred to plastic pots, where oat (soils with alachlor) and soybean (soil with norflurazon) seeds were sown. The herbicide persistence in soil was studied sowing again fresh seeds in each pot. The results showed that the ethylcellulose microencapsulated formulations of norflurazon and alachlor protected against dissipation in soil and remained biologically active longer than the commercial formulation.

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## ABSORPTION AND PERMEABILITY OF CLAYS UNDER PERMEANTS WITH Fe(II) AND Mn(II)

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The protection of groundwater resources from deleterious effects of hazardous wastes is being done by low permeability clay liners. However, it has been shown that certain chlorinated hydrocarbons of the solvent type attack the integrity of clay liners, making them highly permeable. The integrity of compacted clay liners that are exposed to chemical wastes is an important consideration. Concentrated organic chemicals can increase the permeability of compacted clay due to reduction in thickness of the diffuse double layer that surrounds the particles of clay.

Compacted clays are subjected to inorganic permeants to examine the changes in permeability caused by the reaction clays and permeants such as Mn(II) and Fe(II). Tests are conducted in specially designed and constructed mold permeameters that provide precise measurements of pressures and flows.

In this paper, effects of inorganic permeants on the permeability of the compacted clay have been studied. Soil samples used in this study were obtained from the file Landfill located on the Asian side of Istanbul. The soil samples have the hydraulic conductivity,  $k = 10^{-7}$  cm/s and density of 2.70 gr/cm<sup>3</sup>.

In the experimental studies, physicochemical characterizations of the clay and the effect of inorganic permeants on the permeability of compacted clay soil samples have been analyzed, and Mn(II) and Fe(II) have also been measured in the influent and effluent in order to determine the treatment capability of the compacted clay. Absorption of clay soil was studied in batch and continuous reactors. The microstructure (micro-fabric) of the clay was studied by scanning electron microscope.

Keywords: Compacted clay, adsorption, permeability, Mn(II), Fe(II)

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## REMOVAL OF IRON AND MANGANESE FROM WATER BY USING FILTRATION TECHNIQUE

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In oxygen-free aquatic environments such as ground waters and hypolimnetic waters of eutrophic lakes, iron and manganese exist predominantly in the ferrous state Fe(II) and manganese state Mn(II). Even though iron and manganese removal processes used commonly nowadays were invented in the 19th century, there are still significant gaps in our knowledge. The basic process used for iron and manganese removal is to oxidize soluble iron and manganese compounds so that they are converted to insoluble iron and manganese compounds, and these oxidation products are removed by either precipitation and/or filtering. Catalytic effects of the Fe(OH)<sub>3</sub> and MnO<sub>2</sub> on the oxidation of ferrous iron and manganese by aeration have been demonstrated and the kinetics of this catalytic reaction has been formulated by the authors in recent studies. It has been reported that the oxidation rate is linearly increasing with Fe(III) concentrations up to 600mg/l and Mn(IV) concentrations up to 700mg/l respectively.

The aim of this study was to investigate the mechanisms of Fe(II) and Mn(II) removal in slow sand filters. The removal of Fe(II) and Mn(II) in uncoated sand and Fe(II)-Mn(II) coated sand were studied separately.

Model filter is made of 10 cm internal diameter and 50 cm height Plexiglas material. The feeding flow of the reactor is 50 ml/min. Filter was fed with approximately 3 L/hour flow rate and 0,382 m<sup>3</sup>/m<sup>2</sup> surface load per hour.

This study was conducted by filling one reactor with clean sand and another with Fe(II)-Mn(II) coated sand. It is observed that the removal efficiency in Fe(II)-Mn(II) coated sand is higher than that of clean sand due to the fact that Fe(OH)<sub>3</sub> and MnO<sub>2</sub> balls make a film layer by coating sand particles and this film layer causes catalytic effect on oxidation of Fe(II) and Mn(II).

Keywords: Iron, manganese, slow sand filter, coated filters, uncoated filters, autocatalytic effect.

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## THE EFFECTS OF MN(II), NI(II), ZN(II) AND POTASSIUM HYDROGEN PHTHALATE ON FE(II) OXIDATION WITH ATMOSPHERIC OXYGEN.

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As a natural result of iron content of 4.7 % in the earth's crust, groundwaters are rich in iron as well. In oxygen-free aquatic environments, such as groundwaters and hypolimnetic waters of eutrophic lakes, iron exists predominantly in the ferrous state Fe(II). When this water comes into contact with atmospheric oxygen, Fe(II) is oxidized and precipitates as Fe(OH)<sub>3</sub> flocs. Removal of iron is necessary for domestic and industrial uses of this kind water. Iron being as the secondary contaminant in EPA drinking water standards causes undesired metallic flavour and deleterious view when it has higher concentrations than specified values.

However, there are various studies about the effects of organics on oxidation of Fe(II) with atmospheric oxygen in literatures; it is seen that the effects of inorganics are not studied well enough in the literature.

In this study, effects of potassium hydrogen phthalate, Mn(II), Zn(II) and Ni(II) on oxidation of Fe(II) which are increasing due to seasonal changes in surface water sources with atmospheric oxygen were determined. In laboratory-scale experimental system as a batch reactor; raw water obtained from entrance of Omerli Dam Treatment Plant and deionized water were used, oxidation is performed for different concentrations.

Effects of additional organic and inorganic materials on the oxidation mechanism of Fe(II) were investigated. Potassium hydrogen phthalate as an organic material and Mn(II), Zn(II), Ni(II) as inorganic materials were used.

In the study, in Fe(II) oxidation at presence of PHF (potassium hydrogen phthalate), reduction of Fe(III) with an increase in initial concentration of PHF and a decline in catalyst effect of Fe(II) on oxidation were observed. In comparison with oxidation experiments at the presence of Mn(II) and without Mn(II), decelerating effect of Mn(II) on Fe(II) oxidation due to  $[Mn(II)]/[Fe(II)]$  rate was seen. In Fe(II) oxidation with the presence of Zn(II), deceleration in Fe(II) oxidation rate due to presence of Zn(II) was observed. In Fe(II) oxidation study with atmospheric oxygen at presence of Ni(II), it was emerged that Ni(II) does not have an effect on the oxidation.

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## EVALUATION OF POTENTIAL POLLUTION FROM AGRICULTURAL ACTIVITIES AT DURRES REGION (ALBANIA)

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The agricultural region of Tirana-Durres-Kavaja with about 25 000 ha of cultivated land (Arenosol – FAO-UNESCO, 1992) is located between mountains Dajt-Kruje and Adriatik seaside. In this zone lives 1/3 e country population (city of Tirana 800, 000 inhabitants, city of Durres 120, 000 inhabitants and rural part with about 100, 000 inhabitants). The total surface of Durresi watershed is about 26000 ha and in this rural zone there are about 14 000 agricultural farms with 1.7 ha each one. The region is traversed by two small rivers (Ishmi and Erzeni) with 18 m<sup>3</sup>/s and 21 m<sup>3</sup>/s, each one, respectively in summer and winter season. In river Ishmi flows and the Lana river (5 m<sup>3</sup>/s water) where are poured untreated wastewaters of Tirana city, without any treatment. Recent investigations indicate that these rivers are polluted. The soils are shallow and with loamy and sandy soil texture. Durres Region is one of the main suppliers of Tirana market with fresh vegetables and most visited coastal region for summer turistic purposes. The objective of our study consists in budget evaluation of N and P and its potential danger that such products present for the public health and the coastal touristic environment. The contribution definition of non point source and P was the specific objective.

Key words: pollution, nitrogen, phosphorus, manure, fertilizers, agriculture, poultry industries.

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## AIR PREDICTION MODELS OF POLLUTANTS IN AN INDUSTRIALISED AREA OF THE MEDITERRANEAN BASIN

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**Keywords:** Air Pollution, Ambient Air, Prediction Models, Public Health, TSP, PM10, Heavy Metals.

Air quality evaluation was performed regarding atmospheric particles (TSP and PM10), As, Cd, Ni and Pb in a Spanish coastal area during five years (2001-2005) in order to compare these values with other areas in the Mediterranean basin. The study area, Vila-real (Castellón, Spain), is highly industrialised, with businesses involved the non-metallic mineral material industries (ceramic production) and chemical industries (colour, frit and enamel manufacturing) standing out (1). The origin of the contamination in this area is both natural and anthropogenic. The natural origin is due to the resuspension of mineral materials from the surrounding mountains (2) and from the long-range transport of materials from North Africa. The anthropogenic contamination sources are before mentioned industries as well as vehicular traffic. The objective of this study was to assess the concentrations of these contaminants and elaborate a series of mathematical models of them. The goal is to provide a useful instrument to alert the population facing possible episodes of high concentrations of atmospheric pollutants. Once the particle samples were collected in quartz fiber filters, the concentration levels of TSP and PM10 were determined gravimetrically. The chemical analysis of the filters was carried out by ICP-MS (3). Predictive models have been constructed by using Multiple Regression Analysis together with Time Series Models (ARIMA). The SPSS 14.0 statistical software has been employed to analyse the obtained experimental data.

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## HEAVY METAL SPECIATION OF ESTUARINE SEDIMENTS AFFECTED BY ACID MINE DRAINAGE IN THE TINTO AND ODIEL ESTUARY, SPAIN. RELATIONSHIP TO BIOACCUMULATION OF FISH TISSUES

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The particular metal-rich geochemistry of the Iberian Pyrite Belt, the consequences of metal exploitation of its mineral resources and the acid mine drainage (AMD) have been suggested as the main reasons for the relatively high metal levels in the Gulf of Cádiz (SW Spain) [1-2]. Large sulfide deposits and metal-rich wastes have been exposed over centuries to lixiviation processes involving a subsequent mobilization and transportation of metals along the water drainage system towards the open sea, mainly Tinto and Odiel rivers [3]. The highest metal levels in riverine discharges to the sea have been found in the Ría de Huelva, the mouth area of the Tinto and Odiel rivers Estuary, where both rivers come together forming a unique course for a few kilometres before it reaches the sea [4]. Anthropogenic activities can be considered as metal pollution sources as well, specially urban sewage inputs, lixiviation of phosphogypsum deposits and industrial activities along the Ría de Huelva, covering fertilizer plants, paper processing and oil refineries.

As a forward step to understand the mechanisms of transport, mobilisation and trapping, as well as to find their sources, determine their bioavailability and asses the potential impact of such processes on aquatic biota, a study of the heavy metal speciation of sediments along the Ría de Huelva have been achieved. For this purpose, a speciation procedure based on a sequential extraction methodology proposed by the Community Bureau of Reference (BCR) has been followed [5]. Thus, six heavy metals (Fe, As, Zn, Cd, Pb and Cu) in sediments have been separated in four different fractions: labile, reducible, associated to organic matter, and mineral. Also, the concentrations of metal in tissues (gill, liver and muscle) of benthic and pelagic species of area were determined and compared with labile and total metal levels to assess the characteristics of bioaccumulation in two different species of fish.

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## ADSORPTION AND DEGRADATION OF FOUR ACIDIC PESTICIDES IN SOILS FROM SEVILLE

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Adsorption of four acidic pesticides was measured in four soils. In general, sorption of acids increased in the order dicamba < metsulfuron-methyl < 2,4-D < flupysulfuron-methyl. Adsorption was negatively correlated with soil pH and positively with clay content. Two different K<sub>d</sub> predictors equations, which were developed in a previous work for these acidic pesticides in nine English arable soils, and based on selected soil properties as: Log D, organic carbon, and a pesticide descriptor, were tested for the measured K<sub>d</sub> in the present work. Both equations were not successfully applied, mainly due to the negligible OC content in the Spanish soils under study.

Degradation process was also investigated for these pesticides on the selected soils. Results were analysed to (i) identify any commonalities in factors influencing rate of degradation and (ii) test for any link between sorption and degradation processes. No a general pattern could be observed when all pesticides were considered together, but however a strong correlation between adsorption and degradation could be determined for all acidic pesticides studied in this work when these were investigated individually for each soil, concluding that degradation is a very complex process where a depth study of the soil and pesticide properties should be undertaken before supply any assessment about its fate and behaviour, and therefore more studies with more soils of different properties should be performed.

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## SURFACE SEDIMENTS IN THE OPEN AEGEAN SEA

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Surface sediments of the Aegean Sea gathered from 17 sampling stations during 6 oceanographic cruises (1996-2004) have been analysed for the estimation of Zn, Ni, Cr, Cd, Pb, Cu, Fe, Mn and org. C. The samples were collected with a grab sampler of a Smith-McIntyre type. Wet sieving was used. The chemical analyses were conducted on the <63  $\mu\text{m}$  grain size fraction of the sediments since metals from anthropogenic sources are mostly concentrated on the fine sediment particles. Until 1999, the major and trace elements were determined using the A.A.S. technique after total dissolution of the sediment samples, successively attacked with conc. nitric acid, hydrofluoric acid, aqua regia and perchloric acid in Teflon bombs. Since 2000, the X-ray Fluorescence technique was used.

It is noteworthy that sediments in the northern part of the Aegean Sea are found enriched in some of the trace metals like Zn, Cr, Pb and Fe compared to the southern Aegean Sea. Riverine sources in the northern Aegean Sea contribute substantially to the suspended load of the sediments, whereas in the southern Aegean Sea Aeolian inputs play the most important role on the sediment supply. This is clearly reflected on the concentrations of the terrigenous metals.

The correlation coefficient matrix was used to determine the origin of certain metals. Hence, two groups of elements could be distinguished: the first group consists of Zn, Pb, Cr and to a lesser extend Cu, which are strongly related to Fe; the second group consists of Ni and Cu, which are strongly correlated either to Mn or to organic C.

The metal concentrations recorded in this work are similar to those reported for other unaffected Greek marine areas.

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## DETERMINATION AND EVALUATION OF SURFACE OZONE LEVELS IN ESKISEHIR, TURKEY

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In this study, the results of the studies related to the evaluation of ozone (O<sub>3</sub>), which is the most important compound of photochemical smog, and its precursors in the atmosphere of Eskisehir was evaluated. Up to now studies such as continuous and semi-continuous ozone monitoring, passive sampling of ozone and NO<sub>2</sub> which is its one of the most important precursors, determination of NO<sub>x</sub> and VOC emissions which play an important role in the ozone formation by calculation and determination of ozone levels by modelling has been used for the assessment of ozone and its precursors in the study area.

A detailed emission inventory was prepared for the city center. According to the results of the emission inventory, total NO<sub>x</sub> and VOC emissions for 2005 are 2806 tons/year and 414 tons/year, respectively. For both NO<sub>x</sub> and VOC emissions, traffic seems to be the most contributing source which is followed by domestic heating. While the contribution of industrial emissions are approximate to the domestic heating emissions for NO<sub>x</sub>, it has been obtained that the contribution of industrial activities is much lower for VOC emissions. By applying passive sampling to obtain 15-day average values at 7 sites with different characteristics, the average concentration values for winter and summer seasons were obtained as 30 and 16 µg/m<sup>3</sup> for NO<sub>2</sub> and 38 and 54 µg/m<sup>3</sup> for ozone.

The continuous ozone measurements carried out in Anadolu University İki Eylül Campus during 2005 showed that the average monthly ozone concentrations between April-August were above 80 µg/m<sup>3</sup>, and the highest monthly average value was obtained as 91 µg/m<sup>3</sup> in August. The highest observed concentrations were around 160 µg/m<sup>3</sup> in July and August. The AOT40 value which is the indicator of plant exposure to ozone was calculated as 27940 µg/m<sup>3</sup>.hr.

Besides the detailed monitoring and emission inventory studies carried out for the city center and mentioned above, ozone levels were determined for the 100 km \* 100 km domain, including the city center and some important nearby residential and industrial towns, with a resolution of 2 km \* 2 km by using MM5 meteorological model and CAMx chemical model. For these modeling studies, the other important anthropogenic emissions in the study area were also determined and the biogenic VOC emissions which contribute to ozone formation were calculated. In the study area, the anthropogenic VOC emissions, biogenic isopren emissions

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and biogenic monoterpene emissions were determined as 2175 tons/year, 6058 tons/year and 1920 tons/year, respectively. According to this result, the biogenic emissions seem to be important in the VOC budget. When the geographical distribution of ozone is investigated according to the model results, high ozone levels are observed in the rural areas in the north-north west part of the city. Large emission sources in the north-northwest-west part of the city and dominant wind direction of west-north west for summer season play an important role for this distribution.

**Keywords:** Ozone, anthropogenic emissions, biogenic emissions, ozone monitoring, ozone modelling

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## MONITORING OF PESTICIDE RESIDUES IN RIVER WATER OF ALIAKMONAS RIVER IN THE REGION OF IMATHIA (N. GREECE) BY MEANS OF SOLIDPHASE EXTRACTION DISKS AND GAS CHROMATOGRAPHY

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Pesticides contamination of surface waters has been well documented worldwide and constitutes a major issue that gives rise to concerns at local, regional, national and global scales. The uncontrolled use has led to an urgent demand for the development of sensitive and precise analytical methods in order to monitor these compounds in river water.

Aliakmonas is the longer river of Greece and is found completely in Greek territory with total length of 322 km. It rises in the northern "Pindus" Pindus mountains in northern Greece on the border with "Albania" Albania, before flowing southeast then northeast through the Greek "peripheries of Greece" peripheries of "West Macedonia" West and "Central Macedonia" Central Macedonia and flows into "Thermaic Gulf" Thermaic Gulf. It flows through an extensive area, making it one of the most importances to agriculture in Greece. The region of Imathia, in the prefecture of Macedonia in Northern center Greece, is one of the biggest producing areas of peaches in Greece (about 500.000 tons per year). Most of the amount of pesticides used in Imathia region- which is very high- is being applied in peaches cultivation.

At the present study, twenty four modern pesticides from various chemical groups, which used especially for peach cultivation, were analyzed in river water of Aliakmonas.

This work presents the results of the monitoring survey of 84 samples of surface river water which were collected monthly between January 2006 and December 2006. The sampling cruises included seven sites in the banks of the river. Two 2.5-l volumes of water were collected in glass bottles from each sampling site. After filling with water, the bottles were sealed with screw caps lined with aluminium foil. Isolation of the pesticides from the filtered water samples were performed off-line using a standard 6-port SPE manifold from Supelco (Bellefonte, PA, USA) connected to a vacuum pump. The collected samples from rivers, were prefiltered on 0.45-mm HVLP filters (Millipore Bedford, MA, USA) to eliminate particulate matter and were acidified with sulfuric acid. SDB-RPS, disks were first activated by wetting with 6 ml acetone. Then they were washed with 10 ml acetate and were vacuum dried. Methanol (10ml) was then percolated through the disks and without letting the disks to become dry, a 10 ml distilled water and the without letting the disk to become dry, 1000ml water sample (adjustment at pH 3 to pH 3,5). The analytes were eluted with 2x10 ml EtAt:Dichloromethane (50:50). The final extract was dried over anhydrous sodium sulfate. Finally they were evaporated to a final volume of 0.5 ml under a gentle stream of N<sub>2</sub>, with solvent change to Hexane. Recoveries of all analytes were good enough ranging between 85% and 108% in all cases.

In the river water, concentrations of detected pesticides compounds were almost under EU MRL except some samples which were collected from Canal-66. The higher concentrations of pesticides in river waters were measured during the period from June to August 2006.

**Keywords:** Aliakmonas, Water analysis; Environmental analysis; Pesticides.

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## ANALYTICAL DETERMINATION OF SYNTHETIC ESTROGENS IN ENVIRONMENTAL WATERS, SLUDGE AND SEDIMENTS: STATE OF THE ART

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Synthetic sex steroids for pharmaceutical use—ovulation inhibitors, estrogen surrogates during menopause—are nearly exact copycats of natural sex steroids. This is valid for the effects caused as well as for their potency. Besides their advantages in therapeutic uses, some undesirable estrogenic side effects can occur. Owing to their high estrogenic potency, unwanted effects like increased growth of the endometrium and a higher risk of breast cancer can accompany the desired effects during menopause. However we are faced to Endocrine-disrupting effects in the environment. Endocrine-disrupting effects in the aquatic environment, such as the feminization of male fish can be likely attributed to the presence of estrogens in river.

Endocrine-disrupting chemicals (EDC) can enter surface water by a series of mechanisms including direct discharge of industrial and domestic wastewaters, sewage treatment plant effluents, agricultural drains to streams and rivers, overland flow after rainfall events and spillage during production and transport. Worldwide, in municipal sewage treatment plant discharge and in the receiving waters, predominantly estrone, 17 $\beta$ -estradiol and the contraceptive 17 $\alpha$ -ethinylestradiol have been detected. Therefore, a potential contamination of soil with estrogens may be caused by the application of digested sludge from municipal sewage treatments onto agricultural fields. Further, it seems likely that estrogens are present in sediments, and because of their extremely high estrogenic potency, the possible threat to sediment biota cannot be ruled out.

In this contribution, the study of possible routes of exposure for synthetic steroids is considered in the light of recent studies, and the analytical methodology for determining synthetic estrogens in environmental waters, sludge and sediments is critically revised. Special attention has been paid to validation of analytical methods within the field of a global approach involving traceability and uncertainty measurement.



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## IN SILICO SCREENING OF ESTROGEN-LIKE CHEMICALS BASED ON QSAR MODELS

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Increasing concern is shown by the scientific community, regulators, and the public about endocrine-disrupting chemicals (EDCs) that, in the environment, are adversely affecting human and wildlife health through a variety of mechanisms of toxicity, mainly estrogen receptor-mediated. Because of the large number of EDCs in the environment, there is a great need for an effective tool of rapidly assessing ED activity in the toxicology assessment process and in the context of the new European REACH policy.

Here, classification and regression QSAR models were developed to predict the estrogen receptor binding affinity based on a large data set of heterogeneous chemicals and theoretical molecular descriptors from DRAGON. The built OLS regression model, based on eight descriptors, was validated comprehensively (internal and external validation, Y-randomization test) and all the validations indicate that the proposed QSAR model is robust and satisfactory ( $Q^2 = 0.75-0.85$ ). Comparison with similar studies revealed that our model seems to outperform all the others on the whole, although it is impossible to have an absolute measure of comparison.

For the classification models, three nonlinear classification methodologies: Least Square Support Vector Machine (LS-SVM), Counter Propagation Artificial Neural Network (CP-ANN), and k-nearest Neighbor (kNN) were applied, by using four molecular structural descriptors as inputs. All three methods can give satisfactory prediction results both for training and prediction sets, and the most accurate model was obtained by the LS-SVM approach. In addition, our models were also applied to about 58 000 discrete organic chemicals; about 76% were predicted not to bind to an estrogen receptor.

Thus, the proposed models are very satisfactory and externally predictive, and can provide a practical tool for the rapid screening of the estrogen activity of organic compounds, allowing the quick identification of possible environmental estrogens, being based only on chemical structure.

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## PROGRESS WITH THE PBT EVALUATION, UNCERTAINTIES AND PBT ASSESSMENT UNDER REACH

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Substances fulfilling PBT criteria are substances that are persistent, bio-accumulative and toxic, while vPvB substances are characterised by a particularly high persistency in combination with a very high tendency to bio-accumulate, but not necessarily proven toxicity. These properties are defined by the criteria laid down in Annex XIII of the REACH Regulation (Registration, Evaluation and Authorisation of Chemicals) that entered into force in the EU on June 1st 2007. A PBT/vPvB assessment is required for all substances manufactured or imported in the EU in amounts of 10 or more tonnes per year that are not exempted from the registration requirement under REACH.

The objective of the PBT/vPvB assessment is different from the other risk assessment approaches as it seeks not to estimate safe concentrations but to minimise releases of PBT and vPvB substances and thereby exposure of humans and the environment to substances that cannot be controlled with reasonable effort once they have been released. In practice, the PBT and vPvB assessment comprises of 1 or 3 steps (comparison with the criteria and, if these are met, emission characterisation and risk characterisation) that are outlined in a guidance document developed as part of the REACH Implementation Projects. This guidance for PBT/vPvB assessment shall ensure that all existing information as well as information that can be developed with alternative methods (in vitro, QSAR and read-across) is taken into account in the most appropriate way in order to save costs and reduce the need for conducting new animal experiments.

The presentation will illustrate the current status of the evaluation of 127 PBT substances, which has been carried out by the TC NES subgroup for the evaluation of potential PBTs or vPvBs in the context of the EC's Interim Strategy for Management of PBT and vPvB substances. Further, the main elements of the guidance on assessing of PBT/vPvB substances under REACH will be set out and illustrated with practical examples, e.g. brominated flame retardants.

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**ROLE OF POLYCYCLIC AROMATIC HYDROCARBONS AS  
ENDOCRINE DISRUPTORS IN A COHORT OF URBAN  
TRAFFIC POLICEMEN IN SOUTHERN EUROPE.**

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Human exposure to polycyclic aromatic hydrocarbons (PAHs) occurs principally by polluted air and tobacco smoke, dietary intake, and dermal contact. The main purpose of this work was the assessment of human inhalatory exposure to PAHs in urban air, in relation to a suspected and still under consideration characteristics of endocrine disruptors of some of them. This exposure was quantified measuring their concentrations on breathable particulate (PM<sub>5</sub>) singularly sampled in a cohort of urban traffic policemen (smokers and non smokers) that, for their specific working functions, spend their time indoor and outdoor. The second purpose of this study was the quest for a possible correlation between personal exposure to PAHs and the potential consequence on thyroid morphology and functionality.

A group of voluntary was enrolled among traffic policemen working in Torino, an European city located in North-Western Italy having almost 900.000 inhabitants. Sampling period lasted from December 2004 to March 2005; at the beginning of the working shift (7 a.m.) 6 policemen had on a sampler for PM<sub>5</sub> and PAHs. At the end of the working shift (2 p.m.), policemen returned the samplers, answered to a questionnaire, a urine spot and a venous blood sample were collected and a medical examination and a thyroid ultrasound scanning was performed.

The 53 voluntary subjects were subdivided as following: 1: 14 subjects non smokers working outdoor, close to traffic, 2: 20 subjects non smokers working in offices, 3: 19 subjects smokers, with or without traffic exposures.

PAHs concentrations (15 chemicals) were: group 1 134 ng/m<sup>3</sup>, group 2 131 ng/m<sup>3</sup>, group 3 ng/m<sup>3</sup>. No significant differences were observed in the three groups considering: B.M.I., thyrotropin TSH (μ/ml), free fraction of thyroid hormone FT<sub>3</sub> pg/ml and FT<sub>4</sub> (ng/dl), antibodies against anti tireoglobulin Tg Ab (U/ml), and anti-thyroid peroxidase TPO Ab (U/ml). Excluding three cases of previous thyroid troubles, TSH, FT<sub>3-4</sub>, Tg Ab, TPO Ab and thyroid volume did not show neither pathological conditions nor statistically significant differences between exposed or non exposed to traffic. Nevertheless, TPO Ab measured in non smokers, exposed to traffic (16,6%) was three times higher if compared to non smokers non exposed to traffic (5,3%).

In conclusion, our findings show a very low exposition to PAHs in the selected subjects; furthermore, non differences were recorded between outdoor and indoor professional activities. Thyroid effects of this urban PAHs exposure are negligible considering morphology, functionality, autoimmunity, and formations of nodules valuable with an ultrasound scanner. Longitudinal studies are hoped for correctly considering the long term effects of urban traffic on thyroid functionality.

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## POLYCHLORINATED BIPHENYLS (PCBs) IN THE MEDITERRANEAN SEA ATMOSPHERE AND SEAWATER

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Polychlorinated biphenyls (PCBs) are anthropogenic compounds that enter the environment as a result of primary and secondary sources. They bioaccumulate and are considered potent toxicants capable of producing a wide spectrum of adverse health effects in biota and humans such as induction of enzymes, anti-estrogenic effects, disruption of the endocrine system, immunosuppression, carcinogenicity, reproductive and developmental toxicity, skin disease, and cognitive disorders.

Within the framework of the IP THRESHOLDS of Environmental Sustainability, two sampling cruises on board of the oceanographic vessel B/O Garcia del Cid were performed. The first campaign was executed from Barcelona to Istanbul and the second one from Barcelona to Alexandria. Environmental air and water concentrations for the 7 indicator PCBs (CB-28, 52, 101, 118, 138, 153, 180) and other organochlorine compounds were obtained across the Mediterranean Sea. Air sampling was performed as indicated for PCDD/Fs<sub>1</sub> whereas water suspended particulate matter was trapped by using quartz fibre filters (QFFs), and compounds in the dissolved phase were extracted by using a polymeric adsorbent (XAD-2). Results from all sampled compartments allowed the estimation of atmospheric deposition fluxes.

Total air concentration ( $\Sigma 7$  congeners) along the Mediterranean atmosphere ranged from 50-77 pg m<sup>-3</sup> whereas the sample taking at Marmara and Black seas exhibited a value of 172 pg m<sup>-3</sup>. Furthermore, samples of plankton were also collected and analysed for all the Mediterranean allowing to estimate the bioaccumulation of PCBs in planktonic food webs.

1 See abstract of POLYCHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS (PCDD/Fs) OVER THE MEDITERRANEAN SEA for campaign description, air sampling and analyses details

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## DIETARY INTAKE IN PREGNANCY AND THE RISK OF HYOSPADIAS IN 12 EUROPEAN COUNTRIES

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The aetiology of hypospadias is not well understood and the underlying reasons for the increasing incidence of hypospadias in Europe are unknown. It has been hypothesized that the risk of hypospadias is determined in utero and that pregnancy dietary intake (in particular foods possibly contaminated by EDCs) could affect hypospadias risk in the offspring.

In order to test this hypothesis, the prevalence at birth of hypospadias in 12 European countries (Denmark, Finland, Ireland, Poland, U.K., Italy, Spain, France, Switzerland, Germany, Netherlands and Malta) reported by Eurocat Database (2002) was correlated with the average per-capita consumption of selected food items (n=124) in these countries in the corresponding period (FAOSTAT-Database).

Among the food items examined, the following were found to be significantly correlated with the prevalence of hypospadias: fruit ( $r=0,709$ ;  $p<0,01$ ), consumption of pelagic fish ( $r=0,707$ ;  $p<0,05$ ) and aquatic animals ( $r=0,669$ ;  $p<0,05$ ), sugar cane and sugar crops ( $r=0,837$ ;  $p<0,01$ ), and animal fats ( $r=0,580$ ;  $p<0,05$ ).

Our findings, although based on an ecological approach, give additional support to the results of previous research which suggest that dietary exposure in pregnancy to products potentially contaminated with EDCs (fruits, fish and animal fats) may be implicated in the pathogenesis of hypospadias, through the Testicular Dysgenesis Syndrome. High consumption of sugar-rich foods has also been hypothesized as a risk factor in hypospadias through the insulin-related suppression of the sex hormone-binding globulin production, leading in turn to an increase of the free oestrogen level.

This ecological analysis of the relationship between the prevalence of hypospadias and dietary exposures in pregnancy, suggests that the consumption of foods potentially interfering with the endocrine system of the mother, may be associated with an increased risk of this congenital defect.

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## SEX STEROIDS IN TAPES PHILIPPINARUM (ADAMS AND REEVE 1850) DURING THE GAMETOGENIC CYCLE: PRELIMINARY RESULTS

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It is well known that a wide variety of endocrine disruptor chemicals (EDCs) (e.g., organotin compounds, heavy metals, herbicides, and xenoestrogenic compounds) can induce endocrine abnormalities in marine invertebrates often causing reproductive disorders. Despite these phenomena are of great concern mostly in coastal and estuarine environments, only few data are available about the mechanism of action of EDCs, mainly due to a lack of knowledge on the invertebrate endocrine system. In particular, in the clam *Tapes philippinarum* estrogenic effects of nonylphenol (NP) were recently demonstrated, they resulting in vitellogenin-like protein induction, mostly in male clams (Matozzo and Marin, 2005), as NP probably mimics endogenous estrogens.

To better understand the possible mechanism of action of NP, as well as of other EDCs, the presence and patterns of variation of sexual steroids were evaluated during the various phases of the gametogenic cycle of *T. philippinarum*. Adult clams were collected from two licensed areas located in the Lagoon of Venice (Italy) from July 2005 to May 2006, corresponding to following stages: spawning (July), post-spawning (October), spent (January) and gametogenesis (May). The clams were sexed by microscopic observation (400  $\mu$ ) of a smear of gonadal tissue with the exception of the spent stage in which no gametes were detectable.

Progesterone, testosterone and estradiol-17 $\beta$  were measured in the whole-body clam homogenate using specific and opportunely validated microtitre RIAs. Differences in hormone concentrations during annual cycle were assessed by analysis of variance (ANOVA) followed by a Tukey's Post hoc test ( $P < 0.05$ ). In females, all the hormones showed the same profile, with higher concentrations during the spawning period and lower during post-spawning and gametogenesis. In males, progesterone and estradiol-17 $\beta$  never differed among stages and the values were very similar to those of females in non spawning periods. Conversely, testosterone statistically decreased during gametogenesis. All the hormones were unexpectedly high in the spent stage in which no gonadal tissue was observable and females and males were thus jointly processed. Progesterone was the most representative sexual steroid showing levels (about 1 ng/g) six to seven times higher than those of estradiol-17 $\beta$  and testosterone.

Although the results obtained are preliminary and need further validation, the protocols set up to evaluate sexual steroids in *T. philippinarum* represent the first step for future research aimed at understanding the physiological role of these hormones and their potential interaction with EDCs.

Matozzo V., Marin M.G., 2005. Can 4-nonylphenol induce vitellogenin-like proteins in the clam *Tapes philippinarum* Environ. Res., 91: 179-185.

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**DO REPRODUCTIVE CONDITIONS INFLUENCE RESPONSIVENESS  
OF VITELLOGENIN-LIKE PROTEIN INDUCTION IN CLAMS (TAPES  
PHILIPPINARUM) EXPOSED TO 4-NONYLPHENOL?**

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Increasing efforts have been recently addressed to the evaluation of vitellogenin (Vg)-like protein induction as useful biomarker to assess estrogenic contamination in aquatic environments. Vg, the precursor of egg-yolk proteins, is normally synthesised in mature females, but is induced also in males and immature females of both fish and invertebrates after exposure to endocrine disrupting chemicals. Among these compounds, 4-nonylphenol (NP) is widespread in marine coastal areas, coming from various sources, mainly sewage treatment plants. In a previous study, NP was shown to induce Vg synthesis in pre-spawning males of the clam *Tapes philippinarum* after 7-days exposure, whereas no effect was detected in females (Matozzo and Marin, 2005).

In the present work, estrogenic effects of NP were evaluated during sexual resting phase of clams, when gonads are undifferentiated and thus sex not distinguishable by microscopic observation of gonadal smears. Specimens of *T. philippinarum* from the Lagoon of Venice were exposed to the same NP concentrations previously tested (0, 0+acetone, 0.0125, 0.025, 0.05, 0.1, 0.2 mg/l) for both 7 and 14 days. After exposure, Vg levels were determined in haemolymph and digestive gland by the alkali-labile phosphate (ALP) assay. In the haemolymph Ca<sup>2+</sup> levels were also measured, they being possibly related to the presence of Vg-like proteins.

In 7-days treatments, Vg content significantly increased in both haemolymph and digestive gland at the highest concentration tested ( $p < 0.05$ ), whereas no variation was observed in haemolymph Ca<sup>2+</sup> concentration. In 14-days treatments, Vg and Ca<sup>2+</sup> levels showed a similar increasing trend in haemolymph, although significant differences with respect to controls were found at 0.025 and 0.05 mg NP/l for Ca<sup>2+</sup> only ( $p < 0.05$ ). A dose-dependent Vg increase was also observed in digestive gland, significant at 0.1 mg NP/l ( $p < 0.05$ ).

Responsiveness of Vg induction was confirmed in quiescent clams, mostly when measured in digestive gland, indicating applicability of the biomarker throughout the whole reproductive cycle of animals in both laboratory and field studies. A relationship between Vg and Ca<sup>2+</sup> levels was detected in prolonged exposure only.

Matozzo V., Marin M.G., 2005. Can 4-nonylphenol induce vitellogenin-like proteins in the clam *Tapes philippinarum*. *Environ. Res.*, 91: 179-185.

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## DETERMINATION OF THE METABOLITES OF ALKYLPHENOL ETHOXYLATES AND BISPHENOL A IN WATER SAMPLES USING SPE/LC/ MS\*

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The last years a lot of research is carried out on micropollutants in water and effluents that disrupt the endocrine system in humans and animals by mimicking, enhancing or inhibiting the effects of hormones. Among the substances that are suspected to act this way are the nonyl and octylphenol ethoxylates (Alkylphenol Ethoxylates). They are mainly present in household chemicals as non ionic surfactants and during the industrial and urban waste water treatment are dissociated into octylphenol και 4-n-nonylphenol (4-n NP), metabolites that act as endocrine disruptors.

The aim of this work is to develop a simple procedure for the determination of octylphenol and 4-n-nonylphenol, as well as the Bisphenol A substance with similar action, in water and waste water, by using Solid Phase Extraction (SPE) and measurement on Liquid chromatography with Mass detector (LC/MS).

The extraction procedure involved SPE with elution solvents 5ml acetone and 10 ml mixture of solvents tertbutylmethylether/Methanol (9:1). The eluted sample is evaporated to 1ml and the determination is carried out using HPLC with MS detector. The system used is Waters 2695 separation module, with Xterra C18 separation column and mobile phase mixture methanol/Milli Q water with gradient elution and detection on ZQ 2000 Waters.

The qualitative and quantitative determination is achieved using the retention time and the molecular weight under conditions of negative electronspray ionisation with the mass spectrometers ZQ 2000.

The method showed acceptable accuracy and precision. The calibration curves for concentrations 10 -500  $\mu\text{g/L}$  of each substance were linear with correlation coefficient 0,99. The recoveries in replicate spiked water samples ranged from 70 to 80% and the limit of quantitation ranged from 0,02 - 0,1  $\mu\text{g/L}$ .

In 10 samples analysed from urban waste water treatment plants, after secondary and tertiary treatment, the concentrations of octylphenol και 4-n nonylphenol (4-n NP), and Bishenol A were below the quantitation limits.



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This method was developed within the project MENTOR among the Polytechnical School of Crete (Department of Environmental Engineering, Laboratory of Technology and Environment Management) and the State General Laboratory in Nicosia, Cyprus.

The team from the Polytechnical School of Crete in Chania, developed a method for the determination of Ethoxylates using Solid Phase Micro Extraction (SPME) and Gas chromatography with Mass detection (GC/MS)

\* Project MENTOR , KY-EA/0603/11, 2004 – 2006.

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## FATE OF ENDOCRINE DISRUPTING COMPOUNDS IN WASTEWATER TREATMENT PLANTS

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The presence in the environment of chemicals capable of affecting the endocrine system has become a matter of scientific and public concern. These compounds are known as Endocrine Disrupting Compounds (EDCs) and include different categories of contaminants. Sewage and industrial wastewaters and surface runoff are considered as significant sources of these compounds in the environment.

The aim of this study was to investigate the fate of selected endocrine disrupting compounds on full-scale wastewater treatment plants. The target compounds were 4-octylphenol (4OP), 4-t-octylphenol (4tOP), octylphenol monoethoxylate (OP1EO), octylphenol diethoxylate (OP2EO), 4-nonylphenol (4NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), bisphenol A (BPA), triclosan (TCS), estrone (E1), 17 $\alpha$ -estradiol (aE2), 17 $\beta$ -estradiol (bE2), mestranol (MeEE2), 17 $\alpha$ -ethinylestradiol (EE2) and estriol (E3).

The occurrence of target EDCs was studied along the different stages of two wastewater treatment plants. The first one treats mainly municipal wastewater and the second plant receive wastewater from a hospital, in the area of Thessaloniki, Greece. Influent wastewater, samples after each treatment unit, final treated effluents and sludge were collected and analyzed. Wastewater samples were filtrated through fiber glass filters and the target EDCs were determined in dissolved and particulate fractions. Solid phase extraction on OASIS HLB cartridges was employed for the determination of dissolved EDCs, whereas sonication was utilized for the extraction of EDCs from solid samples. N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was used as derivitization agent. The analytical method combine the determination of phenolic compounds (4OP, 4tOP, OP1EO, OP2EO, 4NP, NP1EO, NP2EO, BPA, TCS) by gas chromatography – mass spectrometry (GC/MS) and the determination of steroids (E1, aE2, bE2, MeEE2, EE2, E3) by gas chromatography – tandem mass spectrometry (GC – MS/MS).

The removal efficiency of target EDCs in wastewater treatment plants, the distribution of these compounds between dissolved and particulate fractions and possible correlation with organic carbon (DOC and POM) are presented and discussed.

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## PASSIVE SAMPLING OF SELECTED ENDOCRINE DISRUPTING COMPOUNDS USING POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLERS

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Many organic compounds entering the aquatic environment may pose threat for humans and wildlife. Monitoring the levels of these compounds is necessary to ensure that water quality standards are maintained. Most aquatic monitoring programs rely on collection of grab samples of water at a given time. When the pollutants are present at trace levels, large volumes of water need to be collected. The analysis of grab samples provides only a snapshot of the levels of pollutants at the time of sampling; samples are not time representative and episodic events can be missed. Passive sampling could be an alternative sampling method that gives time-weighted average concentrations of pollutants. This type of sampling is based on free flow of pollutants from the sampled medium to a receiving phase of the sampling device.

Polar organic chemical integrative samplers (POCIS) have been designed to sequester and concentrate waterborne polar organic chemicals. A POCIS consists of a solid material enclosed within a microporous membrane. In this study, two types of POCISs (POCIS pharmaceutical and POCIS pesticide) were studied for their sampling efficiency of selected endocrine disrupting compounds (EDCs). Target EDCs include 4-alkylphenols (nonylphenol, octylphenol), their ethoxylate oligomers (mono- and di-ethoxylates of nonylphenol and octylphenol), bisphenol A, the estrogens (estriol, estrone, 17 $\beta$ -estradiol, 17 $\alpha$ -estradiol) and synthetic steroids (mestranol and 17 $\alpha$ -ethynylestradiol).

Laboratory-based experiments were conducted with POCISs exposed to water spiked with known concentrations of EDCs for 7, 14 and 28 days. EDCs sorbed into POCIS were eluted with suitable organic solvent, derivatised with BSTFA and analysed by gas chromatography – mass spectrometry (GC-MS). From this experiment the kinetic regimes and the corresponding sampling rates were determined. The efficiency of POCISs was also studied in field conditions. Both types of POCISs were deployed at four sites in different aquatic environments (marine, river, wastewater canal) for one week. During this period, grab samples were also collected. The concentrations calculated from POCISs were compared with results obtained from grab sampling.

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## ENDOCRINE DISRUPTING COMPOUNDS IN THE COASTAL ENVIRONMENT OF THERMAIKOS GULF, NORTHERN GREECE

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Endocrine disrupting compounds (EDCs) represent different classes of organic compounds such as alkylphenols, phthalates, polychlorinated biphenyls, pesticides that may cause adverse effects to aquatic organisms. Investigated EDCs in the present study include the alkylphenols, nonylphenol (NP) and octylphenol (OP), their mono- or di-ethoxylate oligomers (NP1EO, NP2EO, OP1EO, OP2EO), bisphenol A (BPA) and the steroids estrone (E1), 17 $\alpha$ -estradiol ( $\alpha$ E2), 17 $\beta$ -estradiol ( $\beta$ E2), estriol (E3), 17 $\alpha$ -ethynylestradiol (EE2), mestranol (MeEE2). Alkylphenols (APs) are used in the production of APEOs that are non ionic surfactants, in the preparation of phenolic resins, polymers, stabilizers, antioxidants. The most significant commercial APEOs are nonylphenol ethoxylates (NPEOs) and octylphenol ethoxylates (OPEOs). Degradation of APEOs generates more persistent shorter chain APEOs with one or two ethoxy units and alkylphenols. NP is included in the Water Framework Directive (WFD) 2000/60/EC while OP is currently under review for inclusion in this category. Bisphenol A is used as an intermediate in the production of polycarbonate and epoxy resins. The investigated steroid hormones include both the natural hormones (E1,  $\alpha$ E2,  $\beta$ E2, E3) that are excreted by mammals and the synthetic EE2, MeEE2 that are used as contraceptives.

The presence of these compounds is examined in the coastal environment of Thermaikos gulf at Northern Greece. Thermaikos gulf is next to the city of Thessaloniki that is a densely populated, commercial and industrial area. Three main rivers along with several streams and canals that receive rainwater, surface runoff as well as wastewater enter the gulf. The importance of the gulf apart from recreation is also economical. The fishing activity is intense and there are many mussel cultivations.

Samples included water, total suspended solids and sediments. Oasis HLB extraction cartridges with acetone as elution solvent were utilized for the extraction of EDCs from water samples. Total suspended solids collected after filtration of aqueous samples and sediments were extracted ultrasonically using ethyl acetate and a mixture of acetone:methanol (1:1) respectively. A further clean up step through florisil cartridges was necessary for sediments. The determination of target EDCs was carried out by gas chromatography – mass spectrometry (GC-MS) after derivatization with N,O-bis(trimethylsilyl)trifluoroacetamide.

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The concentrations of target EDCs in water, total suspended solids and sediments in the coastal environment of Thermaikos gulf are presented in this study. Spatial and temporal variation of target EDCs is discussed. The distribution of the compounds between aqueous and particulate phase is also examined. Moreover, possible relationships among the examined compounds and dissolved organic carbon (DOC) in water, total organic carbon (TOC) in sediments and the mass of total suspended solids are investigated.

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## CONCENTRATIONS OF VOCs AND OZONE IN INDOOR ENVIRONMENTS: A CASE STUDY IN TWO MEDITERANEAN CITIES DURING WINTER PERIOD

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Indoor organic compounds are released from a variety of building materials including vinyl tiles and coverings, carpets, particleboards, wood products, paints, adhesives etc. [1]. Organic compounds associated with paints, varnishes, sealing caulks, adhesives, carpets and other materials as well as human activity processes, such as cleaning, are likely to be a major cause of health complaints associated with indoor air in new or recently renovated buildings [2]. Ozone which has both indoor (photocopiers and other machines) and outdoor (due to ventilation and infiltration systems) sources is a common highly reactive oxidizing agent in indoor environment [3]. Ozone concentrations could be high enough to drive chemical reactions with monoterpenes forming ultrafine particles and irritating gaseous organic compounds.

Building materials represent the largest surfaces indoors and are the largest contributors of VOCs in the indoor environment. This study conducted in the frames of BUMA project (Prioritization of Building Materials Emissions) and aims to thoroughly assess the human exposure to air hazards emitted by building materials and the contribution of outdoor levels to indoor air quality. Herein, is presented indoor and outdoor VOCs and ozone measurements from field campaigns at two urban Mediterranean cities, Nicosia and Athens, during winter period.

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## AN EVACUATION SYSTEM FOR EXTRAORDINARY INDOOR AIR POLLUTION CIRCUMSTANCES

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The problem of evacuating the buildings through the shortest path with safety, has become more important than ever in a case of indoor air pollution (i.e. fire, gas leak, airlessness, smother) happening in complex and tall buildings of today's world.

In this paper it is aimed to present a 3D interactive human navigation and evacuating system for indoor. The developed system generates the optimum path in a 3D modelled building, and provides 3D visualization and simulation. It also generates the guiding expression and provides that information to the mobile devices such as PDA's, laptops etc via internet. That complete system was tested on a complex building model using GPRS and also WIFI internet connections based on the web technologies in a scenario of extraordinary indoor air pollution circumstance. This paper discusses the results gained from the application.

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## TOXICOGENOMIC STUDY OF INDOOR AND OUTDOOR AIR CHEMICAL MIXTURES

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There is a need for addressing the complexities of environmental health issues: understanding, for example, that environmental exposures occur to mixtures of chemicals rather than to individual agents, and that such exposures occur in the context of numerous other potential risk-modifying physiological factors, such as genetic background, gender, stress, developmental period of exposure and diet. These co-occurring risk factors may enhance or mitigate the effects of chemical exposures, and do so in a dynamic fashion across the life span. As such, studies recognizing interactions and mixtures may have marked significance not only for evaluating the efficacy of risk assessment paradigms, but also for the determination of public policies.

In this perspective, the use of toxicogenomics would be the appropriate screening method for assessing biological effects of complex chemical mixtures, allowing us to review the whole spectrum of potential biological response then rather focusing on a pre-defined number of endpoints as in classical toxicological analysis.

In the study presented herein, we focused on typical indoor air mixtures identified in the INDEX review and the interaction of its components (namely class of compounds as aromatics, aldehydes and terpenes). Furthermore we investigated the interactions between the indoor air mix as in INDEX, with a mixture of PAHs isolated from urban air in Milan. The main goal was to identify a specific set of biomarkers for each type of exposure (indoor or outdoor) and to evaluate the combined effects when exposure occurred to both of the mixtures. Three human cell lines were used, derived from skin (HaCat), bronco-pulmonary system (A 59) and liver (HEP G2). Applying a Total Gene Expression assay by Applied Biosystems Microarrays, we could profile large sets of genes modulated by single mixtures exposure, common biochemical pathways and specific molecular responses.

This is the first example of a complete genomic-response on 'early events' following exposure to complex mixtures. Together with physiology-based pharmacokinetic (PBPK) models derived by the assessment of exposure in different situations, we expect that these results should guide further "in vivo" dose response studies addressing specific toxicological endpoints to understand the network of biological interactions induced by human exposure to environmental mixtures.



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## RADIOLOGICAL UNDERGROUND EXPOSURE: THE TAV TUNNEL IN VALLE DI SUSA (ITALY)

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Radiological impact due to indoor exposure, particularly due to permanence underground, is considered by Italian and European laws, which suggest accurate measurements and define action levels. Risk connected to exposure is circumscribed by setting limits on indoor air concentration of nuclides and on consequent doses.

Particularly, inhalation of radon – a radiological decay product of uranium - and its progeny can lead to neoplasms damaging the respiratory apparatus. Harmful concentrations of gas in indoor air can be reached because of its continuous production from uranium, because of its tendency to stratification and other particular conditions.

The estimate of radon potential concentrations and absorbed doses is useful to verify whether dose limits can be respected or not. In every underground building there could be radioprotection problems, and such situations should be controlled.

RESRAD-BUILD (RESidual RADioactivity in BUILDings) is a computer model designed for evaluating radiation exposures within structures.

Natural radiation exposures in an underground building will be illustrated through a case study. In this work, the RESRAD-BUILD model is used in fact to evaluate the dose received by an individual inside a contaminated underground tunnel: the TAV (Traforo Alta Velocità, High-speed Rail Tunnel) which will be situated in Valle di Susa (Piedmont). In the area we are considering, the presence of natural radionuclides slightly exceeds the worldwide mean value, particularly the concentration of  $^{238}\text{U}$ . The scheme of the tunnel is made considering a 15 meters length portion, 4x4 meters section, made of three compartments. The three compartments are in series, and inside them there are nine sources and one receptor. Parametric studies have been performed by means of this model, checking the influence of different parameters on the radon indoor concentration and on the consequent dose to the individual.

RESRAD-BUILD final results show that an air flux of  $0.1 \text{ m}^3/\text{h}$ , entering the first compartment, can be sufficient to lower the dose received by the exposed receptor below  $1 \text{ mSv}/\text{y}$ , which is the population dose limit. An air flux of  $0.1 \text{ m}^3/\text{h}$  is a quite small value: it means that the building inner air should be totally changed every 2400 hours (100 days). This air exchange can be obtained easily both in the construction and exercise phases.

Results show the order of magnitude of the dose the exposed workers receive, notwithstanding the simplifications adopted. They can be useful to make an early estimate of radiological risk. The proposed practical application shows how limits imposed by regulations can be respected in the presence of concentrations of radionuclides slightly exceeding the world average, by means of modest air exchanges.

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**FLIES (FLANDERS INDOOR EXPOSURE SURVEY):  
THE INFLUENCE OF CONTAMINANTS IN AMBIENT AIR ON  
THE INDOOR AIR QUALITY AND CHILDREN'S EXPOSURE**

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**Introduction:** Whereas the ambient air quality in Flanders has been extensively monitored for years, this recent study is the first one on indoor air quality in Flanders for a relatively large set of pollutants and micro-environments.

**Materials and methods:** In 50 Flemish dwellings and 24 other children's micro-environments (day care, school, car,...), indoor (I) and outdoor (O) concentrations of 15 contaminants were measured in Jan - Febr 2006. Except for PM, all pollutants have been measured by diffusive sampling (Radiello, IVL and SKC) during 7 days. The presence of indoor sources, dwelling characteristics and children's (140) time budgets were retrieved through questionnaires. The slope of I versus O MTBE (no indoor sources) (FINF) was applied to breakdown the I concentration of pollutants  $x$  ( $C_{i,x}$ ) in a I generated ( $C_{ig,x}$ ) and an ambient ( $C_{o,x}$ ) fraction :  
EMBED Equation.3 (1)

Ambient ( $A_x$ ) and non-ambient ( $N_x$ ) exposure were respectively calculated as :

EMBED Equation.3 (2) and EMBED Equation.3 (3)

with  $t_{o,j}$  and  $t_{i,j}$ : time fraction spent respectively outdoor and indoor at  $\mu$ -environment. Exposure experienced during transport ( $TR_x$ ) (I or O) was calculated as a separate term. Total personal exposure to  $x$  is the sum of  $A_x$ ,  $N_x$  and  $TR_x$ .

**Results and Discussion:** Indoor concentrations showed a high variability between houses (REF\_Ref159733671 \h \\* MERGEFORMAT Table 1). Median I/O ratios were for most pollutants (with known I and O sources) between 2-5. A FINF factor of 0.86 (95 % CI: 0.59-1.13) was obtained and applied in (2). The MTBE based FINF factor was not suitable for NO<sub>2</sub> and PM<sub>10</sub>. Ambient exposure dominated (66 %) the children's exposure for benzene, while indoor sources dominated (80%) for formaldehyde. For pollutants not shown in REF\_Ref159734227 \h \\* MERGEFORMAT Table 2, the ratio A/N was between that of benzene and formaldehyde. Notwithstanding this indirect evidence for strong contribution of indoor sources to  $C_i$  (and T) for formaldehyde, no clear source -  $C_{ig}$  (or  $C_i$ ) relationships could be found based on the questionnaires

**Table SEQ Table \\* ARABIC 1: indoor concentrations (Ci) (in  $\mu\text{g}/\text{m}^3$ ) in 50 dwellings (results for selected pollutants)**

	median	min	max
MTBE	0,5	0,1	33
Benzene	2,1	0,7	24
Toluene	8,1	1,3	122
m-+p-Xylene	2,3	0,4	18
Formaldehyde	23,7	1,4	124
Acetaldehyde	21,8	1,1	65
TVOC	491	138	2793
NO <sub>2</sub>	21,3	7,1	122
PM10	11,7	2,3	58

**Table SEQ Table \\* ARABIC 2: contribution of A, directly or through infiltration (resp. A,outdoor and A,indoor), N and TR to personal exposure T of Flemish children.**

	benzene	formaldehyde	TVOC
A,outdoor	3%	1%	4%
TR	3%	4%	12%
A,indoor	63%	15%	35%
N	32%	80%	50%

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## ESTIMATING THE ECOLOGICAL PREFERENCE ON BUILDINGS. THE GREEK ENVIRONMENTAL BUILDING ASSESSMENT

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The past decades brought up a real revolution on the perception about the building design. The need for energy use reduction, the syndrome of "sick buildings" and the rise of new technologies created a movement, called "sustainable building". "Green buildings" are not any more futuristic constructions, but products of the technological evolution that discipline on the demands for quality. These are buildings that satisfy, on a large scale, the demands of the users, while at the same time; they reduce to the minimum the consequences on the environment, on people's health and on ecosystems.

Ecological building is related directly to modern architecture. The building designer should have knowledge on energy, on microclimatic, the materials' behavior, on green planting, on the physics of the shell, the acoustic and noise protection, the city planning and on transport. Additionally, the building designer should be capable of solving special problems such as water recycling, alternative waste management or the establishment of a central control system for the automatisms (BMS - Building Management Systems). Finally, the building designer should be aware of the uses of special tools or new ways of funding (i.e. leasing).

Green building is an issue of great importance and has become a relatively new tendency among the world. Green building or sustainable building could achieve a healthier environment for the residents and additionally can contribute to the energy efficiency and conservation both in the field of construction as well as in the field of function of the buildings. Green building uses environmentally friendly resources and materials, contributes to the energy efficiency and conservation, produce heat from the sun, contribute to the water conservation and treat its own wastes. There have been some very successful examples of measuring the level of environmental sustainability of buildings worldwide.

In Greece green building has become a challenge for architects and designers. A pilot rating system for measuring the sustainability of Greek buildings is proposed for green-buildings; therefore there should be a guide for how green-building can be performed and how the buildings can be rated according to their level of sustainability. The international experience can help to propose a rating system that could be undertaken by the Greek building development. Additionally, there are proposed indicators that should take into account for sustainable building.

Key words: green building, sustainable building, eco-building

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## INDOOR AND OUTDOOR NO<sub>2</sub> & OZONE LEVELS IN SCHOOLS OF ESKISEHIR, TURKEY

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Most people in the world spend 80-90% of their time indoors. Therefore, recent attention has turned to a greater consideration of the indoor environment. An appraisal of indoor air quality becomes important for the understanding of the impact of air pollution on human health. Indoor concentrations depend on indoor (heaters, smoking, cooking etc.) and outdoor sources (traffic, combustion processes, industry etc.) as well as the air exchange rates. Schools are among the indoor environments where especially children spend much of their times. In this study, measurements of indoor and outdoor NO<sub>2</sub> and ozone concentrations were carried out in two school buildings in Eskisehir, Turkey. Passive sampling method which is simple, inexpensive and provides possibility for the determination of pollutant distribution over a large area was applied during two-week period in June 2006 in School 1 (S-1) and in March 2007 in School 2 (S-2).

NO<sub>2</sub> is one of the main gaseous pollutants with the important effects on both indoor and outdoor air quality. Health impact of NO<sub>2</sub> includes different respiratory and lung diseases. Also, ozone is a secondary pollutant primarily formed by the chemical reactions of NO<sub>x</sub> and VOCs in the presence of sunlight. It is also among the greenhouse gases and has harmful effects on human health.

In this study, indoor/outdoor NO<sub>2</sub> and ozone concentrations were determined in two high schools situated in different regions of the city with different outdoor characteristics. S-1 is situated in the north part of an industrial area which is in the east of the city and approximately 10 km far from the city centre. S-2 is situated in a suburban and residential area in the south of the city. The major aim of the study was to determine the concentrations of NO<sub>2</sub> and ozone to which children and the other school staff were exposed. The selected indoor environments were class, library, corridor, toilet, canteen, dining hall, teacher's room, laboratory and dormitory. Besides indoor concentrations, outdoor concentrations were also measured at one point in the schools.

In S-1, indoor NO<sub>2</sub> concentrations were found to vary between 6.5-40.0 µg/m<sup>3</sup>, while indoor ozone concentrations were between 2.50-55 µg/m<sup>3</sup>. In S-2, indoor NO<sub>2</sub> and ozone levels were obtained between 14.0-76.0 µg/m<sup>3</sup> and 2.0-15.0 µg/m<sup>3</sup>, respectively. In both schools, NO<sub>2</sub> concentrations were obtained in higher levels especially in dining hall, teacher's room and canteen where cooking and smoking activities are much more performed. Since the traffic is quite low around the regions where the schools are situated, the effect of outdoor NO<sub>2</sub> pollution on indoor pollution was also low. Outdoor NO<sub>2</sub> and ozone concentrations were 18.0 µg/m<sup>3</sup> and 97.0 µg/m<sup>3</sup>, respectively, in S-1, while they were 25.0 and 58.0 µg/m<sup>3</sup>, respectively, in S-2. High concentrations of outdoor ozone were measured for both schools, especially in S-1, since they are remote from the city centre. So, the higher indoor ozone levels in S-1 may due to the source contribution of the outdoor ozone pollution. This ongoing study is proceeding toward collecting more samples for different pollutants from different schools by considering spatial and temporal variations.

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## BENZENE EXPOSURE OF SEVERAL POPULATION GROUPS IN A MEDIUM SIZED SOUTHEASTERN EUROPEAN CITY

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In the present study, an extended measurements campaign was performed in a medium sized Southeastern European city (Ioannina, Greece), in order to investigate the parameters that comprise the exposure to benzene of some characteristic population groups (policemen, gasoline station employees and taxi drivers) in comparison to the general population. The campaign included ambient air monitoring and personal exposure measurements with both passive and active sampling in several microenvironments.

From the measurements, the average urban concentration of benzene was determined equal to  $3.2 \mu\text{g}/\text{m}^3$ , while personal exposure values were 9.8, 25.3, 32.8 and  $21.4 \mu\text{g}/\text{m}^3$  for the general population, the policemen, the gasoline station employees and the taxi drivers respectively.

Active sampling results revealed that driving in a traffic congested road is an activity leading to elevated exposure levels, almost similar to car refueling procedure (up to  $80 \mu\text{g}/\text{m}^3$ ), followed by walking on the roadside of a congested road (up to  $60 \mu\text{g}/\text{m}^3$ ).

Indoor exposure to benzene is in general lower to outdoor, testifying that traffic is the dominant source of benzene emissions in the wider area.

The parameters that significantly raise ambient benzene concentrations are traffic congestion, street canyons, calm wind conditions and the presence of gasoline stations near the inhabited areas.

Risk evaluation due to exposure to benzene revealed that general population runs a risk equal to  $5.3 \times 10^{-5}$ , which increases from 10 to 40% for the examined occupational groups. This variability is depended on the activities pattern of each population group.

Key words: Benzene, human exposure, risk assessment, case study.

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## INFLUENCE OF GAS ENVIRONMENT WITH THE INCREASED CONTENTS OF CARBONIC GAS ON SLEEP OF HUMAN

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Now influence of the anthropogenous factors by health of the human considerably grows. The research of anabolic function sleep represents the large scientific interest. For disclosing mechanisms of adaptation in dynamics of cycle wakefulness- sleep is necessary change of functional condition of organism and central nervous system aside catabolism. As system influence we choose breath by changed gas environment with the increased contents of carbonic gas (CO<sub>2</sub>). As activity of the central nervous system and the mechanisms of sleep are closely connected with by free radical processes, the establishment of influence on sleep of substance - antioxidant – dimethylpyrazolilselelide is logical.

The researches are lead out on 11 examinees 18-23 years of both floors. The breath by gas mix enriched with carbonic gas (partial pressure of carbonic gas 7-8 mm of mercury pole, 1 % CO<sub>2</sub>), was carried out with the help of the device «Samozdrav». The multiparametrical estimation of functional status was made with use the computer polygraph "SAGURA" - "Laboratory of sleep". Intensity of free radical processes in saliva and blood judged on the standard biochemical parameters.

Hypercapnia (gas environment with the increased contents of carbonic gas) causes activation of regenerative functions of brain. It is expressed in increase of general duration of sleep and its phases. The different change of slow-wave and paradoxical phases of sleep testifies to an opportunity of realization of anabolic function of sleep in its different phases. In researches on influence of selenium-contained substances on sleep the participation of slow-wave sleep is established during restoration by decrease of intensity of free radical processes..

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## INDOOR AIR QUALITY IN A PRINTERY INDUSTRY IN ATHENS, GREECE

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The investigation of the pollutants' emissivity by technical equipment in occupational environments and the impact on the indoor air quality are of great concern during the last years. In the present study, representative pollutants' measurements were conducted during the period between 5 and 9 March 2007 in a printery industry in the centre of Athens. In particular, particulate matter (TSP, PM<sub>10</sub> and PM<sub>2.5</sub>), inorganic pollutants (NO<sub>2</sub>, NO, SO<sub>2</sub>, O<sub>3</sub>) and organic compounds (formaldehyde, benzene, toluene, xylene) concentrations were measured during the sampling period, while chemical analysis for As and Pb identification in TSP was conducted.

It is the purpose of the study to examine the pollutants' levels in comparison with the international limits for human exposure in working environments. Measurements took place in five indoor sites of the building, where different activities occurred.

According to the results, the levels of the inorganic compounds (NO<sub>2</sub>, NO, SO<sub>2</sub>, O<sub>3</sub>) did not exceed the limits established by the EU in any case. Similar remarks were drawn for formaldehyde, since the measured concentrations were 2 or 3 orders of magnitude lower than the limit (2.5 mg m<sup>-3</sup>). Benzene, toluene and xylenes concentrations varied between 0.007 and 0.165 mg m<sup>-3</sup>. Additionally, PM<sub>2.5</sub>, PM<sub>10</sub> and TSP levels ranged between 0.08 and 0.16 mg/m<sup>3</sup>, 0.08 and 0.20 mg m<sup>-3</sup> and 0.12 and 0.22 mg m<sup>-3</sup> respectively, presenting quite normal variations. Both As and Pb concentrations in TSP were found low. Despite the location of the building (urban area with intense vehicular circulation) and the age of the constructing materials, all pollutant concentrations presented satisfactory variations. Morning indoor peaks could be attributed to the outcoming pollutants generated by the increased vehicular activity and intruded in the occupational environment through open windows. On the other hand, lower noon and afternoon outcoming concentrations were well treated by the industry ventilation system and no significant influence on the indoor environment was observed. As far as the indoor sources are concerned, despite the constant use of substance such as ink, acetone etc, only local and instant exceedences were detected, not influencing the 8-hours mean values which are comparable with the E.U. limits.



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## ADVERSE IMPACTS OF WASTE WATER TREATMENT – A CASE STUDY

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Industrial metal plating processes coat materials with metals, such as chromium, copper and nickel. After the plating process, excess metals are rinsed off and the rinse water is collected and then treated to remove metals prior to discharge of the rinse water into rivers. This waste water is typically treated with sodium dimethyldithiocarbamate, which will precipitate the metals in the water resulting in aqueous metal concentrations low enough that the treated water can be released into rivers. However, misuse of this treatment can result in adverse environmental impacts.

During a period from June through October, there were three fish kills in the Ohio River downstream from an industrial plating plant. By October, the invasive Zebra mussels in a portion of the river near the plant were gone, there was 100% native mussel mortality in beds nearest the plant, and mussels 8 km downstream from the plant were dead or dying. The net result was that 9,000 fish (primarily fresh water Drum), 10,000,000 gastropods, 1,000,000 freshwater mussels (>20 species, including 2 Federally-listed endangered species, some of which were >30 yrs old), and all benthic organisms within 80 m of the shore near the plant were killed. The water quality parameters during that time were: dissolved oxygen 6-8 mg/L, water temperature 20-25 C, pH 7.0, no microcystin or other algal toxins detected, and no PCBs or other pesticides detected. In the fish, there were no viral or bacterial diseases or unusual parasites.

Other factors were investigated as possible causes of the fish and mussel kill. In the area of the kill, just downstream from the plating plant, chromium concentrations were many times greater in sediments, mussels and fish as compared to levels just upstream from the plating plant. However, it is questionable whether the chromium levels were acutely toxic. Although sodium dimethyldithiocarbamate is typically used to remove metals from waste water, there are reports that it under certain circumstances it can react to form 1-(dimethylthiocarbamoyldisulfanyl)-N,N-dimethyl-methanethioamide, or thiram, a fungicide that is highly toxic to fish and mussels. Analysis of sediment, mussel, and fish samples by lc-ms resulted in positive detects for thiram in sediment and mussel samples. It appears that the plating plant misused the sodium dimethyldithiocarbamate during the treatment of the metals resulting in thiram formation which in turn caused the fish and mussel kill. Although sodium dimethyldithiocarbamate is very effective in precipitating metals from waste water, its use has become controversial, other fish kills attributed to the misuse of this chemical have been reported since this incident.

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## CORRELATION STRUCTURE AMONG CHEMICAL-PHYSICAL VARIABLES MEASURED IN MUNICIPAL SOLID WASTE DISPOSAL

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Innovative methods for monitoring pollutant concentrations in surface and subsurface soil are crucial tasks in environmental research. Actually the main purpose is to develop monitoring strategies able to provide detailed information about the temporal and spatial evolution of contaminants in subsoil, combining fast, not invasive and low cost acquisition procedures for in situ observations. In this context we have recently investigated on the use of magnetic susceptibility measurements in superficial soil as a simple, rapid, cheap and non-destructive proxy variable able to evaluate concentration levels of heavy metals. A monitoring method based on this parameter may give results directly in situ and in real time. It may be easily combined with other geophysical and analytical investigation techniques [1-4]. Here we present the results of a field survey carried out in a municipal solid waste disposal. On a georeferenced sampling grid composed by 32 sampling points, we collected superficial soil and we determined 10 parameters. Particularly we measured: in situ soil magnetic susceptibility (kD) by means of a portable meter (Bartington MS2) equipped with the MS2D probe for in situ investigations at depth 15 m; total concentrations of 7 heavy metals (Co, Cu, Fe, Mn, Ni, Pb, Zn) in laboratory by means of AAS techniques; soil electrical conductivity (C) and pH by means of a multiparametric laboratory instrument. Data analysis was based on a multivariate procedure aimed to reduce the dimensionality of the data. Principal component analysis and clustering algorithm were applied on successive runs, in order to individuate a set of new independent variables and a classification of sampling points, allowing us to characterize the underlying correlation structure. Particularly we pointed out three significant components: one representative of soil parameters (III PC = f(C, pH) 12% of explained variance), one representative of relationship between lead and magnetic susceptibility (II PC = f(Pb, k) 23% of explained variance), and one representative of heavy metal levels (I PC = f(Co, Cu, Fe, Mn, Ni, Zn) 67% of explained variance). For this last, it was possible to individuate two source profiles (Ni, Cu, Zn) and (Co, Fe, Mn). Moreover sub-groups of sampling points characterized by different levels of heavy metals were determined by data matrix and score matrix clustering.

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## FINGERPRINTING THE ORGANIC MATTER CONTENT OF WASTEWATERS: SEQUENTIAL FILTRATION/ULTRA FILTRATION FOR PARTICLE SIZE DISTRIBUTION-BASED COD FRACTIONATION

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During the last decade, olive oil production has become the rising star of agro-food industry, upon start and accelerated realization of the numerous merits of the raw material –the olive-, the product –the olive oil-, as well as the side-products –soap, compost, etc.-, at a global scale. As a natural consequence of the massive production capacity and exercise in the Mediterranean region, wastewaters generated during olive processing and olive oil production have become one of the major concerns of the agro-food-specialized Mediterranean countries (97% share in the global production), including Turkey (7% share,; Paraskeva and Diamadopoulos, 2006). Another industrial sector of significance to the countries in the Mediterranean pot and in which agro-products are used as the raw materials is the textile industry. This sector has also a marked share in Turkey's overall industrial production exercises. Considerable water consumption during the production processes, naturally followed by high amounts of generated wastewaters with extremely variable and complex compositions, entitle the textile industry as a significant area of RTD to work on with an engineering perspective searching for a sustainable solutions to the environment-related problems of the sector. Consequently, scientific, as well as application-oriented, research has accelerated towards generating scientifically sensible, economically feasible, engineeringly applicable, environmentally friendly, hence in overall, sustainable solutions for optimization of the processing and production practices, and for treatment of the wastewaters generated from the abovementioned industrial sectors, as well as for handling of the processing/production left-overs.

For master-minding such kind of a sustainable solution, it's apparent to the members of the RTD community that prior to the development of the know-how for dealing with the problem, the starting point is to get acquaintant with the material in hand, which calls for collecting the comprehensive information regarding the character of the material -the wastewater-, to be dealt with. In this regard, this current study offers an alternative approach for resolving the character of the different wastewaters (textile wastewaters, OMW), with a specific accent on the organic matter content; the former is suggested here to contribute to not only solving, but also to re-phrasing the codes of physico-chemical or/and biological treatment processes to be applied or treatment of them. The suggested approach is an alternative one, cause it makes use of the classical physical segregation technique via filtration or ultrafiltration, yet provides a new means of data collection and evaluation through combing the sequential filtration/ultrafiltration-based sequential segregation of particles' sizes with the organic matter content –in terms

of COD concentrations- within each size category, thus compiling the particle size data and COD data into PSD-based COD fractionation of the investigated wastewater. Experimental results indicate that PSD-based COD fractionation actually gives the COD-fingerprints characteristic for the investigated wastewaters: (i) for untreated textile wastewater; significant COD-fractions at the particulate ( $> 1600\text{nm}$ ) and supra-colloidal ranges ( $450\text{-}1600\text{nm}$ ), and also a major fraction at the soluble range ( $<2\text{ nm}$  size category) (ii) for raw OMW; a homogenous distribution of the COD-fractions with not more than 12% contribution (to the total COD content) at all size categories below  $2\text{ nm}$  (the real soluble range), and accumulation of the dominant COD fraction at the size category below  $2\text{ nm}$  (approx. 67% of the total COD).

This new approach has been tested previously (Sophsnsiri and Morgenroth, 2003; Dulekgurgen et al., 2006; Dogruel et al., 2006), and proved to be successful not only in providing the needed comprehensive information regarding the wastewater character beyond the traditional data-set, through allocating the COD-generating moieties at the size categories where they physically reside at, thus revealing the in situ COD-fractionation fingerprints claimed (and proved, at least for some domestic-, textile-, tannery-wastewaters) to be specific for each wastewater, but also in revealing the fate of the wastewater COD-fractions after exposure to physical-, chemical-, or/and biological treatment alternatives in lab-scale and full-scale applications thus providing useful, non-conventional, and comprehensive information regarding the role of the exercised treatment processes on the shift of distribution of the COD-fractions. It is suggested here that the proposed alternative approach has a strong hold in finding a broad application platform for itself as a powerful and useful tool serving in the field of non-conventional wastewater characterization, and the final output of it mentioned above is expected to serve as a good and meaningful follow-up point for pre- and post-engineering applications namely design, modeling, optimization, retrofitting, etc., in the multi-disciplinary field of environmental science and engineering.

(a)

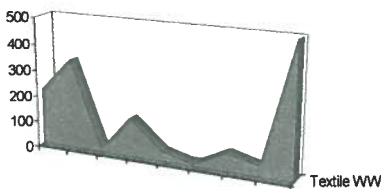
(b)

Fig 1. PSD-based COD fingerprints of the untreated textile wastewater (a) and raw OMW (b)

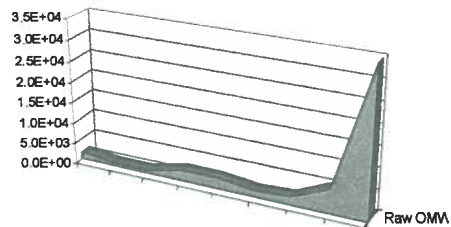
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PSD-based COD fingerprint of an untreated textile WW



PSD-based COD fingerprint of a raw OMW



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## WASTE MANAGEMENT PRAXIS IN THE AUTOMOTIVE INDUSTRY ACCORDING TO ISO 14001

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With its production capacity of 1.268.605 units and its 7.835.693 \$ export income as of the year 2005 Automotive Industry is one of the leading industries in Turkey. It is sustaining its position in environmental protection. More than 60% of the Automotive Manufacturers Association registered member firms are certified according to ISO 14001 and 99% has its own wastewater treatment plant. In implementation of an environmental management system according to ISO 14001, hazardous and non hazardous waste management plays a significant role due to the operational control clause. This study focuses on waste management strategies in the automotive industry with the objective to provide information about the classification, source, segregation, transport, reuse and cycle of the waste.

In the paper the non hazardous waste from the automotive industry is classified and recycle and reuse alternatives are considered. Recycled waste classification and distribution as well as the solid waste amounts per production unit are summarized. The most important part of the reusable waste consists of metals used as raw material in the production followed by packaging material. The segregation of reusable waste at the source, its storage and the delivery are of main concern. In this study examples and different recycle and reuse practices are discussed. The distribution of solid waste sourcing from production as well as the minimization and saving alternatives are also considered.

Further more the paper deals with the segregation at the source, minimization and storage as well as recycle and disposal practices of hazardous waste. The transition of hazardous waste amounts within the years are summarized and the expenses as well savings are evaluated in terms of specific examples.

While managing waste the local legislation is of most concern. A successful management system requires first of all well defined waste categories which can only be achieved due to well determined legislation. In this context the Turkish and EU approaches in waste management are discussed within given examples. The necessary steps which should be taken for waste categorization according to the Turkish legislation are summarized within a flow chart. Emphasis is given to the waste catalogue covering all the waste defined on process basis for a precise waste classification.

In the study the waste management praxis in the automotive industry is outlined and it is shown within examples that ecological approaches like an effective waste segregation can cause economical alternatives and that simple solutions can lead to meaningful savings. The problems involving the infrastructural and legislative difficulties are mentioned. As an outcome the study suggests cooperative approaches to overcome the problems due to the disposal and classification of hazardous waste from the automotive industry and offers solution alternatives by reviewing the legal legislation.

Otomotiv Sanaiyyinde ISO 14001 ÇYS Kapsamında Atık Yönetimi Uygulamaları

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## IMPLEMENTATION OF THE DENITRIFYING PHOSPHORUS REMOVAL PROCESS IN MUNICIPAL WASTEWATER TREATMENT

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Biological phosphorus removal with simultaneous denitrification was implemented and evaluated in a continuous flow bench scale plant for municipal wastewater treatment. The plant operation is based on the activity of two microbial populations which grow under different operational conditions (two sludge system). Denitrifying Phosphorus Accumulating Organisms (DPAOs, sludge I) are enriched under alternate anaerobic – anoxic conditions, whereas nitrifying biomass (sludge II) grows under aerobic conditions. The plant configuration enhanced the growth and predominance of DPAOs, a fraction of Polyphosphate Accumulation Organisms (PAOs) able to remove phosphorus using nitrate (NO<sub>3</sub><sup>-</sup>), instead of oxygen, as the final electron acceptor, so as phosphorus removal was mainly achieved under anoxic conditions (no aeration).

Batch experiments were conducted in order to evaluate the denitrifying phosphorus removal capability of sludge I. The experiments were conducted in two identical batch reactors, one operated under alternate anaerobic – anoxic conditions and the other under anaerobic – aerobic conditions. Specific rates for the processes of anaerobic phosphorus release, substrate uptake, anoxic and aerobic phosphorus uptake and denitrification were determined. The results obtained were directly compared to similar data derived from identical experiments using conventional (mainly aerobic) PAO sludge, originated from a bench scale plant based on the UCT design concept and treating the same sewage as the two sludge treatment plant.

Experimental results clearly indicated the advantage of using anoxic phosphorus removal instead of the conventional aerobic for municipal wastewater treatment. No significant difference was recorded between the anoxic and the aerobic phosphorus uptake rates respectively for the two sludges. This indicates excellent phosphorus removal efficiency for denitrifying phosphorus removal systems with much lower aeration demands and minimized nitrate effluent concentration without extensive recycling in comparison with conventional biological phosphorus removal processes (UCT, A/O, A<sub>2</sub>O etc.).

**Key words:** Biological nutrient removal, denitrifying phosphorus removal, PAOs, DPAOs, anaerobic – anoxic process, activated sludge.



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## TiO<sub>2</sub>-PHOTOCATALYZED DEGRADATION OF PHENOLIC ACID CONTAMINANTS PRESENT IN OLIVE MILL WASTEWATER

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Phenolic acids constitute an important group of pollutants which are reluctant to biological treatment. The photocatalytic degradation of p-coumaric acid and vanillic acid, compounds representative of the polyphenolic fraction typically found in olive processing and wine-distillery has been investigated using TiO<sub>2</sub>/UV photocatalytic technique. Important degradation yields are achieved. The influence of TiO<sub>2</sub> concentration, pH solution and irradiation time on the rate disappearance of p-coumaric acid and vanillic acid have been demonstrated. Finally, liquid samples were analyzed by means of HPLC/MS and GC-MS chromatography to identify reaction intermediates.

Keywords: Phenolic acids; Photocatalysis; Vanillic acid; p-Coumaric acid; photodegradation; TiO<sub>2</sub>; wastewater.

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## THE DETERMINATION OF SELECTED ANTIBIOTICS AND DEGRADATION PRODUCTS IN WASTE WATER

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The thesis focuses on studying antibiotics spreading into the environment where undesirable resistance is formed. Tetracycline, chlortetracycline hydrochloride and beta lactam antibiotics were the studied antibiotics. Beta lactam antibiotics have been used for more than seventy years in the treatment of infections in both human and veterinary medicine. Antibiotics as active substances may take part in biological processes in sewage disposal plants. In our environment undesirable residues of these substances can remain in water and soil. By chronic action of these substances, microorganisms develop resistance to them and subsequently these are not effective in the treatment any more.

The aim of the work was to develop both a suitable pre-analytic method for antibiotic residues isolation from the matrix and an optimal analytical technique for both identification and determination of tetracycline residues and beta lactam antibiotics residues in wastewater. The real samples from a wastewater treatment plant (WWTP) situated in Veterinary and Pharmaceutical university in Brno and from the large-scale wastewater treatment plant in Brno-Modrice were analysed by the optimised method.

Extraction by sonication and refinement using solid phase extraction (SPE) were the separation methods employed. High performance liquid chromatography (HPLC) with diode-array detection was used for identification and determination of the antibiotic residues. The determination of beta lactam antibiotics was conducted with the help of instrumental analytical methods of high performance liquid chromatography and capillary electrophoresis. The optimised method was used both in model systems and for real samples from both WWTPs. Obtained results were evaluated and their interpretation was made.

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## WASTEWATER TREATMENT AND REUSE BY CONSTRUCTED WETLAND SYSTEMS

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Absence of adequate wastewater treatment and contamination of surface waters threaten the health of local residents and health of a valued aquatic ecosystem. Water treatment systems using aquatic plants and wetlands have been widely applied in many developed countries, as well as in developing countries where it would seem these technologies should be well suited. One of the most essential benefits of aquatic pond and constructed wetland systems is their capability for use as a treatment system for water quality improvement, besides being an habitat that has very important ecological functions. Within the recent years, ecological significance of either natural or constructed wetlands is better understood, their utility in water quality control-by operating them as an engineered system in a controlled manner has gained interest in developing countries where the share of national income spared for environmental protection is quite limited. Thus, effective use of this limited economic input depends highly on the cost of environmental protection technologies. In such cases, use of low-cost technologies (including both investment and operational cost) must be of priority importance. Among these technologies, wetlands and stabilisation ponds are the appropriate systems for prevention of water pollution caused by point sources of pollutants. As the operation and maintenance of such systems are quite simple and easy, it is an advantage for developing countries.

Furthermore the constructed wetland technology offers an opportunity to recycle and reuse of wastewater for various purposes such as irrigation, establishing and sustaining the aquatic ecosystems, as well as using the constructed wetlands for removing of contaminants from the surface water flows to drinking water reservoirs as creeks and, may be considered as an easily applicable and most economical solution.

In this paper, the generalised results of experimental studies, which have being conducted for several years at our laboratory and pilot scale systems, have been presented. In one of our earlier studies, conducted between 1998-2000, we have studied the potential use of the constructed wetlands for the wastewater treatment from small settlements and single houses. The experimental results showed that the area requirements for the organic matter removal by intermittent-recycled constructed wetland system is around 1 m<sup>2</sup> per person in order to meet the Turkish Water Pollution Control Regulation discharge standards.

Another study was conducted in order to investigate the possible use of restored or constructed wetlands for water pollution control in drinking water reservoirs. In this study, it was aimed to decrease organic matter (BOD<sub>5</sub>) and nutrient (N, P) loads from the waters joining the drinking water reservoirs like creeks and surface flows, by constructed wetland systems. For this purpose, a pilot-scale constructed wetland-aquatic pond system was built at the campus of

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Marmara Research Center (MAM) of Turkish Scientific and Technological Research Foundation (TÜBİTAK) in Istanbul, and organic matter and nutrient removals on this system was examined. The emergent, floating and submerged plants were used in the systems are *Canna-Cyperus-Typhia-Juncus* (emergent), *elodea-egeria*(submerged) and *Spirodela-Lemna* (floating) respectively. It was determined and compared with unplanted systems in terms of percent removals of HRTs and nitrogen loading rates by relationships between influent and effluent concentrations. Organic matter and nutrient removal performances in different hydraulic and mass loading in one-year period were examined and contributions of plants on treatment were also investigated. The best average nutrient removals were obtained with the floating plants while by the emergent plants was the best for organic matter removal. The average lowest nutrient and organic matter removals were obtained at the submerged plants. It was found that nutrient and organic matter removals could be explained by first-order kinetics. The removal rate constants, regressed from the model were found close to the values depicted in literature. The results show that the best relationship between model and observed values is in the floating plant systems. The kinetic constants ( $k_20$ ) and temperature coefficients ( $\theta$ ) are determined using experimental data and the first-order plug flow model. Furthermore, they are compared with the observed values using equations of predicted effluent concentrations versus temperature and loading rates.

The recent studies of our group include pilot and field scale applications of upflow anaerobic sludge blanket reactor followed by horizontal flow and vertical flow constructed wetlands. One of the systems is under operation for 8 months. The capacity of this system is 2000 pe, and constructed in a village near to Istanbul. The preliminary results gave good effluent quality even under winter conditions. More discussion will be presented in this paper.

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## ADSORPTION-DESORPTION OF PESTICIDES BY SOILS AMENDED WITH WOOD RESIDUES AFTER DIFFERENT INCUBATION TIMES

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In the last years, research to find new and less expensive materials suitable for the adsorption of pesticides and other organic contaminants to protect and prevent the contamination of soil and water by these compounds is being carried out. In this sense, wood residues are materials with a low cost and available in large amounts from forest and industrial activities, which can be used as potential sorbents of hydrophobic pesticides. Lignin is a main component of wood and has a hydrophobic character and hence it could be responsible for the adsorption of hydrophobic compounds.

In this work, we studied the adsorption of pesticides by soils amended with wood residues after different times of incubation of the soils. Three pesticides with different hydrophobic character were studied (linuron, alachlor and metalaxyl). Natural soils were a sandy soil and a clayey soil with organic matter content < 2%. Two different wood sawdust (< 1mm) obtained from pine and oak wood, with a lignin content of 24.4% and 18.2%, respectively, were used to amend the soils at a dose of 5% w/w (equivalent to 40 t C/ha). We obtained the adsorption-desorption isotherms of the pesticides in the natural soils. Soils amended with wood sawdust were incubated at 20°C and a humidity equivalent to 60% of the water holding capacity during 12 months and adsorption-desorption isotherms of the three pesticides studied were obtained at time 0, 5 and 12 months.

Sorption isotherms of pesticides by soils amended with wood sawdust indicated an increase in the sorption coefficients up to 46.0% for linuron and 80.6% for metalaxyl after an incubation period of 12 months. This increase was lower for the clayey soil and the increase was higher for the sandy soil amended with pine sawdust. After this time desorption decreased for linuron or increased for metalaxyl (more soluble compound). Sorption of alachlor by both amended soils kept similar in soils amended after incubation times, although desorption decreased with the time up to 47%. Hysteresis coefficients decreased with the time in all the systems studied. Sorption of pesticides was, in general, higher by oak amended soils than by pine amended soils and it was also higher by amended clayey soil than by amended sandy soil. The amounts of pesticide sorbed varied in the order linuron > alachlor > metalaxyl. The results obtained indicate the influence of pesticide, wood and soil characteristics, and aging time on the adsorption of these pesticides.

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**MONITORING OF DI-(2-ETHYLHEXYL)PHTHALATE, NONYLPHENOL,  
NONYLPHENOL ETHOXYLATES AND POLYCHLORINATED BIPHENYLS IN  
ANAEROBIC AND AEROBIC SEWAGE SLUDGE BY GAS CHROMATOGRAPHY-  
MASS SPECTROMETRY**

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In the last years, the implementation of the Directives 91/271/EEC [1] and 98/15/EEC [2] concerning urban wastewater treatment has increased the number of wastewater treatment plants (WWTP) operating in the European Union and, consequently, the production of sewage sludge. Nowadays, the application of sewage sludge to farmland is the cheapest and one of the most used sludge disposal options. However, as sewage sludge is a byproduct of wastewater treatment, it inevitably contains a wide range of potential contaminants, including nutrients, metals, pathogens, and organic chemical residues. In 2000, the European Union published the third draft of a future sludge Directive entitled "Working document on sludge" [8] where concentration limit values for some organic compounds are included for the first time. Some of the organic compounds included in this document are di-(2-ethylhexyl) phthalate (DEHP), nonylphenol and nonylphenol ethoxylates with one or two ethoxy groups (NPEs) and polychlorinated biphenyls congeners (PCBs) number 28, 52, 101, 118, 138, 153 and 180. The concentration limits established in sludge dry matter (dm) for land application of sludge are 100 mg kg<sup>-1</sup> for DEHP, 50 mg kg<sup>-1</sup> for the sum of nonylphenol and nonylphenoethoxylates and 0.8 mg kg<sup>-1</sup> for the sum of the seven PCBs congeners.

The monitored compounds were extracted from sludge by sonication and measured by gas chromatography-mass spectrometry.

DEHP and NPEs were detected in all of the analyzed sludge samples from both WWTPs at concentration levels in the range of 22.3–600.6 mg kg<sup>-1</sup> and 136.5–2356.6 mg kg<sup>-1</sup> dm (dry matter), respectively. PCBs were detected in all types of sludge analyzed from the anaerobic WWTP but was not detected in any sludge sample from the aerobic WWTP. The sum of concentration of the seven PCBs congeners in the anaerobic WWTP was in the range of 0.1–1.5 mg kg<sup>-1</sup> dm. The concentrations of DEHP, sum of NPEs and sum of the seven PCB congeners were higher than the limits fixed in the third draft of the future Sludge Directive for land application of sludge in 67%, 100% and 17% of samples from the anaerobic WWTP and in 83%, 100% and 0% of samples from the aerobic WWTP, respectively.

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## TREATABILITY OF A SIMULATED SPENT DISPERSE DYEBATH WITH ELECTROCOAGULATION

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Electrocoagulation (EC) using aluminum (Al) and stainless steel (SS) electrodes was investigated for color and COD removal from a simulated spent disperse dyebath. In the first part of the study, EC was optimized for electrolyte (NaCl) concentration (750-3000 mg/L), current density (9-87 mA/cm<sup>2</sup>) and initial pH (3.5-11.5). Optimum EC conditions were established as 2500 mg/L NaCl, pH=7.0 and 44 mA/cm<sup>2</sup> for 100% color and 58% COD removals using Al electrodes (total treatment time=30 min), whereas 100% color and 45% COD removals were obtained for 2000 mg/L NaCl, pH=7.3 and a current density of 44 mA/cm<sup>2</sup> when SS electrodes were employed for 60 min treatment. EC results were compared with color and COD removals achieved via coagulation with alum, ferrous sulfate and ferric chloride at varying doses (200-2000 mg/L). Alum was more effective in color (100%) and COD (64%) removals than ferrous sulfate and ferric chloride. The amount of sludge formed during EC using SS electrodes was approximately 10 times less than the sludge produced during EC with Al electrodes, whereas electrical energy requirements to achieve 100% color and 50% COD removals were 10 and 30 times higher when SS electrodes were employed for EC. In the last part of the study, the effect of spent simulated disperse dyebath pretreatment using EC under optimized reaction conditions on the biodegradability of total (combined) textile wastewater was examined. Activated sludge experiments run for 24 h at a fixed food-to-microorganisms ratio of 0.18 mg CODo/mg MLVSS indicated that although the effluent contribution from the polyester dyeing stage to the total textile wastewater is only in the range of 20-40% on volumetric basis, the COD of the final, biotreated effluent decreased below 100 mg/L when the spent disperse dyebath was subjected to EC.

**Key words:** textile industry; dyehouse effluent; spent disperse dyebath; coagulation; electrocoagulation; biodegradability; decolorization; COD removal.

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## **STREAM AND SOLID WASTE POLLUTION ASSESSMENT AT THE EASTERN BLACK SEA REGION, TURKEY**

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In Turkey, as elsewhere, ever increasing population, rapid urbanization, industrialization, and standards of living have contributed to increasing amount of wastewaters and solid waste originating from municipalities and other sources, and their consequent disposal has been the source of major environmental problems.

Topographical and hydrogeometrical structures of the Eastern Black Sea Region of Turkey don't allow suitable and economical solutions to be found easily for the disposal of wastewaters and solid wastes. All of the municipal and industrial solid wastes mixed with hospital and hazardous wastes are dumped to the nearest lowlands and river valleys or directly into the sea. Although major cities have outfalls, most of the settlements in this region dispose of their wastewaters either directly into the streams or the shallow coastal sea waters without any treatment as point sources. Solid wastes with their high organic and inorganic strength and quantities are the major polluting matters in comparison with the wastewaters.

In this paper, suitability of an applied solid waste planning system for a lot of locations along the Eastern Black Sea coastline and environmental problems associated with the wastewater and solid waste disposal in this region are discussed. Municipal solid waste characteristics of two major provinces, Trabzon and Gümü hane, are determined, and which disposal method can be suitable for the waste management are investigated. The water quality of the De irmendere, Galyan, and Har it Streams, which flow into the Black Sea and are an important water resource for Trabzon and Gümü hane Provinces, respectively, are examined in order to determine the levels of pollution and the results are compared with the relevant Turkish and EU Directives.

**Keywords: Stream Pollution, Watershed Models, Water Quality, Solid Waste, Waste Management, Open Dump, Black Sea,**



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## INTEGRATION OF GIS, RS AND MULTI CRITERIA ANALYSIS FOR LANDFILL SITE SELECTION: ISTANBUL EUROPEAN SITE CASE STUDY

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Waste management is very important process especially for the developing cities because of increasing population, public health concerns and environmental awareness. All stages of this process, which is considered as an important part of the sustainable development studies, are strictly defined depending on the waste type by regulations and laws. Although, they are clearly defined, there are several problems in practice since it has many parameters that should be considered. For example, solid waste storage process should be executed by considering the distance from settlement area, airport, water resources, forests and etc. Topography and geologic/geomorphologic structures of storage area are also important factors that should be observed in practice. Another common characteristic of these parameters is that they vary according to type of the waste. Therefore, management of this process is difficult in practice. Especially selection of the waste storage areas is very important in this concept since an inappropriate landfill site may have negative environmental, economic and ecological impacts.

In this study, management of the solid wastes produced in Istanbul European side is considered as the one of the most important problems, since the metropolis develops rapidly in terms of population and industrial activities. In this concept, integration of Remote Sensing, Geographic Information Systems (GIS), and Multi-criteria Decision Analysis is used to assess the current situation of landfill areas in the study area and to determine alternative landfill areas by considering the criteria stated in national and international regulations. For this purpose, firstly current land cover and land use characteristics of the study area are determined by classifying the SPOT data. In addition to the legal landfill areas declared by the municipality, potential landfill areas are determined by examining the classification results of remotely sensed data.

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In the second step of the study, determined landfill areas are evaluated by considering requirements described by the laws and regulations after verifying them by using 2006 dated IKONOS data. In this concept, two different DEM data with 50 m and 5 m resolution are used for determining the topography and slope of the area.

Additionally, vector maps and classification results of the remotely sensed data are used to designate the other factors, which affect the decision making process, such as surface water, floodplains, transportation network, and etc. Geo-spatial analysis and Multi-criteria Decision Analysis are executed by using GIS technologies in this stage of the study. Finally, alternative landfill areas are determined by executing the analysis over structured GIS and final results of the study are presented as thematic maps.

**Keywords:** landfill, solid waste management, GIS, remote sensing, multi-criteria decision analysis

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## SOURCE SEPARATED URINE AS A SOURCE OF PLANT NUTRIENTS AND A SUGGESTION FOR ITS USE VIA INDIRECT ROUTE

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The new wastewater management concept Environmental Sanitation (ECOSAN) advocates that domestic wastewater is not a waste to be discarded but a source to be reevaluated. One of the primary suggestions of ECOSAN is the separate collection of urine from domestic wastewater at its source. Urine constitutes less than 1% of conventional domestic wastewater by volume however it contains over 80% of the nitrogen, and 50% of phosphorous and potassium therein. With the high level of those plant nutrients within its composition, its further use in agriculture as fertilizer is suggested. As of now, the most frequent application onto agricultural fields has been exercised via the direct route. Storage of source separated urine is recommended before being applied especially for hygienic safety. Storage periods in the order of magnitude of months, specifically up to six months, are reported to be relevant for the complete inactivation of pathogens. With direct application, pharmaceuticals and hormones still remain as potential problems which need further research.

The results obtained in this work show that characteristics of urine samples change drastically throughout storage for pathogenic die off and at the time of application onto agricultural fields, its composition is significantly different as compared to its freshly collected state.

The most significant change occurs with ammonium with an increase of fifteen fold as a result of conversion of urea into ammonium during storage, which is observed to be fast within the first month, accompanied by about three units of increase in pH. The second important change is observed for electrical conductivity which is a critical parameter for agricultural use, which may increase of up to three fold. The variation of potassium concentration is not as significant as the others, with only a slight increase of about 15 %.

This paper aims to give an overview of the use of source separated urine for agricultural purposes which is most frequently considered via direct application together with a summary of the results of observations made during long time storage periods of source separated human urine. Furthermore, as a safer alternative to direct application of urine, a suggestion for processing of urine with the natural zeolite clinoptilolite to transfer plant nutrients in urine onto the zeolite and the subsequent use of the product as a possible slow release fertilizer will be outlined. Supporting laboratory data for the suggested method will also be provided to show that over 90% of the ammonium in urine may be transferred onto clinoptilolite and about 85% may be made available as plant nutrients through washing with tap water, representing elution through irrigation or wash down with rain.

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## PIG SLURRY DEPURATED BY CONSTRUCTED WETLAND

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The most natural way for slurry removal is its application as soil manure. Unfortunately, most of the farmers don't have enough arable land, near their farms, to apply that residue in the proper doses in order to avoid soil and water pollution according to the EU Directives. As a result, it's essential to find technologies which are able to recycle this liquid effluent, solving pig slurry management problem. The aim of the research is testing with constructed wetlands to depurate.

Wetlands are a suitable system to reduce pollution by agrarian effluents and, as in this case, by pig slurries. In this study, we are using two types of constructed wetlands. Farms have a phase separator for the pig slurries by bioaeration process. The solid phase is dried-out and used directly for fertilization. In order to reutilize that water, vertical surface and horizontal subsurface flow constructed wetlands systems are tested in order to know the liquid flow rate that can be remediate depending on the conditions. These constructed wetlands contain two gravel layers of different size and a sand surface layer. The plant specie selected is *Phragmites australis*, because it is adapted to the semiarid climate of the area and also has a fast production of roots and rhizomes.

The pig slurry characteristics of each farm were very different; they depend on area, pig food, cleaning systems, pig farm cycle, etc. In vertical surface flow constructed wetlands (VFCW), some percentages of removal obtained have been: total nitrogen by 60.4 %, ammonium nitrogen by 58.4%, organic nitrogen by 67%, electrical conductivity by 54.9 % and suspended solids by 50.2%. In the horizontal sub-surface flow constructed wetland (HSFCW), its percentage of removal was high: total nitrogen by 69 %, ammonium nitrogen by 51.5 %, organic nitrogen by 92.4 %, electrical conductivity by 34.2 % and suspended solids by 99 %.

Constructed wetlands seem to be an ecological and cheap wastewater treatment. It constitutes a revalorization method of the pig slurries for water recycling. This alternative should be considered among others as a solution to manage safely pig slurries and to minimize disposal risks. In conclusion, pig slurry, treated with these systems, will be able to be reutilized for irrigation purposes.

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## **“IN SITU” AMENDMENTS AND REVEGETATION REDUCE TRACE ELEMENT LEACHING IN A CONTAMINATED SOIL**

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In Mediterranean semiarid regions found, reclamation of contaminated soils such as those affected by mining activities or mine spills is constrained by the climate (dry hot summers with significant fire risk and very low precipitation arriving as irregular torrential rainfall events) and soils with low nutrient and organic matter content. Leaching of contaminants can negatively affect groundwater sources, which are crucial for the sustainability of both natural and agricultural systems in the Mediterranean area. Due to low vegetation cover, run-off losses in such soils may transport trace elements and other contaminants to streams and rivers. This creates conditions that favour higher erosion and disturb normal ecosystem functioning.

The “in situ” stabilization of contaminants was highlighted as a potentially reliable and cost-effective alternative for reclamation of extensive areas moderately contaminated with trace elements.

In this work, various amendments and/or a plant cover were assessed for their potential to reduce trace element leaching in a trace element contaminated soil under semi-arid conditions. The experiment was carried out in field containers and lasted 30 months. Five treatments with amendments (leonardite (LEO), litter (LIT), municipal waste compost (MWC), biosolid compost (BC) and sugar beet lime (SL)) and a plant cover (*Agrostis stolonifera* L.) and two controls (control without amendment but with plant (CTRP) and control without amendment and without plant (CTR)) were established.

Drainage volumes were measured after each precipitation event and aliquots were analysed for pH, electrical conductivity (EC) and trace element concentrations (As, Cd, Cu, Pb and Zn). Soil pH and trace element extractability (0.01 M CaCl<sub>2</sub>) at three different depths (0-10, 10-20 and 20-30 cm) were measured at the end of the experiment.

Incorporation of amendments reduced leaching of Cd, Cu and Zn between 40-70 % in comparison to untreated soil. The most effective amendments were SL, BC and MWC. At the end of the experiment, extractable concentrations of Cd, Cu and Zn were generally lower in all amended soils and CTRP compared to CTR. In all treatments soil pH decreased and extractability of trace elements increased with soil depth.

Results showed that the use of these amendments combined with healthy and sustainable plant cover might be a reliable option for “in situ” stabilization of trace elements in moderately contaminated soils. Although assisted natural remediation techniques do not decrease total trace element concentrations in soil, they have the potential to be a reliable technique for reducing trace element solubility in situ. Therefore, contamination of groundwater and adjacent areas may be prevented and limited in a cost-effective, sustainable manner.

## PERSISTENCE OF DIURON IN AN ORGANIC AMENDED SOIL: A FIELD STUDY

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Addition of organic amendments or organic wastes to soils contributes to improve their physical and chemical properties. The increase in organic matter content upon amendment also affects the fate of other compounds applied to soils such as herbicides. The aim of this work was to study the effect of the application of a solid waste from olive oil extraction (alperujo) on the movement and persistence of diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], which has been an herbicide widely used in olive groves. For this purpose, an experimental olive grove located in Mengibar (Jaen, Spain) was divided in two plots: 1.- Plot without organic amendment (blank) and 2.- Plot treated with alperujo during 3 years at a rate of 17920 kg of alperujo ha<sup>-1</sup>. At the beginning of October 2005, diuron was applied to both plots at a rate of 2 kg ha<sup>-1</sup>. After 7, 14, 21, 28, 49, 70, and 117 days of herbicide application, triplicates from each plot were sampled at 3 depths (0-10, 10-20 and 20-30 cm), air-dried, remains of olive leaves, grass roots, and stones removed and sieved through a 5 mm mesh sieve. Diuron was extracted with methanol 1:2 weight:volume ratio, the extracts were evaporated to dryness, resuspended in 2 mL of methanol, filtered and analyzed by HPLC.

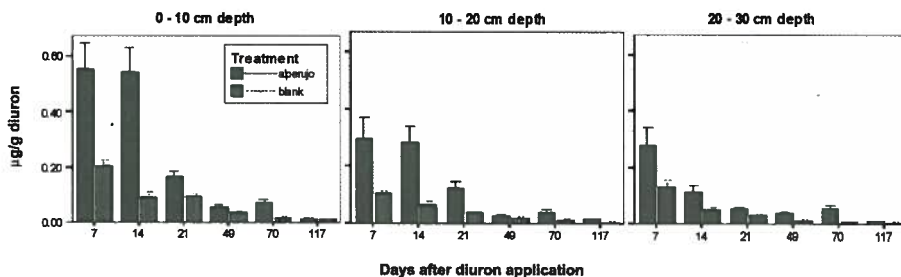


Figure 1. Diuron ( $\mu\text{g}$  of soil) extracted at different depths.

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The total amounts of diuron recovered from soil are shown in Figure 1. Higher amounts of diuron were detected at each sampling depth in plots treated with alperujo. The increase in soil organic matter content upon amendment with alperujo is responsible for the increased sorption and hence, for the higher persistence of diuron in the soil .

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## TOTAL RECYCLING OF OLIVE MILL WASTES BY INTEGRATED PHYSICAL, PHYSICO-CHEMICAL, CHEMICAL AND BIOLOGICAL TECHNOLOGIES

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Olive mill waste waters (OMWW) and olive mill solid-liquid waste (OMW) are by-products of three-phase and two-phase olive oil processing plants, respectively. Both these materials cause disposal problems because of their highly polluting load, which is documented by high chemical oxygen demand (COD) and biological oxygen demand (BOD). However, these wastes may also be regarded as an inexpensive source of inorganic and organic compounds to be recovered because of their potential economic interest.

From OMWW it has been previously recovered and characterized the humic acid-like organic polymeric fraction named polymerin. This complex salified organic polymer has been proposed as an amendment and has shown high sorption capacity of heavy metals such as Cu, Zn, As, Cr(III) and Cr(VI), as well as of ionizable pesticides. It has also been successfully experimented the removal of these toxic compounds from simulated waste waters by cyclic sorption on the cited bio-sorbent.

The hydroxytyrosol triacetyl derivative (triachdrx) was very efficiently produced as a highly pure stabilized antioxidant compound by a short treatment of the organic extracts obtained from the same above OMWW samples deprived of polymerin, with an acetylating mixture in mild and safe conditions (international patent under PCT/IT2005/000781). The purified triachdrx showed the same protective effects against the oxidative stress in human cells as the parent hydroxytyrosol (hdrx), likely because of the biochemical activation of the acetyl derivative into the active hdrx by esterase.

Dry olive mill residue (DOR) from OMW was fractionated by a consecutive continuous solid-liquid extraction with ethyl acetate, n-propanol, methanol and water, obtaining the EAF, PF, MF and WF fractions, respectively. The mass spectrometric analyses showed EAF, PF and MF to be mainly composed of simple phenols, phenolic acids, flavonoids and glycosilated phenols, whereas WF was mainly consisting of polymerin. The identification of oleoside, 6'-b-glucopyranosil-oleoside, 6'-b-rhamnopyranosil-oleoside, and polymerin are reported for the first time occurring in DOR. The saprobe fungi *Coriopsis rigida*, *Pycnoporus cinnabarinus* or *Trametes versicolor* indicated to be able to metabolize both the phenols and glycosilated phenols, but not polymerin. In correspondence, EAF, PF, MF and WF, which proved to be toxic on *Lepidium sativum*, decreased their toxicity after incubation with the selected fungi, WF showing to be also able to stimu-



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late the growth of the selected seeds. The fractionation procedure and the biological treatment of the DOR components could be a methodology for the obtainment of products of high added value in native form and after the bioremediation.

In conclusion, the considered wastes can be totally recycled after integrated physical, physico-chemical, chemical and biological technologies, with three main potential outcomes: i) the reducing of the environmental impact deriving from the discharge of these wastes, ii) the acquisition of substances of agricultural, food, pharmacological and cosmetic interest and iii) the acquisition of bio-sorbents for the clean up of waters contaminated with toxic compounds.

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## WASTE MANAGEMENT PRACTICE IN TURKISH SHIPYARDS

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More than 40 shipyards in Istanbul/Turkey are involved in new construction and repair of ships and generate significant quantities of pollutants, wastes and wastewater. Operations in the ship-building and repair industry are complicated and these activities generate significant amounts of emissions. New ship construction and ship repairing have many industrial processes such as cutting, surface treatment, blasting, painting and coating, solvent cleaning and degreasing, welding and fiberglass boat manufacturing.

The amount of wastes and pollutants are a major risk from environmental and ecological point of view. These wastes can be grouped as particulates, VOC's (styrene, acetone, methylene chloride), metal mists and fumes for pollutants, paint chips, cleaning and paint stripping solvents, oil residues from bilge and cargo tanks, emulsified lubricating and cutting oils and coolants for wastewater and paint chips (containing metals, tributyl-tin), spent abrasives, surface contaminations and cargo tank residues, spent plating solutions and cyanide solutions, waste cutting oil and lube oils for the residual wastes.

To manage these wastes and pollutants in the shipyard industry, these waters should be well defined and characterized. Such as the characterization of copper and zinc concentrations in shipyard wash waters and removal coincident with treatment operations that are targeting tributyltin removal. Copper and zinc were observed to be major components of shipyard wash waters. High concentrations were associated with the large amount of particulate material in the waters generated through wash down and hydroblasting of ship hulls. Also metal cutting during the process of ship scrapping or breaking operations will generate air emissions containing particulate matter, heavy metals, metal ions, oxides of nitrogen, carbon monoxide and ozone.

The best way to reduce pollution is to prevent it at the beginning of the project. Alternatives to reduce the pollution may be to decrease the material inputs, to improve the engineering processes to reuse the materials, to improve the management practices, to use alternatives to toxic chemicals.

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## THE FATE OF KINETIC PARAMETERS ON BIOLOGICAL TREATMENT OF RAW AND ANAEROBICALLY PRE- TREATED WASTEWATER

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In this study, alcohol distillery industry wastewater which having high COD concentration is used. The samples from anaerobic treatment influent and effluent are used in experimental studies. In concept of the study, inert COD fractions of wastewaters, readily biodegradable organic matter fractions, yield coefficient, maximum growth rates, decay rates are calculated. For influent and effluent of anaerobic treatment processes samples, the soluble inert COD fractions are calculated as 0,009 and 0,13 respectively. Heterotrophic maximum growth rates are calculated as 6,47 day<sup>-1</sup> and 6,04 day<sup>-1</sup>, decay rates are calculated as 0,15 day<sup>-1</sup> and 0,12 day<sup>-1</sup> respectively. While the readily biodegradable COD fraction is 0,30 for influent of anaerobic treatment , it is calculated as 0,18 for effluent of anaerobic treatment.

The experimental results show that while inert COD fraction is low at the beginning of the anaerobic treatment processes, this fraction is increasing in outlet of the processes. In contrary, the readily biodegradable organic matter fraction is decreasing outlet of the anaerobic processes.

**Key Words:** Inert COD, readily biodegradable COD, heterotrophic growth rate, decay rate, yield coefficient

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## THE POTENTIAL USE OF VEGETABLE OIL REFINING SLUDGE IN AGRICULTURE

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Land application of sludge provides a means not only of disposing of an unwanted waste product, but also of returning valuable nutrients (nitrogen, phosphorus, and micronutrients) and organic matter to the land. Although current trends in waste management policies favor land application of sewage sludge as opposed to land fill deposition or incineration (Council Directive, 1999/31/EC), applications of industrial sludge to farmland are not common practice due to the risk of accumulation of the heavy metals and organic pollutants in both soil and crops. However, the accumulation of heavy metals and their availability to plants depend strongly on the composition of the sludge, the application rate, soil properties, and the crop species. Therefore, certain industries such as food (vegetable) processing, the tobacco industry, pulp and paper production, fermentation industries, and flour production have considerable potential due to the low heavy metal and high organic matter content of their sludges.

Vegetable oil refining sludge has also potential for agricultural applications because it contains high organic fraction, substantial amounts of plant nutrients, all of which favor its use as a soil fertilizer. Therefore, the objectives of the present study were to investigate the reuse potential of vegetable oil refining sludge in agriculture and to examine the effects of different sludge loadings on plant growth. In this framework, the soil used to grow the plants was amended with sludge at various ratios (0, 165, 330, 495, and 660 t/ha) for lettuce plants grown in pots in a greenhouse. The effects of various sludge loadings on plant growth were investigated by counting the plants and number of leaves, weighing the green plant parts and root, and by measuring the stem length of the plants. The heavy metal content in the green plant parts was also examined to confirm that they conformed to the limits.

Conducted results demonstrated that the sludge used in this study was poor in heavy metals but rich in organic matter, and nutrients thus it can be used as a partial substitute of chemical fertilizer and as a soil conditioner. However, due to the strong alkaline conditions of the raw sludge, symptoms of nutrient deficiency were observed. The alkaline conditions diminished the solubility of the minerals and nutrients, thus stunted growth was observed in the sludge treatments. The highest stem length was obtained in the 495 t/ha sludge application (19.8 cm) which was substantially lower than the control (58.2 cm). Similarly, the difference between the control and tre-

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atments were significant in terms of dry weight of the green parts. The highest dry weight was obtained in the 495 t/ha sludge application (39.5 g/pot) which was considerably lower than in the control (125.1 g/pot). The analyses of heavy metal contents have shown that metal contents have not reached to toxic levels in the leaves even with high sludge loads except lead (Pb) and (Cd) cadmium. The sludge application did not significantly increase the Ni, Zi, Cu, Cr, Mn, and Fe contents of the green parts of the lettuce plants.

Consequently, the results indicated that agricultural recycling of the sludge from vegetable oil refinery treatment plant for crop production is a promising alternative, since characterization of the sludge suggests that it is appropriate for supporting plant growth; moreover, it is an easy, cost-effective, and environmentally friendly method for sludge disposal by the selected industry.

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## TROUBLESHOOTING FOR COD EXPERIMENTS: COMPARATIVE EVALUATION OF OPEN AND CLOSED REFLUX PROCEDURES FOR DETERMINATION OF COD FROM ACETATE

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In biological wastewater treatment engineering and science, the parameter “chemical oxygen demand (COD)” has the central role, not only because it gives the lump-sum of the organic matter content of the bulk liquid before and after treatment, thus serves as the letter “A” of the “wastewater characterization alphabet” of the “language” of diagnostics from which treatment efficiencies are translated to the language of engineering and science for troubleshooting the algorithm of the technical aspects and for comprehending the biochemical conversion processes, but also because it is implemented as the core parameter describing the organic substrate in mechanistic activated sludge models functioning through the mathematical expressions of biochemical conversion processes and in between the model components describing the features of the biomass, the wastewater and the other environmental (existence and function-related) conditions, all connected and portioned through the links of kinetics and stoichiometry.

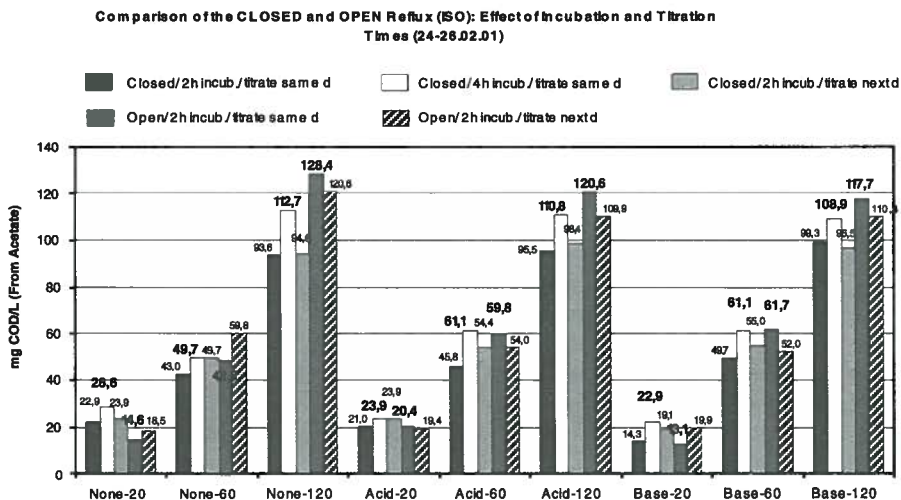
Revolutionizing the grasp and exercise of biological wastewater treatment engineering and science, the merit of these models depends on realistic description of the fundamental biotransformation processes and on accurate and comprehensive characterization of the wastewater, with a specific accent on differentiation of -i.e., COD fractions- in regard to microbial degradation kinetics. Considering the microbial physiology, transmembrane porins permit direct influx and outflux of hydrophilic small particles (<1 nm thus physically categorized as “soluble”), across cell membrane by forming membrane channels with a typical diameter of around 1 nm. Some of the largest porins also mediate the transport of particles with nominal molecular weights as high as 5 kDa (Brock et al., 1994). Once the particles have the direct/transmembrane porin-mediated access to the microbial cell interior, they are rapidly metabolized (in minutes), in case they happen to be biodegradable. If to exemplify for mechanistic modeling, the soluble readily biodegradable COD fraction consists of relatively small biodegradable particles, which are easily transported across cell membrane and then metabolized within a presumably short time span, whereas it takes longer for utilization of the particulate biodegradable COD and the soluble slowly biodegradable COD -or the rapidly hydrolysable COD- fractions since these comprise of larger particles necessitating extracellular breakdown prior to transport into cells for degradation (Wentzel et al., 1999; Hu et al., 2002).

Acetate, or when dissolved in water acetic acid, is one of the chemicals used very commonly as the C-source to support the microbial growth in lab-scale biological wastewater treatment applications with suspended or attached growth processes. By its nominal molecular weight

and heterotrophic utilization rate of, it fits to the above descriptions of “soluble” and “readily biodegradable” C-source. Yet, due its single carboxyl group, it is susceptible of showing resistance to oxidation reactions of even with extreme nature as in COD experiments and in ozonation. The resistance is speculated to originate from the fact that there is no oxidized-intermediate before formation of the end-product of chemical oxidation, since acetate is directly oxidized to CO<sub>2</sub>. In this regard, the primary objective of this study is to determine how much of information loss is experienced and how much of a bias is introduced by the globally exercised COD-measurement techniques for diagnosing the amount of acetate as a C-source for microbial growth (and/or storage). The tools selected here are also the techniques to be troubleshooting: determination of COD in accordance with the procedures outlined in the Standard Methods for Examination of Water and Wastewater (APHA et al., 1998) and International Standard ISO 6060: Water Quality-Determination of the Chemical Oxygen Demand (International Organization for Standardization, 1986).

The experimental sets used for the troubleshooting exercises included: (i) preservation (keeping at +4oC and preserving via addition of NaOH, or H<sub>2</sub>SO<sub>4</sub>, or without any acid-base addition); (ii) reaction time (2 hours or 4 hours); (iii) titration time (same day or next day of reaction); (iv) control reactions (with KHP); (v) different COD concentrations (20, 60, and 120 mg COD/L); all in duplicates, resulting in 48 samples for the closed reflux and another 48 samples for the open reflux experiments. Collected and processed data revealed that the best experimental results, in terms of recovering the most of the theoretical COD in the COD experiments, were obtained by the combination of: preserved sample (via acid or base addition); extended reaction time (4 hr instead of conventional 2 hrs); titrating on the same day of boiling.

Fig.1 Overall results: comparative evaluation of the impact of the experimental conditions (closed or open reflux, sample preservation, reaction time, titration time, concentration) on the level of experimentally recoverable COD originating from acetate.



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## PREPARATION, CHARACTERIZATION AND APPLICATION OF ACTIVATED CARBON DERIVED FROM OLIVE STONE IN WASTEWATER TREATMENT

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Olive stone waste generated in the olive oil production process, was used to prepare a GACs by two activation processes: physical and chemical activation under different conditions, to develop carbons with substantial capability to adsorb toxic metals from wastewater. Preparations were carried out using different oxidizing gases in the physical activation e.g. CO<sub>2</sub>, steam and air and also at different chemical ratios using H<sub>3</sub>PO<sub>4</sub>. Effect of carbonization temperature and time are the important variables, which had significant effect on the pore structure of carbon. Developed activated carbons were characterized by various analysis e.g. SEM, I.R, density, pH, ash content and phenol test. Pore volume and surface area of carbons were estimated by BET method. The best prepared carbon showed surface area, total micropore volume and average pore diameter of 848m<sup>2</sup>/g, 0.4cm<sup>3</sup>/g and 11Ao, respectively. This carbon was tested in application for treatment of industrial wastewater containing Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Mn<sup>2+</sup> ions. From two different industrial facilities (i) dyeing unite and (ii) painting unit. The investigated carbon was effectively sufficient in these applications due to all the metals were removed and thus the treated water can pass into rivers without any risks.

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## INVESTIGATION OF IN-SEWER TREATMENT PROCESSES

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The necessity to assess sewer systems and wastewater treatment plants (WWTPs) as parts of the wastewater system has been well realized for several years. It is clear that both sewer systems and WWTPs affect the quality of the receiving waters. Besides, sewer systems strongly influence the amount and quality of the influent arriving at the WWTPs. Thus, the interactions between sewer systems and WWTPs are very important when discussing wastewater systems (Langeveld, J.G. et al., 2002).

Research should be focused on the interactions of sewer systems and WWTPs to be able to maximize the reduction of the environmental impact of water systems at minimal cost. Besides, it should be considered that a sewer is not just a collection and transport system but also a process system (Jacobsen, H.T., 2002).

Many chemical, physical and biological transformations of wastewater in sewer systems may take place and cause significant changes in the composition during transportation.

Especially in gravity sewers some part of the organic matter is removed before reaching the WWTPs. Formation of sulfide under anaerobic conditions is one of the most well known examples. Sulfide is a serious health risk for humans and a malodorous compound which also create corrosion problem in sewer networks.

If it is considered that the hydraulic retention time of 10 km. long sewer with a velocity of 0.5 m/s is about 5.5 hours and is compared with hydraulic retention time of a conventional biological treatment plant the importance of retention time is understood.

The objective of the present work was to investigate biological and chemical transformations in sewers and to examine the opportunity of operating the sewer system as a bio-reactor.

Therefore a lab scale plant was designed to examine the changes in COD,  $\text{NH}_4\text{-N}$ , TKN and Total Phosphorus in different circulation times. In this study wastewater velocity was adjusted as 0.5-0.1 m/s and two different slopes were studied. Removal efficiency of COD was obtained as 40-85 % while it was 40-80% for  $\text{NH}_4\text{-N}$ , 40-60% for TKN and 30-90% for Total Phosphorus.

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Consequently experimental results showed that considerable reduction of pollutant loads could take place during the transportation of wastewater in sewer lines.

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**ADSORPTION PROPERTIES OF ACTIVATED CARBON FROM  
PEACH STONES PREPARED BY CHEMICAL ACTIVATION WITH K<sub>2</sub>CO<sub>3</sub>**

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Adsorption properties of activated carbons from peach stones prepared by chemical activation with K<sub>2</sub>CO<sub>3</sub> were investigated using acidic dye in aqueous solution. It was found that the overall adsorption process was best described by pseudo-second order kinetic model. Equilibrium data were fitted to the Freundlich and Langmuir isotherm equations and the equilibrium data were found to be well represented by Langmuir isotherm equation. The calculated adsorption capacity for Acid Yellow 11 (AY11) on activated carbon was  $4.08 \times 10^2$  mg g<sup>-1</sup> at 20°C. Activated carbon from peach stones prepared by chemical activation with K<sub>2</sub>CO<sub>3</sub> was found to be a promising adsorbent for the removal of dye from aqueous solution, due to its high adsorption capacity.

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## COMBINED ANAEROBIC TREATMENT OF DOMESTIC WASTEWATER AND LANDFILL LEACHATE AT PSYCHROPHILIC TEMPERATURES

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In recent years anaerobic treatment of many dilute industrial and domestic wastewaters were reported to be treated successfully owing to the presence of large amounts of biocatalyst (anaerobic sludge) despite the eventually low operational temperature of the treatment plant (Banik and Dague, 1997; van Lier et al., 1997). Landfilling has gained significant importance for ultimate disposal of solid wastes which increases the amount of young landfill leachates in Turkey. One of the most convenient methods for leachate control is to treat them (~2% by volume) with domestic wastewaters (Yangin et al., 2002). In this study, the aim was to investigate low temperature influence on the UASB reactor performance treating medium strength pre-settled raw sewage and leachate without any additional heating. Therefore, around 1.0% of pre-settled leachate by volume was mixed with pre-settled domestic wastewater as the feed for a lab-scale continuous-flow Upflow Anaerobic Sludge Bed (UASB) reactor which was operated for about 3 months at room temperature ( $15\pm 2^\circ\text{C}$ ). The performance of the reactor was evaluated by monitoring COD<sub>tot</sub>, COD<sub>sol</sub>, SS, and VSS removals as well as pH, and alkalinity. Besides, biomass concentration was measured at each Organic Loading Rate (OLR) change. Since the UASB reactor was inoculated by the granular sludge taken from a full-scale mesophilic ( $35^\circ\text{C}$ ) UASB reactor treating alcohol distillery wastewater, it was fed with synthetic sewage for the biomass to be acclimatized to relatively low temperature value. The reactor was then fed with raw domestic wastewater at the same HRT of 12 hr. Raw sewage (average COD<sub>tot</sub>@250 mg/l) was pre-settled before it was mixed with the young leachate (with 1.0% by volume) in order to increase the initial COD<sub>tot</sub> to 500-600 mg/l. Since raw sewage reflected a very weak strength character, the aim was to increase the influent organic concentration to relatively medium strength character by leachate addition before fed into the psychrophilic UASB reactor. Results indicated average COD<sub>tot</sub> and COD<sub>sol</sub> removals of 58% and 32%, respectively (OLR=0.5 kg COD/m<sup>3</sup>.day) only with raw sewage feeding. During pre-settled sewage feeding, average COD<sub>tot</sub> and COD<sub>sol</sub> removals were observed as 14% and 37%, respectively (OLR=0.3 kg COD/m<sup>3</sup>.day; HRT=8 hr). Low organic removals could be attributed to very dilute influent (weak strength) characteristics of both raw and pre-settled sewage. Anaerobic treatability results indicated higher COD<sub>tot</sub> removals with 1.0% leachate addition. Average COD<sub>tot</sub> and COD<sub>sol</sub> removals were obtained as 60% and 67% (OLR=1.3 kg COD/m<sup>3</sup>.day; HRT=10 hr) at  $15\pm 2^\circ\text{C}$ . Thus, COD<sub>tot</sub> removal was significantly affected by influent COD concentration rather than operational temperature. By leachate addition into domestic wastewater at appropriate ratios, not only were leachates controlled but also a significant increase in biogas production could be observed. Average biogas production was calculated as 0.25 m<sup>3</sup>/kg

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COD removed/day with leachate addition whereas almost no biogas productions were observed in the cases of either pre-settled or raw domestic sewage treatment. Apparently, low influent COD resulted in low substrate levels inside the reactor and also in a low biogas production rate. Besides, a considerably large fraction of methane and carbon dioxide gases might have been escaped in dissolved form in the effluent (Uemura and Harada, 2000). Although results indicated sufficient COD removals in this study, low nutrient removal was one of the most significant problems in the psychrophilic UASB reactor that necessitated an additional post-treatment as expected at all anaerobic processes.

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**A NEW APPROACH FOR WASTEWATER AND SEWAGE SLUDGE  
DISINFECTION: INACTIVATION OF SALMONELLA SPP. BY  
LOW-FREQUENCY ELECTROMAGNETIC FIELDS**

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The conventional treatment of sewage sludge may contain high concentrations of pathogenic microorganisms and treatment is required to minimize the risk health if it is to be agricultural reas. Landfill is the most common method in the final disposal of sewage sludge in Turkey. The present study concerns microbial inactivation by low frequency electrical fields in batch treatment chamber with parallel plate electrodes. Salmonella spp. was chosen indicator microorganism. The aim of this study was to investigate Salmonella spp. inactivation liquid and semi-solid media. In this study, an electrical apparatus for inactivating microorganisms in sewage sludge was designed. In this system, the energy of electromagnetic fields can physically cause direct breakage of DNA strands. Also, a continuous AC electric field (50 Hz, 6 kV m<sup>-1</sup>) applied to sewage sludge containing Salmonella spp. in order to evaluating the inactivation effect of the electrical apparatus. Finally, with electrical treatment, Salmonella spp started to inactivation after 20 minutes. The number of viable Salmonella spp. decreased 97 % and 2,22 log reduction with applied electric field (50 Hz, 6 kV cm<sup>-1</sup>) at 40 minutes.

## BATHING WATER QUALITY ASSESSMENT IN ANTALYA BEACHES: LEVELS AND HEALTH RISKS OF FECAL INDICATORS IN SEAWATER AND BEACH SAND

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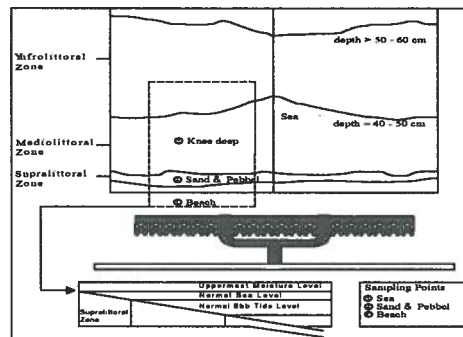
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The presence of fecal contamination within water column and sediment in the sea and sands in recreational areas may health risk for bathing users in the sea side. Untreated storm water runoff from cities and rural areas is a significant source of beach water pollution. In addition important local sources include waste from boats and from malfunctioning septic tanks. As a result of variety of water uses and the constant pressure of people on swimming areas, these areas have increasingly become contaminated with pathogen bacteria. The amount of international (transient foreigner) and national tourists visiting Antalya are increasing every year because of the tourism activities. This area is visited 6-7 million tourist during the dry season for recreational activity.

The microbial context of sediments at the sediment-water interface in bathing areas is receiving increased attention. The sediments may contain 100-1000 times the number of fecal indicator bacteria contained in the overlying water. Stream sediments have been shown to contain fecal coliform (FC) at concentrations higher than 100-1000 times those observed in the overlying water column. Studies in the survival of bacteria indicate that sediments present an environment for growth. Stream sediments contain fecal coliform at concentrations higher than those observed in the overlying water column. Ten sampling points along the Konyaalti and Lara beaches selected and monitored dry season. The microbial water quality at two beaches, Konyaalti Beach and Lara Beach, in Antalya, Turkey was obtained microbial indicators (total coliform, Fecal coliform, *E. coli* and enterococcus) for purpose of evaluating effects between microbes and for identifying possible sources of contamination. The objective of current study was to evaluate two beach sites sediments or sands survival of microbes in supralittoral zone and mediolittoral zone from April to September 2007. Water samples were collected from depth of ankle deep and knee deep in the mediolittoral zone (Fig. 1). Sand samples were collected from supralittoral zone for non-bather or children. The levels of fecal indicators, especially *E. coli* were obtained in sand than in water in most sampling site. This study provides the first original data on the microbiological content of sand along Antalya Beaches and sea water microbiological quality.

Figure 1. Selected sampling sites for assessment health risk in beach



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## TREATMENT OF NAPHTHALENE SULPHONIC ACIDS USED AS DYE ASSISTING IN TEXTILE INDUSTRY BY ELECTROCOAGULATION

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Wastewaters originating from the textile dyeing and finishing industry often contain highly complex mixtures of biologically persistent naphthol- and naphthylamine sulphonates. Naphthalene sulphonic acids and their sodium salts are widely used as dye assisting chemicals. These dye auxiliaries often being applied as dispersing and levelling agents are very water soluble due to the presence of at least one sulpho group and hence of a hydrophilic character. Naphthalene sulphonates may have negative impacts on natural water ecosystems as the derivatives of naphthalene compounds are only poorly biodegradable. Therefore, conventional treatment methods such as biological (activated sludge) processes have proven to be quite ineffective and alternative, advanced treatment methods need to be explored for the efficient abatement of naphthalene sulphonates. Electrocoagulation on the other hand, seems to be a promising treatment process to treat these dye assisting chemicals.

The purpose of the present study was to explore the treatability of a commercial naphthalene sulphonic acid formulation being frequently applied in the cotton and polyamide dyeing process to improve the fixation of reactive and acid dyes onto the fibres, by electrocoagulation using stainless steel electrodes and to compare the organic matter removal performance of electrocoagulation with that of conventional coagulation carried out using ferric chloride, ferrous sulphate and aluminium sulphate (alum). The naphthalene sulphonic acid formulation (BOD<sub>5</sub>: 0 mg/g; COD: 1400 mg/g; TOC: 414 mg/g; acute fish toxicity LCo: 100 mg/L) was supplied by a local textile factory and used as received. Aqueous naphthalene sulphonic acid formulation with an initial COD of 300 mg/L was used in the experimental study. Electrocoagulation experiments were performed in order to optimize the reaction conditions in terms of applied current density and electrolyte (NaCl) concentration at an initial reaction pH of 5. A wide range of coagulant doses (i.e. varying between 160 and 1600 mg/L for ferric chloride) was tested in the coagulation experiments conducted using a Jar-Test apparatus. Coagulation experiments revealed that COD removal efficiency moderately increased with increasing coagulant dose from 45 % (for 160 mg/L ferric chloride) to 62 % (for 1600 mg/L ferric chloride). While for alum 300 mg/L was sufficient to achieve 60 % COD removal, 500 mg/L ferric chloride and 760 mg/L ferrous sulphate was required to obtain 60 % and 63 % COD removal, respectively. Electrocoagulation results obtained for NaCl concentrations of 1000-2000 mg/L at a current density of 22 mA/cm<sup>2</sup> (corresponding to an applied current of 5 A) and an initial pH of 5.0 indicated that over 70 % COD removal could be achieved within a reasonable reaction time of 60 min. On the other hand, an increase in the applied current density did not significantly enhance the COD removal performance. Hence electrocoagulation of naphthalene sulphonic acid formulation proved to be effective method in removing organic matter even at the lowest current density applied in the present study. The results of experimental study were also evaluated and discussed in terms of sludge production rates.

**Keywords:** Coagulation; electrocoagulation; naphthalene sulphonic acid formulation; stainless steel electrodes; textile dyeing process.



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**PROPOSALS ON THE CITY OF NIKEA REFORM  
OF STREETCLEANSING COLLECTION SYSTEM.  
APPLICATION OF CLEAN INDICATORS METHODOLOGY**

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This proposed study is focused on the sector of city-street cleansing collection system, an important sector of every urban municipality not only for health protection but also for environmental protection and life quality improvement reasons. The Nikea Municipality is one of the largest in the province of Attica and Piraeus prefecture with more than 110,000 residents. This specific area is over-populated, with twenty (20) large public squares, narrow streets and an important main road network as well. The majority of its residents belongs to medium and low income class, while in several cases there is almost no town planning.

In this context, this paper analyzes the existing situation of a continuously aggravating problem related to increasing quantities of litters, traffic and abandoned vehicles. Besides, the existing work force in the street cleansing sector presents serious drawbacks, such as the large percentage of temporary labourers or workers with special needs, lack of suitable equipment, etc. Given the time evolution (both qualitative and quantitative) of the litter form and applying the methodology of clean indicators, one may categorize the streets of the city, comparing the existing situation -in the street cleansing sector- with the desirable one.

This classification is based on two methods. The first method is devoted to finding the characteristics of the road net, including the width and the length of the streets and pavements that surround every building block of the area under investigation. The second procedure is concentrated on estimating the analytic composition percentage per weight and per building block of litter sources in Nikea, performing on the spot detailed experimental measurements. These experimental measurements include the litter percentage produced by the domestic solid waste as well as from various natural processes such as the fall of leaves, the public gatherings etc. At the same time, foreign and Greek bibliography is used in order to calculate the litter percentage resulting from the circulation of pedestrians and vehicles.

For the accomplishment of this project, data from the Hellenic National Statistical Organisation (e.g. the 2000 inventory of buildings) and from the Nikea's planning department (for the years

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2001-2006) as well as from the Municipality's circulatory official study are taken into consideration. In addition, a significant number of photomaps, covering either the whole of the city or individually "sensitive" points, is also utilized.

Subsequently, the scientific methodology required to be adopted, considering the placement of appropriate litter bins at suitable points and the state of art concerning the street cleansing technology, is described in detail.

Moreover, proposals are made for the best management of existing human resources (55-60 sweeper employees) along with the necessary rearrangement of the entire street cleansing department in order to provide the best available services to the citizens. Taking into account the important role of the human factor in the litter production, suggestions that can be applied in a Municipality such as Nikea are made, in order to achieve the best possible citizen's awareness of environmental issues, contributing also to the reduction of the litter production.

Finally, the present paper examines the total cost of the proposed interventions through an appropriate techno-economic study. For this purpose reliable data from the local and the international market are gathered, while the developed financial evaluation model takes into consideration the time evolution of the local economy major parameters (e.g. capital cost, annual inflation rate, labour cost etc.). In an attempt to obtain realistic and applicable results, the entire analysis is related to the municipality administration's desirable city cleanness level, using the appropriate clean indicators.

Recapitulating, a complete analysis of the street-cleansing collection system of Nikea municipality is described. The suggested revisions are based on detailed information about the current situation and take into account the economic status of the specific municipality. In the authors' opinion, the revised plan -if adopted and properly applied- should not significantly impede the local municipality financial budget, while it improves the services offered by the local authorities. Several additional urban municipalities may use equally well the proposed street-cleansing collection management plan with similar benefits.

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## CHARACTERIZATION AND TREATMENT OF GOLD REFINERY EFFLUENTS

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Refining operations of precious metals like gold and silver play an important role in gold and silver manufacturing. Both raw ores from gold mines and used gold and silver objects should be refined and purified for further processing and thus gold and silver refining processes are essential for the manufacturing operations of precious metals. Refinement of gold, silver and other precious metals like platinum, palladium, iridium, etc. is conducted in two steps. The first step is the low-grade materials refining which includes blast furnace or electric furnace smelting, where gold is recovered up to 98% together with pure copper and silver. The second step of purification is the high-grade materials refining and the selection of refinement procedure depends on the final purity requirement of gold and the presence of platinum group metals in crude gold. Molten chlorination is applied for 99.5% gold grade and the purified gold is cast into bars for marketing or into anodes for electrolytic refining up to 99.99% purity, if the melt is free of platinum group metals. In case other precious metals are present in crude gold, wet chemical processes are applied where gold is dissolved in aqua regia (nitric and hydrochloric acids mixture), insoluble silver chloride is collected and pure gold is precipitated as the product of the reaction with sodium bisulfate.

This study involves the investigation of waste generation in a gold refinery where high-grade gold recovery is conducted using wet chemical processes. The investigated plant produces 110 tons of pure gold, 45 tons of pure silver and 35 tons of copper and zinc annually. Two different types of industrial wastewaters are generated in the plant during manufacturing operations, (i) wastewaters from wet chemical processes and (ii) wastewaters from stack gas washing operations performed to reduce NOX emissions due to the acids used. The wet chemical process wastewaters were generated at a flowrate of 5m<sup>3</sup>/day and have acidic character. The wastewaters from stack gas purification are alkaline wastewaters since NaOH is used in the process. Water is continuously re-circulated in the gas purification system and dumped batch wise one the absorption capacity is exceeded. The stack gas treatment wastewater is discharged approximately once a week corresponding to an approximate wastewater flowrate of 1 m<sup>3</sup>/day.

The wastewater characterization studies have revealed that the acidic industrial wastewaters (pH = 0.6) have high heavy metal content where the alkaline stack gas washing unit wastewaters carry low concentrations of metals. Nevertheless alkaline wastewaters should also be carefully treated due to the high pH value of 13.8.

A series of chemical treatability tests have been applied to these wastewaters and five different treatment scenarios with more than 95% metal removal were obtained have been evaluated in terms of economical feasibility and practical ease of application for the selection of the best treatment scheme. The optimum treatment procedure has been determined as the neutralization of acidic wastewaters with NaOH initially up to pH=4.0 and then mixing with alkaline wastewaters where the pH is balanced around 6.0. The final precipitation is obtained by raising the pH value 9.0 for maximum metal removal.

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## USAGE OF TREATED DOMESTIC WASTEWATER IN IRRIGATION: AN EXAMPLE OF TURKEY

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The objective of this study is to determine the water storage requirement for irrigational purpose and potential irrigational lands for the characteristic regions of Turkey using the meteorological data taken from 16 meteorological stations of the areas with abundant irrigational lands. In order to use the treated domestic wastewater in irrigation, the required volume for municipal wastewater storage was calculated depending on the vegetation types grown in these regions using data from these sixteen stations. In addition, the area of the potential irrigational land was determined using all of the generated domestic wastewater from the residential areas close to these 16 stations. The Blaney-Criddle Method, which was developed for dry and semi-dry regions in United States of America (USA), was used in this study. This method is often used by the Turkish State Hydraulic Service for dry and semi-dry regions in Turkey because of the fact that these regions in Turkey are similar with the regions in USA which are used to develop the Blaney-Criddle Method in terms of the climate and properties of the arable lands. The results are shown in the graphics of the manuscript.

The results of this study point to these conclusions:

Natural systems, due to being economical and practical along with giving chance to the utilization of wastewater are better to be well considered for Turkey.

There is a great potential of wastewater usage in irrigation, since it provides the nitrogen and the phosphorus demand of the plant while needing less fertilizer.

In the regions where 16 meteorological stations are located as the representative of Turkey, storage volume and the required area are acceptable for wastewater usage in irrigation in Mediterranean and Southeastern Anatolia Regions together with an additional water supply and if tolerable winter conditions predominate.

Although additional work could be needed on the seasonal wastewater storage maps and local assessment of the populated areas, storages and irrigated areas are especially good enough for the low populated areas, Thus, decision on the types of the irrigated plant and water becomes more important as well as the nutrient demand of the plant should be carefully evaluated.

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Irrigation with the treated wastewater will lower the costs of water and wastewater treatment and thus presenting an interesting study for the economists.

Since considerable losses will be observed in the cases of leaking and evaporation, the required storage volume and the area could be calculated more precisely if monthly and annual evaporated and leaked wastewater amount is known.

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## TREATMENT OF PULP BLEACHING EFFLUENT BY CATALYTIC OZONATION PROCESS

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Ozonation has gained considerable attention for water and wastewater treatment due to its higher oxidation and disinfection potential. However, low solubility and instability of ozone in water limit the usage of ozonation process. When ozone is used together with various catalysts for treatment, efficiency of process could be improved by increasing the hydroxyl radical concentration which in turn could reduce the cost of process. Heterogeneous catalytic ozonation is one of the treatment technologies developed in recent years. In this work, heterogeneous catalytic ozonation was applied to pulp bleaching effluent and the obtained results were compared with those of ozonation and homogeneous catalytic ozonation processes. The wastewater was taken from an integrated pulp and paper plant in which a six-stage bleachery (C/E-H-D/E-D) process is applied to the cooked softwood and hardwood kraft pulp. Ozonation was applied to segregated CEH and CEHDED stage bleaching effluents as a pretreatment operation in order to increase their biodegradability. Granular activated carbon (GAC) and iron and manganese ( $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ) ions were used as heterogeneous and homogeneous catalysts, respectively. The effects of pH and catalysts concentration on applied ozonation process were investigated and the efficiencies of the processes were evaluated by the variation in BOD<sub>5</sub>/COD ratio, AOX, color, aromatic compound concentration, chloride concentration, and molecular weight distribution (MWD) of the pollutants in effluents. Although an increase in the pH of sole ozonation from 7 to 10 did not cause any improvement for color removal of CEH effluent, positive effects on all other investigated parameters were observed. By O<sub>3</sub>/pH=10 process, BOD<sub>5</sub>/COD ratio of CEH stage wastewater was increased to 0.3, which was initially 0.1. On the other hand, aromatic matter and color degradation were 78 % and 88 %, respectively, with a 2.05 mg O<sub>3</sub>/mg COD of specific ozone consumption. The flow rates of CEH and DED stage wastewaters are equal, but strength of DED effluent was quite lower. However, the process efficiency was not affected by the application of ozonation to CEHDED stage effluent. Both  $\text{Fe}^{2+}$ (5mM)/O<sub>3</sub>/pH=7 and  $\text{Mn}^{2+}$ (5mM)/O<sub>3</sub>/pH=7 processes resulted 50 % of COD reduction for CEH stage effluent while BOD<sub>5</sub>/COD ratio reached to 0.25 with  $\text{Fe}^{2+}$ (5mM)/O<sub>3</sub>. 33 % of COD degradation obtained by O<sub>3</sub>/pH=10 process was enhanced to 50 and 63 % by GAC(10g/L)/O<sub>3</sub>/pH=10 and GAC(10g/L)/O<sub>3</sub>/pH=7, respectively. Also, heterogeneous catalytic ozonation at pH 7 led the decrease in absorbed specific ozone from 2.2 to 1.3 mg O<sub>3</sub>/mg COD. Both O<sub>3</sub>/pH=10 and GAC(10g/L)/O<sub>3</sub>/pH=10 processes were found to be effective for the removal of AOX (up to 84 %), although the degradation rate was comparably higher in the case of heterogeneous catalytic ozonation process. Only 25 % of the compounds found in the wastewater have low molecular weight (MW < 1000). The ratio of these compounds were increased to 46 % within the first 30 minutes by GAC(10g/L)/O<sub>3</sub>/pH=10 process and these results are in agreement with variation in BOD<sub>5</sub>/COD ratio. Combination of ozone with GAC not only cause degradation of adsorbed pollutants but also lead regeneration of GAC which determined by comparison of sequential usage potential of activated carbon.

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**GENERAL PLAN FOR THE INTEGRAL TREATMENT, MANAGEMENT  
AND VALORISATION OF WASTE GENERATED DURING  
THE PRODUCTION PROCESS OF VIRGIN OLIVE OIL.**

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The main objective of this project is to demonstrate the environmental and economic advantages and the technical feasibility of a new system to manage the waste originated during the production of the virgin olive oil. The plan consists in recovering the maximum water quantity in the origin. Therefore, it is recommended that olive mills carry out the remaining successive extractions of oil in a 3- phase system (50% of water) with the related savings in transport and in the drying costs in the extraction plants (which is twice, the one proposed). The alpechin would be treated in the plant where after being concentrated, it will be used for solid and liquid production of organic fertilisers and the water for the irrigation of the olive grove. In total, this supposes a cost of treatment of a 1/3 of the cost of the current process with the extraction plants, moreover it will be the additional advantage of water recovery.

The plan bears the construction of a demonstration plant. This plant incorporates a new process in three steps: a quick separation of solid products, a thermal concentration of liquid products and a final treatment of the remaining water. The benefits will be: total absence of solid and liquid waste, smaller treatment costs, additional revenues in the olive mill, some benefits for the extraction plant (olive pomace/cake 50% water) and energy self-supplying.

The plan has been supported by the EC with the concession of the project LIFE05ENV/E/000292 called: "Processing Plant for the Integral Treatment and Valorisation of the Wastes Generated during the Olive Oil Production Process" (OLIVEWASTE).

Other objectives would be the execution and legislative adaptation of several European normatives. These regulations concern to Water management, Residues and Environmental protection (2000/60/EC, 75/442/EEC, 86/278/EEC Directives, etc...). Other aim of the project will be to carry out activities of knowledge dissemination, which should have an important character of demonstration of the techniques used. Finally, the mobilization of all the involved sectors to achieve the attainment of these objectives will be essential.

This project has a duration of 3 and a half years and a budget of 4.524.561 Euros. The European Commission has subsidized 45,65 % of the costs through its LIFE Programme. The participants in the project are Fundación CARTIF, TRAINALBA S.L, ENERMAN S.A, AYUNTAMIENTO DE BAENA and DELEGATION DE CÓRDOBA.



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**EFFECTS OF DE-OILED TWO-PHASE OLIVE MILL WASTE  
ADDITION TO SOIL ON SORPTION, DEGRADATION  
AND LEACHING OF THE HERBICIDE TERBUTILAZINE**

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Semiarid Mediterranean soils under intensive continuous cultivation have a net deficit of C. The continuous centrifuge two-phase process generates a large amount of an olive mill waste known as alperujo. This by-product is usually sent for further chemical and heat treatment in order to obtain a second extraction olive-oil with generation of a de-oiled two-phase olive mill waste (DTPOMW). DTPOMW has very high organic matter content and, therefore, can be used to add organic C to degraded soils. The effective use of DTPOMW as a soil amendment requires information on the net impact on the behaviour of other compounds used in agriculture, such as pesticides.

In order to investigate the effects of the addition of DTPOMW on the sorption, desorption, degradation and leaching of the herbicide terbutylazine, experiments were conducted on soils samples collected from a field study on an olive grove soil amended five years with three levels of DTPOMW (0, 27 and 54 Mg ha<sup>-1</sup>, annually). Terbutylazine sorption isotherms on unamended and amended soils were obtained by short-term equilibration (<24 h) tests. Dissipation of terbutylazine in the soils was studied at 40 % of field capacity. Leaching experiments were studied in handpacked soil columns.

The DTPOMW application significantly increased terbutylazine sorption capacity and K<sub>f</sub> was increased by 190 % when 54 Mg of DTPOMW ha<sup>-1</sup> was annually applied to the soil, revealing the affinity of terbutylazine for this organic amendment. The DTPOMW also influenced terbutylazine desorption from the soil. Dissipation studies revealed that biodegradation of this herbicide was reduced after DTPOMW application. A greater vertical movement of the herbicide in soil columns was observed in unamended soil compared to the soil amended with the higher rate of DTPOMW. However, DTPOMW addition accelerated the vertical movement of the herbicide through the soil, independently of the annual applications of amendment received. Thus, greater percentage of water soluble organic carbon in DTPOMW-amended soils can facilitate transport and accelerate the leaching of the herbicide.

Key-words: De-oiled two-phase olive mill waste; terbutylazine; sorption, degradation, leaching



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## LONG-TERM IMPACTS OF SUGAR CANE WASTERWATER IRRIGATION ON FERRALITIC SOILS

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In areas with extensive production of sugar cane, disposal of the residues from manufacturing plants of this agricultural product represent a major concern (Cruz et al., 1991; Gloeden et al., 1991). This agroindustrial material can be used as a substitute for chemical fertilizers, as they contain significant amounts of organic matter and plant nutrients. Application of by-products from the sugar cane industry could be one of the most economical and suitable methods to solve two problems: wastewater disposal and increasing soil fertility.

The objective of the present study was to determine the effect of sugar cane wastewater irrigation for 40 years on ferralitic soils from the La Habana province in Cuba. More specifically the effect on: a) some physico-chemical properties of the soil, b) the iron and manganese oxides content, c) the mobility of Cu, Zn, and Co in the profile, and d) crop yield. Results were compared with those obtained under traditional mineral fertilization.

The study area is located in the province of La Habana, in Cuba. Soils were classified as Ultisols according to the Soil Survey Staff (1999). They are Ferralitic Yellow soils with parent materials of calcareous rocks.

Fertilization with the wastewater caused a decrease of soil pH down to a depth of 100 cm. However there was an increase in electrical conductivity because of the large concentration of potassium in the wastewater. The amendment also increased the organic matter content along the whole profiles.

The formation of organo-mineral complexes produced little change in the particle-size distribution, but an increase in the poorly crystalline iron oxyhydroxides in the upper horizon up to 22%, and the crystallinity of iron oxyhydroxide in the soil decreased substantially. This was likely due to dissolution and reprecipitation of these oxides by the acid pH of the wastewater. Total and poorly crystalline manganese contents also decreased. The amendment material increased the mobility of metals because of the formation of water soluble complexes with organic ligands. The results showed that the long-term wastewater irrigation could be of agricultural interest due mainly to its organic matter concentration, but micronutrient concentrations in the upper horizons were negatively affected because complexed metals favored their transport throughout the soil profile, which may eventually lead to deterioration of groundwater quality and/or micronutrient deficiency.

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## RECYCLING OF WET OLIVE CAKE "ALPERUJO" THROUGH TREATMENT WITH FUNGI AND SUBSEQUENT VERMICOMPOSTING

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The wet olive cake or alperujo, a semi-solid waste produced during the two-phase extraction of olive oil, is the main waste produced by the olive oil agroindustry in Spain. This olive waste has a high C/N ratio, recalcitrant nature and contains toxic compounds as polyphenols, which prevent their direct application to agricultural soils.

*Pleurotus ostreatus* is a macrofungus which use polysaccharides from various lignocellulosic wastes to produce the oyster mushroom for human consumption. In addition, it has been demonstrated his ability to degrade phenols, detoxifying the phenolic wastes used as substrates. *Eisenia fetida* is the most common epigeic earthworm used in vermicomposting. Vermicomposting has already been described as a useful process for stabilizing different natural and anthropogenic wastes.

The aim of this study was to evaluate the changes recorded in a wet olive cake after degradation with *Pleurotus ostreatus* (4 months) and, thereafter with *Eisenia foetida* (4 months). These changes were assessed by determination of some enzymatic activities, organic matter and elemental composition in this olive waste at the beginning and at the end of both subsequent degradation processes.

Predecomposition of wet olive cake with *P. ostreatus* reduced appreciably polyphenols content, total organic carbon, hemicellulose and cellulose and increased N, P, K, micronutrients content and some enzyme activities (dehydrogenase, glucosidase and urease). Subsequent vermicomposting of the predecomposed wet olive cake improved the agronomical quality of this waste, which displayed optimal C/N ratio, null phytotoxicity and, in general, higher enzyme activities and nutrient contents. These results revealed that the combination of both treatments was a feasible and economical method to recycle wet olive cake. The finished organic product obtained was stable, mature and enriched in nutrients, therefore, it could be used as organic amendments, mulching products and soil remediation amendments

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## ENHANCED DIURON SOIL SORPTION USING MEDITERRANEAN AGROINDUSTRIAL WASTES

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The sorption of pesticides by soils is a very important process because it strongly influences the applied pesticide amount that can reach target organisms and that can be degraded, volatilised or leached. Pesticide soil sorption is dependent on both soil and pesticide properties, with sorption, generally, augmenting with the increase of organic matter and/or clay content in the soil.

Olive oil and wine production are important industries in the mediterranean region. These industries generate huge amounts of wastes (among others, wet olive cakes, grape marcs, vinasse biosolids), which management is regarded as a serious environmental issue. Recently, different solutions have been proposed for the efficient reuse of these wastes, previously composted or vermicomposted, such as its addition to soils in remediation or agricultural purposes.

Diuron is a systemic ureic herbicide with a moderate persistence in soil. It is used for plant protection, in agriculture intensive systems, so soil and water contamination by this xenobiotic is highly probable.

The aim of this study was to evaluate the effect of the addition of three vermicomposts obtained from olive (wet olive cake) and winery (spent grape marc, vinasse biosolid mixed with vine shoot) wastes on sorption of Diuron (as DiuroKey 80% w/w from Industrial Química Key) in two mediterranean agricultural soils with low organic carbon content (3.6 and 9.3 g kg<sup>-1</sup>).

In the unamended and organically amended soils, sorption isotherms fit the Freundlich equation well ( $R^2 > 0,949$ ,  $P < 0,01$ ). In the amended soils with the three assayed vermicomposts, Kf values fold between 5 and 2 times the Diuron soil sorption capacity. The higher increases in the values of the sorption coefficient (Kf) due to the vermicompost amendments took place in the soil with lower organic carbon content. Comparatively, higher Diuron sorption was recorded when vermicomposts from winery wastes, which have higher organic carbon and lignin content, were added to both soils. Diuron sorption decreased after incubation, for 6 weeks, of the soils with the assayed vermicomposts. These decreases were less appreciable when the soil had been incubated with vermicompost from olive wastes.

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## THE BULKING AND BULGING PROBLEMS THAT CAUSING BY FILAMENTOUS MICROORGANISMS

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In this study, the flock structure, the filamentous microorganisms and not filamentous microorganisms of the samples which are taken from Adasu Wastewater Treatment Plant have been investigated. With the analysis results between water and sludge quality have been made a contact.

First; some information has been given about the characteristics of the wastewater, the treatment methods and the pollution parameters and the pollution analysis parameters. The microorganisms in the wastewater have been referred.

Afterwards; the activated sludge process and the important microorganisms in the thesis subject have been discoursed and some information about the reasons and precautions of the bulking problems have been given.

In the conclusion chapter, the samples of the treatment plants have been investigated by microscopically. The information has been given about the investigation methods and the stains methods which are applied and the photos of the types which are fixed and the flocks have been taken. With this results between the analysis results have been made a contact. Some information have been given about that will make about this topic and the precautions will take.

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## INVESTIGATION OF ACID PHASE PRODUCTS USING COW RUMEN BASED ANAEROBIC MIXED CULTURE

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Isolated from cow rumen, gram positive anaerobic bacteria were used for fermentation volatile fatty acids (VFAs), alcohols and other intermediate products from glucose in a laboratory scale model completely stirred batch reactor operating at  $35\pm 1^\circ\text{C}$ . The purpose of the study was to determine the gram positive anaerobic bacteria activity and its effects from the change of hydraulic retention time (HRT, 1-48 h), sludge retention time (SRT, 5-20 d). The heat treatment ( $90^\circ\text{C}$  for 1h) of the anaerobic microflora from cow rumen was able to select partial gram positive bacteria spores; this product was used as a seed for batch system. The glucose was used as lone substrate of all study stages. For seven HRTs and four SRTs, the results indicate that at pH: 5,  $5\pm 1$  and 3 g/l organic loading rate (OLR), a maximum VFA production 2650 mg/l (as HaC) and 12,44 %  $\text{H}_2$  concentration was achieved at HRT: 4 h. Nevertheless, at HRT: 1.5h, pH:  $5.5\pm 1$  was also the optimum pH for the maximum  $\text{H}_2$  production among four pHs evaluated from 5 to 6. There was a significant accumulation of VFA (mainly, acetic acid, propionic acid and butyric acid), alcohols (ethanol, propanol), and formic acid during the entire study.

**Key Words:** Acid phase; Cow rumen; VFA; Hydrogen production; Anaerobic treatment

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**WITHIN BOG VARIATION OF <sup>210</sup>Pb PROFILES:  
IMPLICATIONS FOR DATING PEAT CORES**

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In order to study the spatial variability associated to the reconstruction of metal atmospheric deposition during the last century in the northwest of the Iberian Peninsula, four peat bog cores (CHL1, CHL5, CHL8 and CHL13) were taken from in the Chao de Lamoso bog (Serra do Xistral, NW Spain). Bulk density, <sup>210</sup>Pb and Pb profiles showed significant differences amongst the four replicates. In core CHL1, bulk density data increased with depth from 0,10 to about 0,13 g·cm<sup>-3</sup>, while in the other cores the mean bulk density value was constantly lower (0,10 g·cm<sup>-3</sup>). Unsupported <sup>210</sup>Pb and Pb profiles exhibited secondary maxima at layers between 8 and 24 cm depth in cores CHL5, CHL8 and CHL13. These differences suggest that the accumulation mechanisms, degradation of organic material and compaction are not homogeneous in the same peat bog. Building of an age model of the peat core was attempted by using the common <sup>210</sup>Pb method (i.e. CRS, CF:CS models) constrained with <sup>137</sup>Cs and <sup>241</sup>Am activity profiles. Maximum Pb concentrations correspond to peat layers dated at early 1970s. However, derived lead net accumulation point to maximum deposition between 1949 and 1965. This is in disagreement with historical patterns of lead emissions that peaked in the 1970s, and illustrates the spatial variability in the peat bog record. These results suggest that use of classical models without explicitly consider the role of processes such as organic matter decomposition and lead mobility in peat bogs is not advisable and that estimations (of chronologies and fluxes) obtained using single cores may not be representative for a given area. Here we discuss the need for further elaborate modeling of peat bog chronologies by using radionuclides.

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## EFFECT OF CHEMICAL TREATMENT ON THE AROMATIC CARBON CONTENT AND PARTICLE SIZE DISTRIBUTION-BASED ORGANIC MATTER PROFILE OF OLIVE MILL WASTEWATERS

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Countries along the Mediterranean coast are among the main manufacturers and consumers of olive oil. The characteristics of the liquid waste generated in the small-to-medium scale facilities largely depend on the type of extraction process (the traditional press method or the continuous three-phase centrifugation process) employed. Olive mill wastewater (OMW) is characterized by its high COD (25-300 g/L) and TOC (10-100 g/L), strong, dark brown color as well its biologically difficult-to-degrade polyphenolic content (including phenols and polyalcohols). Its high organic load mainly originating from a variety of sugars, tannins, acids, pectins and lipids imposes serious wastewater management and disposal problems. In the last decade great effort has been out forward to develop efficient physicochemical, as well as biological treatment solutions for the treatment of OMW. To our knowledge, most of these studies have focused on the treatability of synthetic wastewater and single model pollutants selected to mimic effluents from this industry.

In the present study we have investigated the physicochemical treatability of actual OMW (total COD = 52774 mg/L; filtered COD (through 0.45 mm) = 45516 mg/L; TOC = 18650 mg/L; DOC = 14600 mg/L; oil and grease content = 7930 mg/L; UV280 = 1.0668 m<sup>-1</sup>; UV254 = 1.0728m<sup>-1</sup>) received from a mill located in Edremit/Turkey, by coagulation-flocculation with FeCl<sub>3</sub>, hydrated lime and anionic polymer (10 mg/L) at varying pH's (5, 8.5 and 9) and doses (1500 and 3000 mg/L), Fenton's oxidation at different H<sub>2</sub>O<sub>2</sub> doses (50 and 100 mM in the presence of 5 mM Fe<sup>2+</sup> catalyst at pH = 3), and electrocoagulation using iron electrodes at different current densities (22 and 44 mA/cm<sup>2</sup> at pH = 4.5 and 1000 mg/l NaCl electrolyte). Obtained experimental results were compared with those achieved by employing a commercial polymer at different doses and pH's. The experimental study focused on the impact of chemical treatment on the aromatic carbon content (represented by the UV280 parameter) and particle size distribution (PSD)-based COD fingerprint of the wastewater sample. PSD-based organic matter profile of the investigated OMW as well as the TSS-VSS values (1365-1125 mg/L, respectively) indicated that the raw OMW had a rather soluble character and approximately 67% of the OMW total COD cumulated at the size category below 2nm (<1 kDa) (i.e. 11% of the total COD content was at the 2-3 nm size category), speaking for a considerable aromatic carbon fraction. Results have indicated that 30% soluble COD and 20% DOC removals could be achieved by chemical precipitation using FeCl<sub>3</sub> as coagulant at pH 5.0.

Results of the experimental studies were evaluated and discussed in terms of chemical treatment of OMW and its effect on the PSD-based organic matter profile.



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## PHOTOCATALYTIC TREATMENT OF PHENOL WITH VISIBLE LIGHT IRRADIATION

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The problem of pollution reduction in aqueous streams containing refractory compounds is of great importance for many industries. Among the harmful organic compounds in industrial wastewaters, phenol and phenolic substances have attracted more attention because of their toxicity and frequency of use in industrial processes producing wastewater contaminated by phenol as a pollutant. Traditional biological and physical-chemical processes (adsorption, membrane processes, chemical oxidation etc.) can generally be used for phenol removal. Chemical oxidation is one of the potential alternatives to remove phenol and phenolic substances from wastewaters. In the past decade, considerable attention has focused on photocatalytic degradation of phenol as titanium dioxide (TiO<sub>2</sub>) has proven to be the most excellent photocatalyst for the oxidative decomposition of many organic compounds under UV irradiation. However, the relatively wide gap of TiO<sub>2</sub> limits further application of the material in the visible light region ( $\lambda > 400$  nm). The aim of the present research is to investigate the feasibility of removing phenol by the modified TiO<sub>2</sub> catalysts which were responsive to visible light irradiation. For this purpose, new developed N-doped TiO<sub>2</sub> catalysts and S-doped TiO<sub>2</sub> catalysts adsorbed with ferric iron were used in the present study. Phenol oxidation was experimentally investigated in terms of phenol removal, intermediate formation and TOC removal pattern. The degradation rate for the mineralization (depletion in TOC content) of phenol was also calculated for all experiments.

With these intentions degradation of aqueous phenol solution containing  $2.6 \cdot 10^{-4}$  M initial phenol concentration with catalyst powders was investigated under both UV and visible light irradiation. Titanium dioxide Degussa P25 as the photocatalyst was used for a reference experiment for the degradation of phenol in both light sources. Experiments were conducted at pH 3.0 and 8.0 with a constant catalyst concentration of 1 g/l. 75% TOC removal was achieved under UV light irradiation at the end of the 6 hr reaction time using Degussa P25, while there was no observable removal with visible light photocatalysis. 12-19% TOC removal efficiencies were achieved in 6 hr reaction time for N-doped catalysts under visible light irradiation at pH 3.0. The degradation rates for the mineralization were found 0.0216 and 0.0482 mol / l hr for N-doped catalysts at pH 3.0. S-doped catalysts proved to be more efficient as compared to the N-doped catalysts at the same experimental conditions. The degradation rates for the mineralization were calculated as 0.1237 and 0.1505 mol / l hr for S-doped catalysts. S-doped catalysts were also effective under UV light source with removal efficiencies up to 70%. However, 90% TOC removal efficiencies were also obtained under visible light photocatalysis.

Results of the experimental studies were evaluated and discussed in terms of applicability of modified TiO<sub>2</sub> which were responsive to visible light irradiation for both phenol and TOC removals.



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## OZONATION OF OXYTETRACYCLINE IN MANURE AND WASTEWATER

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Modern animal farms regularly and widely use antibiotics either directly or as food additives for disease control and prevention as well as for promoting growth, and thus the yield. The waste produced such antibiotic use builds up antibiotic pollution. Biologically resistant antibiotics are found in soil and natural water resources as well as manure in measurable concentrations. Such antibiotic wastes, if not treated properly, would lead antibiotic resistance in microorganisms found in these natural resources, which in turn could be a serious threat to human life.

Keeping all the above in mind, this study aims to research the removal process of tetracyclines, which are widely used veterinary antibiotic, ozonation in both manure and wastewater.

In the first part of the study, cow manure samples that was synthetically polluted with oxytetracycline (OTC), was subjected to ozonation process. The effects of antibiotic concentration, humidity and ozonation processing time to ozonation yield were interrogated. A 40 mg/kg increase in manure OTC concentration resulted in a 20% reduction in antibiotic removal by ozonation. OTC removal yield was found to be about 60% less in humid (50%) manure compared to dried manure. A 59% OTC removal was achieved with 0.3 g ozone/mg OTC in five minutes. However, increasing the processing time to 90 minutes could only achieve a 23% increase in the antibiotic removal yield.

In the second part of the study, the wastewater produced after cleaning of animal barns imitated by mixing two different concentrations of OTC (5-10 mg/L) to synthetically prepared wastewater that was prepared from manure samples. The imitation wastewater purification was tested under two different pH (5 and 8.5), and ozone dose (11g/m<sup>3</sup> and 32g/m<sup>3</sup>) values. To test the effect of defined parameters to ozonation process, eight different experiment sets using 23 factorial design were constructed. Ozonation yield was determined through OTC removal, and variations in bacterial toxicity and BOD5/COD ratio. Almost complete antibiotic removal was achieved by ozonation process, independent of oxidation process conditions. Increasing ozone dose and pH efficiently increased removal rate while antibiotic concentration had a minimal effect, if any. A 1.4 min<sup>-1</sup> OTC removal rate was achieved under high pH and ozone dose conditions. The BOD5/COD ratio was increased almost 10 times with 0.48 g absorbed ozone per liter of wastewater. In addition, initial 20% bacterial toxicity was completely eliminated.

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## OZONATION OF ANTIBIOTICS IN SYNTHETIC PHARMACEUTICAL WASTEWATERS

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Recently various antibiotics have been detected in the effluents of municipal sewage treatment plant and also in natural sources. Antibiotics are classified as emergent pollutants due to their toxic effects to living organisms that would upset the ecological balance. Moreover, the presence of antibiotics in natural systems may lead to the development of multi-resistant strains of bacteria. Wastewater from antibiotic formulation processes in pharmaceutical industry can be a potential source for the environmental pollution with antibiotics if they would not be treated properly.

Considering the above-mentioned facts, the present investigation aimed to study the pretreatment of antibiotic formulation effluent by ozonation process to produce biodegradable products. Four different wastewater bearing cephalosporine (ceftriaxone sodium), penicillin (penicillin VK and amoxicillin), and quinolone (enrofloxacin) group antibiotics at typical concentrations encountered in pharmaceutical formulation effluent were synthetically prepared. The oxidative performance of ozonation was evaluated in terms of COD, aromaticity, and absorbance removal at specific wavelength for the antibiotic active substance, and biodegradability enhancement as BOD5/COD and specific oxygen uptake rate (SOUR), as well as ozone utilization during the course of process. In addition, degradation of antibiotic active substance was verified by HPLC analysis.

The results of ozonation process indicated that the complete removal of each antibiotic active substance was achieved within the short time period. Depending upon the type of antibiotic 65-81% COD and 20-98% aromaticity (UV254) removals were obtained with a 2.96 g/L.h applied ozone dosage at pH=7 (COD<sub>i</sub>=900 mg/L). Ozonation brought about a rise in the BOD5/COD ratio of enrofloxacin wastewater from an initial 0.02 to a maximum of 0.33 and BOD5/COD ratios of ceftriaxone sodium, penicillin VK and amoxicillin wastewaters were increased from 0 to 0.07, 0.28 and 0.42, respectively, an observation which clearly demonstrated the formation of biodegradable ozonation products. SOUR value of penicillin VK, amoxicillin and enrofloxacin were also enhanced to 26, 13 and 35 mg O<sub>2</sub>/g MLSS.h by the application of ozonation for an hour, while for ceftriaxone sodium, this value was increased only to 8 mg O<sub>2</sub>/g MLSS.h in accordance to BOD5/COD ratio.

The combination of UV or H<sub>2</sub>O<sub>2</sub> with ozone did not improve the treatment efficiency of enrofloxacin formulation wastewater in terms of COD removal. On the other hand, by the application of photolytic ozonation, about 20% increase was provided in UV254 removal and oxygen uptake rate of enrofloxacin formulation wastewater compared to that of mere ozonation.

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## THE ADSORPTION OF MTBE ON COALS

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Environmental pollution is an inevitable effect of developing technology. These environmental pollutions are primarily air, water and soil pollutions. One of the organic contaminants causing water pollution is MTBE, methyl tert butyl ether. Since 1979, in order to produce high-grade gasoline, MTBE has been using as an additive material for gasoline instead of Pb and Mn compounds. Exhaust emission considerably decreases if gasoline mixture contains certain amount of MTBE. However MTBE could easily mix to water and soil by the way such as leakage of pipeline and storage tanks and so on. It is well known that MTBE has toxic and harmful effects on muscle and nerve system and it causes unpleasant smell and taste in water even very low concentrations. In order to remove harmful effects of MTBE, it is required its concentration in water to be less than 20 ppb. The removal of MTBE in water is too difficult due to its high solubility and resistance to chemical decomposition.

To remove the organic compounds in water, the most effective method is the adsorption of them on the activated carbon. Granular activated carbon and some synthetic resins are good adsorbents for MTBE at lower concentrations, however these adsorbents are so expensive. It is necessary to use cheap and abundant materials in nature to make the adsorption process feasible. Therefore a bituminous coal and a lignite have been chosen as adsorbents in this study.

In this research, these abundant materials (bituminous coal and lignite) that have different chemical and porous structures have been used to adsorb MTBE in water. Three different size fractions (-212  $\mu\text{m}$ , 212-300  $\mu\text{m}$ , +300  $\mu\text{m}$ ) of each coal were used in adsorption tests. The BET surface area and particle size distributions of the coals were performed for characterisation. The adsorption results were evaluated in terms of Langmuir and Freundlich adsorption models. Depending on the initial MTBE loadings, the type and particle sizes of the coals, considerable amounts of MTBE were removed from water. Our findings showed that the coals used in this study may be used to be able to remove MTBE in water.

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## NUTRIENT CONCENTRATIONS IN THE INNER SARONIKOS GULF AFTER THE SEWAGE SECONDARY TREATMENT

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The environmental quality of Saronikos Gulf has been studied during the last fifteen years, within the framework of a monitoring program, providing important evidence of environmental change and increasing our ability to manage the ecosystem of Saronikos Gulf, especially after the operation of the Sewage Treatment Plant on the Psittalia Island.

In this paper we present the nutrient distributions of the last year investigation (September 2005 – September 2006) in the Inner Saronikos Gulf after the operation of the Secondary Sewage Treatment Plant, in order to assess the environmental impacts of the secondary treated sewage discharge of the city of Athens.

The inner Saronikos Gulf is rather shallow (maximum depth ~100m) and is affected by the Athens municipal treated sewage outfall that is discharged south of the Psittalia island. Until 1994, the sewage of the city of Athens was discharged untreated into the surface waters of Saronikos Gulf. Since 1994, the sewage generated by the city of Athens (population more than four million) has been primarily treated in Psittalia Treatment Plant, and since the end of the year 2004 the sewage of Athens city has been secondary treated. The treated sewage effluents are discharged into the Inner Saronikos Gulf through multi-port diffusers in water depth of 63 m.

The oceanographic data collected monthly over a grid of 5 main stations in the Inner Saronikos Gulf during one year (September 2005 – September 2006). During the warm period (May–November), the sewage plume has been detected in the pycnocline or below it at depths >50m, whereas during winter, the sewage plume has been detected at the surface of the water column.

The sewage plume is characterised by relatively high nutrient concentrations (ammonium, phosphate and nitrite). The highest nutrient values recorded at the station located close to the Psittalia sewage outfall which is affected directly by the sewage outfall, for the period September 2005 – September 2006 was 1.330  $\mu\text{mol/L}$  (in September 2005 at 50m) for phosphate, 19.20  $\mu\text{mol/L}$  (in September 2005 at 50m) for ammonium and 1.105  $\mu\text{mol/L}$  (in October 2005 at 50m) for nitrite. Nitrate and silicate concentrations showed an increase with depth as well as with distance from the sewage outfalls, which probably is related to organic load mineralization.

It is noteworthy, that high nutrient concentrations were recorded near the bottom of the stations located southwest of Psittalia during the year, with the only exception in February 2006, due to the low temperature and the homogenization of the water column.

The temporal variation of nutrients during the period 2000 – 2006 in the Inner Saronikos Gulf showed a slightly decreasing trend, which cannot yet be related for certain to the operation of the secondary sewage treatment plant

## STABILIZATION OF HEAVY METALS BY USE OF CONSTRUCTION AND DEMOLITION RESIDUES (CDRS): A PRELIMINARY APPROACH

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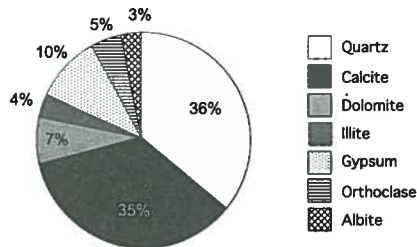
The capacity of residues from construction and demolition activities (CDRs) for immobilizing heavy metals in contaminated soils was studied. For this purpose, a high number of lixiviation tests have been performed.

In accordance with the Spanish legal provisions, (RD January 18, 2005) it is necessary the development of in situ treatments for residues, avoiding the generation, transport and elimination of these materials. The use of in situ methods is also recommended by EPA as a suitable methodology.

The aim of this study was to evaluate the possibility of using residues coming from construction and demolition activities, or residues coming from the mining of calcareous materials, as immobilizing agents of metals.

Physico-chemical and mineralogical characteristics were determined in contaminated soils and in the residues used as possible stabilizers. The results suggest that in addition to their suitable use as soil amendments, these materials have a great potential for the purpose considered here.

	Contaminated soil ppm	Lixivates mg/day.m <sup>3</sup>	% Retention
Zn	34275	17	75
Pb	6123	5	90
Cd	15742	6	80



Results of leaching tests using a 1:1 CDR : Contaminated soil mixture

	<2 μm	2-50 μm	>50 μm	% CaO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% Others
CDR's	18.3	38.3	43.2	33.2	30.2	88.3	28.3
Contaminated Soil	16.2	36.4	39.6	3.9	38.8	15.3	42.0

Average granulometric and chemical composition

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## PRODUCTION OF METHANE FROM DISTILLERY WASTEWATER USING ANAEROBIC CO- DIGESTION

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Anaerobic digestion offers the advantage of energy gain by producing biogas. The co -digestion process, which can be defined as the simultaneous treatment of two or more organic waste streams by anaerobic digestion, offers great potential. In addition, there are a lot of benefits of co-digestion: improved balance of nutrients, synergistic effect of microorganisms, increased load of organic matter and better biogas yield. In areas, where large industrial complexes are limited, co-digestion of different agricultural and industrial effluents is an attractive method for environmental protection and energy savings. There are a number of wastewaters readily available for anaerobic digestion deriving from olive oil production, table olive processing industries and winery – distillery activities that leads to extensive soil and water pollution due to high COD, TKN, and TP concentrations by low pH. Those effluents can be digested together with pig breeding wastewaters under synergistically increase biogas production.

Within this study, combined anaerobic digestion of distillery wastewater with pig manure, was investigated under thermophilic conditions (55o C) during a period of three weeks. The cumulative methane production reached 450 ml CH<sub>4</sub> /g VS (volatile solids) after 20 days, while TKN and COD removal was high. These results indicate a promising solution for distillery and pig breeding wastewater treatment.

The aim of the present work was to investigate how a thermophilic digestion system will react by the addition of distillery wastewater to pig manure in a co-digestion process. COD removal, VFAs concentration, pH variation as well as methane production in the laboratory scale experiments were monitored.

**Key words:** Anaerobic co-digestion, biogas production, pig manure, distillery wastewater.

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## BIOSORPTION OF COPPER (II) FROM AQUEOUS SOLUTIONS BY USING SACCHAROMYCES CEREVISIAE

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The discharges of heavy metals from industrial activities are major environmental problem due to their accumulation in organisms and causing toxicity. Recently, low-cost adsorbents such as yeast, algae, and bacteria were used for heavy metal removal from wastewaters. Therefore, in this study *Saccharomyces cerevisiae* yeast was used in order to remove Cu (II) from aqueous solutions. *Saccharomyces cerevisiae* yeast is an inexpensive, commonly available, source of biomass.

The effects of initial pH (1-6), contact time (5-1440), initial Cu(II) concentration (25-200 mg/L) and temperature (25-45oC) were investigated in a batch experimental system. Optimum pH value of biosorption by yeast was found to be 6 for this study. The maximum adsorption capacity of *Saccharomyces cerevisiae* was determined as 49 mg/g for Cu(II) metal biosorption at optimum experimental conditions (pH 6, contact time 24 hour, yeast dose of 1g/L, initial Cu(II) concentration of 100 mg/L, temperature 25oC).However, maximum biosorption of Cu(II) by *Saccharomyces cerevisiae* was obtained at temperature of 45oC as 66mg/g. It could be concluded that copper biosorption by *Saccharomyces cerevisiae* increased with increased temperature in the range of 25-45oC.

The experimental equilibrium data fitted to Freundlich adsorption isotherm model. As a result, yeast (*Saccharomyces cerevisiae*), one of the low-cost adsorbents, can be used for removal of copper (II) from aqueous solutions.

**Keywords:** Biosorption, heavy metal, copper, yeast, adsorption isotherm

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**A STUDY ON THE TOXIC SUBSTANCES IN A STREAM  
ORIGINATING FROM DUMPSITE OF A TOWN ( Sivrice, Türkiye)**

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The present study aims at determining the heavy metal pollution generated from domestic solid wastes (dump sites) of a town which is stored along the bank of a stream. For this purpose five sampling sites were selected along the stream. First sampling site is chosen from the upper part of the stream as a reference station. Three stations were in the middle and lower parts of the stream along which domestic solid wastes are spreaded over. The last station is located at the region before the stream discharges into Lake Hazar which has a great significance for both fisheries and recreation purposes. From selected sites, water and sediment samples were collected at monthly intervals during the wet season when runoff was possible. The concentrations of Fe, Cu, Cr, Co, Zn, Ni, Mg, Ca, As and Pb in both water and sediment samples were analyzed by means of an Atomic Absorption Spectrophotometer and ICP. Water temperature pH and conductivity of stream water were measured in the field. Heavy metal concentrations in water samples were found decrease in sequence of Mg>Ca>Fe>Cu>Cr>Ni>Zn and in sequence of Ca>Mg>Fe>Cr>Co>Cu>Ni>Zn in the sediments. Heavy metal concentrations in sediments were found to be by far higher than that recorded in water samples. The concentrations at the sites adjacent to domestic solid wastes were higher than that recorded in the clean water region. These findings may indicate the existence of heavy metal contamination in the parts of the stream originating from water percolating through dump site. The values of each heavy metal at each sampling station were compared with those of water quality criteria of EPA and Environment Canada.

**Key words:** Heavy metal, dumpsite, Kürk Stream, Lake Hazar, Türkiye



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## SOIL FACTORS RELATED TO HEAVY METAL BIOAVAILABILITY AFTER SEWAGE SLUDGE APPLICATION

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The aim of this study is to know the influence of some soils properties (texture, oxidable organic carbon, pH, carbonates and electrical conductivity) on heavy metal bioavailability (Zn, Cu, Ni, Cd, Cr and Pb) in barley (*Hordeum vulgare*) after the use of two sewage sludges (with high and normal heavy metal contents) as soil amendments. It is also an objective of this work assessing if the extraction with DTPA is a good method to estimate bioavailability.

For these purposes, 36 agricultural soils were selected (Table 1). Two kinds of sewage sludge were applied to each soil with a doses of 50 t/ha. The first one (common level of HM, Table 2) was obtained from the wastewater treatment plant of Aspe (Alicante, Spain) and the second one (polluted sludge, Table 2) by adding salts of the metals to the first one. The soil/sludge mixtures were done along all the soil thickness, and were placed in cylindrical plastic pots (11 cm length, 11.5 cm internal diameter). Assays were performed in triplicate.

**Table 1. Ranges and means of the soils used in the study.**

	pH	EC( $\mu$ s/cm)	CO <sub>3</sub> <sup>2-</sup> (%)	Ox.OrgC(%)	Sand (%)	Lime (%)	Clay (%)
Range	5.48-9.09	38-2370	0.02-78.70	0.22-2.00	22.46-90.46	2.14-59.71	0.54-39.47
Mean	8.13	277.1	25	0.81	60.79	22.87	16.3

**Table 2. Total and extractable with DTPA heavy metals in common and polluted sewage sludge.**

	Cu (ppm)	Zn (ppm)	Pb (ppm)	Ni (ppm)	Cr (ppm)	Cd (ppm)
Common	206.98/22.75	646.06/94.52	38.98/8.69	14.30/4.40	35.62/2.24	0.84/0.05
Polluted	1704.88/358.91	4021.15/1687.13	1086.09/201.88	372.11/253.07	1989.65/3.64	39.87/18.21

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The experiment was carried out in a greenhouse (mean temperature and relative humidity of  $22 \pm 5^\circ\text{C}$  and  $70 \pm 10\%$ , respectively). Soils mixed with sludge were kept at approximately 60% VHC with deionized water by weighing periodically, and they were incubated for four weeks before planting out the seeds. Thirty-five Barley seeds were sown per pot and reduced to twenty plants after two weeks. The plants were harvested eight weeks after sowing.

The plants were separated into shoots and roots, and soil samples were collected from each pot. Total and extractable-DTPA heavy metals were determined in roots and soils respectively. Additionally, two small pots with the same mixtures, but without plants, were used (per treatment) in order to check the bioavailable heavy metals. One was analyzed before seedling and after the incubation period, and the other at the same time that the plants were harvested, to check the effects of plants in the extraction with DTPA.

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## EFFECTS OF EXTRACELLULAR POLYMERIC SUBSTANCES (EPS) AND PHYSICO-CHEMICAL PROPERTIES OF ANAEROBIC GRANULES ON SLUDGE SETTLING

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An upflow anaerobic sludge blanket(UASB) reactor with a volume of two liter was operated at constant VLR (12.5 kg COD /m<sup>3</sup> day) The effect of substrate type(molasses, dye and chemical industry ) on the extracellular polymeric substances (EPS material) and on the surface charges of the granules was evaluated for the sludgesettling in the UASB reactor. A high diameter floc (2.3 mm), high biomass concentration (35-78 g/l,) high methane percentage(72%) optimum SVI and low water content (55%) of sludge was observed in the reactor feeding with molasses and dye containing wastewaters. The COD removal efficiencies and effluent VFA were 98% and 200 mg/L in reactor feeding with molasses, respectively. Lower sludge size and lower water content of of sludge in molasses feeding reactor provide a good performance for dewaterability of anaerobic sludge. The extracellular polymeric substances (EPS) and protein content are high in reactor feeding with molasses. Increases of volumetric loading rate (VLR) cause increases in EPS production. It was observed that there is a close relationship between EPS, granule diameter, granule quality.

As the substrate concentrations increased the surface charges increased in all reactors. The surface of sludge is negatively charged in UASB reactor feeding with molasses and dye industrywastewaters. The sludge surface in UASB reactor feeding with molasses exhibits low surface charges while the surface charge of granules(sludge) in the dye and chemical waste water feeding sludge are high negatively charged.

The specific methanogenic activity (SMA) is higher in granules feeding with molasses and dye wastewater compared to the other substrate used . The results showed that sludge surface properties depend to the substrate properties. Furthermore granule diameter, SMA of sludge, EPS content and the surface charge affect the settleability (sludge volume index) and dewaterability of anaerobic sludges feeding with molasses and synthetic dye wastewater.

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**PROGRESS IN USE OF FERRATE (VI) AS AN OXIDANT  
WASTEWATER TREATMENT: OXIDATION OF P-COUMARIC ACID  
AND VANILLIC ACID BY FERRATES K<sub>3</sub>FeMnO<sub>8</sub>**

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Oxidation of p-coumaric acid and vanillic acid, representative compounds of the polyphenol typically found in olive processing and wine-distillery wastewaters, has been investigated using ferrates K<sub>3</sub>FeMnO<sub>8</sub>. The iron (Fe VI) is derivated from K<sub>3</sub>FeMnO<sub>8</sub> which has properties such as high stability, oxidizing power. Fe (VI) product non-toxic elements at the base of Fe (III); thus, this makes ferrate (VI) an environmentally friendly oxidant for wastewaters.

This paper aims to explore K<sub>3</sub>FeMnO<sub>8</sub> as an alternative olive-mill wastewater (OMW) chemical treatment.

Herein, the removal of polyphenolic acid by environmentally-friendly oxidant, ferrates (VI) K<sub>3</sub>FeMnO<sub>8</sub>, is sought by studying the reaction time oxidation between Fe (VI) and polyphenolic acid as a function of pH and concentration of ferrates. In dilute solutions (10<sup>-4</sup>M), contaminants are removed by Fe (VI) in minutes. From different analytical techniques (HPLC/MS and GC/MS), various intermediate compounds have been reported.

**Keywords:** Ferrates K<sub>3</sub>FeMnO<sub>8</sub>,; iron (VI); Vanillic acid; p-Coumaric acid; wastewater; environmentally friendly Oxidant; chemical treatment; olive mill wastewater.

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## HEALTH-CARE WASTE MANAGEMENT IN COASTAL AREAS

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Rapid developments in medical technology and increased packaging have contributed to huge expansions in the volume of medical waste produced in Turkey. Much of the problem, however, lies not in the increasing volume of infectious waste but in the large quantity of nonhazardous solid waste with which it becomes mixed. Despite training programs, much non hazardous waste ends up in the red bags designating medical waste; once it finds its way into a red bag, even a soda can or a paperclip must be treated as potentially infectious.

In order to control the medical wastes, the implemented Turkish Medical Waste Control Regulation (TMWCR) came into force in the year 2005, as a part of the Environmental Act. According to the regulation, all healthcare institutions are obliged to collect, transport and store medical wastes as mentioned in the regulation whereas the Metropolitan Municipality is responsible for the final transportation and disposal of these wastes.

Medical wastes generated in the hospitals in Antalya Province, are transported in special transport vehicle and dumped in the, mostly, unsanitary landfills. The management of these wastes generated along the 640 km coastal zone has its difficulties.

In Antalya city proper waste management is carried out. The wastes are collected and deposited in the sanitary landfill of the city in accordance with the legislation. In the hospitals, especially in the Akdeniz University Hospital substantial improvements regarding waste minimization and separation at source is achieved. But unfortunately the same improvements in the health care facilities along the coast couldn't realize.

The amount of waste produced by the year 2020 is calculated as 20 tons/day. Nearly half of it will be produced in facilities along the coastal zone. Due to high summer population, lack of suitable land, scattered facilities and stringer environmental issues, it is not possible to solve the problem at source. A regional solution considering the province as a whole is needed.

In scope of this study a sustainable health care waste management scheme (production-end disposal), concerning the whole province is developed.

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## COMBATING BULKING SLUDGE WITH PHYSICAL AND CHEMICAL METHODS

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The successful application of the activated sludge process requires that the sludge floc settles and compacts well in the settling tanks. The major problem in activated sludge operation is the development of poor settling sludge. When this occurs, suspended solids (SS) pass to the effluent in concentrations that often exceed regulatory standards for SS and other discharge parameters. Many sludge settling problems can occur, and their causes are not the same. One of the most commonly identified activated sludge solids separation problems is caused by filamentous bacteria.

Non-specific methods are often used to combat with bulking or floating sludge. The use of strong oxidizing agents such as chlorine and hydrogen peroxide is among these methods. One disadvantage of using chemicals is that floc forming bacteria are also influenced negatively. This can lead to the failure of the treatment process. Additionally the use of chemicals results in an increase in sludge mass, which has to be disposed. During the last years the use of lowfrequency ultrasound to combat filamentous organisms in bulking sludge is gaining importance.

The use of ultrasound is mainly linked to one characteristic aspect of powerful sound fields in liquids – the acoustically induced cavitations. This means the formation of vapor filled bubbles due to the alternating pressure conditions. It is reported that as a result of sonication, the thin filaments are much more exposed to the shearing forces than the flocs and are cut up into small pieces. Since the remaining flocs are not interconnected by filamentous organisms any longer, the activated sludge bulky flocs become smaller and much more compact after sonication. Additionally, the settling properties of the activated sludge would be improved. And due to the smaller sizes, bacteria are better supplied with substrate, which increases their selection advantage against the filamentous organisms.

Bulking sludge phenomena is also a serious problem in treatment plants located along the coastal zone of Antalya. The main goals of this study are the identification of filamentous microorganisms found in the aeration tank of the Antalya main WWTP (75000 m<sup>3</sup>/day) and determination of the effectiveness of physical-chemical methods on combating these micro organisms. During the study the average SVI is determined as 241 ml/g which indicates bulking characteristics of the sludge. In samples which are taken from the aeration basin, the filamentous bacteria are identified according to "Dichotomous identification key" according to Jenkins, D. The identified major organisms are type 1701, type 021N; *Microthrix parvicella*; *Thiotrix* spp. and *Sphaerotilus natans*. Combating the filamentous bacteria with sonication resulted that ultrasound application has affected the floc structure of the activated sludge and improved the settleability of the sludge. Similar results are achieved with chlorine and hydrogen peroxide applications.

In this study the results of the experimental work conducted in the main WWTP of Antalya will be introduced in detail.

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## SLUDGE MANAGEMENT PROPOSAL FOR TOURISTIC COASTAL AREAS

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Antalya Province which is located on the Turkish Mediterranean coast is the most preferred tourism destination in Turkey. The local economy is based on tourism and any problem on the coastal zone will have negative effects on the tourism. For that reason, planning, design and implementation of the treatment plants located in this region have to be managed carefully to control pollution and to protect the environment. Along the coastal zone of Antalya there are more than 20 regional waste water treatment plants and, additionally numerous plants of the hotels under operation. These plants based on biological processes. As the quality of the treated waste water accomplishes with the discharge standards of the Turkish Water Pollution Control Regulation which is in accordance with Water Framework Directive, there is no need to consider it as a pollution source. But, however, the treatment and disposal of the produced waste water sludge is the remaining problem which could not be solved yet.

Presently, sludge use and disposal options include biogas production, land application, cocomposting, landfilling and incineration.

Land application is the largest beneficial use for sewage sludge. Since municipal sludge are a by-product of the foods we eat, they contain important nutrients such as nitrogen, phosphorus and potassium. Proper land application provides a way to recycle these nutrients and return them to the soil safely. Sludge can also be processed into heat-dried pellets that are marketed as fertilizers and soil conditioners. The pelletization process also reduces disease causing organisms. Golf courses, parks, cemeteries, nurseries and municipal landscaping projects provide markets for pelletized sludge products.

Composting is another way to recycle nutrients and organic matter in sludge. The benefits obtained from using sludge composts include increased water and nutrient-holding capacity and increased aeration and drainage of soils. Composted sludge also provide the soil with low levels of plant nutrients. Sludge compost is currently being produced and marketed by municipalities in the EU.

Currently the sludge produced in the province is not used in the agriculture and incineration is too expensive. Therefore as alternative disposal methods energy recovery via biogas production, landfilling and co-composting are remaining.

In this study based on the amount and the characteristics of sludge produced in the treatment plants along the coastal zone, regional sludge management scheme is developed.

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## THE USAGE OF GIS IN LANDFILL SITE SELECTION

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Antalya, Turkey

Most of the municipal solid waste generated in Turkey is disposed via landfilling. Only a little amount of municipalities dispose the wastes in sanitary landfills. The majority of the 3617 municipalities dispose the generated waste in unsanitary landfills. In frame work of the EU assessment process increased attention is given for the construction of new landfills. It is proposed that for the next 10 years more than 80 new landfills should be constructed. Parallel with the escalation of environmental degradation and awareness, municipal landfill siting is becoming increasingly difficult. Especially along the coastal zone of Antalya the suitable areas are very rare. In spite of accordance with the regulations, a suitable site can not be accessed due to NIMBY sendrom induced reactions of the neighborhood. It is calculated that the amount of waste to be landfilled will vary between 7.5 million m<sup>3</sup> and 2.7 million m<sup>3</sup> by the year 2030, according to the degree of waste separation at source. In scope of this study suitable landfill area with 2.5 million m<sup>3</sup> is investigated.

As it is evident that many factors must be incorporated into landfill siting decisions, it is also important to consider that many of these criteria conflict. Balancing the importance of these variables is very difficult and has posed challenges to decision makers. This study will attempt to utilize a Geographical Information System (GIS) approach to determine an optimal landfill siting along the coastal zone of Antalya. MapInfo will be used as the GIS tool since it is able to perform suitability analysis using Multi-Criteria Evaluation (MCE) analysis. A MCE analysis investigates a number of possible choices for a siting problem, taking into consideration multiple criteria and conflicting objectives. Weights will be generated for each factor using a pair-wise comparison and the eigenvector weight function. These weighted factors will be combined with constraint maps that create areas of absolute unacceptability.

In framework of this study, in order to make use of the GIS tool, several maps of the region are prepared: Geomorphology, soil properties, land use, land value, land slope, proximity to water bodies, proximity to streams, distance to population centers, proximity to local wells are digitized. For the final decision, map-layer screening approach is conducted for siting the landfill and the final map that identifies regions that are most suitable for the location of a landfill site is generated.

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## PACKAGING WASTE MANAGEMENT: ANTALYA CITY CASE STUDY

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After realizing the reality of natural resources is unlimited, need for finding suitable methods of recycling, recovering and reusing of waste materials have been taken much more attention. These methods are extremely important considering the packaging waste material proportion is 35 % of the total solid wastes in Turkey. Increased life expectation and development of packaging industry resulted in widespread usage of packaging material. Since the percentage of packaging material in total solid wastes is in increasing trend, recycling and recovering of packaging material became economically valuable. Approximately one million tone of packaging waste is recovered each year in Turkey. Significant amount of these wastes are collected from the streets and landfills under the unsanitary conditions. Separation of recoverable wastes at source is necessary to create more efficient recycling system. In order to achieve sustainable packaging waste management in Turkey, "Packaging and Control of Packaging Waste Material" law based on EU Directive of Packaging Waste Material (94/62/EC) came into force in 2004.

To provide sustainable packaging waste management, a project covering the aspects of sustainable waste management was initiated in a pilot region of Antalya Muratpaia Municipality in 20 888 houses. This project is extended to the whole Antalya City within 5 years. The waste composition in pilot region is determined as follows: paper (66 %), glass (17 %), plastics (12 %), metal (3 %) and 2 % non-recyclable material. Enlargement of the project to the whole Antalya City and recycling of metal, paper, plastic and glass packaging waste will not only protect natural sources but will also provide economical gain, energy savings and reduction landfill space. This project will also contribute to reach EU Landfill Directive aimed to decrease the amount of waste which will be landfilled to 50 % till year 2009 and to 35 % till year 2016. In this study, the results of the project will be evaluated and proposals for sustainable packaging waste management in Antalya City will be introduced .

Key Words: Packaging waste management, Recovery, Recycling, Reuse, Separation at source

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## THE DETERMINATION OF SELECTED „MUSK“ COMPOUNDS IN WASTE WATER AND SEWAGE SLUDGES

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Synthetic musk compounds are fragrance substances commonly used as fragrant constituents of detergents, cleaning and washing agents, and cosmetics (creams, perfumes, deodorants). At present, there are more than three thousand synthetic fragrances being used for perfuming commercial products. However, some musk compounds have proved to accumulate in the environment as well as in mammal tissues of human body, and hence classified as persistent organic pollutants (POPs). Recently they have been analyzed in different compartments of environment especially in water ecosystems where they get after application via waste water.

This thesis was focused on some synthetic fragrances produced by the AROMA Prague Co. This thesis deals with optimization of analytical methods for analysis of musk compounds and their later analysis in water samples. Semipermeable membrane devices and solid phase micro-extraction were considered as optimal methods for analysis of these compounds in water. In both cases the analysis was carried out by high resolution gas chromatograph coupled to mass selective detector. Musk compounds were finally detected in the influent and effluent of Brno waste water treatment plant and waste water treatment plant of Brno University of Veterinary and Pharmacy with the use of optimized methods.

The aim of this study was to perform optimisation of a method for determination of selected fragrances in sewage water and sewage sludge. Different extraction techniques for the separation of studied compounds from solid matrices were compared. The identification and quantification of analytes was also carried out by high resolution gas chromatography - mass spectrometry (HRGC/MS).

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**A RAPID METHOD FOR DETERMINATION OF TOTAL LAS IN SEWAGE SLUDGE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) AND CAPILLARY ELECTROPHORESIS (CE) AFTER MICROWAVE EXTRACTION**

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Linear alkylbenzene sulfonates (LAS) are the most common synthetic anionic surfactant used in domestic and industrial detergents, with a global production of  $2.4 \times 10^6$  tonnes per year. After use and disposal, LAS may enter the environment by one of several routes, including by direct discharge to surface water or discharge to water from sewage treatment plants. Sewage treatment plants break down LAS only partly: some of them remain in effluent and other fraction is adsorbed in sewage solid. A rapid method for the extraction and determination of total LAS from sewage sludge based on microwave extraction and HPLC-FL and CE-UV determination is proposed.

The main factors affecting the extraction efficiency (extractant volume, microwave power and irradiation time) were optimised using a fortified sludge. The extraction of total LAS is carried out by using an extraction time of 10 min and 5 mL of methanol.

For HPLC-FL determination, mobile phase acetonitrile-water was used, comprising 60 % (v/v) from 0 to 1 min and a flow rate of 1 ml min<sup>-1</sup> programmed to 100% acetonitrile between 1 and 2 min and a flow rate of 2 ml min<sup>-1</sup>. The final composition was maintained for a further 5 min.

The determination of total LAS by CE-UV was performed in a borate buffer (10 mM, pH=8.8). The separation voltage was 20 KV and the temperature of the capillary was 25 °C. Injections were performed in the pressure mode and the injection time was set at 5 s. The determination of total LAS is carried out in less than 7 minutes. The method did not require clean-up or preconcentration steps. Detection limit for total LAS in the sludge was < 5 mg Kg<sup>-1</sup> using both determination methods.

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**EVOLUTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)  
AND HEAVY METALS IN SLUDGE SAMPLES FROM CONVENTIONAL  
WASTEWATER TREATMENT PLANTS.**

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This paper presents results on the presence and evolution of PAHs and heavy metals for a conventional activated sludge wastewater treatment plant (WWTP). PAHs analysed were the 16 PAHs recommended by the EPA. On the other hand, 13 heavy metals were studied (Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Ti and Zn). The physico-chemical soil parameters were measured in triplicate by standard methods approved by the Spanish legislation (MAPA, 1986) for soil analysis and standard techniques compiled by the APHA (APHA-AWWA-WPCF, 1992).

The sewage sludges originated from the Guadalete WWTP site in Jerez de la Frontera (Cádiz, Spain). PAHs were extracted from the sewage sludge by microwave energy. High performance liquid chromatography coupled with diode array and fluorescence (HPLC-DAD-FL) detectors were used. Heavy metals were analysed by ICP-AES.

The results showed that total PAHs concentration (sum of 16 EPA PAHs) varied between 6757  $\mu\text{g g}^{-1}$  dry matter (DM) for compost and 4176  $\text{ng g}^{-1}$  DM for secondary sludge. The most abundant PAH was pyrene. The highest concentrations of heavy metals were also found in compost (1035  $\text{mg kg}^{-1}$  DM) and lowest concentration in secondary sludge (485  $\text{mg kg}^{-1}$ ).

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## ARSENIC REMOVAL FROM WATERS BY ZERO-VALENT IRON: COLUMN STUDIES

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Pollution of water resources by arsenic is a well-known environmental problem that can pose severe human health implications. The occurrence of arsenic in groundwater is due to natural processes such as weathering of arsenic minerals as well as to anthropogenic activities including mining, industrial waste discharges and application of certain herbicides and pesticides. The most common forms of arsenic occurred in groundwater are As(V) (arsenate) and As(III) (arsenite); arsenite is more toxic and more mobile than arsenate. High arsenic concentrations in groundwater have been found in several countries. According to European legislation, the arsenic concentration in drinking water should be below the limit of 10ng/L (98/83/EC). Relatively high concentrations of arsenic, exceeding the proposed limit, have been determined in many areas in Greece.

Several technologies have been proposed for the removal of arsenic from waters such as coagulation, precipitation, ion exchange, reverse osmosis, nanofiltration and adsorption. Zero valent iron (ZVI) is a material that has been used for the removal of several organic and inorganic contaminants from aqueous samples. This material has been also used for the arsenic removal. The removal efficiency of ZVI depends on the type of ZVI material, the composition of groundwater, the arsenic concentration and the speciation of arsenic in treated water and the experimental conditions.

In this study the arsenic removal efficiency of zero valent iron was investigated. Columns loaded with fine and coarse sand and ZVI were employed. The experiments were conducted using tap water spiked with arsenate, arsenite, and a mixture of arsenate-arsenite which passed through the columns downward using a peristaltic pump. The pH and Eh values and the concentrations of total arsenic, arsenate, arsenite, total iron and ferrous iron in treated water were measured. Arsenic was measured by using hydride generation with flame AAS (HG-AAS). Speciation of arsenic was performed by passing the samples through arsenic speciation cartridges. Total Fe was measured by flame AAS and Fe(II) was measured by a UV-Vis spectrometry using the phenantroline method. The efficiency of arsenic removal by ZVI was evaluated using field water samples with different physicochemical characteristics and naturally occurred arsenic concentrations.

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## HEAVY METALS SPECIATION IN SEWAGE SLUDGE STABILISED WITH FENTON'S REAGENT

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Analysis of total heavy metals concentration in sewage sludge is not suitable as a way of the assessment of their impact on the environment and living organisms. Toxic effect of heavy metal compounds is connected with their bioavailability. That is the reason for the necessity of speciation of heavy metals in the sludge. Heavy metals speciation is especially important during chemical stabilization of sewage sludge with strong oxidants in acidic environment, e.g. Fenton's reagent. At low pH heavy metals are much better leachable than under neutral conditions. During chemical stabilization also oxidation of organic matter occurs. This process may affect the form of heavy metal compound in the sludge.

The aim of the investigation was to evaluate changes in forms of metal compound in the sewage sludge stabilized with Fenton's reagent (0.5 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 1 to 100  $\text{cm}^3$  of  $\text{H}_2\text{O}_2$  per 10 g of the sludge). Stabilisation lasted for 1 h at room temperature. Metals speciation was performed before and after chemical stabilization of the sludge. The results indicate that in acidic environment metal compounds were leached from the solid phase to the supernatant, however no correlation was found between the dose of Fenton's reagent and the amount of the compounds leached. The changes in the forms of heavy metals in the sludge before and after chemical stabilization weren't statistically important.

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## CHANGES OF SELECTED MICROPOLLUTANTS CONTENT IN CHEMICALLY STABILISED SEWAGE SLUDGE

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Polycyclic aromatic hydrocarbons (PAHs) and adsorbable organic halogens (AOX) are ubiquitous pollutants of sewage sludge. Due to their toxic and mutagenic properties evaluation of their fates during stabilisation processes of sewage sludge is of great interest. In 2000 European Union has developed the draft of a working document on sludge which included limit values for selected organic compounds, including PAHs and AOX.

The present study has been conducted to evaluate the fates of PAHs and AOX in supernatant during chemical stabilisation of sewage sludge with Fenton's reagent.

Chemical stabilisation was performed with supernatant separated from digested sewage sludge. 1 L of supernatant were filled into 2 -L glass reactors and chemically stabilised with 1 g of solid  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 7,5 to 150 mL of  $\text{H}_2\text{O}_2$  (30%) per L. Stabilisation lasted for 2 hours at room temperature.

Total PAHs concentration in supernatant was equal to  $10.1 \mu\text{g.kgd.m.}^{-1}$ . The most abundant compounds were phenanthrene and fluoranthene. The less abundant ones were 6-ring compounds. Chemical stabilisation of supernatant with Fenton's reagent significantly decreased PAHs content in supernatant, however no correlation was found between dose of Fenton's reagent and concentration of individual compounds.

In contrary to the behaviour of PAHs, AOX concentration in supernatant increased after chemical stabilisation with Fenton's reagent.

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## IMPACT OF SEWAGE SLUDGE ADDED TO THE SOIL ON LEACHING PAHs, PCBs AND AOX

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PAHs, PCBs and AOX are the most toxic hydrocarbon among EPA-list recommended to checking up in environment. It has to be taken into account not only valuable compounds of soil but also these that can be accumulated in soil and have toxic influence on microorganism. In spite of low solubility, PAHs, PCBs and AOX could be leached from deposited industrial wastes and from stored sewage sludge with smallest particles by rain fall and could migrate in water and soil. The objective of that researches were determination of dynamic of PAHs, PCBs and adsorbable organic halogens (AOX) leaching by water from soil amended with sewage sludge. Sewage sludge from municipal biological and chemical treatment plant was used during studies. In the studies stabilised sewage sludge was used and sewage sludge modified on calcium oxide (CaO). Sewage sludge was added to soil samples in the range 5 g dry mass /L. Control sample was soil without sludge amendment. Leaching were done under static conditions. Static leaching was lead using water extract method. A liquid to solid phase (dry mass) ratio (L:S) was 10:1. Sterile water three times was added to soil and soil with sewage. The water extracts was carefully separated from solid phase. PAHs, PCBs and AOX concentration determined in solid samples and in water extracts. The content of 16 PAHs listed by EPA and 7 kongeners of PCBs were determined. Gas chromatography - mass spectrometry (GC-MS) was used to qualification and quantification of PAHs and PCBs. AOX were determined according to DIN EN 1485 procedure by Chemisches Laboratorium Dr.Wessling GmbH and Co.

The results showed the presence of PAHs, PCBs and AOX in the soil and in sewage sludges both in digested and in modified CaO. The highest PAHs, PCBs and AOX concentration were determined in the water extract from soil amended with sewage sludge modified with calcium oxide. Therefore, the application of sewage sludges can influence long term PAHs, PCBs and AOX accumulation in soils. Thus, the monitoring of these organic micropollutants concentration in sewage sludges in agriculture is necessary. On the base of realised studies and obtained results that was concluded that soil amended with sewage sludge under atmospheric falls conditions is real PAHs, PCBs and AOX contamination threat both for water environment and for soil.

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## SPECIATION OF HEAVY METALS IN SOIL AMENDED WITH SEWAGE SLUDGE

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The results of the investigation into leaching of selected heavy metals from soils fertilized by sewage sludges are presented in this study. The studies were carried out using biochemically stabilized and thickened sludges as well using soil originating from an agriculture area. Digested sludges as well as digested, chemically stabilized sludges were added to the soil. The following investigations were made: in the control soil (without added sludges), in the soil with added digested sludge and in the soil with added digested sludge after liming. Selected heavy metals were determined in the above mentioned sludge samples. Form of metal compounds were analyzed before and after sewage sludge amendment.

Then, water extracts in the control soil, in the soil with added digested sludge as well as in the soil with added digested sludge after liming was prepared according to PN-Z-15009. Water extracts were prepared 3-times using redistilled water which was added to the both soil sample and soil with added sludges in the amount considering solid to liquid ratio ( $S/L$ ) =1:10. In the obtaining water extracts the concentration of ions of selected heavy metals was determined. The following heavy metals: Pb, Cd, Ni, Cu, Zn in formerly digested samples were analysed using atomic absorption spectrometer.

The total concentration of 5 heavy metals in the control soil was 5,4 mg/kg.d.m, whereas in the soil fertilized with digested and limed sludges was 389 and 466mg/kg.d.m., respectively.

The sum of studied heavy metals in the extracts obtained from soil containing digested sludges as well as limed sludges was 0,465mg/L and 0,558 mg/L, respectively, whereas in samples taken from the control soil was 303mg/L.

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## THE ANAEROBIC PRE-TREATMENT OF HIGH STRENGTH LANDFILL LEACHATE

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The leachate produced sanitary landfill, can cause environmental hazards due to its very high concentration of contaminants. The production and migration of leachate from a landfill into groundwater and nearby surface waters causes the pollution of these sources and soil. For this reason, the treatment of landfill leachate is necessary prior to ultimate discharge.

The aim of this study was to investigate the anaerobic pre-treatment of sanitary landfill leachate containing high concentrations of organic compounds. The study presented also contains the characterization of young landfill leachate used.

The characterization of leachate was carried out in different seasons of a year. It was observed that the landfill was a young landfill and leachate had high concentrations of contaminants. The characterization of leachate was affected by various hydrological factors.

Since the leachate contained high concentrations of organic matter, it was initially treated in anaerobic reactor. The up-flow anaerobic sludge blanket reactor (UASBR) with a 16.7 L of total volume was used in the anaerobic treatability studies.

The anaerobic treatability studies of leachate contain the determination of optimum hydraulic residence time, the effects of hydraulic residence time, high pH and  $\text{NH}_3$  level on the performance of the organic matter removal. The optimum hydraulic residence time was determined as 2.35 days and the COD removal efficiency of the UASBR was achieved as more than 90%. In the anaerobic treatment, the inhibition of free ammonia may occur when pH is greater than 8. In this study, anaerobic reactor was operated at high pH level without decreasing in removal efficiency and acclimated to elevated pH levels.

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## SURFACTANT DEGRADATION BY MEANS OF PEROXI - ELECTROCOAGULATION

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In the early 1960's occasional instances of foaming were observed both in wastewater treatment plants and in surface waters receiving effluents. This phenomenon was shown to be due to the use in detergent products of a poorly biodegradable surfactant; which, consequently, was insufficiently removed during the treatment process. Industry reacted rapidly by replacing the problematic surfactant with a biodegradable equivalent. Since this time the removal of detergent surfactants in wastewater treatment plants has been the subject of much research; by industry, academia and regulatory authorities.

Surfactants have widely been used in textiles, food, paints, detergents, cosmetics, oil recovery, mining, pulp and paper industries. The anionic types in the present study have relatively low biodegradability. Oxidation methods by ozonation or photocatalytic treatment is a relatively costly method. Peroxi-electrocoagulation method is efficient and less expensive. In this method, hydrogen peroxide was added into the system, fenton reactive has been formed in the process. Hence it would be of much practical and academic interest to look into surfactant wastewater treatment by peroxi electrocoagulation method.

Electrocoagulation (EC) is an electrochemical wastewater treatment technology that is currently experiencing both increased popularity and considerable technical improvements. EC is a complicated process involving many chemical and physical phenomena that use consumable electrodes to supply ions into the wastewater stream. The process has also been employed successfully to treat different industrial wastewaters. The purpose of this study to conduct experimental tests employing the peroxi-electrocoagulation process in treating the surfactant wastewater.

Electrocoagulation is an electrochemical method of treating polluted water whereby sacrificial anodes corrode to release active coagulant precursors (usually aluminium or iron cations) into solution. A kinetic model was adopted to represent the oxidation of surfactant wastewater.

Experiments were conducted to examine the effects of pH, current density, conductivity, amounts of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) on the surfactant removal.

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Two types of tests were performed in the experimental work: Two commercial anionic surfactants were chosen. First group we can examine sodium dodecyl sulfate (SDS), second group we can do the same experiments with sodium dodecylbenzenesulfonate (DBS), then we check the results. The laboratory test system consisted of an electrocoagulator unit with a power supply, ampermeter and voltmeter. Experiments were conducted to examine the effects of pH, and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), waiting period, electrolysis time, NaCl concentration effect, current density and concentration.. The obtained solution was detected directly. All the tests were performed at ambient temperature. The performance of the system is strongly dependent on the working conditions. All chemicals were of analytical grade quality and were used without further purification.

Anionic surfactants can be achieved by the electro fenton reactive, both at laboratory and pilot scale.

**KEY WORDS:** Electrocoagulation, Detergent, Surfactant Wastewater, Fenton Oxidation, Peroxy Coagulation

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## COMPARISON AND MODELING OF THE HYDRAULIC PERFORMANCE OF A MEMBRANE SEQUENCING BATCH REACTOR (MSBR) FED WITH SYNTHETIC WASTEWATER AND LANDFILL LEACHATE

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The aim of this study was to investigate the hydraulic performance of a Membrane Sequencing Batch Reactor (MSBR) for wastewater treatment. A hollow fiber ultra-filtration membrane module was used for the separation of the biomass from the treated effluent. The MSBR was fed for over three months with synthetic wastewater of gradually increasing strength in terms of COD and TN concentrations (COD varied from 465 mg l<sup>-1</sup> up to 4800 mg l<sup>-1</sup>, whereas TN varied from 65 mg l<sup>-1</sup> up to 570 mg l<sup>-1</sup>). For the following six months, the MSBR was fed with "mature" landfill leachate from the municipal solid waste landfill of Thessaloniki (North Greece).

The average quality of the raw leachate was 2456 mg l<sup>-1</sup> COD, 375 mg l<sup>-1</sup> TN and 8.2 mg l<sup>-1</sup> PO<sub>4</sub>-P. During the synthetic wastewater operation, there was a constant increase in the MLSS content of the MSBR (from 3500 mg l<sup>-1</sup> up to 13000 mg l<sup>-1</sup>). The HRT varied between 1.7 and 10 days and the average permeate flux value was around 11.2 l m<sup>-2</sup> h<sup>-1</sup>. During the landfill leachate operation, on the other hand, the biomass concentration varied between 7000 mg l<sup>-1</sup> and 15300 mg l<sup>-1</sup>, whereas the HTR was kept constant at 10 days. The MSBR was run under both supercritical and sub-critical hydraulic conditions. During the supercritical operation, the average permeate flux value was around 8.3 l m<sup>-2</sup> h<sup>-1</sup>, while the corresponding sub-critical value was around 4.3 l m<sup>-2</sup> h<sup>-1</sup>. The SRT was practically infinite as almost no sludge wastage ever took place during the overall nine-month experimentation period. The hydraulic performance of the MSBR was assessed by calculating the membrane permeability from the recorded experimental data (TMP, permeate flux and temperature). Finally, the variations of the membrane permeability over time were mathematically correlated with the MSBR basic operational parameters.

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## **COPPER AND ZINC CONCENTRATIONS IN FEEDSTUFFS OF DIFFERENT LIVESTOCK ACTIVITIES IN MIDDLE GREECE**

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Heavy metals are main soil contaminants that can reach through mobilization surface water (lake, rivers) and sometimes also the groundwater level. One possible source of soil contamination with heavy metals is the free disposal of solid wastes from livestock farming activities. On the other hand heavy metal levels in the solid wastes depend on the concentrations that are present in the feedstuffs and feed mixtures using by the farmers.

In the framework of an "Archimedes" project, financed by the Greek Ministry of Education, the correlation of Cu and Zn concentrations between feedstuffs and wastes levels due to different livestock activities (cows, pigs, sheep and poultry) in the area of Larissa/Middle Greece over a period of one year was studied.

In the first phase of the project samples from feedstuff and feedstuff mixtures used by farmers from the four different livestock activities were collected every 3 weeks and analysed by Atomic Absorption Spectroscopy (Varian 220FS SpectraAA) for the quantification of Zn and Cu. Statistical analysis for sample size, mean values as well as minimum and maximum and standard deviation using the SPSS program has been performed.

The first results show relatively high concentrations (ppm level) of Zn and Cu in the feedstuffs that can affect the concentration levels not only in the solid and liquid wastes (manure, urine, etc) that are free disposed in the environment, but also their presence in agro-industrial products like milk or meat that can threat human life.

In the second phase of the project the influence of the Zn and Cu concentrations in feedstuffs to the corresponding concentrations in the liquid and solid wastes of the above livestock activities will be studied.

**Key words:** zinc, copper, livestock, feedstuffs, environmental pollution

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## **THE PORT WASTE MANAGEMENT SYSTEM: EVALUATION OF TURKISH PORTS**

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Ports are the most important gateway for trade in all over the world. They are subject to a variety of activities, including maritime transport, shipping, and marine services. Ports generate, receive and handle a great deal of many different kinds of waste every year and it is viewed by many port authorities as one of the most important environmental issues. The waste reception facilities in ports vary in capacity and type. Many of these waste reception facilities are designated for bilge and ballast water handling. The need for proper facilities for ship waste to be discarded at ports is essential to reduce the probability of increased marine pollution from ships.

The International Convention on the Prevention of Pollution from Ships (MARPOL 73/78) provides an international framework on port reception facilities for ship-generated waste and cargo residues. These already stipulate that ports should provide reception facilities for vessels to safely dispose and manage various types of wastes. In recent years, developing a Port Waste Management Plan and establishing an efficient ship waste handling system designed to ensure proper waste management services in compliance with international legislation attracts a great deal of interest for ports.

In view of this, Port Waste management planning is an economical, environmental, technical and administrative issue for international areas and Turkey. In This article, the following subjects will be presented; types of ship-generated waste, port waste reception procedures, port waste management system and evaluation of Turkish ports waste reception facilities.

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## CLIMATIC DISTURBANCES TO THE WATER CYCLE IN THE WESTERN MEDITERRANEAN BASIN: ORIGIN AND PROPAGATION TO REGIONAL - EUROPEAN AND GLOBAL SCALES

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To analyze the changes perceived in the Western Mediterranean summer storm regime, we used meso-meteorological information from the results of several projects on atmospheric pollution in Southern Europe. The first step was to develop a procedure to disaggregate the daily rainfall information into three components: frontal, summer storms and Mediterranean cyclogenesis ; from this, several hypotheses were derived on the most probable processes implicated. The results indicate that the rainfall regime in this Mediterranean region is very sensitive to variations in the surface air mass temperature affected by land-use.

Land-use perturbations accumulated over history may have induced changes from an open, monsoon-type regime with frequent summer storms over the mountains inland to a regime dominated by closed vertical recirculations, where feedback mechanisms favor the loss of storms over the coastal mountains and additional heating of the sea surface temperature during the summer. This, in turn, favors Mediterranean cyclogenesis and torrential rains in autumn-winter. Because these intense rains and floods can occur anywhere in the basin, perturbations to the hydrological cycle in any part of the basin can propagate to the whole basin and adjacent regions. Furthermore, present levels of air pollution can produce greenhouse heating, amplifying the disturbances and pushing the system over the critical thresholds level.

These questions are relevant for the new European Union (EU) water policies in southern Europe and for any other region dominated by monsoon-type weather systems.



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## EFFECTS OF NEW ANTIFOULING PAINTS ON THE MACROFOULING BIOCOENOSIS OF HARD SUBSTRATUM IN THE LAGOON OF VENICE

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Biofouling is the natural association of sessile marine animals and plants encrusting submerged hard substrata and steady structures, the biotic composition and succession of which depends on geographic place, type of substratum, physico-chemical characteristics of the seawater and seasonal climatic conditions. In the lagoon of Venice, the climax of this biocoenosis is reached in summer-autumn and is represented by colonial ascidians of the Botryllinae family as dominant species. Macrofouling growing on artificial objects constantly immersed in the seawater causes severe economic damages, which result in continuous maintenance of the structures and high costs due to hydrodynamic loss of the boats also involving a sensitive increase in fuel consumption and atmospheric pollution. Therefore, the study of antifouling compounds from 1970s with the introduction of organotin compounds as principal biocides is fundamental for the future of naval engineering with which it parallelly evolved. However, the severe disadvantages for environmental impact of organotins involved a strict international regulation of their employment with the purpose of reaching their total elimination within 2008. As a consequence, from 1990s, the research of alternative biocides, to be applied as antifoulings in paints for covering immersed objects, remarkably increased aiming to produce new chemical formulations effective on the biofouling and also compatible with the preservation of marine ecosystem.

The purpose of our research was to evaluate the effects of some new antifouling paints in commerce, containing Cu<sub>2</sub>O, CuSCN, Sea-Nine 211, Diuron, TCMS pyridine, Zinc pyrithione, Zineb and Endosulfan as principal or booster biocides, on the ecological succession of hard substratum macrofouling employing wooden and steel panels immersed for one year in two stations of the southern Venice lagoon, different for bathymetric and hydrodynamic characteristics. Some biodiversity indexes (species richness, biocoenosis structure, covering-abundance index, similarity index) were used to describe the evolution of biocoenosis.

Results, compared with control and TBT-treated panels, enabled us to highlight the disturbing activity of the antifouling paints, that results in the selection of resistant and dominant species, often different to those of the natural climax. We have established an order of biocidal efficacy of the assayed antifouling paints: TCMS pyridine, Diuron, Irgarol 1051 < Cu<sub>2</sub>O, CuSCN, Zn pyrithione, Zineb, Endosulfan, Sea-Nine 211 < TBT. None of the paints assayed is more powerful than that containing TBT and the biocidal efficacy depends on the type of matrix (hard or self-polishing) and the presence of biocidal boosters able to enlarge the toxic effect. In consideration that the wide use of these antifouling paints is accompanied by a continuous leaching of their active substances in the environment, our data evidence the dangerousness of these xenobiotics towards the coastal marine biocoenoses, in particular to fragile ecosystems like the lagoon of Venice and suggest the necessity of a revival of a more careful toxicological study of the paints already in commerce and a research of new antifouling systems which don't use chemical biocides.

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## PROTEOMICS AND ABSOLUTE TRANSCRIPT EXPRESSION SIGNATURES IN FREE-LIVING MUS SPRETUS TO MONITOR TERRESTRIAL ECOSYSTEMS

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Biomarkers provide evidence of exposure/effect to pollutants in bioindicators. The mouse is the best-known vertebrate model organism and *Mus spretus* the best characterized aboriginal species. This non-protected rodent attains high population densities, typically inhabits marshlands, and feeds on plants, seeds and insects around its burrow. Here we investigated the suitability of novel bioassays to monitor terrestrial ecosystems using free-living *M. spretus* mice as bioindicators.

We first evaluated whether the quantitation of mRNA molecules of key genes is a reliable bio-monitoring end-point. To this end, we examined the *M. spretus* expression levels of 19 transcripts encoding different cytochrome-P450s and glutathione transferases. Mice dwelling at the Doñana Biological Reserve (SOL) were compared to those from an industrial settlement (PS). Transcript quantitations showed: i) gender-related differences in the expression of most Cyp and Gst genes; ii) the concomitant up-regulation of Cyp1a2, Cyp2a5, Cyp2e1, Cyp4a10, Gsta1, Gsta2, Gstm1, and Gstm2 mRNAs in liver of PS males; and iii) outstanding qualitative and quantitative differences between the hepatic expression signature of PS males and that promoted by paraquat (superoxide-generator herbicide). Even with the focused set of Cyp and Gst transcripts quantified in this study, our data indicate that animals living in a particular polluted site display a characteristic expression signature in line with the types of substances contaminating the area of concern.

Though control of mRNA levels is crucial in regulating protein production in mammals, major end-points are protein levels and activities. Therefore, we next evaluated the suitability of high-throughput proteomic methods (2-DE protein separation and MALDI-TOF-PMF analysis) in assessing the biological effects of polluted terrestrial ecosystems on inhabitant *M. spretus* mice. Metal analysis, biochemical assays and transcript level quantifications were carried out in parallel to assist the interpretation of proteomic data. Animals from three sites along the "Domingo Rubio" stream were compared with mice from SOL negative reference, using specimens from PS and rice fields as positive controls. Our study revealed contrasting differences in the proteome of animals dwelling at different polluted environments, with specific increases and decreases in selected groups of proteins and changes that appear as coordinately regulated. Identified proteins were sorted into different cell functions: axonal transport and cell division, autophagy-related proteolysis, biotransformation, adaptation to oxidative stress, and central pathways of glucid, fatty acid, amino acid, methyl and urea metabolism. Importantly, whereas some of the observed protein expression changes may protect mice from the toxic effects of pollutants, others would make the animals more susceptible.

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### 3D COASTAL EROSION ANALYSIS OF KILYOS-KARABURUN REGION USING MULTI-TEMPORAL SATELLITE IMAGE DATA

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The largest metropolitan city of Turkey is Istanbul. More than 300 000 people per year have been immigrating to the city. Istanbul is a cultural and historical city which is growing in east-west direction. Open mining areas located between Kilyos and Karaburun enlarge towards east-west direction parallel to the Black Sea. The coastal zone in this region has been changed due to open mining activities conducted since 1980. In the beginning, the coal was extracted from the land placed on the forest areas. After the surface coal being exhausted, sea was filled within the waste extracted from mining areas and new areas for coal production were opened. Forest areas and sand dunes were destroyed by open mining activities performed because of lack of environmental precautions. As a result of filling of materials extracted from open mining areas into the sea, ecosystem and topographic structure were totally damaged. Coastline was a straight line and full of beach sand in 1984 which can be identified on 1984 Landsat 5 TM image. After 1980s, coal production located very close to coastal line was started. As a result of production, obtained soils covering the coal in open mining areas were transferred to sea and the coastline has fairly changed.

The primary objective of this study is, determination of the coastal erosion occurred in the part of Black Sea coastal zone using multitemporal satellite sensor data and interpretation of the obtained results. LANDSAT satellite sensor data were used in this study. Satellite images received in 1984, 1992 and 2001 were rectified into the UTM coordinate system and a layer stack image including 16 bands pertaining to these years was formed. To determine the coastal changes occurred in 1984, 1992 and 2001, a new RGB image including infrared band from each year was constituted. As a result of study influences of open mining areas and waves on the coastal line morphology were analyzed by means of remotely sensed data.

In this study, open mining area induced changes in coastal zone were analysed using surface and spatial profile obtained from Multitemporal remotely sensed data belonging to 1984, 1992 and 2001 years. Several spatial profiles which are parallel each other with equal distance along and vertical to the coast line are extracted to calculate amount of waste extracted from open mining areas and load in the sea from the satellite images. For this purpose bathymetric map which has 5 meters interval of the study area is used. In conclusion it is found that the amount of filled material into the sea between 1984 and 1992. Some of the filled materials were disappeared by the wave effect in the period of 1992 and 2001. Also, both changes in sea and land were determined.

Keywords: Istanbul, coastal erosion, spatial profile, 3D

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## CONDITIONS OF ELIMINATION OF ENVIRONMENTAL POLLUTION IN INSECT MANAGEMENT

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Environmental pollution caused by present insect growth regulators applied in plant protection (pesticides, fungicides etc.) and/or their biodegradation products (mainly metabolites of soil aerobic microorganisms) has been widely described in the literature. Such pollution is especially hazardous for ecosystems with limited sources of water. Degradation products are sometimes more detrimental to human health than the applied compound.

In this paper a synthesis of a series of peptides is described and their sterilizing effect proved on reproduction of insects having different development (Diptera, Orthoptera, Hemiptera). Compared to untreated controls, the hatchability was considerably decreased, in some cases down to less than 20%. Using the determination of ATP/ADP content and viability of HeLa S3 cells exposed separately to various concentrations of the tested oostatic peptides and/or their biodegradation products, no toxic effects were found. The biodegradation products of a certain peptide (amino acids and peptides with shortened sequences) were obtained using HPLC after peptide incubation with microbial strains isolated from the soil collected on site.

A chosen oostatic pentapeptide H-Tyr-Asp-Pro-Ala-Pro-OH was applied (e.g., in drinking water) to several model insects to analyze its accumulation and/or degradation in body parts using different procedures such as morphological and histological observations, studying of influences of selected inhibitors of enzymes, effects of insect operation (e.g., an oostatic effect in allatectomized females of the bug *Pyrrhocoris apterus*), application of the pentapeptide radiolabeled by us in Tyr1 or Pro3 or Pro5 and measurement of total radioactivities of isolated tissues and/or radio-HPLC of tissue extracts or hemolymph, respectively. Using such procedures, the mode of action was proposed and the conditions of application optimized.

The paper summarized laboratory studies of a new tool in insect control having a high biological activity and no toxic impact.

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## TOXICITY OF FUNGICIDE TEBUCONAZOLE TO AN ESTUARINE AND A FRESHWATER ORGANISM

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Two Toxkits® microbiotests with 2 species from different aquatic environment (estuarine and freshwater) has been used to evaluate the toxicity of Tebuconazole, pesticide widely used as fungicide in rice crop areas like Albufera Natural Park (Valencia, Spain) to avoid and treat rice blast disease, caused by phytopathogenic fungus *Pyricularia oryzae* during summer period. Albufera Lake has two differentiated aquatic areas, estuarine due to influence of seawater intrusion and a second area fed by freshwater from irrigation channels and ravines.

To evaluate the effect of the pesticides on marine and freshwater environments, it is necessary to use different microbiotests with representative organisms for different kinds of water. For this reason, we have selected Artoxkit M® with *Artemia franciscana* as marine-estuarine organism and Thamnotoxkit F® with *Thamnocephalus platyurus* as freshwater organism. Toxkits® are based in dormant or immobilized biological material from which live test organisms can easily be hatched. All bioassays were performed according to the Standard Operational Procedure provided in the Toxkit®.

Tests organisms were exposed to different concentrations of Tebuconazole (Purity >99%) for a period of 24 and 48 hours to evaluate acute toxicity. Concentration of Tebuconazole assayed were: 15, 13.75, 5, 1.71 and 0,43 mg/L to Thamnoxkit F® and 30, 20, 10, 7.5 and 3,25 mg/L to Artoxkit M®. LC5048h. values were obtained using Probit regression included in SPSS+ v.14 Statistical Software.

Results show that *Thamnocephalus platyurus* (LC50-48h.= 4.50 mg/L) is more sensitive than *Artemia franciscana* (LC50-48h = 19.77 mg/L ). NOEC and LOEC values were 13.75 mg/L and 1.43 mg/L, respectively, to *T. platyurus* and >30mg/L and <3.35 mg/L, respectively, to *A. franciscana*.

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## USE OF CULTURE COLLECTION (GAZI MACC/TURKEY) FOR HEAVY METAL EFFECTS, TOXINS AND PRESERVATION OF MICROALGAE

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The Gazi Microalgae Culture Collection (GAZI-MACC) contains diverse groups and strains of algae. Gazi-MACC would benefit from replacing with preservation. In these collections some species used for tolerating and morphological changes against heavy metals and some of used variety experimental studies like determining of microalgae toxins and systematic researches. Gazi Microalgae Culture Collection is charged with several tasks:

- Custody of a national resource;
- Provision of a living resource for the science base;
- Receipt of deposits subject to publication;
- Safe, confidential and patent deposit services;

Collections are in a unique position as custodians of genetic resources and therefore have a key role to play in the conservation of genetic resources. Collections add value to received and collected biological material. This is done through purification, expert preparation, authoritative identification, description, determination of biochemical and other characteristics, comparison with related material, safe and effective preservation, evaluation of value for biological control uses, and indication of importance of beneficial and detrimental attributes. They often provide samples of deposited organisms free of charge to the depositor and participate in capacity-building projects to help establish facilities and expertise in country. Gazi-MACC seeks to protect the rights of the country of origin of organisms in its collections. Depositors of strains benefit from the added value, secure storage of their isolates and, in particular, relief from the burden of distribution and ensuring the continued availability of the strain. A mix culture is been accumulated in this collection for medicine study also.

Key words: Microalgae, Culture collection, Toxins, Heavy metals, Systematic, Turkey



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## A DIFFERENT WAY FOR AN EARLIER BIO-INDICATION OF ENVIRONMENTAL POLLUTION

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In the eukaryotic genome a peculiar kind of non-coding DNA is present, which is able to answer to the environmental factors by quantitative variations of some of its sequences (reviewed in Bassi 1999, Plant responses to environmental stresses, Lerner ed. - New York, pp. 161-170). These variations are very different from mutations, in that they are quantitatively significant, usually (but not always) transitory, and clearly non-random in that the same effects accompany specific environmental stimuli. The above answer of the repetitive/non-coding DNA to the stresses is immediate, always present and very probably it constitutes the first answer of an organism to the environmental signal. Therefore, it has been suggested that "repetitive/non-coding DNA could act as a mediator between the environment and gene expression, by "receiving" the messages from the environment, modifying itself accordingly, and hence determining, by the conformational effect, the expression of specific sets of genes" (Bassi, 1990, Biol. Rev., 65: 185-225).

From the considerations above, it becomes clear that repetitive/non-coding DNA behaviour could usefully be utilized as a way to discover in advance the presence of an influence of environmental pollution on the organisms. Moreover, this method could permit to individuate the influence of environmental pollution on the organism also in those cases in which the whole biological organism can't be used as bio-indicator, as the natural organic defences are able to eliminate others kind of morphological or physiological variations.

In the present work, using different experimental approaches, we observed the repetitive/non-coding DNA behaviour in answer to metals in two kinds of Bryophytes, very different from one another from a physiological and ecological point of view, the aquatic moss *L. riparium* and the terricolous moss *F. hygrometrica*. In fact, from a genetic point of view, the genome of Bryophytes is organized in such a way that its repetitive/non-coding DNA modifications are particularly easily identifiable by the modern cyto-molecular techniques and can be quantified also directly in situ, without separating the DNA from its natural position inside the cell (Bassi et al., 2006, Plant Bios., 140: 80-86).

Our results show that in both mosses the repetitive fraction of genome answers to lead, cadmium and also zinc treatment by an amplification of some G-C rich non-coding DNA sequences; this DNA amplification is measurable already after fifteen days of the plant exposure to the metals and is quantitatively proportional to the time of metal action; moreover it stops upon removal of the metal from the culture medium. Present results are discussed on the lights of the utilization of repetitive/non-coding fraction of genome as an earlier bio-indicator of environmental pollution.

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## IDENTIFICATION OF ANTHROPOGENIC PRESSURES ON ANTINIOTI LAGOON, A NATURA 2000 SITE IN NORTHERN CORFU (GREECE)

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Antinioti is a coastal lagoon located at the northern coast of the island of Corfu. The lagoon is included in the NATURA 2000 Network, as the site is characterized by a variety of habitats (bogs, marshes and water fringed vegetation) and is of great importance for several species of flora and fauna, such as the threatened *Lutra lutra* (otter). The lagoon also provides home for fish (*Valencia hispanica* and *Aphanius fasciatus* are listed in Annex II of the Directive 92/43/EEC), amphibians (*Emys orbicularis* and *Mauremys caspica*) and reptiles (e.g. the colubrid snake *Elaphe quatuorlineata*). The biodiversity of this site is increasing because of the occurrence of an interesting avifauna including threatened waterfowl and birds of prey (e.g. *Ardea purpurea* and *Circus aeruginosus*).

Antinioti lagoon is also very important for the economic development of the area, supporting fishing, leisure activities and tourism. Although, for the time being, the verified reasons for decline of the natural environment of this site have had small to moderate influence on the animal taxa, it could be said that increasing human activities will soon disturb this sensitive ecosystem. The greatest threats to the site and its preservation come from: a) increasing of human habitation and tourist development, b) unorganised leisure activities, c) the unreasonable use of fertilizers and pesticides in nearby cultivated areas (e.g. olive groves), d) the lack of information to the local community about the importance of the wetland.

We performed, for the first time, chemical analysis on water and sediment samples collected from the Antinioti lagoon, in order to assess the quality status of the site and thus contribute to the selection of proper conservation and management measures in the area. The samples were analysed for nutrients, pesticides, organic matter and heavy metals (Fe, Mn, Cu, Cd, Pb, Zn, Ni). This paper will focus on the heavy metals concentrations as they are known to enter the food chain through bioaccumulation, seriously affecting the quality of fisheries.

The lagoon communicates with the sea through two canals, a natural and an artificial one. Physicochemical parameters and low dissolved metal concentrations at stations close to these canals revealed marine characteristics and determined the boundaries of the system. Higher metal concentrations on both dissolved and suspended phases were detected in the internal part of the lagoon. Significantly high concentrations of Pb and Cd in sediments and particulate matter were detected at one site, suggesting the influence of an external source of pollution. Moreover, a stream which flows into the lagoon was identified as the main contributor of metal inputs to the system. Sediments with a relative high metal content could act as a long-term, secondary source of these metals in the water column, through diagenetic procedures. Analysis of heavy metals in the tissue of fish collected from the lagoon will supply further information concerning the quality status of Antinioti.



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## ENVIRONMENTAL RESIDUES IN GAME ANIMALS: 5 YEARS IN RESEARCH EVALUATION

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From time immemorial, hunting is a fundamental source of high-value animal proteins. For millennia it was a tool of Mankind for conquering spaces for Agriculture and Husbandry, provoking as a consequence the slow and progressive confinement of wild and game animals in increasingly restricted areas. During last few decades this trend changed considerably: mountains and valleys become more and more unpopulated, natural environments are expanding and reconquering the spaces already took out by the work of Mankind. In the same time a widespread and increasingly ecological and nature-oriented conscience involved a wider population, bringing about the reintroduction of wild animals, extinct in those environment since many years.

The Biella Province (Piedmont Region, North-west Italy) territory: 180,000 inhabitants, a surface of 913 km<sup>2</sup>, covered by rice fields in the plane and for more of 50% of the territory by hills and mountains, ranging from 300 to 2,500 meters. Agriculture and Husbandry are more and more diminishing and wild and game animals: foxes, wild boars, roe deers, chamois, deers, fallow deers, are populating or repopulating moors, woods and the abandoned valleys. At the same time the environmental pollution, i. e. the fallout originating from industrial activities: 1,100 textile factories are still working in Biella or from vehicular traffic: 24,000 registered motor vehicles only in the Province, is constantly increasing.

As a routine, medical investigation and food inspection for the detection of animal diseases or zoonoses (i. e. Tuberculosis, Brucellosis, trichinellosis) are carried out by the Veterinary Service of Biella (part of the Piedmont Region Health Service). Considering the outstanding importance of the animals as sentinels of environmental hazards, since 2001 we started a program of sampling liver and kidneys of wild and game animals: roe deer (*Capreolus capreolus*), chamois (*Rupicapra rupicapra*), wild boar (*Sus scropha*), in order to investigate the spread of some residues, like heavy metals: Lead (Pb), Chromium (Cr), Cadmium (Cd) and PCB (polychlorobiphenyles). Since hunting season 2001/2002 to 2006/2007 samples were taken at the checkpoints for game animal diseases control and the chemical analysis were performed by officially accredited Laboratories.

This paper deals with the results of five years of investigations in the field of surveillance and monitoring of environmental health hazards and their impact on life, applied to game animals. The data obtained have been analysed in order to assess the safety of animal products and byproducts for human consumption (food and feed safety) and for starting a process of methanalysis, that can be employed for implement an Evidence Based Prevention (EBP).

**HEMATOLOGICAL INDICES OF THE AZOV  
SEA ROUND GOBY NEOGOBIUS MELANOSTOMUS**

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To use hematological indices in the functional diagnostics of different fish species one should, first of all, to collect data describing the so-called "norm". Of course, the state of each species is described by its own set of qualitative and quantitative hematological characteristics. At present there is a well-developed hematological statistics for species of high commercial value: sturgeons, salmon, carps etc. However, in recent years due to ecological changes in the Azov Sea caused by climatic, hydrological and biotic processes, the commercial value of the goby *Neogobius melanostomus* Pallas (1814) has increased. So a necessity appeared to collect primary statistic data in order to determine the hematological "norm" of this species.

The fish state was assessed according to available/absent morphological and microstructural disorders. Blood samples were taken from the caudal vein, the fixed preparations were stained by Romanovsky technique. The following blood parameters were determined: leucocytic formula, index of leucocytes' shift, erythropoiesis intensity. Morphometric analysis of erythrocytes included size measurements of cells. Based on morphometric indices we computed ovalization (ratio of cell length to its width) and the volume of erythrocytes. A total of fifty males and females were checked.

Results of samples studied are presented in the Table.

	Index of leucocytes' shift	Lymphocytes	Monocytes	Segmento Nuclear Neutrophils	Rodnuclear Neutrophils	Eosino- phils	Erythro- poiesis Intensity
Average	0.24±0.04	79.74±2.08	1.11±0.22	10.79±1.01	8.37±1.53	0.00	2.11±1.05
min	0.09	57.0	0.00	5.00	3.00	0.00	0.00
max	0.72	89.0	3.00	20.00	27.00	0.00	15.00

White blood corpuscles. In general, healthy fish had mature forms of lymphocytes, while young cells were single. Neutrophils were represented by segmentonuclear and rodnuclear leucocytes. Eosinophils were extremely rare. Macrophages were not observed in blood at all. Thrombocytes. There were thrombocytes of two types: solitary cells with oval nuclei and cytoplasm elongated from both ends, and groups of small rounded cells of intensive violet color forming sometimes great aggregations glued by their own cytoplasm.

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Erythrocytes. Morphologically the red blood cells consisted of mature erythrocytes and immature forms of erythropoiesis (normoblasts, basophilic and polychromatophilic erythrocytes. Both ellipsoid and round cells were found on one and the same smear in all the fish tested. Orthochromic erythrocytes had an ellipsoid form, while polychromatophilic and basophilic normoblasts were round. The round goby's erythrocytes were mainly ellipsoid. The length of erythrocytes averaged  $10.96 \pm 0.16 \mu\text{m}$ , the width and mean corpuscular volume accounted, respectively, to  $8.35 \pm 0.12$  and  $587.2 \pm 37.3$ . Morphometric parameters of males and females were similar.

Erythrocytes' nuclei were found, as a rule, in the centre of homogenously colored cytoplasm. Some specimens had erythrocytes with deformed nuclei. The erythrocytes with anomalous nuclei numbered 2-3%. Vacuolization of cytoplasm and nuclear shadows were also observed.

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## MODELING THE MOBILITY OF Mn IN COASTAL SEDIMENTS COVERED WITH CYANOBACTERIAL MATS

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In coastal marine environments with shallow, warm and calm waters, it is sometimes possible to observe the presence of organosedimentary forms (algal mats) which are produced by sediment trapping, binding and /or precipitation as a result of the growth and metabolic activity of microorganisms, principally cyanobacteria.

The typical property of these forms is their laminated structure in which different functional groups of microorganisms occur in vertically stratified layers.

These structures are observed in coastal areas of the temperate and tropical zone as well as in some Greek coastal areas.

The aim of this work was to study the distribution and mobility of Mn among the main layers of coastal cyanobacterial mats in a closed bay at Anavissos on the coast of Saronikos Gulf in Greece. The area of Anavissos was selected due to the ideal existing conditions for the development of such formations.

The pH, temperature, dissolved O<sub>2</sub>, salinity and conductivity of the porewater in the anoxic layer were measured in situ with customized needle electrodes. The pH varied between 6.8 and 6.9, the PO<sub>2</sub> between 0.01 and 0.02 atm, and the temperature between 18.1 °C (in winter) and 22.1 °C (in summer).

Small sediment cores were collected and separated into three discrete layers according to their structure. The Mn of each layer was extracted according to a modified BCR sequential extraction method, which separated the metal into four fractions according to their lability. The determination of Mn in each fraction was carried out by the furnace atomic absorption method.

The main results of our study were: (a) The % contribution of each fraction of Mn presented no significant differences between the three layers of the sediment, (b) the most abundant fraction of Mn was that associated with the crystalline grid of the sediment (about 59%), (c) the Mn connected to small inorganic particles and carbonates prevailed over all the labile forms of Mn, and (d) the surface layer of the sediment was slightly depleted in Mn associated with organic compounds and sulphides.

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After processing the physicochemical measurements, we calculated the ratios  $Mn^{+4}/Mn^{+2}$  and  $Mn^{+3}/Mn^{+2}$  in the porewater of the anoxic layer of the sediment. The values extracted were an indication that most of the Mn was in the form of  $Mn^{+2}$ .

Finally, the high mobility of  $Mn^{+2}$ , in combination with the results of our determination, can lead to the proposal of a model that will attempt to simulate the mobility and distribution of Mn in sediments covered with cyanobacterial mats.

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## DETERMINATION OF NUTRIENT STATE IN THE MOUSTOS LAGOON, GREECE

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This study concerns the Moustos lagoon, located in eastern Peloponnesus, Greece, in the region of the town of Astros. Moustos forms part of the Natura 2000 network and constitutes a significant coastal ecosystem, being a shelter of migratory species and a range of flora and fauna. The maximum depth measured in the lagoon was 4.7 m. Two artificial canals (a main and a secondary one) sustain communication with the sea whereas an accessible carstic spring supplies the lagoon with brackish water (salinity 13.0o/oo), being the main drainpipe of the limestone masses of the region. The inflow of water from the sea causes the mixing of water masses of different salinity. Occasional flooding results in the creation of a salt marsh around the lagoon.

Two samplings were conducted in July 2004 and March 2005 and water samples were collected from a grid of six stations: the spring, three stations across the centre of the lagoon, one in the main communication channel and the sea (at the channel mouth). The nutrients were determined using standard spectrophotometric methods.

The abiotic parameters measured in situ showed good oxygenation of the system (6.5-10.0mg/l), also obvious through the abundant lagoon vegetation. Temperatures in the lagoon were higher during the summer sampling (27.4oC) and in surface water layer in comparison to the near-bottom one in both seasons. It is an indication for a weak stratification in the water column. Salinity values were 15o/oo on average on the surface water and about 26.2o/oo, in deeper water layer. It seems that the spring water flows almost surficially without being mixed with the deeper 'trapped' water masses, which in turn are influenced by seawater penetration through the Quaternary deposits.

The nutrient levels of the lagoon system were determined. NO<sub>2</sub> - were quite low in both seasons (0-0.5 µmolN/l). NO<sub>3</sub> - were especially high in the summertime (78 - 146 µmolN/l) and high in winter (27.4-38.2 µmolN/l). NH<sub>4</sub><sup>+</sup> values ranged 2.9-8.2 µmolN/l in July and 0.24-0.78 µmolN/l in March. Organic nitrogen was determined 5-43 µmolN/l in summer and 75.6-97.7 µmolN/l in winter. Total nitrogen values were similar in both seasons (104-161 µmolN/l). It is seen that in the summer the inorganic forms of nitrogen dominate in the brackish lagoon, whereas in winter there is the opposite trend. PO<sub>4</sub>-3 values were very low 0-0.10 µmolN/l. SiO<sub>4</sub>-4 concentrations were high in both seasons (77-120 µmolN/l) showing that silicate is of terrigenous origin.

The relatively high concentrations of nutrients in the lagoon indicate a eutrophic environment, which given the significance of the ecosystem requires monitoring.

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**ECOTOXICOLOGICAL EVALUATION OF A SOIL  
CORE FROM A DISUSED INDUSTRIAL SITE CONTAMINATED  
BY HYDROCARBONS AND HEAVY METALS**

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A soil core from a disused industrial area near Naples (Italy) characterized by hydrocarbons and heavy metals contamination has been investigated.

The samples were collected on a vertical soil profile at different depths: 30, 60, 90, 120, 150 and 180 cm.

The hydrocarbons levels were high (2500-7500 ng g<sup>-1</sup>) along all the soil core profile, but the greatest values were measured at 90 and 120 cm. Heavy metals were more abundant in the intermediate layers, and among they arsenic and zinc were at concentrations greater than those established from the Italian law (D.M. 471/99).

The ecotoxicological evaluation was carried out by acute and chronic toxicity tests with organisms belonging to different trophic levels: the bioluminescent bacterium *Vibrio fischeri*, the green microalga *Selenastrum capricornutum*, the plants *Sinapis alba*, *Lepidium sativum* and *Sorghum saccharatum*, the cladoceran *Daphnia magna*, and the ostracod *Heterocypris incongruens*. These batteries of toxicity tests were applied to the whole soil, aqueous and organic extracts matrices.

In the contact bioassays on the whole soil samples, 120 cm resulted the most toxic one with bacterium *V. fischeri*; a significant biostimulation was observed for all samples with phytotoxicity tests, except at 180 cm, where a little inhibition was obtained. Ostracod test showed a little toxicity only for the sample at 30 cm.

The samples relative to the deeper layers of the soil core showed toxic effects in most cases.

Soil extracts from deeper layers of the soil core were the most toxic, mainly towards bacteria and unicellular algae.

Among the different toxicity tests performed, bioluminescence and algal inhibition growth were the most sensitive ones with all matrices. *D. magna* was the less sensitive organism: it has shown a significant mortality only with aqueous extract at 60 cm.

Moreover inorganic contamination, linked to aqueous phase, was mainly identified by *S. capricornutum* chronic toxicity test.

The results obtained with the batteries of ecotoxicity tests evidenced the highest toxicity in the lower layers of the analyzed soil core, for all matrices. In particular, the higher toxicity of deep samples, where high concentrations of PAHs and paraffins were measured, was emphasized by toxicity tests carried out with organic extracts.

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## CADMIUM UPTAKE BY HOLM OAK (*QUERCUS ILEX* SUBSP. *BALLOTA*) IN POLLUTED SOILS: DESCRIPTIVE AND EXPERIMENTAL APPROACHES

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Soil and air pollution are regarded as possible factors for forest decline. Trace elements have usually low natural concentrations. However, different human activities have altered their biogeochemical cycles, and increased their levels both in agricultural and forest soils during the last decades. Cadmium, a trace element, is easily mobile in soils, usually having a high soil/plant transfer coefficient. Therefore, the risk of cadmium accumulation in aboveground biomass of forest systems (and then into different levels of the food web) may be higher for Cd than for other low-mobility trace elements.

In this work we study the Cd accumulation patterns in holm oak (*Quercus ilex* subsp. *ballota* Desf. Samp.), under field and controlled conditions. This oak is the dominant tree species in most of the sclerophyllous forests in the Mediterranean region, and is frequently used in the afforestation of degraded sites. Field studies were carried out in the Guadiamar River Valley (Seville, SW Spain). This area was affected by a huge mine-spill in 1998 that polluted the soils with several trace elements. In 2005, soil and plant (leaves) samples were taken along a pollution gradient in the Guadiamar Valley. Different life-stage (juvenile saplings and adult trees) were considered. Greenhouse experiments were carried out with holm oak seedlings, exposed to different Cd concentrations (0, 20, 80 and 200 ppm).

Under field conditions, the total Cd concentrations in soils ranged from 0.07 mg kg<sup>-1</sup> (unpolluted sites) to 3.05 mg kg<sup>-1</sup>. There was a broad heterogeneity in some soil factors that potentially affect trace element bioavailability, such as soil pH and organic matter. Despite the relatively high soil concentrations, the leaf concentrations ranged from 0.015 to 0.70 mg kg<sup>-1</sup>, which were within the normal ranges for higher plants. The average soil/plant (leaves) transfer coefficient was 0.35, and was not affected by soil pH neither by organic matter content. Under controlled conditions, holm oak seedlings showed a high retention of Cd at the root level (up to 1500 mg kg<sup>-1</sup>). From roots to leaves, less than a 0.4% of Cd was transported in all treatments. These results suggest that holm oak presents effective mechanisms of Cd retention at the root level, and thus avoiding its transport to the leaves and negative effects on photosynthetic tissues. Although the risk of Cd bioaccumulation in holm oak leaves is low, the severe soil pollution by Cd could negatively affect plant ecophysiology (growth rate, root functioning) as well as other ecological processes at the belowground forest subsystem (soil microbial activity, nutrient mineralization, and other related variables).



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## WILL COASTAL WETLANDS BE STILL ALIVE FOR BIRDS? AN OVERVIEW OF WEST MEDITERRANEAN REGION OF TURKEY

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Study was performed from 1988 to 2004 at Manavgat River, Titreyengöl, Bogazkent/Kocagöl, Kurgunlu Waterfall, Yamansaz Marshes, Demre/Santa Claus Bird Paradise, Avlan and Patara Lake and Dalaman wetlands, and counted bird species in each site was 187, 155, 214, 152, 159, 208, 91 and 216, respectively. It was seen that only Demre and Patara lakes have been protected areas at costal band of west Mediterranean region of Turkey and the others, like Bogazkent/Kocagöl, have been damaged and some of these, like Avlan Lake, have been dried especially by human. The main defined problems and/or threats to these areas are overpopulation, urbanization, golf course and hotel constructions, agricultural activities, pollution, absence of environment conscious or education at local people and natural environmental variation, and for birds; uncontrolled hunting, decreasing water level, burning reedbeds and filling up water bed. We could also say that laws and agreements to protection of wetlands and birds do not enoughly practiced before and now by governs in Turkey. As a result, reduction to present threats for wetlands must be arranged cooperatively by governs, specialists and local people. We have to protect and leave these areas for future not only to birds but only to human to live in a healthy environment.

**Keywords:** Wetlands, Birds, Batı Akdeniz, Mediterranean, Kıyı sulakalanları

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## METALLOMICS: A NEW TOOL FOR ENVIRONMENTAL POLLUTION ASSESSMENT

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Many biomolecules in bioindicator animals are biomarkers of environmental stress. These biomolecules frequently contain heteroatoms (atoms different of C, H, O, N), that can be used as tags for the identification of both small (amino acids, oligopeptides) and large biomolecules (proteins, nucleic acids, and polysaccharides). In this case a very sensitive element detector like ICP-MS which cope for the simultaneous analysis of metals, metalloids and non-metals elements can be used as molecule tracer. This analytical approach based in the use of heteroelement tags is called "metallomics"(1) and the "metallome" is the overall distribution of heteroelements in the cell compartments.

Metallomics is focused on unknown molecules that can be isolated from biological matrices using the atomic detector copupled to a unidimensional or multidimensional chromatographic unit por the complete separation and isolation of the different heteroatom-biomolecule. Latterly, these molecules have to be identified with a sensitive unit for structure elucidation, usually tandem mass spectrometry. This Metallomics Analytical Approach (MAA) (2) is being very successful and important contributions have being providing in environmental studies: Environmental Metallomics (3).

The application of MAA to different examples in relation to assess the potential pollution of Doñana Natutal Park are considered and commented and the possibilities of the approach os discussed.

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## THE ENVIRONMENTAL CONDITIONS IN AN HISTORICAL VALUE LAKE (KOUMOUNDOUROU LAKE, ATTICA, GREECE)

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Many lakes and lagoons have been examined and described worldwide with regard to their environmental status. In a similar case, Koumoundourou Lake, which is located in a highly industrialised area on the NE inshore side of the Elefsis Bay (N38°02'-E23°37') and separated from the sea by a terrestrial ca 15 m zone, was studied in order to assess its environmental status. The catchment area of the lake is characterised as suburban and extends over 39.8 km<sup>2</sup> with mean slope 8%, while the elevation ranges from 0 to 540 m. This lake is a typical meromictic shallow ecosystem with a depth of ca 1.5 m, while close to the ancient fount named Reita which supplies with water the ecosystem the depth does not exceed 2.5 m. The water surface of this brackish lake covers an area of ca 143.000 m<sup>2</sup> and its level is by 1.40 m higher than the sea water level. The perimeter of the lake estimated at ca 1.300 m, while the maximum length and width is ca 600 and 400 m, respectively. This area is strongly connected with the ancient Greek civilisation, as it was dedicated to ancient Goddess Demeter and Kóren. The ancient inhabitants of the city of Athens used this lake within the context of the great religious festivity of the 'Elefsis Mysteries'. Close to the north place of the lake there are some ancient remains, probably of a sacred place. During those past times the fishing activities were aloud only to the ancient priests. According to ancient inhabitants' beliefs the Koumoundourou Lake's waters became chthonic from the Evoikos Gulf (East of Attica prefecture). The first lighthouse in Greece was also established on the top of the northern hill. The Koumoundourou Lake's area regarding the geology is characterised from quaternary alluvial deposits and fans. These materials overlie karstic limestone and dolomites of the Middle Tertiary to Lower Jurassic. Annually, the height of the rainfall is ca 360 mm and the mean annual evaporation has been referred at ca 1630 mm. In general, the climate of the lake's region is characterized as a Mediterranean subtropical due to the fact of the observed short annual temperature range, while the various conditions and local activities create a microclimate. On the biotic aquatic characteristics phytoplankton (*Amphora* spp., *Gomphonema* spp., *Cocconeis* spp., *Melosira* spp., *Navicula* spp., *Nitzschia* spp., *Surirela* sp., *Synedra* spp., *Ceratium* spp., *Merispomedia* spp., *Chroococcus* sp, etc) and benthic communities (*Tubifex tubifex*, *Nereis* spp., *Chironomus* spp., *Gomphus* sp., *Prionospio* spp., *Capitella capitata*, *Glycera convoluta*, *Abra prismatica*, *Nereis diversicolor*, *Pectinaria koreni*, *Corophyllum volutator*, *Tanais covolinii*, *Nassa* sp, *Hydrobia ulva*, etc) have been collected and examined. Regarding the various plants (*Juncus* spp., *Carex* spp., *Phragmites australis*, *Chara hispida*, *Ruppia cirrhosa*, etc) they were also recorded, while the lake is inhabited as well by various *Mugil* spp. and *Anguilla anguilla* species. Physicochemical analysis was also applied to the collected samples, with the obtained values and the heavy metal concentration indicating degradation of the ecosystem.

Nowadays, in conclusion, the wide area of the lake characterised of a big range of anthropogenic activities, where the final product are the various pollutants (heavy metals, oil hydrocarbons, oil refinery, etc). This situation in relation with the various natural conditions is leading the ecosystem towards degradation on the lake's soil and waters. Additionally, the aquifer has also been polluted.

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**ATRAZINE EFFECTS ON GROWTH OF THE DIATOM  
RHIZOSOLENIA SETIGERA EHRENBERG**

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The effects of the herbicide atrazine were examined on clonal cultures of the diatom *Rhizosolenia setigera*. The growth of *R. setigera*, expressed as cell density, in cultures exposed to 20 and 50 $\mu$ g L<sup>-1</sup> atrazine, was stimulated reaching a final cell density of 17.5% and 32.1%, respectively, over the control. On the contrary, cultures of *R. setigera* growing at 70 and 100 $\mu$ g L<sup>-1</sup> atrazine concentrations showed decrease in final density, compared to control, of 40.5% and 41.0%, respectively. The results of chl-a measurements showed different responses of the cells to various atrazine concentrations. In cultures containing 20 and 50 $\mu$ g L<sup>-1</sup> atrazine, chl-a concentrations were always found higher than the control, reaching at the end of the experiment an increase of 48.0% and 58.5%, respectively. Chl-a concentrations in cultures growing in the presence of 70 and 100 $\mu$ g L<sup>-1</sup> atrazine showed a remarkable increase, only after the 6th day of the experiment, reaching final percentage of 86.8% and 139.0%, respectively. The above findings are compared and discussed with the results of cell density, in association with the variations observed on cells size.

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**THE STUDY OF BIOLOGICAL PHENOMENON ADEN SEA:  
GREENNESS, LIGHT EMISSION AND HARMFUL ODOURS**

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The study aims to disclose the causes of greenness, emission of light and harmful odours in Aden beaches. Water samples were collected during the period of January- March 2006, and were examined by light microscope connected to CCD camera.

The result has revealed the presence of green gelatinous colonies, the diameter of one colony is about 1 cm. The colonies contain microalgae called *Phyaeocystis* sp. and *Vibrio* bacteria. We were used several bacterial cultures to isolate two bacteria species that belong to *Vibrio* genus: *V. fischeri* and *V. harveyi*.

The source of lighting and the harmful odours resulting from bacterial metabolic activity, while the greenness resulting from the algae.

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## APPLICATION OF THE METHOD OF MAGNETIC PERMEABILITY IN SOIL - ECOLOGICAL RESEARCHES

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All soils to a greater or lesser extent possess magnetic properties that is connected first of all by that basic elements of a mineral part of soils are characterized by obviously expressed paramagnetic features, and also, because of presence in them of connections of iron and ferromagnetic qualities. At an estimation of magnetic properties of ground first of all take into account sizes of magnetization, a magnetic susceptibility, magnetic permeability, residual magnetization.

Magnetic characteristics of soils reflect quantity and quality contained in them iron oxides. Presence of ferrous minerals, the form of their presence and concentration with high accuracy reflect features of material structure of rocks of anyone lithological shape. Practically all geological formations in the nature are magnetic, the majority of them low magnetic. The basic magnetic minerals meeting in the nature, are: magnetit, titanomagnetit, maffemit, pirrotin, natural iron. The most widespread, and also having the greatest value of a magnetic susceptibility, is magnetit. In soils a chemical compound ferromagnetics rather monotonous. Among new ferromagnetics in overwhelming majority prevail magnetit and maffemit.

At studying physical properties of soils data on their magnetic properties have important value. It is shown, that the knowledge of magnetic parameters of soils helps to allocate types and subtypes of the some soil (Babanin, 1973), to diagnose form of iron in soils (Vadunina, Babanin, 1972), to identify - ground (Virina, Faust, 1973).

It is shown, that under magnetic characteristics - it is possible to construct their magnetic structure which is defined {determined} by a structure of ground, its capacity, distribution of substance on genetic horizons. Changes of a magnetic susceptibility (with depth are reflection of intra-soil processes and can be used as the objective data with a view of soil diagnostics (Babanin, etc., 1995).

Magnetic permeability ( $\mu$ ) of soil is offered to be determined in the air-dried samples of soils sifted through a sieve in diameter of 3 mm, with use of the device in which basis of work the principle of change of size of inductance of the coil is put at a premise of a sample of soil inside of the coil. Depending on magnetic permeability of a sample, inductance of the coil changes. The coil is included in an oscillatory contour of the low-power high-frequency generator with constant initial capacity (49,52 Pf) and inductance (128 mkGn). Frequency of fluctuations about 2 MHz also is measured by the built - in digital frequency meter. Accuracy of measurement of frequency - 100 Hz.

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## METAPROTEOMICS OF SOILS FROM DOMINGO RUBIO STREAM (SW SPAIN)

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The Domingo Rubio stream (DRS) flows into the Tinto River before it joins Odiel River to form Huelva Estuary (SW Spain). Its lower and middle courses are under tidal influence, receiving elements of pyritic origin from the Tinto River and hazardous wastes from nearby chemical plants and petrochemical complex. Its upper course is under intense agricultural activity, mostly strawberry crops. The biological effects of pollutants are studied at Cordoba University by using several biochemical biomarkers. Recently, new endpoints are being searched using Proteomic approaches. Metaproteomics intends the proteomic analysis of mixed microbial communities in a soil under certain circumstances. In a multidisciplinary project centered in DRS and in cooperation with the State University of Campinas, this metaproteomic approach is being used to study soils from 3 DRS sites, exposed to metals, hydrocarbons and pesticides, and 1 reference soil relatively free of contaminants. Samples were obtained at 0-20 cm depth and refrigerated at 4°C for geological characterization and quantification of different kinds of contaminants, and for subsequent metaproteomic studies.

Two types of metaproteomic studies were carried out, both *in vitro* and *in situ*. For those of the first type, the microorganisms thriving at control soil were grown in LB medium and exposed for  $\leq 24$  h to 4 mM Cr(VI) and/or 3% phenol. Control microorganisms and those exposed to pollutants at various times were collected, disrupted and their soluble proteins separated in 2-DE polyacrylamide gels (18 cm, 4.0-7.0 pH) using three replicas per sample. Over 2,500 protein spots were resolved per gel. Image analysis of the proteomes obtained in the different conditions showed significant differences in expression of several proteins.

For the *in situ* study, the proteins present in soil samples were extracted for 2-DE analysis. Due to their charge, the presence of humic and fulvic acids or humins would interfere with the IEF separation of proteins, giving "horizontal streaking". Thus, different purification methods were tested with the extracted proteins before 2-DE analysis. A protocol has been optimized, that allows for the separation of  $\geq 1,000$  well-resolved proteins. These *in situ* proteomes are being compared in the three contaminated and the reference soils studied. Preliminary results show significant differences in protein expression. The spots differentially expressed in both the *in*

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situ and in vivo proteomes will be excised from the gels, treated with trypsin and analyzed to MALDI-TOF peptide-mass fingerprint analysis, followed by de novo sequencing by tandem mass spectrometry and bioinformatics search for protein identification.

The preliminary results already obtained in this pioneering work suggest that Metaproteomics approach can be applied to in situ studies of soils from real ecosystems and not only to in vitro studies, as usually done up to now. This predicts new and brilliant perspectives to the use of Proteomic methodologies for complete characterization of polluted environments.

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## RESPONSE OF BIOCHEMICAL BIOMARKERS IN CRABS FROM THE DOMINGO RUBIO STREAM (SW SPAIN)

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The Domingo Rubio stream (DRS), located South of Huelva province (SW Spain), flows to the left bank of Tinto River just before joining Odiel River into Huelva Estuary. At both DRS margins there is an intensive agricultural activity, mostly strawberry crops, that release great amounts of biocides and fertilizers, reaching maximal levels at the upper course. The lower and middle courses of DRS are under tidal influence and receive heavy elements of pyritic origin from the Tinto River and hazardous wastes from the nearby chemical plants and petrochemical complex, located at the New Port Industrial Area.

DRS pollution status was studied by following pollutant biological effects in digestive gland extracts of *Carcinus maenas* crabs collected with live traps at DRS mouth, using as reference animals collected at clean areas of Cadiz Gulf (CG), in the Atlantic Ocean. As biomarkers sensitive to metals/organic chemicals we assayed the activities of primary (GSH-peroxidase -SeGSHPx-, catalase -Kat) or ancillary antioxidant enzymes (glucose-6-P -G6PDH- and 6-P-gluconate dehydrogenases -6PGDH), of phase I (cyt P4501A -EROD) or II (GSH transferase -GST) biotransforming enzymes, lipid oxidative damages (malondialdehyde -MDA) and glutathione content and redox status (GSH, GSSG). Two esterases (carboxyl- -CbE- and acetylcholinesterase -AChE) were assayed as responsive to pesticides.

MDA levels were ~2-fold higher in DRS crabs compared to those from CG, suggesting that animals living at DRS are chronically exposed to metals and/or organic contaminants that generate reactive oxygen species, leading to lipid oxidative damages that generate oxidized by-products, such as MDA. The oxidative stress of DRS animals was confirmed by the glutathione redox status, 2-fold more oxidized in DRS compared to CG. SeGSHPx was similar in crabs from problem and reference areas. In contrast, three key antioxidant enzymes, Kat, G6PDH and 6PGDH, diminished in DRS animals compared to CG crabs, by 4-fold, 2,7-fold, and 7-fold, respectively. These drastic decreases in antioxidative enzymes could derive from inactivation or inhibition promoted by metal binding to these proteins, or from enhanced proteolytic degradation due to oxidative stress. A statistically significant decrease was also found in EROD activity linked to cytochrome P4501A. No significant differences were observed when the CbE activity of DRS and CG animals was compared. On the contrary, both GST and AChE activities increased 2-fold in crabs from the polluted area, probably as an adaptation to massive pesticide exposure.

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A Proteomic analysis of soluble gill proteins is being carried out in crabs living at DRS and at CG looking for proteins with significantly altered expression that could be useful in subsequent studies as new and unbiased pollution biomarkers. This so-called "Environmental Proteomics" approach, already carried out in wild mice from several DRS sites, will help to establish the biological effects of pollutants in a multidisciplinary project centered in DRS, aimed to develop new methodologies for the massive analysis of environmental data.

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## TOXICITY OF SOILS AFFECTED BY A PYRITE TAILING SPILL

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Science-based approaches for determining the ecological risks arising from contaminated sites are currently being developed. Biosensors provide an obvious means for monitoring truly bioavailable and bioaccessible contaminants in soils. Many biosensors have been successfully used to measure the toxicity of heavy metals and other pollutants in environmental samples. EC50 values for metals toxicity of pore water, extracted from soils amended with individual heavy metals concentrations, on *Vibrio fischeri* (Microtox®) and *Escherichia coli* have been reported by different authors (Mowat and Bundy, 2002; Paton et al., 1997; Dawson, 2005). However, metal contaminated soils are usually polluted with a variety of compounds and thus represent complex situations in terms of toxicity assessment.

In this study two different bacterial biosensors, Microtox® Acute Toxicity Test (Azur Environmental) and *Escherichia coli* HB101 pCD607 (Ratray, et al., 1990) were performed in pore water extracted from 25 soils affected by the pyrite mine spill in Aznalcóllar in 1998, polluted with high concentrations in As, Zn, Cu, Cd and Pb (Aguilar, 2004). Pore water was extracted in a 1:2 soil:water mixture (Flynn et al., 2002) and the solid-solution heavy metals partitioning coefficients ( $K_d$ ) were determined according to the calculation from Sauve´ et al. (2000). The luminescence express as a percentage of the luminescence of the control (Milli-Q water) sample.

Both biosensors (*V. fisheri* and *E. coli*) were sensitive to those pore water containing the highest heavy metal concentrations. Although *E. coli* tended to be more sensitive to soil solution heavy metal concentrations than *V. fisheri*, showing a large range of observable effects. Luminescence values determined for both *E. coli* and *V. fisheri* showed significant negative correlations ( $p < 0.001$ ) with the Cu, Zn, Cd water soluble concentrations. Cu, Zn and Cd exhibited the lowest  $K_d$  values indicating that a small proportion of these metals was retained by soils. Cubic functions of Cu, Zn, Cd and  $K_d$  values against luminescence explained the relation between heavy metals and biosensor responses, as has been previously reported for soils individually amended with these metals (Dawson et al., 2005).

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## BIOMONITORING OF CHLORINATED PESTICIDES AND PCBs IN THE EASTERN ADRIATIC COASTAL WATERS USING MUSSELS MYTILUS GALLOPROVINCIALIS AS INDICATOR

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As the result of increasing urbanization, agricultural activities and industrial development, coastal waters of the Eastern Adriatic (Croatian coast) have been exposed to contamination particularly by organic pollutants. However, the frequency of survey activities in the past decade has been reduced, as the consequence of the warfare in Croatia.

Therefore, a biomonitoring of chlorinated pesticides and PCBs, using mussels *Mytilus galloprovincialis* as very popular and widespread indicator organisms, was performed during 2002-2005 period along the Eastern Adriatic coast. The main objective was to provide information on the present extent and spatial distribution of chlorinated hydrocarbons, in order to determine baseline conditions and evaluate anthropogenic influence in the study area.

The general pattern of organic contaminants distribution was characterized by higher PCBs concentrations in relation to chlorinated pesticides, reflecting the prevailing influence of industrial sources of contamination over the agricultural ones. The average value and concentration range was 102 (10.7-287) ng/g dry wt for PCBs in comparison to 10.3 (2.3-25.1) ng/g dry wt for DDTs compounds. Much lower average concentrations were obtained for HCB, lindane, aldrin and dieldrin (0,14; 0.25; 0.84 and 0.75 ng/g dry wt), respectively.

Regarding spatial distribution, the elevated contaminant concentration was generally found in mussels collected near urban and/or industrialized centres with high input of industrial, harbour and urban wastewaters. Although not conclusive, no significant temporal decline of the level of contamination by chlorinated hydrocarbons at the Eastern Adriatic coastal area was observed.

The comparison of obtained data for PCBs and DDTs compounds in this work with previously published for Mediterranean regions might indicate a lower level of contamination at the investigated area. Moreover, all established concentrations were far below the maximum permissible level of chlorinated hydrocarbons in mussels for human consumption, prescribed by the Croatian legislation.

However, continued biomonitoring is necessary for reliable assessment of temporal and

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## ECOTOXICOLOGICAL EVALUATION OF THE EFFECT OF LAMBRO TRIBUTARY ON SEDIMENT QUALITY OF THE RIVER PO (ITALY)

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Many studies investigating the water quality of the River Po, the main river in Northern Italy, pointed out the Lambro tributary inflow as the primary source of contaminants over the entire Po river course. In spite of its relatively small mean-contribution of about 70 m<sup>3</sup>/s to the 750 m<sup>3</sup>/s of the Po river flow, the River Lambro discharges as high pollutant loads as to affect concentrations in Po river waters even downstream from the mixing-stretch.

The Lambro input is thus reported to significantly contribute to the transport of pollutants over the downstream part of the main-river course, carrying trophic as well as toxic loads to the Adriatic Sea. Particularly, the toxic contamination has been more recently investigated in a comprehensive study of Po river sediments. The contemporary evaluation of sediments collected downstream from the confluence of the main tributaries all over the 600 km river course, identified the Lambro confluence as one of the Po river-sites of major toxicological hazard and pointed out the toxicity testing on sediment solvent-extracts as most effective descriptors of sediment toxic potential.

Two ecotoxicological models were used in this study with the aim to highlight the effect of the toxic contribution of the River Lambro by evaluating changes of Po river sediment-quality over the 20 km-stretch downstream from the confluence of the two rivers.

Sediment samples were simultaneously collected in low-flow condition during late-winter period at five reaches selected both 5 km upstream, and downstream at ca. 6, 11, 16, 21 km from the Lambro inflow. The solvent-extracted fine fraction of sediment samples was used to measure the toxic potential as *Selenastrum capricornutum* 72h EC50 and *Ceriodaphnia dubia* 48h EC50, in terms of equivalent grams per litre of test-solution.

The results obtained from both the test-organisms allowed to clearly discriminate sediment-quality changes over the river-stretch, showing a similar up to downstream toxicity trend. The lowest toxicity was just measured upstream while the highest in the first downstream sample and as far as 21 km downstream the sediment toxicity was still 2-3 folds higher than in the upstream site. The role of Lambro input, as heavily affecting changes of the toxic potential of Po river sediments, was also supported by the physicochemical characterization of samples and by the analytical data of persistent organic chemicals from a parallel study of the same sediments. When compared with the previous study on the entire Po river course, the actual sediment-contamination levels were similar, or slightly lower, confirming the toxicological hazard of the river sediments downstream from the Lambro input. When compared with the previous ecotoxicological results, similar algal-toxicity values were also measured. Particularly, the good relationship linking toxic potential with contamination levels suggests the good agreement between present and previous results, and supports the toxicological approach as an effective descriptor of sediment contamination.

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**SPECTRAL CHARACTERIZATION OF FLUORESCENT EOM  
(EXTRACELLULAR ORGANIC MATTER) RELEASED BY THE  
BLUE-GREEN ALGA SYNECHOCYSTIS SP.**

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The primary production of phytoplankton, which is an essential source of food in aquatic ecosystems, involves both particulate biomass and dissolved organic matter, the latter being released by living cells into the extracellular medium. The EOM (Extracellular Organic Matter) is a complex and mostly unidentified mixture of organic chemicals. While a consistent literature has shown that a number of different compounds can be released by different algal species, relatively little is still known about the chemical composition and the relative contribution of the released compounds within the multi-component organic mixture.

The idea of fingerprinting EOM by fluorescence, which was born with the need to investigate the origin and the accumulation mechanism of massive quantities of mucilages in the Adriatic Sea, revealed appropriate to discriminate between EOM produced by different algae.

A biological method, based on the natural accumulation of EOM in laboratory-cultures, has been recently developed, as a strategy providing progressively high-concentrated EOM-samples. While the increasing concentration of the fluorescent compounds makes possible to define the production trend in monospecific cultures, the fluorescence analysis of EOM produced by a number of algal species revealed effective for a species-specific EOM characterization. The biological preconcentration system, combined with the synchronous fluorescence technique, was used in this study to provide the spectral characterization of the EOM produced by the blue-green alga *Synechocystis* sp.. With the aim to confirm the specific fingerprinting capacity, the spectral responses of *Synechocystis* EOM were also compared with the fluorophoric composition of EOM from different producer-species.

During 7 months the blue-green alga was aseptically grown in controlled conditions supporting long-lasting stationary growth of living cells. A series of filtered EOM samples from differently aged cultures was analyzed by synchronous fluorescence spectroscopy in a wavelength range of 250-500 nm using a  $\Delta\lambda = 25$  nm.

While both protein and humic-like fluorescence were recorded in all EOM samples, only the latter progressively increased following the accumulation-trend over time in stationary-cultures. While increasing as intensity, the humic-like fluorescence, with ex-max at 365 nm, was keeping a distinctive spectral shape. When compared with different producer-species from the same blue-green or from different algal groups, the spectral features were clearly discriminating *Synechocystis* EOM, based on additional bands or ex-max location.

These results support the ability of the combined biological and fluorescence approach to identify links between the released mixture of chromatophoric compounds and the producer species.

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## APPLICATION OF A TROPHIC INDEX (TRIX) FOR WATER QUALITY ASSESSMENT IN KALAMITSI COASTS (IONIAN SEA) AFTER THE OPERATION OF THE WASTEWATER TREATMENT PLANT

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In order to assess possible impacts on the quality of the coastal waters in Kalamitsi area, induced by the operation (July 2004) of the Wastewater Treatment Plant (WWTP), a monitoring program was applied on seasonal basis, during the period March 2001 - July 2006. Samples obtained from three stations were analyzed and data on chlorophyll- $\alpha$  (Ch), oxygen saturation (aD%O), mineral nitrogen (mN) and phosphorus ( $PO_4$ ) were used in order to develop the trophic index TRIX (mN,  $PO_4$ ), modified for the present case study as follows:

$$\text{TROPIC INDEX} = 2,5 \cdot (\text{LOG} [\text{Ch} \cdot \text{aD\%O} \cdot \text{mN} \cdot \text{PO}_4] - [0,5])$$

In the study area the trophic index TRIX depends mostly on aD%O ( $R^2 = 0,48$ ). Trophic index displayed similar values in all stations, having a weighted mean value 5.2 (good to mediocre water quality). No significant difference between stations was detected before or after the WWTP operation.

The TRIX mean values per sampling estimated before and after the operation of WWTP did not reveal any significant difference, indicating no or minor influence of the treated waste discharges on water quality. However, the TRIX standard deviation values per sampling displayed significant higher values after the treatment plant became operative, suggesting pressures probably attributed to the discharges of WWTP.

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**EFFECTS OF BEACH ALTERATION ON NESTING ACTIVITIES  
OF LOGGERHEAD TURTLES (CARETTA CARETTA) AT BELEK  
AND DENIZYAKA BEACHES IN ANTALYA, TURKEY**

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This study was carried out at Belek and Denizyaka beach during the nesting season (from may to september) at the year of 2004. It was observed that the changing in beach topography had resulted with nesting success variation in breeding season.

After the surface studies, lengths of the Beachs for 2004 are as follows: 4740 meters (Belek) and 2500 meters (Denizyaka). The whole beach is divided in two parts. On the Belek Beach side there are 30-46 meter wet zones and 100-300 meter near this there are hotels and resorts.

Keywords: Caretta caretta, Belek, Denizyaka, Beach structure, Nesting



## SOIL REMEDIATION BY USE OF INDUSTRIAL SLUDGES. TOXICOLOGICAL EVALUATION USING MICROTOX BIOASSAY

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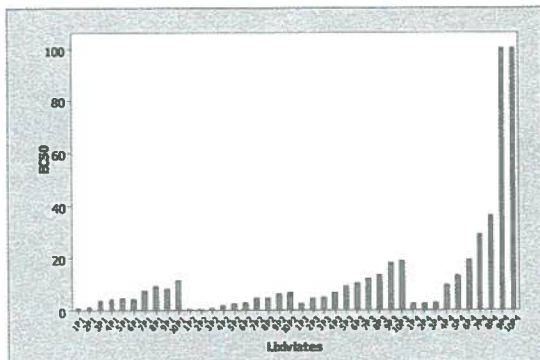
The addition of marble cutting sludges to soils was assessed as a possible way of remediating pollution by heavy metals. Two soil samples from a site affected by mining activities and two other soil samples obtained from a highly industrialised area were used for the study and were mixed with marble cutting sludges providing four stabilised samples from which forty lixiviates were obtained. The potential danger of polluted soils and the stabilisation effect was studied by applying Microtox® test.

The characteristics of the samples are shown in this table and we could see that soils showed acidic pH values. S3 showed the highest Zn, Pb and Cd content, while S2 had the minimum level of Zn and Cd. Finally, S1 showed the lowest Pb content. The marble cutting sludges had a basic pH, low EC and a very low metal content, being mainly composed of calcite and dolomite.

	pH	Pb (mg kg <sup>-1</sup> )	Zn (mg kg <sup>-1</sup> )	Cd (mg kg <sup>-1</sup> )
<b>S1</b>	4.11	4200	5900	35.2
<b>S2</b>	3.43	7500	640	0.4
<b>S3</b>	6.15	12703	66395	83.2
<b>S4</b>	2.34	5998	4979	36.2
<b>Marble cutting sludges</b>	9.47	1.3	6.2	0.5

All lixiviates from non-stabilised samples, except 9S3 and 10S3, were sensitive to the test. EC50 values obtained could be explained both by the presence of soluble heavy metals and by their acidity.

In lixiviates from stabilised samples, the test was only positive in the first lixivate of one sample.



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## GENETIC BIOTRANSFER OF 5-FLUOROURACIL AND ITS AQUATIC TOXICITY

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5-Fluorouracil (5-FU) is continually applied in the cancer therapy and ends up in the sewage water by human excretions, which reach the aquatic environment. In the environment this pharmaceutical residue and its potential toxic effects has been recognized as one of the emerging research areas in environmental chemistry. The increasing attention on 5-FU as potential pollutant, is due to that it does not have similar physico-chemical behaviour (eg Kow) than other harmful xenobiotics (vPvB) which may be persistent or produce adverse effects. In addition its continuous introduction in the environment may make it a 'pseudopersistent' substance. In this study, a radio-labelled [2-<sup>14</sup>C] 5-FU was used in the laboratory basis experiments. 5-FU is considerably accumulated by the green microalgae *Scenedesmus vacuolatus*. The genetic materials of the algae (DNA) are again offered to the ciliate, *Tetrahymena pyriformis* as DNA enrichment in addition with proteose peptone yeast (PPY) extract nutrient medium. Substantial amounts of 5-FU have been evaluated in both organisms used. Also the toxicity of 6-thioguanine has been measured. Our results indicate that the genetic accumulation of 5-FU can be biologically transferred to the other organisms.

Key words: 5-Fluorouracil, genetic biotransfer, aquatic environment

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## APOIDEA®: THE HONEY BEES AS ENVIRONMENTAL BIOINDICATORS

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In general, different species of Apoidea family have been used to evaluate Environmental Biodiversity and Environmental Management System. Competing communities of active groups of herbivore insects (for example Hymenoptera Aculeata) exhibit good bioindication properties for land ecological systems. The latter ones in particular change their structure under the influence of biocenosis changes (anthropogenic in particular) in the ecosystem or under the influence of changes in the hygric conditions or in the mosaic of habitats within the landscape.

On the other hand, honey bees (*Apis mellifera*) are good biological indicators because they indicate the chemical impairment of the environment.

In pesticide monitoring, the critical mortality threshold is about 250 bees/week/station, each monitoring station consisting of two beehives provided with underbasket traps. Only when the threshold value is exceeded, chemical analyses are conducted on dead bee samples in order to determine the active ingredients responsible for bee death. Some of the new insecticides do not cause high bee mortality, but they can severely affect honey bee behaviour, even at low doses. Therefore, in addition to bee mortality, also the development of the colony should be monitored.

Heavy metal pollution can be monitored with both bees and honey. It is, in fact, possible to integrate the data derived from these two matrixes to provide more complete information regarding the presence of contaminants in the environment. Honey can be used to obtain an average value regarding a vast area, because honey derives from nectar that has been collected in many places over several days. Bees can provide more detailed information than honey, because the pollution detected on them is ascribable only to a few days preceding their capture.

Since the incident of 1986 involving the nuclear plant of Chernobyl, studies in the absorption and transfer of radionuclides to beehives have remarkably increased, and nowadays this research continues with the monitoring of long-life radionuclides such as Cs-137 and Sr-90. Pollen and bees were shown to be good, highly sensitive indicators of radioactive contamination.

Recently, we used honey bees for the environmental detection of the phytopathogenic microorganism *Erwinia amylovora*, the causal agent of "Fire Blight", the most destructive bacterial disease affecting Rosaceous plants. It was shown that honey bees could reveal the presence of *E. Amylovora* in both already disease-affected areas and areas where no evident symptoms had yet appeared on the plants.

Keywords: Environmental bioindicators, *Apis mellifera*, monitoring, pesticides, heavy metal, radionuclides, *Erwinia amylovora*.

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## EVALUATION AND MONITORING OF SPATIAL CHANGES IN SAKARYA SUBBASIN USING REMOTELY SENSED DATA

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Sakarya River Subbasin which is under stress of water pollution is examined in this study. The focus of the study is determination of temporal, spatial and structural changes at the study area. The study area is located at the west-northern part of Turkey and surrounded by the several watersheds. The watershed, contains high tablelands and large plains which has a smooth surfaces. The total length of the Sakarya River is 510 km where water requirements of the urban settlements and industry are being served in the area. Additionally this river is also used for discharging of waste water of the settlements. This region is under threat of earthquake and announced as the first degree zone due to geomorphologic characteristics the region where a severe earthquake was happened in the 1999. After the earthquake within the region this area lost the previous characteristics of land use and urbanization. Hence there are drastic changes in the structural characteristics.

In order to analyze the land use/cover and spatial changes, SPOT XS (20m) and SPOT PAN (10m) satellite sensor images within the year of 1999 and 2006 were used. The spatio-temporal changes within the watershed was determined via using image enhancement and classification algorithms. Additionally digital elevation model of the study area is produced and merged with these satellite images in order to enhance the spatial analysis in three dimensions. The achieved results are discussed.

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## ANALYSIS OF WATER PRACTICES AND WATER SAVINGS IN ISTANBUL BY MEANS OF GIS

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Over population, pollution, deforestation and natural disasters are among the major problems faced by the world today. The increasing population and industrial development have put further pressure on the supply of fresh water. Water stress is increasing at the developing countries. In many countries agricultural and other economic activities can only be successfully carried out if there is sufficient fresh water. Water sourced problems will play a very important role in near future. Thus, saving water is becoming very crucial.

Usage and saving of water is totally depends on conscious level of the public. There is a clear parallelism between this level and water saving. In order to measure this level several different methods can be used. In the recent years Geographic Information System (GIS) is become more popular among the other methods.

GIS as a computer-based tool for mapping and analyzing spatial data and events that take place in the earth is also a useful tool for water management aspect. GIS can be used to store, retrieve and display geographically referenced data of the area. It has the power to create maps, integrate information, visualize scenarios, solve complicated problems, present good ideas and develop ultimate solutions.

In this study, Istanbul which is the largest city of Turkey with the over 12 million population was selected as study area. Istanbul has been divided into 32 administrative districts and 4 of these districts (Kadikoy, Bakirkoy, Bahcelievler and Sariyer) were chosen. While choosing these districts, general outlook of the areas like cultural situation and development degree were considered.

To measure conscious level of the public a survey which has 20 questions were prepared and this survey was conducted. Totally 595 survey was realized in the selected districts. After the entire questions take place at the survey was graded all surveys were evaluated. Obtained results were classified and average conscious level of the public was calculated for each neighborhood in the selected districts.

Spatial and non spatial data were stored in GIS data base and several different queries and analysis were carried out. Some of the queries done based on the survey results are; distribution of conscious level, distribution of education and sexual distribution. Obtained results are discussed and displayed on several maps.

Keywords: GIS, conscious level, water saving, Istanbul.

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## PHYTOPATHOGENIC FUNGI IN ANTALYA/TURKEY

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This study aims to identify the species of parasite fungi found on flowering plants in the city of Antalya. The research area goes from the southern east border of Beydagları-Forest in the west, to the Kurgunlu-Çakırlar border in the North, to the Kurgunlu-Lara border in the east and borders with the sea in the South.

The infected plant samples were collected in between February 2000-May 2001. From a total around 911 infected samples, 114 were found to be infected by fungi. The results of the studies carried out on the host plant species in the area reveal a total of 92 parasite fungi species and the total taxa number is 94. Six of these fungi belong to Oomycetes, 18 Ascomycetes, 25 Basidiomycetes, and 45 Deuteromycetes. In the study area, the following orders are represented by these taxa numbers: Peronosporales 6, Sphaeriales 1, Hypocreales 1, Erysiphales 13, Pleosporales 2, Dothideales 1, Uredinales 19, Ustilaginales 6, Moniliales 20, Melanconiales 5 and Sphaeropsidales 20.

Three of 48 identified fungi genera, and 36 of 92 fungi species found in the study area are new for the microfungal flora of Turkey. In addition to, 7 of the plants infected with fungi are new for Turkey and 1 species is a new host for science.

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## SUSTAINABLE ENVIRONMENTAL MANAGEMENT IN COASTAL AREAS – SCIENTIFIC CONCERNS

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Coastal tourist resorts are increasingly threatened by economic and demographic pressure, and the marine ecosystems are in decline around the globe. From a wastewater management viewpoint, the developments should be evaluated within the context of maintaining the critical balance between tourist attraction and preserving water quality. In coastal tourist areas, the quality of the receiving water is, on the one hand, the prime concern for the value of the resort, and on the other hand, it is quite susceptible to pollution and especially to nutrients likely to create eutrophication problems. Tourism should contribute to sustainable development and be integrated with the natural, cultural and human environment. It should ensure an acceptable evolution as regards its influence on natural resources, biodiversity and the capacity for assimilation of any impacts and residues produced.

Water scarcity is also the most crucial environmental problem in tourist resorts. It is exacerbated by the deteriorating quality of water resources due to population fluctuation and other activities. In view of water scarcity, especially coastal touristic areas suffering from water shortage, have to take measures to increase water use efficiency and stimulate greater conservation. This can only be achieved through a realistic environmental management strategy. Within this context, major issues necessary for the environmental basis of sustainable tourism have to be carefully considered and developed for the sustainability of tourism activities.

This paper provides a critical overview of the basic environmental principles for sustainable tourism along sensitive coastal areas and discusses the application procedure by using the outcomes of an extensive study carried out on the coastal zone of Turkey. In this manner, expected water quality, wastewater characteristics and pollution profile, and appropriate treatment technologies are outlined and effective recommendations are offered for future activities.

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## EVALUATION OF GENOTOXICITY IN POLLUTED SOIL BY BENZENE

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Benzene is classified as a human carcinogen, and an association between exposure to benzene and the development of leukemia is well established. The aim of this study was to detect genotoxic effects with short-term genotoxicity tests performed on polluted soils. Analysis of soil samples, coming from an Italian refinery, was carried out in order to evaluate the mutagenesis induction. The evaluation of the genotoxic effects was performed by studying Micronucleated cells (MC) and DNA damage by Comet assay in root meristems of *Vicia faba* seedlings grown on soil samples polluted with benzene. The phytotoxicity was also investigated by the reduction in length of the primary root of *Vicia faba* seedlings. The comet assay on plants has become a useful method for the assessment of the environmental genotoxic impact. It may complement other test systems measuring different endpoints of genotoxicity. The micronuclei test has been used for detecting genotoxic damages in seedlings grown on a polluted soil. The genotoxic effects were evaluated by the frequency of MC and AA in root meristems of *Vicia faba*. A DNA-based biosensor for the detection of genotoxic compounds in soil samples, was assembled by immobilising double stranded calf thymus DNA on screen-printed electrodes. The interactions between DNA and environmental pollutants can cause variations of the electrochemical properties of DNA when a DNA damage is present.

Furthermore in a simulation, in Tor Mancina area (near Rome) benzene genotoxicity was evaluated. Two sets of lysimetric boxes were set up, testing two different types of soil, sandy and clay-loamy soil, cultivated with lettuce (*Lactuca sativa* L.); half of the boxes were polluted with benzene dissolved in soybean oil, while the other ones were used in terms of comparison. The contamination effects on soil functional qualities and plant nutrition were tested; DNA damage with short-term genotoxicity tests and DNA biosensor, on polluted soils and on gravitational water, was detected.

Interestingly, agreement was found between biosensor results and other methodologies. Such DNA biosensors could be useful as early warning devices in areas subject to ecological risk. They may represent an easy and fast way of analysis of polluted areas, especially for in-field experiments, because the analysis of a sample can be performed in only 11 minutes instead of hours, days or weeks that are generally needed for the common genotoxicity tests.



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## HAZARD IDENTIFICATION OF IMIDACLOPRID TO AQUATIC ORGANISMS

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Imidacloprid, belongs to the group of neonicotinoids, and has been increasingly used since 1991. At the moment it is the insecticide with the world's fastest growing sales and is considered a possible replacement for widely used organophosphorus pesticide, diazinon. It is used mainly to control sucking insects on crops e.g. aphids, leafhoppers, thrips, whiteflies, termites and pets e.g. fleas. Imidacloprid is not intended for use in water but it may enter aquatic environment with spray drift or accidental spills, leading to local point-source contaminations. Therefore, the presence of imidacloprid in aquatic environments may affect aquatic organisms. Considering the fact that imidacloprid is a very widely used insecticide, the toxicity of imidacloprid and its commercial formulations on different aquatic organisms should be evaluated to exclude its adverse impacts on aquatic ecosystems. Until now, the toxicity of imidacloprid to aquatic species has rarely been assessed due to the former belief that the compound is relatively immobile in soil and does not leach to groundwater.

Due to the paucity of data on adverse effects of imidacloprid on aquatic organisms the purpose of this study was to identify the potential hazard of imidacloprid and its commercial liquid formulation Confidor SL 200 to organisms from different trophic levels. The toxicity tests with bacteria *Vibrio fischeri*, mixed bacterial community, crustacean water flea *Daphnia magna*, algae *Desmodesmus subspicatus* and fish *Danio rerio* were performed to assess the acute and chronic effects.

The obtained results indicate that imidacloprid and Confidor SL 200 are not highly toxic to tested organisms. The highest acute toxicity was observed in a case of *Daphnia magna* (48h EC50 = 56.6 mg/L) and the commercial formulation was slightly more toxic than imidacloprid alone. Bacteria *Vibrio fischeri* revealed lower toxicity than daphnids, but there was no effect on mixed bacterial culture even at the highest tested concentration. The least sensitive species in our study were the algae *Desmodesmus subspicatus* with a 72 h IC50 at 389 mg/L of imidacloprid. The adverse effects on reproduction of *Daphnia magna* were detected at 2.5 mg/l of imidacloprid after chronic exposure (21d NOEC = 1.25 mg/L). The significant discrepancy of toxicity between imidacloprid and the commercial formulation was not found in most cases.

In the future, higher environmental levels of imidacloprid are expected due to its increasing use. We suggest that further ecotoxicological studies with a broader spectrum of aquatic organisms are performed before imidacloprid is classified as safer than currently applied pesticides.

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## KINGFISHER SPECIES AND THEIR RECENT HABITAT LOSE IN TURKEY

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The number of kingfisher species, exist in Turkey, is 3 belonging to different Kingfisher families (Alcedinidae, Halyconidae and Cerylidae). According to the results of our observations and evaluations realized between the years 2002 – 2006 the most wide spreaded Kingfisher species between them is the European Kingfisher (*Alcedo atthis*). This species is represented with more individual than the other Kingfisher species. Other Kingfisher species, White-breasted Kingfisher (*Halcyon smyrnensis*), which is rarely other than and has a limited range. The last species, Pied Kingfisher (*Ceryle rudis*) has a lower dispersion and the number of individuals is quite low. Estimates place the population at around 200 breeding pairs in Turkey. These three Kingfisher species are faced with different threats. The most important of these threats is increased construction of dams in their habitats. For example, only one dam project in SE Turkey will be effect 20 % of the European population of the Pied Kingfisher.

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## GENOTOXICITY TESTING OF ARSENIC, LEAD AND CADMIUM IN RADISH PLANTS GROWN ON POLLUTED SOILS

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Among contaminants, some metals(oids) such as arsenic, cadmium and lead have shown toxic effects when they are accumulated to some extent. However, the adverse effects of some of these metals(oids) depend not only of the concentration by itself, but on factors such as the presence of phytochemicals in the matrix. Thus, these synergies are needed to be evaluated. To test the genotoxic and antigenotoxic effects of metals(oids) over living organisms, the Somatic Mutation and Recombination Test (SMART) of *Drosophila melanogaster* has been shown to be an excellent indicator.

The main objectives of this work were: i) to study the uptake and accumulation of arsenic, lead and cadmium in radish (*Raphanus sativus* L.) plants, and ii) to establish the genotoxic and antigenotoxic properties of the edible parts of this vegetable.

Metal(oids) concentrations in the edible part of the radish plants were always below the maximum limit set established for these toxic elements in vegetables. The human health implications of arsenic, lead and cadmium accumulated in parts of radish plants are discussed.

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**ECOTOXICOLOGICAL ASSESSMENT OF TWO MINING PONDS  
FROM CARTAGENA-LA UNION MINING DISTRICT (SE SPAIN) AFTER  
TWO YEARS REMEDIATION PROGRAMME**

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Mine soils from Cartagena-La Unión Mining District, SE Spain, possess elevated concentrations of heavy metals and constitute a high risk of pollution for the environment. Chemical stabilization of heavy metals, by adding carbonates and organic wastes, combined with phytostabilization were used as a remediation technique in two representative mining ponds. Monitoring of remediation and assessment of the potential threat to ecosystems and human health caused by polluted soils is generally approached by chemical characterization. However, to get a realistic view on the actual risk of the contaminants depending on their bioavailability, it is necessary to complement the chemical analysis with ecotoxicity testing. These tests provide a direct measure of ecotoxicity and an account for all bioavailable known or unknown toxic components in a soil. Therefore, the combined physico-chemical characterization and ecotoxicological evaluation may improve the description of the potential threat of contaminated and remediated soils on ecosystems. The aim of this study was to assess the water extractable ecotoxic potential of mine soils amended with organic wastes and carbonates. Water extracts of two years amended and not treated soils samples were assessed with *Vibrio fischeri* luminescence inhibition test; algae growth inhibition test; *Daphnia magna* test, and *Vibrio fischeri* and *Pseudomonas putida* growth inhibition test. Results showed a reduction of ecotoxicity in amended soils compared to no treated soils in all the tests, except for *V. fischeri* growth inhibition test that was no sensitive for one soil type. Moreover, where inhibition percentages were higher enough to calculate EC50 values, such as in *Pseudomonas putida* and algae growth inhibition tests, these values increased with amendment addition showing the decrease of ecotoxicity. Ecotoxicological and chemical analyses demonstrated that after two years of remediation, risks related to heavy metal mobility and toxicity were reduced in both mining soils.

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**MONITORING COMPLEX MIXTURE OF POLLUTANTS ON  
LIXIVIATE POOL OF A MEDITERRANEAN LANDFILL AND ITS  
STREAM USING WOOD MOUSE AND ARTHROPOD BIODIVERSITY.**

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Anthropogenic activity introduces into the environment several chemicals, most of them biologically active or bioavailable for some organisms. These xenobiotics constitute a source of stress for natural communities, with long-term effects on the populations and ecosystems. Several models of ecotoxicological risk assessment have been described. We have previously proposed a method based on toxicological information divided into four blocks, i.e., systemic toxicity, genotoxicity, reprotoxicity and effects on populations (Borràs and Nadal, 2004). Part of this data are shown in this study.

Wood mouse and arthropod populations were caught in four sites: VG, area next to the lixiviate pool at the Garraf landfill; 2VG, bed of the dried watercourse draining the Garraf landfill, 2 Km downstream from the lixiviate pool; 4VG, bed of the same watercourse, 4 Km downstream from the lixiviate pool and CVG, area with geological and phytogeographic features similar to the studied landfill, but devoid of any known source of contamination (used as reference).

Blood parameters (erythrocyte, lymphocyte, monocyte and granulocyte count), body measures and serum biochemistry (GOT, GPT, BUN, Creatinine and Total Protein) were analysed in wood mouse, *Apodemus sylvaticus* (N=48). Arthropod biodiversity was calculated by Margalef Index.

Red and white blood cell counts in VG showed differences with respect to the other studied sites. Hepatic biochemistry parameters suggested positive effects in lixiviate pool area and in the landfill stream but no clear results were observed in renal parameters. No relationship was observed between body measures and other studied parameters. Finally, decrease in biodiversity was observed in VG using Margalef Index.

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**DICENTRARCHUS LABRAX L. MULTI-BIOMARKERS RESPONSE  
TO THE AVEIRO LAGOON WATER CONTAMINATION (PORTUGAL)**

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The Aveiro Lagoon at the north-western coast of Portugal, has been under an increasing anthropogenic pressure for several decades, contributing its water quality degradation. The aim of the research work was to monitor the effects induced, by the complex mixture of different contaminants present in the Aveiro Lagoon water, using several biomarkers in *Dicentrarchus labrax* L. (sea bass). Thus, sea bass were captured at five Aveiro Lagoon sites: Torreira(Tor), Gafanha(Gaf), Rio, Laranjo(Lar) and Vagos(Vag) in Autumn 2005. The following biomarkers were measured as metallothioneins (MT) and antioxidant responses - catalase (CAT), glutathione peroxidase (GPx), glutathione reductase (GR), glutathione S-transferase (GST), content and thiois. Lipid peroxidation (LPO) was also measured. Liver DNA integrity decrease was also determined as genotoxicity indicator. The results revealed that the highest liver CAT, GR activities, LPO and thiois contents were found in sea bass caught at Tor. LPO and GR were lowest in Lar. Sea bass caught at Rio demonstrated the lowest liver GST, GPx, CAT and thiois, whereas the highest liver GST, GPx activities and MT were measured in fish at Vag. Moreover, the lowest liver DNA integrity was found in sea bass caught at Gaf. The results concerning the current study demonstrate that multi-biomarkers should be used in the Aveiro Lagoon continuous monitoring.

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## AVEIRO LAGOON (PORTUGAL) FIELD SURVEY - LIZA AURATA GILL AS A TARGET ORGAN FOR CONTAMINANT INDUCED TOXICITY EVALUATION

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The objective of this study was to monitor Ria de Aveiro (Portugal) contamination, by measuring antioxidants (thiols, GR, GST, GPx and catalase), metallothioneins (MT), peroxidative damage (LPO) and genotoxic responses (DNA integrity) using golden grey mullet (*Liza aurata*) gill. *L. aurata* were captured in the Autumn of 2005, at 6 sites (Torreira-Tor, Barra-Bar, Gafanha-Gaf, Rio, Laranjo-Lar and Vagos-Vag). Fish caught in Rio had the highest thiol levels whereas in Tor fish had the lowest levels. GR activity was higher in fish from Gaf and the lowest activity was found in fish from Rio. GST and GPx activities were found higher in fish from Lar and lower in Tor whereas catalase was highest in Gaf and lowest in Bar. MT levels were higher in fish caught in Lar whereas Bar and Rio were respectively, the sites where the fish had the highest and the lowest LPO levels. The lowest gill DNA integrity was found in fish from Gaf. Gill multi-biomarker responses have demonstrated their utility in coastal lagoon monitoring.

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**GOLDEN GREY MULLET (*LIZA AURATA*) LIVER OXIDATIVE STRESS AND  
GENOTOXICITY RESPONSES IN THE ENVIRONMENTAL CONTAMINATION  
ASSESSMENT**

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Several Aveiro lagoon (Portugal) contaminated sites were assessed in the Autumn of 2005 using golden grey mullet (*Liza aurata*) hepatic antioxidant responses (thiols, glutathione reductase - GR, glutathione S-transferase - GST, glutathione peroxidase - GPx and catalase - CAT. Moreover, metallothioneins (MT), lipid peroxidation (LPO) and DNA integrity were also evaluated. Fish were captured at 6 different sites (Torreira-Tor, Barra-Bar, Gafanha-Gaf, Rio, Laranjo-Lar and Vagos-Vag). Fish caught at Lar showed the highest GR activity whereas the lowest was found in fish collected from Rio. *L. aurata* GST and GPx activities were highest in Tor and lowest in Lar. *L. aurata* CAT, showed the highest activity at Vag and the lowest at Rio. MT levels were higher in Lar than in the other sites. The LPO highest levels were found in fish collected from Vag whereas Tor was the site with fish having the lowest LPO levels. *L. aurata* liver showed the lowest DNA integrity at Rio. This data demonstrates the importance of the adopted multi-biomarkers as applied in *L. aurata* in sea coastal water pollution monitoring.



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**WILD GOLDEN GREY MULLET (*LIZA AURATA*) KIDNEY  
ANTIOXIDANT AND DNA DAMAGE RESPONSES TO AN AQUATIC  
CONTAMINATED ENVIRONMENT**

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Golden grey mullet (*Liza aurata*) was captured in October 2005 at the Aveiro Lagoon (Portugal) six different locations (Torreira, Barra, Gafanha, Rio, Laranjo and Vagos). This coastal lagoon is contaminated by chloralkali plant (metals), pulp and paper mill factory (resin acids), harbour activities (PAHs) known to influence the oxidative status and DNA integrity levels of aquatic animals, often proposed as biomarkers of effect. Thus, this field research goal is to investigate the role of several biomarkers: catalase (CAT), glutathione peroxidases (GPx), glutathione reductase (GR), glutathione S-transferase (GST), thiols, lipid peroxidation (LPO) and genotoxicity (DNA integrity decrease), measured in kidney. The current study demonstrated the highest kidney CAT activity in *L. aurata* caught at Vagos and lower in Gafanha. GR had the highest activity at Laranjo. However, the lowest GR and GST activities were observed in kidney fish at Torreira. GPx activity was higher in fish caught at Laranjo. Kidney thiols were higher in fish at Rio and lower at Torreira. Moreover, the highest kidney LPO levels were observed in fish caught at Vagos and the lowest at Torreira. In terms of genotoxicity, the lowest kidney DNA integrity was found in Rio. *L. aurata* kidney demonstrated a different sensitivity to Aveiro Lagoon different exposure locations where different water contaminants may be present.

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**SEASONAL ASSESSMENT OF A CONTAMINATED COASTAL  
LAGOON (RIA DE AVEIRO, PORTUGAL) USING DICENTRARCHUS  
LABRAX L. ERYTHROCYTIC NUCLEAR ABNORMALITIES**

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Ria de Aveiro, a coastal lagoon, located in northern west region of Portugal has been the main receptor of anthropogenic discharges resulting mainly from chlor-alkali and pulp/paper plants, harbours and dry-dock activities as well as municipal and domestic effluents. In this perspective, European sea bass (*Dicentrarchus labrax* L.) erythrocytic nuclear abnormalities (ENA) assay which provide a measure of genetic damage, was applied to monitor this complex water pollution. Fish capture was carried out between spring 2006 to winter 2007, at six locations (Torreira-TOR, Barra- BAR, Gafanha-GAF, Rio Novo do Príncipe-RIO, Laranjo-LAR, Vagos-VAG) along the lagoon.

In spring, a significant ENA induction was observed at BAR, RIO, LAR and VAG in comparison to reference site (TOR). In summer, the ENA induction was significant at all the studied sites. In autumn, ENA induction was significant only at GAF, LAR and VAG. In winter, BAR, GAF, RIO and LAR were the sites showing a significant ENA induction when compared to TOR. This investigation finding provides a rational use of ENA applied to European sea bass which may be successfully employed for biomonitoring anthropogenic contamination in both Atlantic and Mediterranean European coastal waters.

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**SEA BASS (*DICENTRARCHUS LABRAX* L.) GILL ANTIOXIDANT,  
METALLOTHIONEIN, LPO AND GENOTOXIC RESPONSES TO THE  
AVEIRO LAGOON WATERBORNE CONTAMINATION (PORTUGAL)**

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The aim of the present study was the biomonitoring of a polluted coastal lagoon, Ria de Aveiro (Portugal), by assessing European sea bass (*Dicentrarchus labrax* L.) gill antioxidants enzymes viz. glutathione peroxidase (GPx), catalase (CAT), glutathione reductase (GR), glutathione S-transferase (GST) as well as non-enzymatic antioxidants viz. thiols. Metallothionein (MT), lipid peroxidation (LPO) and DNA damage were also evaluated. Fish were caught in autumn of 2005 at five locations (Torreira-Tor, Gafanha-Gaf, Rio Novo do Príncipe-Rio, Laranjo-Lar, Vagos-Vag) along the lagoon. *D. labrax* showed antioxidants enzymes induction viz. GPX (Gaf, Vag), GR (Gaf, Vag), CAT (Lar) and GST (Gaf, Lar, Vag) when compared to the reference site (Tor). Thiol induction at Gaf, Rio, Lar and Vag and MT induction at Vag was also observed when compared to Tor. Nevertheless, fish caught from Gaf showed DNA integrity decrease and LPO increase. These investigation findings provide a rational use of adopted multi-biomarkers applied to European sea bass and can be successfully employed for biomonitoring anthropogenic contamination in both Atlantic and Mediterranean European coastal waters.

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## DICENTRARCHUS LABRAX L. KIDNEY OXIDATIVE STRESS AND GENOTOXIC RESPONSES TO CONTAMINATED COASTAL WATERS

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Ria de Aveiro is a coastal lagoon (Portugal) which used to receive anthropogenic discharges resulting from, chloralkali and pulp/paper plants, harbour and dry-dock activities as well as municipal and domestic effluents. The present research work was carried out to check the various oxidative stress and genotoxic biomarker responses in European sea bass (*Dicentrarchus labrax* L.) kidney due to this complex water pollution. Sea bass were captured in autumn of 2005 at five locations (Torreira-Tor, Gafanha-Gaf, Rio Novo do Príncipe-Rio, Laranjo-Lar, Vagos-Vag) in Ria de Aveiro. Lipid peroxidation (LPO), catalase (CAT), glutathione peroxidase (GPx), glutathione reductase (GR), glutathione S-transferase (GST), thiols and DNA strand breakage were the biomarkers studied. Among all the sites, LPO was increased in fish collected from Gaf; and DNA integrity decrease was observed in fish collected from Gaf and Vag in comparison to Tor. Kidney CAT was induced at all the study sites whereas, GPX, GR and thiol were induced in fish collected from Gaf, Rio and Lar only. Interestingly, kidney is vulnerable towards peroxidative damage at Gaf and its antioxidant potential is also very strong. Thus, the assessed biomarkers were able to express site-specific responses, demonstrating their utility on coastal water health assessment.

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## EFFECTS OF GLOBAL CLIMATE CHANGE ON SMALL MAMMAL COMMUNITIES IN ITALY

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The balance of evidence from a large number of studies suggests that climate change is affecting both animal and vegetal species. Shorter hibernations, advanced breeding, weight reduction, advanced migrations, biodiversity loss and shift in geographic range have been observed. In this framework, the identification of suitable bio-indicators could be an important tool for monitoring and predicting the effects of climate change on species and ecosystems.

Small terrestrial mammals (Rodentia, Soricomorpha) have been chosen as bio-indicators of environmental stress because of their roles in terrestrial ecosystems (e.g. primary and secondary consumers, wood renewers, preys, pathologies spreaders) and their ability to characterize different bioclimates. This study represents the first attempt to investigate the effects of global climate change on Italian small mammal communities. Literature, unpublished and recently collected data, obtained from the observation of cranial bones found in Barn owl (*Tyto alba*) pellets, have been used to reconstruct the micromammal biocoenoses. Faunistic data cover a period of about thirty years. Twenty-two roosts, located all over the peninsula, were grouped into two main bioclimatic regions, according to the Bioclimatic Map of Italy. Temporal variations of several indexes (biotic diversity, trophic level, thermoxerophily indexes, etc.) have been analysed for all small mammal communities. An increase of thermo-xerophilous species (e.g. *Suncus etruscus*, *Crocidura suaveolens*, *Rattus rattus* and *Mus domesticus*) has been observed in several small mammal communities, irrespective of land use and bioclimatic region. The increase is consistent with the tendency toward temperature rise and precipitation decrease recorded in Italy during the last thirty years.

The persistence of this trend would lead to serious consequences in terrestrial ecosystems, such as biodiversity and species evenness reduction. In conclusion, small mammals have been proved useful indicators, not only in ecosystem description, but also in climate change studies. In this perspective, a long-term monitoring of Barn owl's diet should be carried out.

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**GLOBAL WARMING: ATMOSPHERIC METHANE  
SOURCES AND LANDFILL METHANE OXIDATION  
(REVIEW)**

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The methane gas which has 20 times more absorption capacity of infrared radiation in comparison to CO<sub>2</sub> is in third place considering its addition to global warming. Discussions about what would be the dramatic results of the climate changes which happen before their estimated times have been main issues in the world agenda for the recent three years. Therefore, in this review which also consists of studies of decreasing natural and anthropogenic sources and degrees and effects of methane emission which plays an important role in rapidly increasing global warming. Especially, researches about to decrease methane emissions in landfill areas which produces methane emissions show that it could be decreased more than 90% methane which is released to atmosphere. In the meantime, by taking precautions other methane emissions which come out by atmospheric resources could be minimized by appropriate methods and to get successful results.

**Keywords:** Global warming, methane oxidation, climate change, methane mitigation, landfill methane

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## DYNAMIC RISK ASSESSMENT OF ECOLOGICAL DISASTERS

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The damage to the aquatic environment following an accidental spill of dangerous substances is determined by a number of parameters. In broad terms, these refer to the intrinsic properties of the substance itself (aquatic toxicity, persistence, bioaccumulation, solubility in water, etc.), the fate of the substance in the aquatic environment (evaporation, sedimentation, dilution, chemical reactions, degradation, etc.), the physical conditions of the aquatic environment (flow rate, dimensions, physicochemical properties of the water, prior pollution, etc.), and the population and sensitivity of aquatic habitats. Current state of the art in environmental risk assessment is based on the use of static risk metrics (comparing the Predicted Environmental Concentration of the toxicant against its Predicted No Adverse Effect Level), which fail to account for the dynamic nature of ecological disasters.

To obtain a better estimate of toxicity we need to consider the details of the disaster-impacted exposure conditions, i.e. the temporal profile of pollutant speciation in the external medium and the ability of the organism's physiology to handle the internalised concentrations within a given timeframe. The dynamic framework developed herein recognises that the bio-uptake flux is a key parameter in determining toxicological effects. Overall, current challenges for dynamic risk assessment include (a) the need for better understanding of the fate and transport properties of complex mixtures, characteristic of ecological disasters; (b) rendering the concept of mode of action (MOA) and multiple MOA usable for ecotoxicological risk assessment; (c) properly accounting for chronic combined effects (in particular with regard to reproductive and developmental toxicity); (d) modelling pulsed exposure (especially for ecological disasters) and solving the problem of the different time scales of the dynamic system: fast ecological dynamics versus the relatively slower physiological processes; (e) accounting for latent effects (silent toxicity).

This work presents a novel approach to addressing ecotoxicological risk in the case of ecological disasters, introducing biology-based concepts for assessing dose-response relationships between environmental concentrations of toxicants in the aquatic environment and health effects on aquatic organisms such as muscles, shellfish and other fishes. Our approach, which is based on biology-based dose-response modeling, takes into account the physiological processes controlling bio-uptake and metabolism of toxic chemical species in a dynamic time frame. This allows for creating dose-response-time estimates of toxicity, which extend the use of conventional "static" risk metrics. The dynamic toxicity model developed estimates target organ concentrations and physiological response as a function of time. This improves our understanding of the dynamic relationships between concentration exposure and hazard to aquatic species. Furthermore, we identify appropriate biological tissues that may serve as biomarkers sensitive to acute and transient exposure to waterborne contaminants such as heavy metals. The implementation of the methodology is shown using the mortality of tilapia (a tropical fish species) due to arsenic contamination as example case.

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## OCCURRENCE OF VETERINARY DRUGS IN THE ENVIRONMENT: SUSTAINABLE AGRICULTURE

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During the last twenty years, industrial livestock farms have been replacing the traditional family sized farms, especially in EU candidate countries such as Turkey but also in China, which is one of the biggest producer in South Asia. This has led to intensified farming practices where large numbers of animals are reared on relatively small areas, with large waste production posing disposal problems. The intensification of livestock production with its associated increased demand for fodder has encouraged farmers to rely more heavily on chemicals (fertilizers, pesticides, antibiotics, vaccines, disinfectants, etc.) and imported feeds, and therefore very often the manure is not longer considered as an useful soil conditioner. Regardless of this fact large quantities of solid waste and slurry, far in excess of crop requirements, are collected and applied to arable land. The mobility of the drugs or drug metabolites in the soil system predicts, if the drug threat the ground water, affect the terrestrial or aquatic organisms. Unlike priority pollutants, the behaviour and effects of veterinary medicines in the environment has not been extensively studied. Consequently, despite of a relative high usage of some veterinary medical products very little information on consumption, release, fate and effects of this group of substances is generally available. The presentation provides information on the Environmental Impacts of Agriculture and Aquaculture Operations, Required Regulations to Control Environmental/Human Health Impact, Organic Farming



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## **ALTERNATIVE PRODUCTION WAYS TO REDUCE WASTE AND POLLUTANTS OF PROCESSES IN TURKISH SHIPYARDS**

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Ship building industry, known to be one of the oldest productive facilities of mankind, is one of the major sources of pollutants to the environment. Shipyards are often categorized into two basic subdivisions: Shipbuilding and ship repairing. Some shipyards build only large ships and also have repair and dry dock facilities. Other shipyards have facilities for building small and medium sized vessels such as patrol boats, fire and rescue boats, water taxis, ferries, tug boats, fishing boats and shallow drafted barges

This paper focuses on shipyard processes, their pollutant emissions (solid, liquid and air) and alternative ways to reduce these wastes and pollutants resulting from shipbuilding and ship repair activities. New ship construction and ship repairing industries have many industrial processes, similar facilities, and support shops in common. The shipbuilding and repair industry processes are consist of surface preparation, welding, painting and coating, metal plating, surface treatment, solvent cleaning and degreasing, machining and metalworking, vessel cleaning, and fibreglass operations etc.

There are several wastes and pollutants being released during shipbuilding and ship repairing processes. Minimising or avoiding these wastes and pollutants is the most important point to protect enviroment and echology. Especially the climate change, mostly being discussed and studied for recent years, will be effected by improving these shipyard production processes. In this study, to prevent the pollution and waste production, the alternative production systems to current production processes are being investigated such as dry ice blasting to replace sand or grid blasting to prevent blast wastes, using tin-free paints to replace antifouling paints to reduce VOC and PM emissions, using underwater welding and plasma welding instead of electrical arch welding to minimise welding fume and hazardous pollutants, etc.

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## MODELING THE IMPACTS OF CLIMATE CHANGE ON THE WATER QUALITY OF WATERSHEDS

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The Hydrological Simulation Program-FORTRAN (HSPF) has been used to investigate the impacts of climate change on the water quality processes in hypothetical watersheds under different vegetation covers. A scenario has been constructed by extracting trends in temperature, precipitation, cloudiness, humidity and wind velocity using statistical methods from GCM simulation results conducted by the Canadian Climate Center for a grid cell coinciding with western Turkey which is located in the Aegean and Mediterranean Region of the country. These trends have been used in creating daily values for meteorological time series utilized by HSPF as the driving force behind the hydrological and water quality processes. The scenario is based on the SRES A2 scenario of the IPCC. The four types of watersheds investigated are a barren watershed, a pasture, a watershed covered with coniferous forest and one with a deciduous forest. The quality of water in terms of conservative contaminants like dissolved solids leaving the watershed as surface-runoff, interflow and groundwater outflow has been chosen as the variable to be investigated on a monthly basis (computed from daily simulation results). Simulations have been conducted for a time period of 47 years beginning in the water year of 2004. The results show that, though overall changes are modest on a yearly basis, there are significant differences on a monthly basis for hydrological variables, manifesting themselves as increased droughts and floods in certain months. Consequently, changes have been observed in water quality variables affecting the usability of the watershed water output and the sustainability of the use of the watershed for various purposes. The results can be used by watershed managers in planning the future use of watersheds and in determining the distribution of different vegetation types in rural watersheds. It is also demonstrated that HSPF is a powerful tool in the continuous simulation of the effects of climate change on the hydrological and water quality processes of watersheds.

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## **THE EFFECTS OF CLIMATE CHANGE ON RIVERS IN THE MEDITERREANEAN REGION OF TURKEY**

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Predictions about climate change revealed that countries in the Mediterranean region will be affected mostly by increased maximum seasonal temperatures and decreasing precipitation. Therefore, it is likely that in the near future dry and hot climatic conditions will be prevailing in this region. These changes also affect environments such as rivers whose temperature directly related to air temperature. Since air temperatures will get higher and drought seasons are expected, the sustainability of fresh water resources will become more important for the future. Therefore fresh water resources must be monitored continuously or at regular intervals and the effects of climate change on these must be investigated. Turkey has a lot of fresh water resources like rivers, lakes and ground water reservoirs but the water demand also will increase with increasing temperatures. Therefore monitoring and future predictions are the most important studies for determining the management alternatives of water use. In this study, statistical assessment of temperature changes of the main rivers in the Mediterranean region of Turkey is carried out. Depending on the results of the river temperature predictions related to air temperatures, possible effects of these changes on these environments are investigated. Also by using air temperature - water temperature relationships the trends can be extrapolated to near future to reflect the water temperatures at that time. Results of these studies show that some rivers in the Mediterranean region will be warmer than nowadays in the future and seasonal fluctuations will be important. Also in this study, the possible effects of these changes to ecosystems are discussed and the possible management alternatives are put forward.

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## **SURFACE WATER MONITORING OF THE FUNGICIDES TEBUCONAZOLE AND TRICICLAZOLE IN THE ALBUFERA NATURAL PARK (VALENCIA, SPAIN).**

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Albufera Natural Park sited in Valencia (Spain) is a flora and fauna very rich area surrounded by rice fields in which pesticide spraying is a regular practice. The lake has functioned since the last century as a freshwater reservoir for the demands of rice crops. The lake water level is regulated by sluices situated at its three outlet channels which flow into the Mediterranean Sea.

So that, knowledge of realistic environmental concentrations of sprayed pesticides has to be taken into account to asses the adverse impacts these chemicals may have on non target organisms in aquatic ecosystems. Tebuconazole and Triciclazole are widely used as fungicide in this area to avoid and treat rice blast disease in the ANP, caused by phytopathogenic fungus *Pyricularia oryzae* during July and early August. The residue occurrences of these compounds in Albufera Lake were monitored during the summer period of 2003-2005.

Water samples were collected from six stations: four located in-lake and two others at their related irrigation channels. They were chosen because they represent important inlets of pesticide on ANP and define two spatial zones of the lake with different nutrient loadings. Water samples were also collected from an experimental rice plot after treatment with two commercial formulated BIM® (Triciclazole 75% a.i.) and Folicur® 25EW (Tebuconazole 25% a.i.) at recommended doses by the manufacturer.

After sampling, Solid Phase Extraction (SPE) procedure with C-18 Empore® disks and GC-MS/MS techniques were applied to extract and quantify tebuconazole and Tricilazole fungicides.

The results showed that water pollution due to Tebuconazole and Triciclazole residues were higher in the channels than in-lake sampling points. The highest residue in the studied channels were, 2,7 µg/L for Tebuconazole and 6 µg/L for Triciclazole and finally, the analyzed values for in-lake sampling points were 0.9µg/L and 0,5 µg/L, for Tebuconazole and Triciclazole respectively.

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## **IZMIR BIRD PARADISE CHANGE DETECTION ANALYSIS: REMOTE SENSING AND GEOGRAPHIC INFORMATION SYSTEM INTEGRATION**

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Wetlands are one of the most important natural areas of the world since they nestle several kinds of animals and plants some of which are the member of endemic species and perform vital ecosystem services including carbon sequestration, water quality protection and flood mitigation. Unfortunately wetlands are destroyed by the human induced effects such as urbanization or pollution for decades. To conserve these valuable natural areas, many precautions should be taken and sustainable management strategies should be developed. In this concept, it is important to understand the relationship and interactions between the human and natural phenomena for obtaining better strategies. Accurate and reliable change detection of land use and land cover is inevitable component of this procedure. To manage and monitor natural resources and developments change detection is beneficial because of its quantitative analysis. New technologies are currently in use to introduce this relationship. For example, integration of geographical information system and remote sensing data has become important techniques for change detection applications.

Turkey has several wetlands and 9 of these areas are defined as "A" type wetland according to the Ramsar agreement which was signed by Turkey in 1994. Izmir Bird Paradise, which belongs to Gediz Delta, is one of these wetlands with its 20400 hectares of areas, 205 different kinds of birds and several coming up endemic plants. However, this area has been threatened by drying out of marshes, unplanned urbanization, agricultural facilities and water pollution for years. A significant ecological disaster has been experienced especially up to the year of 2002 when the area selected as first degree nature protection zone. Therefore, Izmir Bird Paradise is selected as the study area for performing monitoring studies to determine dimensions of the experienced ecological disaster. For this purpose, integration technique and post classification technique are used to determine the change in Izmir Bird Paradise. 1987 and 2000 dated Landsat ETM data and 2006 dated ASTER data is used in this purpose. Results of the remote sensing studies are integrated with the vector maps and map data of the area by using geographical information systems. Results of the previous studies on monitoring the effects of the water pollution are also considered in this framework.

**Keywords:** ecological disaster, wetland, remote sensing, GIS.

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## INTEGRATED COASTAL ZONE MANAGEMENT AND CAGE SITING FOR MARINE AQUACULTURE

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Sustainable development requires mutual reinforcement of economic growth, social welfare, and environmental protection. Throughout the World, it has been rather difficult to achieve this goal due to the generally conflicting decisions over the three components. The environment has, in most of the cases, been the one sacrificed for economical growth. It is therefore a challenge to ensure sustainable development at either local, national, or international levels. It is a challenge since it requires a compromise among the different views of various stakeholders over the management of environmental resources. Tools are needed for such a compromise. Integrated Coastal Zone Management (ICZM) is one such tool for the management of coastal environmental resources. There are two components of ICZM. One of them is the scientific while the other being managerial components. The scientific component is geared towards determining the best decisions with the support of science and data. The managerial component, on the other hand, is interested in the mechanisms needed for the successful application of the decisions taken. This work is related to the scientific component and specifically to the virtue of employing the scientifically determined decisions in the management of environmental resources.

Recently there has been a dispute in Turkey over the sites of marine aquaculture fish cages especially in one of the most popular touristic regions, Bodrum, Mugla. Currently the ministries of tourism and environment require that the majority of the existing cages be moved. On one side, there are tourism sector and environmental authorities while on the other there are agricultural authorities and farmers. The tourism sector claims that disrupting tourism activities, these cages reduce the tourism revenues. The environmental authorities blame the cages for environmental pollution specifically for the spoil of marine water quality. As the supporters of farmers, the local and central agricultural authorities object either of the claims. This is in no way a desirable end. And there are already sixty appeals of farmers to the courts against the current ruling. There may be many to blame for this issue. However, in essence, it has stemmed from the lack of ICZM programs over the region. More specifically, the sites of cages had not been determined with a sound decision making procedure at the first place. Even for the newly appointed sites, such a procedure is not applied. It is our belief that if there had been ICZM programs in place for coastal zoning, fish cage sites might have been determined more scientifically. There would be two main requirements to this however. The first one is the data needed. And the second one is the tool to apply science, basically to perform the required analyses. Traditionally, a Geographical Information System has been employed for the second requirement while the data was collected in a way that was isolated from the involved state and local organizations. Today, the well accepted way of meeting these two requirements of a ICZM program is through a Spatial Data Infrastructure (SDI). In this work, it will be shown that how a sound fish cage siting would be performed under the SDI vision incorporating all stakeholders.

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## RODENT DENSITY AND CLIMATE IN CENTRAL ITALY: A MODELLING APPROACH

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The identification and the long-term monitoring of suitable bio-indicators is essential in a climate change framework. The main purpose of this research was to evaluate the relationships between climatological parameters and density population of Rodents in Central Italy (Majella National Park).

Two species of small mammals, the Yellow-necked mouse (*Apodemus flavicollis*) and the Bank vole (*Myodes glareolus*), have been studied according to the Capture-Mark-Recapture method in a grid 10x10 of livetraps. Faunistic data have been collected for fifteen years (1988-1995/2000-2006). Density values (N/ha) and climatological parameters (temperature, rainfall, snow cover) have been correlated using linear and non-linear functions. Our results show differences between the two species. The density of the Yellow-necked mouse is more affected by precipitation, expressed as number of rainy days and as the total amount of rainfall. In fact, rainfall increases the mobility of this species and trophic availability. The density of the Bank vole is more influenced by snow cover: during snow conditions the impact of predators is less. On the basis of this correlations a model has been developed using neural networks. For the first time this model has been applied on two rodent sympatric populations in Italy. The model allows us to reconstruct small mammal densities year by year, beginning from the different values of climatological parameters. Furthermore, it will allow us to redesign past densities of the two species, and to predict their future densities according to different climatic scenarios estimated by climate scientists.



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**BIOMONITORING OF DOÑANA NATIONAL PARK  
USING THE ALGERIAN MOUSE (*MUS SPRETUS*)  
AS A SENTINEL SPECIES**

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The aim of this work was to analyse the biological effects of man-made activities on Algerian mouse (*Mus spretus* Lataste, 1883) living in Doñana National Park (DNP) and its surroundings (SW Spain). Biomonitoring was performed, before and after the accident in Aznalcollar pyrite mine (April 1998) to investigate the environmental risk due to the realising of chemical wastes in the Guadiamar river, which reaches the DNP marshlands.

Mice (N=420), used as bioindicators, were collected from different sites, outside and inside the Park, over five years (1995-1999). The experimental design included the use of chemical, biochemical, genetic and fenetic markers to detect possible biological effects induced by xenobiotics in somatic and germ cells and in the palatal ridge morphology and to evaluate the relationship between biomarker response and adverse ecological effects. To assess genotoxic damage bone marrow and peripheral blood micronucleus test with application of Giemsa staining was performed; the immunofluorescent antikinetochore staining (CREST) was applied to discriminate aneugenic and clastogenic damage. In addition sperm cells were assayed with sperm abnormality test and blood cells were analysed with the Comet assay. Concentrations of some heavy metals (Pb, Cd, Zn, Cu) and arsenic were measured in the animal livers.

The comprehensive data analysis have indicated that biological damage observed in mice could be the effect of the contaminants released by the flooding and the toxic spill of the Aznalcollar mine, after the mining accident. In particular, the increase of micronuclei frequency was significantly higher in mice sampled at the sites outside the Park, directly affected by the spread of the contaminated mud, than in those sampled in areas inside the Park no directly affected.. Furthermore results showed that a chronic contamination was present, not only after, but also before the mining accident in some areas of DNP. In addition, it was observed that the effect of contaminants released by the collapsed dam was still present one year after the disaster, in this area characterised by seasonal floods in the marshlands.

This study suggested that biomonitoring had to be carried out in Doñana to determine the long-term biological effects of the environmental pollution and risk for the ecosystems in this protected area. However, this never took place.



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## PRODUCTION OF BIOMASS AND FIXING OF CO<sub>2</sub> FOR FORESTS IN THE REGION OF MURCIA (SPAIN)

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The atmosphere is a common resource to all nations and the climatic change is a world problem, since the emission of greenhouse gases that provoke the climatic change affects not only the country that produces them but also the rest of the countries. Kyoto's Protocol turns the CO<sub>2</sub> especially, and generally speaking the remaining greenhouse gases, in a limiting aspect, which establishes some determining factors and some effects that are transcendental both for the industry and for the economy, and in conclusion, for the way of current life.

The presence of forests affects directly the energetic balance of the climatic system, therefore, the indiscriminate cutting of big extensions of trees and the destruction of the ecosystems that support the primary production of the oceans, destabilizes the climatic system more than the burning of fossil fuels. The plants take water through their roots, and through the leaves, they perspire it in the shape of vapor. With this cycle they contribute to significant increase of the levels of evapotranspiration. The cutting of forests unleashes important climatic alterations, as less water vapor is released from the soil up to the atmosphere, which at the end supposes the decrease of the rains in the zones affected.

By means of a series of functions developed for every species, which cover all the diametric classes from minor feet up to major feet, a series of modular values are obtained, that are applied to the data group obtained from the Third Forest National Inventory of Spain (Ministry of Environment, 1997-2006), multiplying the number of feet by diametric class by the modular value of every fraction of biomass. The aim of the work is to estimate the arboreal total biomass of every species in the region of Murcia separated by fractions. Also the annual total increases of biomass are obtained, as well as the quantity of fixed CO<sub>2</sub> and its annual increase, also according to fractions of biomass. The present forest species in this region are: *Quercus ilex*, *Pinus pinaster*, *Pinus nigra* and *Pinus halepensis*.

	Total Biomass ( <i>Quercus ilex</i> )	Total Biomass ( <i>Pinus pinaster</i> )	Total Biomass ( <i>Pinus nigra</i> )	Total Biomass ( <i>Pinus halepensis</i> )
Total biomass 3FNI (1999)	983162	522896	540522	6330957
Annual increase biomass	69694	25993	17949	204818
Total fixed CO <sub>2</sub> 3FNI (1999)	1713897	980624	1009710	11594071
Increase CO <sub>2</sub> annual fixing	121494	48746	39030	375089
Fixed CO <sub>2</sub> in 2004	3414808	1663063	1556129	16636416
Fixed CO <sub>2</sub> in 2006	3536302	1711809	1595158	16996584

**Table 1: Global balance (Mg) in Murcia for *Quercus ilex*, *Pinus pinaster*, *Pinus nigra* and *Pinus halepensis*.**

## FIXING CO<sub>2</sub> BY THE FOREST OF ILLES BALEARS, IN THE MEDITERRANEAN REGION

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The climatic change is a very complex problem that, of not being approached can affect negatively in all the spheres of life. The countries subject to the general commitments to answer the climatic change, develop national programs to take measurements, as the regulations necessary for the sustainable management of the "carbon sinks", general term in which the forests and other ecosystems that can eliminate from the atmosphere more gases of greenhouse effect that those that they emit, are included. The industrialized countries signatories of Kyoto's Protocol, promised to reduce the emissions of greenhouse effect gases to the atmosphere, between the years 2008-2012, up to placing them in 5.2 % below the emission figures of the year 1990. To help to obtain this aim, Kyoto's Protocol contains the so called "mechanisms of flexibility", which are a set of three initiatives that allow the exchange of reductions between countries. The terrestrial ecosystems are fundamental to balance the concentrations of CO<sub>2</sub> in the atmosphere. The forests constitute a great deposit of carbon. This deposit can decrease when forests are cutted or degraded, which would lead to the release of great quantity of carbon to the atmosphere. On the other hand, this deposit can go up with the growth of the forests, the regeneration and the reforestation.

In this work of investigation it is studied the different species described according to the Third Forest National Inventory of Spain in the Balears Islands, realized by the Ministry of Environment, in the year 1999. The present forest species are: *Quercus ilex*, *Pinus halepensis*, *Olea europaea*, *Ceratonia siliqua*, *Juniperus phoenicea* and other hardwood species. With different functions that are established for every species and that include all the diametric classes, a few modular values are obtained, that are related to the information of the number of feet, taken of the Third Forest Inventory. The aim of this work is to determine the CO<sub>2</sub> accumulated in the different species of the forests of the Balears islands, in Spain, and the annual increases, according to the different fractions; total biomass, radical biomass and air biomass.

	Total Biomass ( <i>Quercus ilex</i> )	Total Biomass ( <i>Pinus halepensis</i> )	Total Biomass ( <i>Olea europaea</i> )	Total Biomass ( <i>Ceratonia siliqua</i> )	Total Biomass ( <i>Juniperus phoenicea</i> )	Total Biomass (Other hardwood)
Total fixed CO <sub>2</sub> 3FNI (1999)	6521506	9363780	3406457	914164	442121	539548
Increase CO <sub>2</sub> annual fixing	228433	234424	318267	47582	17749	13489
Fixed CO <sub>2</sub> in 2006	9948005	12589485	8180463	1627898	708356	719345
Fixed CO <sub>2</sub> in 2008	10633304	13234626	9135265	1770645	761603	755449
Fixed CO <sub>2</sub> in 2012	11547038	14094815	10408333	1960975	832599	803427

**Table 1: Balance of CO<sub>2</sub> (Mg) in Illes Balears for *Quercus ilex*, *Pinus halepensis*, *Olea europaea*, *Ceratonia siliqua*, *Juniperus phoenicea* and other leafy species.**

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## INFLUENCE OF CLIMATE CHANGES ON MARINE ECOSYSTEM AND FISH STOCK IN THE ADRIATIC SEA

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The warming that occurred in the last few decades influenced various aspects of variability of biotic parameters in the sea, from benthos and plankton to fish populations. These influences can be noted at interannual, decadal and secular scales in connection with climate oscillations important for the Adriatic like North Atlantic Oscillation (NAO) and Mediterranean Oscillation (MO). Since changeable atmospheric forcing shows interannual variability connected to hemispheric processes, it is expected that marine ecosystem and fish stock variations are influenced by atmospheric processes on spatial scales larger than the Adriatic. The evidence for this is observed through variations in sea surface temperature, advection, mixing, upwelling and some other parameters that control productivity, growth and migration of marine organisms.

In this paper, the influence of climate changes on regional atmospheric forcing, important for the marine ecosystem in the coastal zone of the eastern Adriatic Sea, has been recognized as a key factor which controls variations in primary production and fish stock from decadal to long-term scales.

To analyze interannual and decadal variations of fish population under the regional atmospheric influence, various atmospheric parameters (wind speed, air pressure, air temperature) and fish landings data (9 fish species from demersal to pelagic ones) were used. Both steady and abrupt regional atmospheric variations were recognized in the air pressure and the air temperature series. The wind speed was used as an indicator of mixing and upwelling, since upwelled waters enrich the surface coastal waters with nutrients, supporting primary productions and consequently the abundance of fish. The data were analysed using principal component analysis and correlation techniques.

It is obvious that synchronicity exists between the variability of wind speed and fish stock. The major features obtained through the analysis point that:

- regional atmospheric forcing was significantly correlated with hemispheric climate variability in such way that support steady and abrupt changes;
- regional space and time variations of wind speed and the sea surface temperature were highly correlated to fish abundance along the eastern Adriatic coast, which all pointed to the conclusion that climate changes through regional atmospheric variations have significantly impacted the marine ecosystem.

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## REMOVAL OF PETROLEUM AND PETROLEUM POLLUTION IN THE MARINE ENVIRONMENT

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Petroleum and Petroleum Products (PPP) have gained a great significance during the last decade. The world started to face a new kind of sea pollution as a result of the industrialization and development of new technologies based on petroleum as well as the transportation of petroleum by tankers and increase in the marine traffic. Although tankers and ships carrying petroleum are known as the main sources of oil pollution in the marine environment, in reality cooling waters of refineries, petrochemical factories, ships operating with fuel oils, researches conducted in the seas are the main sources of petroleum seepage into the seas. Also a huge amount of PPPs has been brought into the marine environment by the rivers.

In the research conducted, different types of PPP are mixed with the seawater in a tank of 136x66x98 cm and wave simulation was applied. Then different types of dispersants available at the local market were sprayed with pressure on the PPP layer. After approximately three hours, samples from different depths were taken and analyzed for the oil content. The same procedure was repeated by increasing the concentration of the dispersants and the most efficient dispersants in the removal of PPP pollution were determined. Then these dispersants were tested for their toxicity effects on fauna at different concentrations. The toxicity tests were conducted with fish named platy.

The results of the research indicated that the two dispersants of the eleven ones tested were efficient in the removal of oil pollution and they also have no toxic effect on the fauna.

The results of the research will be presented in detail with tables and figures at the final manuscript.

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**INFLUENCE OF CEMENT DUST EMISSION ON OLIVE TREES  
AROUND TARTOUS CEMENT FACTORY IN SYRIA: A CASE STUDY  
FOR THE EASTERN MEDITERRANEAN REGION.**

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The concentrations of total suspended particulate (TSP), particulate less than 10 microns (PM10) and particulate less than 3 microns (PM3), were measured in different sites in the surrounding area of Tartous cement factory.

The effects of cement dust emission on the growth of olive trees have been investigated. The results show that the TSP, PM10 and PM3 concentrations in the air were higher than world health organization (WHO) standards at the factory site as well as in the surrounding area within a diameter of 3 – 4 km.

The study shows that branch length, branch weight, amount of chlorophyll and number of leaves were decreased significantly. The average weight of the annual dust fall on leaves was 34.5, 26.4 and 10.9 g/m<sup>2</sup> at the sites around the cement plant, while in the reference site a value of 1.9 g/m<sup>2</sup> was measured.

**Key Words:** Influence of cement dust emission, olive trees, cement factory, TSP, PM10, Tartous, Syria.

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**SEX RATIO ESTIMATIONS OF LOGGERHEAD SEA TURTLE  
(CARETTA CARETTA LINNEAUS,1758) HATCHLINGS BY NEST  
TEMPERATURES AT OLYMPOS-ÇIRALI BEACH, TURKEY**

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There are many different scientific and protection studies about sea turtles in the world and also in Turkey. In this study, hatching success and hatchling sex ratios in the loggerhead turtle (*Caretta caretta*) were estimated by placing electronic temperature recorders in 12 nests at Olympos-Çıralı beach during the nest period in 2006. Over the season, the mean temperature in the middle third of the incubation period ranged from 28.9 to 31.9°C, and incubation periods ranged from 42 to 60 days. The nesting and non-nesting emergence of loggerhead turtles, nest distribution and nest distance from the sea also were recorded. Consequently, hatchling numbers, which reached to the sea, dead numbers, non-growing-eggs and non-hatchling numbers were determined.

As a result, totally 290 emergences of loggerhead turtles and from this emergences 96 nests were determined. From 8367 eggs, 7344 hatchlings and from this hatchlings 6445 hatchlings reached to the sea and rest 899 died either in the nest or on the way. Only from two nests there was no hatchling. Olympos-Çıralı has a relatively high proportion of female hatchlings (%75). For endangered sea turtles, the knowledge of hatchling sex ratios at different beaches, coupled with appropriate conservation measures, can make an important contribution to their survival. The climate change and increased temperature will effect this organisms.

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## CHARACTERIZATION OF SUPEROXIDE DISMUTASE ISOFORMS IN TILAPIA FISH AND VARIATION INDUCED BY MICROCYSTIN-PRODUCING CYANOBACTERIA

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Toxic cyanobacterial blooms are extremely widespread and occur throughout the world in fresh and salt water and various terrestrial habitats, causing serious water pollution and public health menace to humans and livestock. As a worldwide problem, cyanobacterial blooms have been also studied and detected in many countries in the Mediterranean region (Spain, Portugal, France, Maroc, etc.). The intact cells as well as the toxins released after cellular lysis can be responsible for toxic effects in both animals and humans, being actually associated with fish kills. The most abundant cyanotoxins are microcystins (MCs), heptapeptides that have been shown to induce oxidative stress in fish. MCs are able to modify enzyme activities related to oxidative stress and other components of the cellular defence system.

In order to minimize the negative effects of oxidative stress, fish, like other vertebrates, possess an antioxidant defence system, which utilizes enzymatic and non-enzymatic mechanisms to maintain the balance between reactive oxygen species generation and protection from damage by ROS. One of the most important antioxidant defence enzymes is superoxide dismutase (SOD). SOD transforms superoxide anion radical ( $O_2^-$ ) into less reactive species, molecular oxygen and hydrogen peroxide ( $H_2O_2$ ).

In the present work, we characterized different isoforms of SOD in Tilapia fish (*Oreochromis* sp.) and studied the possible alteration of the SOD isoforms induce by toxic cyanobacterial material. Two groups of fish were intraperitoneally exposed to a single dose of 725  $\mu$ g/kg MC-LR. Two control groups were injected the same volume of vehicle, 0.9%, w/v saline solution. Treated and control groups of fish were sacrificed at two different times: 1 day and 7 days after exposure. Homogenates of liver, kidney, muscle, intestine and gills were analysed by polyacrylamide gel electrophoresis and isoelectric focusing under non-denatured conditions. SOD activity was developed in gel by inhibition of nitrotetrazolium blue reduction. The different active isoforms appearing as colorless bands on a blue background. Identification of the diverse isoforms was attained by the use of specific inhibitors.

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## STATISTICAL ANALYSIS OF SHIPPING ACCIDENTS IN TURKEY'S AEGEAN AND MEDITERRANEAN COASTAL REGION

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Turkey's Mediterranean region coast and Aegean coast which take place in the east part of the Mediterranean Sea have length of 4347 km. Their coastal regions have a potential for shipping transportation. Shipping traffic in these coastal regions yearly basis, an increase both in vessel traffic (17000 vessels) and in size of transportation is observed. This situation increases also the risk of accidents in the Aegean and Mediterranean coastal region. These accidents cause a direct influence on the every day life and livelihood of the local people, as well as marine fauna and flora due to oil pollution. Coastal regions of the Aegean and Mediterranean sea is ecologically fragile and sensitive ecosystem. Oil pollution causes damage to tourism, fish farming, marine park, recreation, marine reserves. Because of this, a substantial conflicts take place amongst these usage demands. It needs management in terms of sustainable development. Although shipping transportation makes a contribution to Turkey's economy, it can negatively affect coastal regions. These drawbacks emphasize the priority of performing accident analysis.

In this study, 465 shipping accidents occurred in the Aegean and Mediterranean coastal region during the period between 1995 to 2006 will be analyzed by correspondence analysis in respect to months and years. Then a categorical classification of the main causes of accident, accidents locations, time, type of vessels involved in the accidents by registry flag and sizes will be presented. The results will be obtained by SPSS (Statistical Programming for the Social Sciences) 13.0. Within this study, data derived from records of shipping accidents issued by the Turkey Maritime Department.

Correspondence Analysis (CA) is a descriptive/exploratory technique designed to investigate the relation between row and column variables of a two-way contingency table, similarities and differences among categories grafically. One of the goals of Correspondence Analysis (CA) is to transform numerical information into graphical displays ("maps") and related numerical statistics. The goal of this study is to investigate the relationship between variables as "year and cause of accident", "year and flag", "month and vessel type", "month and flag", "month and cause of accident", "locations of accident and cause", "flag and time", "tonnage and flag", "cause of accident an location" etc... It will be seen that both of the numerical statistics and graphical displays includes very detailed informations about data sets. Both of the relationships



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between the categories in a variable and the categories which possess different variables will be detected and interpreted in details by graphics of Correspondence Analysis. Graphical displays provide rich information in crucial decision making.

The resulting outputs provide the following benefits:

- To seek answers to questions such as "What happened?", "How did accident happen?", "Why did accident happen?", "Where did accident happen?", "What can be done to prevent it from happening again?"
- To determine risky location in terms of shipping accidents.
- To review in order to promote the current navigational safety control and security precaution
- To determine dominant factors which may influence shipping safety and marine environment in terms of risk and threat for Aegean and Mediterranean coastal region.

The specific aim of the study is to examine a general profile of the shipping accident causing pollution in coastal water, present proper data for decision makers in order to help effective decision making and planning, focus on the accident problems for decision makers and stakeholders therefore providing benefits for the evaluation of the need for preventive measures.

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