

**11th International Symposium
on**

Environmental Pollution and its Impact on Life in the Mediterranean Region

**October 6th to 10th, 2001
Limassol, Cyprus**

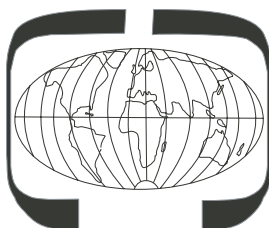
jointly organized by

The Mediterranean Scientific Association of Environmental Protection
(MESAEP)



and

The Society of Ecotoxicology and Environmental Safety
(SECOTOX)



ABSTRACT BOOK

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Under the auspices of His Excellency

the Minister of Agriculture, Natural Resources and Environment
Mr. Costas Themistocleous

in collaboration with

Ministry of Foreign Affairs, Republic of Cyprus

European Commission, JRC Ispra, Environment Institute and Institute for Health and
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GSF - National Research Center for Environment and Health, Institute of Ecological
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THE DILEMMA OF GOLD MINING IN THE MEDITERRANEAN REGION

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Gold is one of the rarest elements of the earth. Its concentration in the upper layer is ~ 4 mg/t (ppb), in sea-water the concentration is 0.01 mg/m³. Very likely, the largest amount of gold is present in the oxide shell and exists in the form of pure gold or gold tellurite res. gold selenite. From there it comes by hydrothermal process to the upper layer of the earth and can be isolated by different processes. The largest gold mine may be Witwatersrand in South Africa 1,000-3,000 m under the surface. Most of the real gold mines, where gold can be isolated by

THE STATE OF THE MARINE ENVIRONMENT IN THE MEDITERRANEAN AREA

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One of the most important seas in the world is Mediterranean Sea. It is the largest inland sea surrounded by three continents. European civilization was born on the shores of this sea, which encompassed the civilized world in the ancient and medieval times.

Nowadays the pollution in the above sea is extended. The Mediterranean Sea serves at a steadily growing rate as the recipient of multitude of waste discharges from residential areas, industrial activities and touristic complexes. Records show a substantial increase in recent years, both in volume and composition of effluents, discharged into Mediterranean Sea. This discharge occurs in the vicinity of all the major cities of the basin and has drastically modified the ecosystem in these areas. Urban liquid wastes comprise mainly dirty water from domestic or industrial washing, detergents and lubricating oils. Industrial liquid wastes comprise wastewater, oils, detergents, solvents, organic and inorganic chemicals and heated cooling water.

Oil transport and transportation generally through Mediterranean Sea is also increasing. There are some 2000 active ferry lines, 1500 cargo vessels and 2000 commercial vessels operating in the Mediterranean Sea each year. The region has 305 ports of all sizes and purposes. The region of ports with urbanization is notable.

The annual number of international tourists is expected to be about 200 million by this year. In spite of marked improvements, the task of handling the liquid and solid waste in summer is overwhelming.

To these facts, pollution from major Mediterranean rivers must be encountered. These rivers drain geological and residential areas far away from coastal line. Very large quantity of sediment entered into Mediterranean Sea every year this way.

The extent of pollution was recognized and a very valuable step was taken. The Mediterranean states in a meeting in Barcelona in 1975 adopted an action plan for the protection of Mediterranean Sea against pollution. This is the well-known MED POL programs. The whole project was a success. Fortunately, the modern technology enables us to go back to careful management of the coastal areas and bring again Environmental balance and Sustainable development.

The marine environment has received man-made radionuclides from many sources: the detonation of nuclear weapons in the atmosphere, the controlled discharges of low-level liquid effluents from the nuclear power industry, and fallout arising from accidents such as the Chernobyl reactor accident, in 1986. These various sources have, collectively, introduced a wide range of nuclides both globally and locally.

A radiological impact assessment for S.E. Mediterranean area has been carried out with co-operation of various specialists in the different branches of radiation protection both for man and the environment. It was based upon investigations, which have been carried out in the past and present original contributions.

SUSTAINABLE CHEMISTRY IN EDUCATION AND RESEARCH

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In many traditional experiments for the education of chemists there is a considerable potential of generation hazardous substances of significant toxicological relevance. As we first could ascertain, considerable amounts of highly toxic dioxins and furans are formed, e.g., while performing the Beilstein-Test for simple qualitative detection of halogenated organic com-

STRATEGY FOR EFFECTIVE WATER MONITORING: FROM DATA TO CONCRETE INFORMATION

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To sustain quality and multifunctionality of surface waters, pollution status, trends, and possible effects of the “cocktail of chemicals” on Human Health and the Ecosystem have to be predicted and evaluated, by integrated monitoring strategies. There are about 100,000 chemicals listed on the EINECS. Two approaches are used to manage these chemicals. For most chemicals an emission-oriented approach is applied to prevent unnecessary pollution. This approach is successful in preventing point-source pollution but cannot always be applied in cases of diffuse pollution. The effect-oriented approach is often hindered by the lack of information on sources, use, fate and effects for most chemicals. This implies that the risk of not managing important chemicals is high. It is also the main reason why environmental quality standards are available for only few chemicals out of the thousands which could be present in the water.

Despite these obstacles, the ultimate goals of monitoring remain the provision of concrete information for risk assessment and risk management and clear identification of priorities for decision making . Monitoring has therefore to go beyond providing only data or fulfilling regulatory obligations. It has to provide prediction rather than remaining retrospective. From a study done in 1995 by European Laboratories and funded by DG XI, it was found that Existing monitoring activities throughout Europe are still associated with the following three major problems which need urgently to be addressed. a)High Cost / Low efficiency and Effectiveness, b) Deficiencies in the information gained (annually 300-350 millions EURO are spend for monitoring water quality in EU, a huge No of data are collected but still information gained is not sufficient), c) Lack of harmonization throughout Europe. Due to these and despite the improvement of EU Regulations and control measures, European Water sources continue to show signs of deterioration with increasing evidence of threats to human health and the ecosystem .To address these deficiencies cost effective integrated –holistic investigation and evaluation schemes need to be developed. These schemes must have enhanced and broad detection capabilities and should be tailored made to provide concrete information. Several basically different approaches are available. All approaches have inherent drawbacks that limit their applicability in the risk management process. Advantages, drawbacks and cost-benefit aspects of these monitoring strategies will be discussed and integration of selected aspects will be proposed for an integrated investigation strategy. Once the investigation approach is defined there are still additional challenges to be met: a) How can we cope with parameters which need to be monitored but for which limits do not exist ? b) How can we address the issue of combined effects of the “cocktails” of chemicals to which man and ecosystem are exposed to? and c) How can out of hundreds of data, concrete information be extracted and presented in way that main problems, causes and priorities can be clearly identified? Obviously, integrating evaluation schemes to meet these challenges and to provide information for management, forecasting and prevention are needed. Our evaluation perception has to be change from the quality evaluation based solely on legal limits towards a broader evaluation based on Environmental Quality criteria or targets for chemicals and their mixtures. Furthermore, to extract from data concrete information, scientifically sound aggregation of interrelated parameters into “pollution type” related indices i.e pesticides or industrial or eutrofication indices have to be developed. These indices can be the tools by which data will be transformed into concrete information. As an example the development in Cyprus (within a Life EC funded project) of an integrated investigation and evaluation scheme based on Quality & Effect Indices, will be presented.

**ENVIRONMENTAL EDUCATION IN PRIMARY SCHOOLS -
RESULTS OF A RESEARCH WITH SPECIAL REFERENCE TO PUPILS COMING
FROM THE MEDITERRANEAN**

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In primary and secondary schools of Germany many minorities are being educated. Teachers have to be especially devoted to them. That is difficult in so far as the preoccupation with each minority needs special information. To meet these tasks teachers depend on results to natural awareness and environmental consciousness, which has to be made available by intensive researches. - The main minority in Germany are people of Turkish origin. In a three years' project of research therefore investigations have been made on children of third and fourth classes of Turkish or German origin respectively and on Turkish adults living in Germany as well about their natural awareness and environmental consciousness, both in order to be compared between Turkish and German children and adults. Children of third and fourth classes have been selected because they are already able to understand the topic of the research, and the questionnaire. And the children are not yet separated in different types of schools. So one can get results, which yet show the whole spectrum of relations to nature and environment. - The relations to nature and environment of Turkish adults living in Germany are different from German adults especially if the Turkish people have grown up in Turkey. That leads via education by their parents to a different awareness of nature and environmental consciousness of Turkish children. One has further to take into consideration that the Turkish children living in Germany, are often born and have grown up in Germany or have changed their residence manifold. Because of that children of Turkish origin living in Germany have also experiences with the German way of becoming aware of nature and environment. Thirdly exist parts of natural awareness and environmental consciousness, which have been developed by the children themselves, using experiences they have made. So it had to be taken into account that children of primary schools of Turkish origin perceive nature and environment triple differently from children of primary schools of German origin. The result is an identity, which has been called "patchwork-identity". That means that there are parts in their identity of Turkish origin, others of German origin and thirdly parts, which are originated by the children themselves. These parts are mingled and depend on each other. The identity of these children of Turkish origin, having grown up in Germany or in both countries is also different from children, grown up in Turkey. Nevertheless is it instructive to look as far as possible for typical Turkish parts of relations to nature, which have overcome in this patchwork-identity. - To complete the research, a survey on teachers of Primary schools has been made to get notice of their awareness of the relation to nature and environment of children of Turkish origin. All these results can help to teach children from Turkish origin in a way that meets with their special natural awareness and environmental consciousness.

THE CURRENT REVISION OF THE ENVIRONMENTAL RISK ASSESSMENT OF CHEMICALS UNDER THE EU REGULATION

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The evaluation and control of risks of chemical substances occupies a prominent place on the current agenda of the EU Environment Council of Ministers, recognising that “the new chemicals policy must develop streamlined, pragmatic and effective procedures to overcome the present lack of knowledge about the properties, use and exposure of existing substances as well as the slow pace in the development of risk assessment and risk management measures...(Environment Council Conclusions of 7 June, 2001)”.

The development and harmonisation of risk assessment methods is the key for a successful risk management, therefore the European Chemicals Bureau initiated in year 2000, in co-operation with Member States, CEFIC/ECETOC, NGOs (WWF) and OSPAR (Marine Risk Assessment) the revision of the Technical Guidance Documents (TGD) in support of the Commission Directive 93/67/EEC on risk assessment for new notified substances and the Commission Regulation (EC) 1488/94 on risk assessment for existing substances, and on Directive 98/8/EC concerning the placing of the biocidal products on the market.

Based on the last five years experience in performing risk assessment in the EU, a number of areas needing revision were identified during the discussions of the risk assessments prepared for individual substances in the course of the Technical Meeting for New and Existing Substances. Some TGD methodologies have already been further developed in order to resolve urgent problems arising from these discussions. The revision process is currently ongoing, and widely varying aspects of the risk assessment are under discussion, including both aspects from the exposure assessment as well as the ecotoxicological effects assessment. New emission scenarios, release estimations, and predictive models for the elimination processes have been developed. The release to the environment from waste water treatment plants, or via waste disposal have been revised. The new concept on “unintentional” releases has been introduced and guidance given. The strategy for effects assessment for sediment and soil organisms has been improved, and new guidance for the calculation of the Predicted No-Effect Concentration (PNEC) using statistical extrapolation techniques is given. Major challenges are the inclusion of an approach for the marine risk assessment as well as the risk assessment of biocides.

INTEGRATED ENVIRONMENT AND HEALTH PROTECTION: THE IMPLEMENTATION OF THE PRECAUTIONARY PRINCIPLE

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Traditional safety assessment methodologies do not represent the actual safety performance of technological innovation when they are based on either limited deterministic analyses or probabilistic risk assessment using frequently controversial criteria and/or data sets. The current trend towards enhanced public and industry awareness of the external cost of technology warrants the development of an enlarged perspective of technological risk. A multi-aspect definition is proposed in this work, whereby risk encompasses the probability of occurrence and consequences of:

- (a) direct insults to human health,
- (b) direct and indirect insults to the natural ecosystem, and
- (c) macrosocietal repercussions of specific technological choices.

This approach of technological risk assessment has the potential of being a low-cost, high-benefit strategy for the internalisation of technological externalities mainly in the long term. It may minimise the risk and the consequent financial burden of regulatory policies imposing “over-protection” obligations to the industry. Such constraints driven by legislation are frequently instigated after inspections based on traditional safety reports not adequately depicting the actual safety performance of technology. Moreover, the combined approach will reduce the societal risk caused by “under-protection” owed to inherent uncertainties and frequent limitations of information resources.

Embedding precaution in the culture of decision-making at various levels will require a combined “top-down” and “bottom-up” approach. It requires not only mandates on government agencies and proponents of potentially harmful activities to exercise precaution, it is also a structure and procedures that build experience in applying precaution from the bottom up – among citizens, in firms, and in all levels of government. Finally, it requires both top-down and bottom-up changes in the way science is conducted for public policy. The broad recommendations presented herein determine the types of changes that would need to occur to institutionalise the precautionary principle as an overarching guide to environmental health decision-making.

1. Institute a guiding duty to exercise precaution in environmental and health legislation.
2. Reconfiguring environmental science for public policy.
3. Refocus policies, guidance, and priorities toward seeking safer alternatives to hazardous activities and opportunities for prevention. This is a clear driver for the development of innovative, clean technologies, countering criticisms that the precautionary principle is only used to stop technologies.
4. Institutionalise precautionary decision-making procedures (precautionary assessment).
Precaution can be established as a guideline to environmental decision-making only to the extent that procedures guiding a precautionary analysis of hazards are in place.

The concept of “risk preoccupation threshold” could be of help in terms of identifying risk values, which can be defined as acceptable by the European citizens. Clearly, such a notion would require an evaluation of the opportunity cost generated when a policy is defined and economic, human and natural resources are geared towards a given direction. Not investing these resources to face other areas of risk imposes a societal cost, which has to be taken into consideration for overall cost-effective policy-making.

ENVIRONMENTAL PERCEPTION AND CONSERVATIONAL EDUCATION

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Environmental, conservational and ecological education programmes nowadays are standard practice in the life of many pupils. This is either due to a teaching tradition favouring outdoor experiences within the subject Biology or due to the common belief that current environmental problems increasingly require educational outdoor settings to engage adolescent concern for the environment (*e.g.*, Leeming *et al.* 1995). Consequently, various educational approaches are assumed to foster environmental literacy and support a willingness to take environmental action.

The most important essential and crucial precondition of measuring perception is providing a consistent and age-adjusted empirical instrument. On the basis of some thousand pupil responses of selected European countries and some developmental studies such an instrument was extracted with sufficient proof of its validity and reliability (Bogner & Wiseman 1999). Five primary factors covering utilitarian and preservational subscales were selected to measure adolescent environmental perception.

Under the precondition of identical designs and identical instruments, different educational programmes may be monitored and compared as well by focussing on a consequent pre-posttest basis. All programmes favoured outdoor settings and lasted for at least four days. It is an interesting finding that all three experimental treatments were able to increase some of the surveyed primary factors, at least, and it can be stated that educational programmes can shift adolescent preservational and utilitarian preferences. However, remarkable differences within the three studies prevail. Firstly, the evaluation study within a German National park focussed on a nature face-to-face experience detailing the satisfying result that four of the five tested subscales were affected in terms of increasing the adolescent perception (Bogner 1998). Secondly, the Swiss evaluation study focussed on a conservational programme featuring an endangered migration bird; two of the five tested subscales were (positively) influenced (Bogner 1999). Thirdly, the evaluation study within a French nature park field centre monitoring an ecological education programme provided proof that two of the five subscales were affected; both were dealing with utilitarian preferences (Bogner 2001).

Consequently, empirical analysis of three different surveys, monitoring three different educational approaches, provides sufficient support for the hypothesis that pupils get influenced towards a selected environmental perception primary factor set. It appeared that the experimental condition of educational programmes results in significant shifts within certain aspects of this adolescent perception. In the case of the present programmes, utilitarian and preservational preferences as well were influenced, *i.e.*, the whereabouts of human dominance over nature, the interference with environments and existence of human altered nature were conceived and understood in a more sensitive manner as well as green environments were better recognised as something generally interfered by human beings. Altogether, it is a very encouraging result that education programmes interact with the utilitarian and preservational sector and increase the pupils' sensibility towards nature and environment.

APPROACHING THE KYOTO TARGETS: THE ROLE OF RENEWABLE AND TECHNOLOGY INNOVATION AT LOCAL SCALE

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Renewable diffusion may offer a good chance to slow down resource depletion and to diminish environmental pollution, favouring the achievement of three objectives:

- greater competitiveness;
- supply safety;
- environmental protection.

These issues are more topical in relation to the necessity of reducing greenhouse gases (GHGs) emissions, as stated by the Kyoto protocol which establishes severe emissions limits for 38 industrialised countries. The Italian Government agreed to reducing the overall GHGs emissions by at least 6.5% below 1990 levels in the commitment period 2008 to 2012, defining the guidelines for national policies in the CIPE Decision n. 137 of November 19, 1998. In such a document, the decrease of fossil fuel consumption and the increase of renewable share are considered strategic objectives. This implies that joint efforts must be made by researchers and Local Authorities to promote suited interventions aimed to reduce fossil fuels consumption, to substitute fuels with higher carbon percentages, and to increase energy saving share, translating at local scale (urban and regional) the national and international objectives.

In this framework it is necessary to investigate the potentiality of the supply side as well as the features of the demand sectors, to assess the feasibility of renewable use and technology innovation. The reorganisation of the energy system configuration must be based on an overall optimisation of the different activities, to develop synergetic interventions. A comprehensive modelling approach is then recommended to carry out a systemic analysis which emphasises the relationships and feedback among the different sectors, allowing the planners to harmonise laws issues and resources use, in order to obtain an improvement of environmental quality. Among the available instruments, bottom–up optimising models represent the most effective tools to perform a multi-objective analysis of an energy system. In fact being energy and technology oriented such models allows users to take into account directly efficiency improvement and technology innovation, comparing technology performances in terms of consumption, costs and emissions. Moreover, they make possible the evaluation of the global environmental impact of energy activities, defining the optimal strategies of resource management sector by sector.

In this work we present a local scale application of the R-MARKAL model to investigate the contribution of renewable and high efficiency technologies in the achievement of the CO₂ emissions reduction targets. The case study will examine the electric and thermal energy demand of a district of Basilicata Region (the Agri Valley) interested by a recent increase of anthropogenic activities. It will be examined the effects of more stringent environmental bounds on energy system configuration as well as changes in resources availability, fuels and services prices, characterising the environmental and economic impact of the different model choices.

**POLLUTION: THE GAP BETWEEN UNDERSTANDING AND
LAWS IN THE MALTESE ISLANDS**

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Malta is a very small nation state, with under 400,000 people. From these it has to supply as does, say, France, Government, University, Schools, Health Service, Social Services, Transport, etc. Taxes fund these, so wealth-creators also are necessary. It is unsurprising, with so few to draw on, that many specialities are missing, pollution being one. With voters unwilling to raise taxes, they are likely to remain missing (unless crises occur).

In theory, five departments control water quality: Water Services, Health, Sewage, Police and (if from farming) Agriculture. In practise, somebody's job can be nobody's job. Environmental appreciation and popular pressure for quality environment improvements are very low (although increasing). As a sensible senior policeman said, 'Environmental stuff is rubbish.'

While the Environmental Impact Assessment (legal) requirements are extremely high, they cannot be applied to unrecognised pollution. Water table analyses are not released, surface water ones are not done, and no one in authority looks for pollutions (unless there is an immediate public health risk).

There is no blame. Malta is overstretched. Since raising tax and using environmental controls mean losing elections, how can a Government act? Yet the pollution of inland surface waters, trivial in the 1980s, is now as proportionately bad as, say, Britain and Germany, and likely to be much worse by 2010.

Because Malta is so small in population, and in area of country side, the stresses and their effects are more obvious than in better resourced countries. As often, Malta is a micro-cosm, where phenomena are striking enough to be understood, and subsequently noticed in other countries.

**SUSTAINABLE CONSTRUCTION IN GREECE:
HARMONIZATION AND IMPLEMENTATION**

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This paper presents research conducted during the period of 1998 to 2000 in the Department of Geotechnology and Environmental Engineering concerning the sustainable Construction in Greece in accordance to European Directives and their application towards Olympics 2004. Four objectives leading to sustainable construction i.e. Resource Efficiency Energy Efficiency (including Greenhouse Gas Emissions Reduction), Pollution Prevention (including Indoor Air Quality and Noise Abatement), Harmonisation with Environment (including Environmental Assessment) Integrated and Systemic Approaches (including Environmental Management System), Resource Efficiency, Energy Efficiency (including Greenhouse Gas Emissions Reduction), Pollution Prevention (including Indoor Air Quality and Noise Abatement) , Harmonisation with Environment (including Environmental Assessment), Integrated and Systemic Approaches (including Environmental Management System). A characteristic example of sustainable construction the rowing and canoeing centre in Schinias, Marathon Attica is presented. Finally, suggestions are made for future research.

PUBLIC RESPONSE TO THE MULTI-FUNCTION SMART CARD USE IN URBAN TRAFFIC AND ENVIRONMENT APPLICATIONS

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The city of Thessaloniki is active in the Telematics applications in its transport network. The objective mainly is to reduce the use of private car in the city centre and consequently to improve the urban environment and air quality. These applications range from the introduction of urban road and congestion pricing for vehicles using the city network till the promotion of using public transport, guidance through road side information terminals and the use of multi-service smart card.

The European project DISTINCT (Deployment and Integration of Smart Card and Information Networks for Cross sector Telematics) is one of the projects sponsored by the Directorate General XIII of the European Commission, promoting the smart card applications in order to favour public modes of travel instead of car usage.

In the framework of the DISTINCT project, Thessaloniki is one of five European cities selected to analyse and test the effect of using multi-function smart card in city applications. The card is being developed for transport services such as tolling, parking and public transport payments and being extended to a city card which include health record and access to information. The idea behind that is to encourage the use of smart card in transport and probably increase the number of users of public transport.

A pilot application has been realised in Thessaloniki during 2000, providing high school students by smart cards for public transport use. The aim of the pilot is the study of the public response to the multi-function smart card use in urban traffic and environment applications and specifically, the improvement of card services, the dissemination of the card potential for traffic and urban environment improvement and the promotion of public transport use.

The majority (74%) of the pilot application participants characterises the smart card system as “good” or “very good”. Comparatively to the present conventional urban public transport system, the users consider the smart card system as much better. The majority (79%) of the users is ready to continue using the DISTINCT smart card in the framework of the urban public transport system. Also, the majority (78%) is positive to the expansion of the smart card system in all the components of the urban public transport. The main sectors, where it is observed the higher interest for expanding the smart card system are: the telephone cards, the tolling electronic payment, the parking electronic payment and the taxi payment.

This pilot application showed that there is a very positive public response to the multi-function smart card use in urban public transport. This response reinforces the idea of using smart cards for the improvement and promotion of public transport and hence, reducing the use of private car in the city centre. Consequently, an improvement of urban traffic and environment is expected.

**DEVELOPMENT OF OCCUPATIONAL EXPOSURE LIMITS
WITHIN THE EUROPEAN UNION**

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The setting of Occupational Exposure Limits (OELs) together with other associated measures forms an essential part of the strategy of the European Community's legislative framework on the protection of workers from risks related to exposure to chemical agents. The objectives of the programme for the protection against chemicals at the workplace are to prevent or limit the exposure of workers to chemical agents at the workplace, and to protect those workers who are likely to be exposed to such agents.

In order to ensure that the proposals made by the European Commission reflect the most recent scientific and technical data, the Commission is assisted by the Scientific Committee of Occupational Exposure Limits (SCOEL) consisting of highly qualified scientific experts.

On the basis of the evaluation of the health effects of hazardous chemical agents and after consulting the Advisory Committee on Safety, Hygiene and Health Protection at Work, the Commission proposes European objectives in the form of Indicative Occupational Exposure Limit Values.

In the following the procedure for setting OELs and the progress of this programme will be outlined.

**HYPHENATED CHROMATOGRAPHIC METHODS
IN ENVIRONMENTAL ANALYSIS**

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Environmental analysis needs methods for organic trace analysis in complex matrices (soil, sediment, plant and animal tissues).

So, the combination of effective clean up with effective separation and sensitive detection is necessary.

For that purposes hyphenated methods (e.g. HRGC/HR MS, HPLC/MS-MS, CE-MS, CE/ICP-MS, TA/QMS/GC-MS) were developed and successfully applied on emission and immission monitoring and ecotoxicological evaluation as well as on biological monitoring.

THE RICAMARE CONCERTED ACTION : OBJECTIVES AND ACHIEVEMENTS

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The International ENRICH/START Workshop on “Global Change and the Mediterranean Region” held in Toledo, Spain, 25-28 October, 1996. developed a set of priorities in the various scientific fields of relevance for global change research in the Mediterranean region. A number of integrative issues were identified, deserving special effort and preparation before new scientific ideas and projects emerge, and policies are enacted.

In order to achieve these goals, the so-called RICAMARE concerted action was set up by the European Commission, START and other donors. The associated RICAMARE network consists of individuals and institutions interested in such research in countries within the European Union and in other Mediterranean countries, particularly in the Maghreb and Eastern Mediterranean countries.

Three major activities were led:

- I) Development of the regional research agenda;
- II) Promoting training and capacity building;
- III) Promoting diffusion of research and awareness of global change and its implications.

Within activity I, four tasks were undertaken, addressing the assessment of the state of the art and further development in four crosscutting issues:

- 1) land-use, land-cover changes and water,
- 2) global change and biodiversity conservation;
- 3) evaluating the costs of climate change;
- 4) development of a concerted data assessment, assimilation and validation for global change.

Each of these tasks were the focus of a dedicated workshop, producing a review of the stage of knowledge, a proposal of a set of joint initiatives, and a strategy suggestion to develop them in connection with the main concerned actors.

Within activity II, five dedicated courses were (or are to be) organised, covering the physical, socio-economic, biological, and water resources components of the system. This plan is quite consistent with the activity I topics and aims at consolidating a scientific community having to take into account conclusions and recommendations from that activity.

Within activity III, efforts were dedicated to improve the diffusion of research results, by disseminating information, especially to the widest community of scientists and policy makers, through a dedicated website, publications and presentations in symposia. Setting up the framework of a future major regional conference which could bring together scientists and policy makers, as well as NGO's to evaluate the achievements and needs, particularly in terms of policy, for ensuring a sustainable development of the region under the impending threats of global change, was also considered .

AIR QUALITY IN EUROPE-ACHIEVEMENTS IN THE PAST AND FUTURE NEEDS FOR POLICY-SCIENCE INTERFACE

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European urban and con-urban areas, in particular large cities, struggle with the problems of high levels of air pollutants. At present about 60% of the European population is living in cities. For the next decades it is foreseen that this percentage will further increase. The substantial growth of the urban population is associated with a further increase of the macro- and micro-economic activities in the cities including energy generating and transportation activities (traffic), building construction etc. and with increased air pollution problems.

Local and national authorities are seriously concerned about elevated concentrations of ozone, of fine particles and of mutagenic and/or carcinogenic compounds e.g. benzene in ambient air. Here the Commission with its services is asked to contribute with directives and proposals to the amelioration of the air quality through the European territory. Evaluating the whole situation on air quality in Europe in the last decades after the implementation of the existing and partly revised air quality directives, it can be stated, that generally there is a clear improvement of many air pollution indices. However, we are far from saying that Europe's urban air quality can be characterized as satisfactory.

CARBONACEOUS MATERIAL, LONG-CHAIN CARBOXYLIC ACIDS AND PAHS IN URBAN AREA OF ROME: CONCENTRATION LEVELS AND SOURCES

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Carbonaceous material is a large fraction of urban aerosol and it is classified into Elemental Carbon (EC) and Organic Carbon (OC). EC in particles is emitted from combustion sources. Because most combustion sources are anthropogenic and generally EC does not undergo chemical transformations, EC is a good indicator of primary anthropogenic primary pollution. OC in particles species are emitted from primary emission sources either anthropogenic or biogenic sources. They can be also generated from chemical reactions among primary gaseous OC species in the atmosphere. OC and EC fractions in fine particles vary depending on the area air quality.

The long-chain carboxylic have been identified as major constituent of organic aerosol. The main important sources for these compounds in the urban areas can be both anthropogenic and biogenic emission and secondary formation from gas phase precursors.

The Polycyclic Aromatic Hydrocarbons (PAHs) are considered to be the pyrolysis products of incomplete combustion of organic matter. Produced during combustion processes, PAHs are introduced into the atmosphere and are attached to fine carbon particles. When exposed to O₃, NO₂, N₂O₅ and other oxidants, PAHs react in the atmosphere slowly yielding oxy-PAHs, nitro-PAHs and Polycarboxylic Aromatic Hydrocarbons.

In this paper we have measured the ground concentration of Particulate Matter (PM), Total Carbon (TC), EC and OC in two Monitoring Stations in Rome. The first station is situated downtown Rome (near S.M. Maggiore Cathedral) where the traffic emission flux is strong. The second station is located in the inner a green park (Villa Ada Park): this site is not directly influenced by anthropogenic emissions.

The results show that in Rome the TC contribution is about 30% of PM and the OC/EC vary between 0.5 and 1.5. The long-chain carboxylic acids and PAHs constitute about 5% of total aerosol mass. The long-chain carboxylic acids give a significative contribution to OC during the spring- summer periods, especially. This behavior can be attributed probably to biogenic emissions and secondary formation during photochemical processes.

The PAHs and in particular those with potential carcinogenic and mutagenic activities are about 0.5% of OC instead their transformation products, e.g. nitro-PAHs, oxy-PAHs and Polycarboxylic Aromatic Hydrocarbons are at very low levels.

WHY ARE SEMIVOLATILE ORGANIC CHEMICALS (SVOC'S) DIFFERENT? – THE ALTERNATE ROLE OF SVOC'S IN THE INDOOR-ENVIRONMENT –

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Aesthetic and health effects were observed by the presence of semivolatile organic chemicals in the indoor environment. The so called “fogging effect” or “magic black phenomenon” – dark walls and surfaces as dirty by carbon black on new painted or renovated walls – is a serious aesthetic problem and must be cleared regarding reasons. This effect may be caused or influenced by the massive occurrence of SVOC's as residues of semivolatile compounds from indefinite sources, may be in glues, plastics (plasticisers or monomers), paints, carpets, and a number of additives used in the building technology and from cleaning agents. The occurrence and fate of semivolatiles as residues from biocide compounds is well known. The surprisingly persistence of some compounds under indoor conditions lead to a prolonged presence in enclosed areas, ventilation is often not able to reduce the SVOC concentrations because of the adsorption (and accumulation) on surfaces, also on particles and aerosols. The earlier observed pathway of semivolatiles biocides seems to be adapted in the case of “magic black phenomena” by adsorbing SVOC compounds on surfaces playing a role as sticky viscous interlayer to catch and accumulate or binding of (black) particles coming from indoor and/or outdoor sources.

For both group of semivolatiles, biocides and sticky viscous interlayer is common, that the ventilation cannot ameliorate the situation. The SVOC coming from the sources will transport through the air but SVOC will adsorb on surfaces also of particles. In contrast to volatile organic compounds VOC's, the duration of evaporation of SVOC is much longer, than in the case of VOC's. Strategies to reduce indoor pollution by this compound are also different. The limited evaporation period of VOC can be accelerated by elevated temperature (so called “bake out” technique) and good ventilation, in the case of SVOC the identification and effective reduction of the sources are only effective.

In some cases, semivolatile compounds are linked to (unpleasant) smell. “Natural” reasons as mould are often the sources. Also synthetic chemistry can be the source of smell. In the case of semivolatiles the sensory impression or the organoleptic result support the thesis, that the evaporation takes a long period of time and activity to reduce or stop smell needs the identification of sources, also secondary sources and the need to remove them from the indoor system. While VOC can be absorbed on some specific materials like polyurethane or PVC foam as part of the furniture or carpet of the enclosed spaces and develop as a secondary source, in the case of semivolatiles the whole indoor surface is a potential “secondary source”.

Summarised we can conclude, that it is necessary to identify and avoid massive SVOC sources in the indoor spaces, above all with unpleasant smell or other biological effects. The rising number of cases with “magic black phenomenon” shows the necessity of precautions by the building technology, construction of furniture and composition of public household products. VOC can be managed by reducing solvents, threatening products to loose volatile residues and always by good ventilations.

COMPARATIVE EVALUATION OF THE AIR QUALITY IN ATHENS AND THESSALONIKI VERSUS EC NEW STANDARDS

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The air pollutants present similar temporal evolution in the urban areas of the European countries. The cases of Athens and Thessaloniki (the capital and the second city of Greece respectively), considered as metropolitan areas of European importance, are interesting examples in order to examine the parameters influencing the relationship between pollution sources and air pollutants and to identify their temporal trends.

The temporal trends of the air pollutants: CO (carbon monoxide), Pb (lead), SO₂ (sulphur dioxide), NO₂ (nitrogen dioxide), O₃ (ozone), PM10 (particulates with aerodynamic diameter lower than 10 μm) and TSP (Total Suspended Particulates) in the urban areas of Athens and Thessaloniki, during the period 1984-99 are examined statistically. A regression analysis was applied and the temporal linear trend: $y = ax + b$ of these values, the regression coefficient (a) and the correlation coefficient $|r|$ are examined.

The air pollutant concentrations resulted from the monitoring networks of the Ministry of Environment, Physical Planning and Public Works (for Athens), Ministry of Macedonia-Thrace and Municipality of Thessaloniki (for Thessaloniki).

The improvement of fuel quality, the technological innovations in industry, the emission sources control programmes and the recent considerable renewal of the vehicle fleet (gasoline engine passenger cars equipped with three way catalytic converters, autobuses and taxis with new technology diesel engines) contributed significantly to the decreasing trend of air pollutants: SO₂, CO, Pb and suspended particulates. This trend is not observed in the case of photochemical pollutants: NO₂ and O₃. Suspended particulates are still above the EU standards, although their trend is decreasing. These results show that despite the temporal trends, the suspended particulates and the photochemical pollutants are the most important problem of the urban atmospheric environment today.

The above mentioned evolution leads the authorities to integrated planning choices in order to improve the urban environment. Among them is the establishment of new air quality standards in combination with actions for the limitation of air pollutant emissions. In this framework, the European Union published two new directives: a) Directive 1999/30/EC, which determines the limit values for the air concentrations of SO₂, NO₂, NO_x, PM10 and Pb and b) Directive 2000/69/EC, which determines the limit values for the air concentrations of CO and C₆H₆. It is important to underline that the new air quality standards are lower up to 50% in many cases or they have to be during the decade 2001-2010.

The above mentioned air pollutant levels in Athens and Thessaloniki are also evaluated by means of the European Commission new air quality standards in order to identify the environmental policy needed to fulfil the implemented requirements.

TRACE ELEMENTS CHARACTERIZATION AND DETERMINATION IN AIR PARTICULATE MATTER COLLECTED ONTO FILTERS

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Trace elements (TE) released in the atmosphere from the anthropogenic sources represent part of the pollutant agents which may be responsible of serious problem to the public health. Depending of their concentrations and their chemical and physic-chemical forms adverse and/or toxic effects are well established for many trace metals that can be released in the air from different pollution processes. Knowledge of the concentrations in the total suspended air particulate (TSP) besides to represent an important parameter is not sufficient for a more close evaluation of the possible impact onto the public health. This has been already recommended by the health organizations which suggest to analyze the “inhalable” particulate; i.e. the fraction containing the particles with an aerodynamic equivalent diameter (AED) of less than 10 μm (PM10) and, more recently, the finest fraction of 2.5 μm AED. In this work, the PM10 has been further investigated to obtain the TE concentrations in the finest “respirable” fractions involved in the different tracts of the respiratory system. By mean of inertial multistage impactors, the air particulate has been size fractionated in the three subsequent fractions: *alveolar* (particles of 0-1.1 μm nominal diameter), *bronchial* (1.1- 4.6 μm) and *tracheo-pharynx* (4.6 < 9 μm). Since the concentrations to be determined are very low (of the order of ng/m^3) special requirements are necessary: (i) high sensitive analytical techniques able to provide multielemental analysis at trace levels; (ii) severe protocols to be followed in the samplings and in the overall analytical procedures to minimize contamination's and/or losses; (iii) quality control of the data obtained by analyzing, with the same procedure, selected standard reference materials.

This work, beside to present the data obtained in the analysis of more than 30 elements in the different air particulate fractions (collected in urban as well as in rural areas) focuses the attention to the analytical problems encountered in this type of determination. In particular, the possible source of errors deriving from blanks of the filtering membranes, analytical procedures, samples homogeneity, samplings times and standards are presented and discussed. Finally, a first attempt to obtain information on the chemical composition of the TE contained in the air particulate matter was accomplished by determining their solubility in distilled water and in physiological solution (0.9% NaCl). To this purpose, leaching experiments have been carried out on the PM10 air particulate fraction. The study gives information about the actual concentration (ng/m^3) in the different air particulate fractions as well as the leaching trend of more than 25 elements. The majority of elements have been determined by Instrumental Neutron Activation Analysis (INAA) while lead and cadmium measurements were carried out by Electrothermal Atomic Absorption Spectroscopy (ET-AAS).

THE GREEK ENERGY CONSUMPTION FUEL-MIX IN VIEW OF GLOBAL CLIMATE CHANGES

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The continuous increase of energy consumption in Greece is directly related to the effort of the Greek citizens to obtain same life quality standards as the rest EU countries. Furthermore, this anticipated increase is basically covered either by imported oil or locally extracted lignite, thus producing significant amounts of hazardous gasses, like CO₂, SO_x and NO_x. On the other hand, the natural gas penetration in the local energy market is still moderate, while the exploitation of the existing plethora of renewable energy resources is minimum.

At the same time, the international community realizes that Global Warming, along with the corresponding climate change, is one of the worst enemies of our planet for the 21st century. Therefore, an action plan was agreed by the whole of the parties, which participated at the recent international conference for the Environment in Kyoto. On top of that, the Greek Ministry of Environment, Physical Planning and Public Works has prepared its own “National Program for the Climate Change” since 1995.

Almost five years later, the proposed study evaluates the National targets’ fulfillment, along with our country’s contribution degree in the EU effort to restrict dangerous air pollutants emissions. During this work, a systematic effort to analyze time evolution of domestic energy consumption fuel-mix in view of the recent climate changes is presented. Additionally, the corresponding emissions of the “greenhouse gases” are estimated according to the primary fuel used. The results obtained may clarify the existing situation and assist the Greek society in taking vital decisions regarding the energy production sector for the next few years, seriously considering the significant global and local climate changes.

**MILITARY USE OF DEPLETED URANIUM:
A MODEL FOR ASSESSMENT OF ATMOSPHERIC POLLUTION
AND HEALTH EFFECTS IN THE BALKANS**

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It is widely held that the weak radioactivity of Depleted Uranium (DU) – lower than natural Uranium – makes its radiological dangers slight. However, DU radiation is indeed “feeble” (i.e. low specific radioactivity, radiation with low penetration capacity) as compared to several other sources, but its biological effects (chemical and radiological) cannot be neglected.

Military use of DU for penetrators has widely spread during the nineties. After the Desert Storm War (1991), it has been widely used in the mediterranean area during the Balkan wars (Bosnia 1995, Kosovo 1999). Its main uses deal with A-10 Aircraft ammunition and Cruise missiles.

Starting from the NATO maps that specify quantities and places of DU bombings in the Balkans, we have set up a model to evaluate atmospheric pollution due to DU, and its health effects on Balkans population and NATO military men.

A credible scenario of a tank attack by an A-10 aircraft, using DU ammunition, is considered to evaluate the DU source term. Population distribution and meteorological data have also been collected for the Balkan area. Dispersion models for atmospheric pollutants are applied.

In order to evaluate the radioactive hazard, we evaluated the Effective Dose Equivalent (EDE) to man, and then the Collective Dose. The calculations have been made using the GENII1 program, which is an internationally acknowledged and utilised software. Hazards due to DU chemical toxicity have been evaluated too, however they seem to be less important than radiological ones.

The results, based on an estimate of the cases expected to occur in population as well as in the armed forces, show that we can reasonably expect soldiers and population to develop certain tumours caused by DU. Occurrences will be quite small, however not negligible, and could be verified with a correct epidemiological campaign and follow-up.

(Footnotes)

¹ B.A. Napier et al. (1990), GENII – *The Hanford Environmental Radiation Dosimetry Software System*, PNL-6584, Pacific Northwest Laboratories (USA)

**VOC AND OTHER ODORIFEROUS SUBSTANCES DETERMINATION
STRATEGIES IN AMBIENT AIR AND EMISSIONS FROM DIFFERENT SOURCES.
EVALUATION OF EPISODES.**

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Due to an increasing public demand for a greater quality of ambient air, there is a growing interest in the analysis of odoriferous episodes, which can sometimes be a significant nuisance to great sectors of the population. There is interest also in the application of preventive and/or corrective measures when appropriate.

The compounds that have odoriferous properties can be both inorganic (as sulphidric acid, ammonia,...) and organic (such as thiols, thioethers, amines, FAV's, ...). Their origin may typically be found in the emissions of chemical plants, coffee roasteries, abattoirs,... and from processes taking place in waste-water or sludge treatment plants, landfills and other environmental treatment systems.

It must be said that the bad odour phenomena can be studied from an organoleptic point of view (applying qualitative and/or quantitative olfactometric methods) as well as doing an exhaustive speciated chemical analysis of the different odoriferous compounds present in the samples. Both techniques can be used complementarily. Since the samples to study can be very complex, there is a need for planning a number of operations which imply "in-situ" tests, by using specific analysers such as for sulphidric acid, or by semi-quantitative colorimetric tubes to determine carbon disulphide levels and/or in-lab analysis using spectrophotometric or chromatographic techniques on samples obtained by absorption with different solutions (such as for ammonia), derivatisation with EFS traps (in the case of carbonilic compounds), using reactive-coated filters (for mercaptanes), confinement in canister or teflon bags or trapping on different adsorbents (like the carbonaceous type for thioethers, esters,... or silica-gel cartridges for aromatic amines, alcohols,...),...

The main operative strategies that must be applied to the study of odoriferous episodes are discussed and a general master-scheme proposal is presented. Moreover, a number of examples concerning the study and evaluation of different typical situations are discussed, such as: land-fill, waste water and manure treatment plants emissions analysis, and the odoriferous impact in ambient air determination from chemical and composting plants emissions.

INFLUENCE OF PARTICLE SIZE DISTRIBUTION ON HEAVY METAL AND PGE CONTENT IN URBAN SOILS OF NAPLES (ITALY)

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Heavy metals and Platinum Group Elements (PGE) content in urban soil is mainly related to anthropogenic sources and in particular is due to vehicle emissions. However, with the introduction in Italy of catalytic converters and unleaded fuel at the beginning of 90's, a decrease in soil Pb content has been observed, while a gradual increase of PGE occurred.

This work aims to study heavy metals concentrations in soil samples and related grain-size fractions (2000-500 μ m; 500-63 μ m; <63 μ m) collected in 5 selected sites including green areas, public parks and high traffic intensity sites in the metropolitan area of Naples (about 120 Km² and 1.054.600 inhabitants). The town is set in a depression located between the Campi Flegrei volcanic field to the West and the Mt. Somma-Vesuvio to the East and delimited by the Mediterranean sea. The flat area is filled with alluvial, marine and lacustrine sediments, while the hilly area is constituted by volcanic rocks erupted by several volcanic center ranging in time from the Upper Pleistocene to recent. The urban area is constituted by bedrock represented by the "Neapolitan Yellow Tuff", buried by incoherent pyroclastic deposits, originating during several eruptions from the Campi Flegrei.

In order to assess the influence of natural and anthropogenic sources of heavy metal and PGE in soils, we have collected top (0-10 cm) and, as reference, bottom soils (40-60 cm) from a profile opened at each site. In the same area a sample of dumped soil was collected close to the main road, to evaluate the effect of vehicular pollution.

All soil samples and related fractions were analyzed for total Cd, Cu, Pb, Zn, Pt and Rh contents by ICP/MS following aqua regia digestion. Hg was determined by Direct Mercury Analyzer-80 (DMA-80).

Some other major and minor elements were determined as well for background characterization of soils. Data concerning PGE elements represent the first attempt to measure these elements in urban soils of Naples.

The complete set of data is presented and discussed allowing interesting preliminary considerations.

POLYCYCLIC AZAARENES (AZA-PAH) IN PARTICULATE MATTER

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Particulate matter samples have been collected from urban ambient air (Milan, Italy), biomass burning, tobacco smoke and vehicle exhaust to study the qualitative and quantitative variation of polycyclic aromatic compound in order to obtain estimates of the relative impact of emission sources on air quality, identify pollution sources, and obtain apportionment of vehicle exhaust in urban air. In this paper, the method development and analytical results for polycyclic azaarenes (aza-PAH) are presented.

Twenty target species (2-4 aromatic rings) were selected among those expected to be present in the particulate matter. The use of GC-MS and LC-MS with various ionization techniques was investigated (electron impact; chemical ionization with CH₄ or NH₃; atmospheric pressure chemical ionisation; electrospray). Particles collected on Teflon filters were extracted in an automatic Soxhlet extractor for 24 hours with dichloromethane. Extracts were evaporated down to 100 µL and various procedures for clean-up to avoid matrix interference were evaluated.

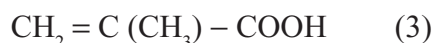
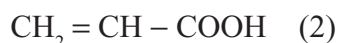
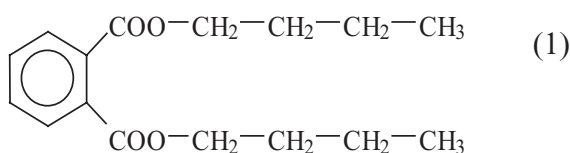
A number of the aza-PAH were identified in the samples at concentration levels in the ppb range. The most abundant aza-PAH were 1-aza-benz[a]anthracene, 7-methoxy-isoquinoline and several isomers of methyl-quinoline. Highest concentrations were found in tobacco smoke followed in turn by urban air, vehicle exhaust and bio-mass burning.

PHOTOCATALYZED DEGRADATION OF SELECTED ORGANIC POLLUTANTS

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Wastewaters of the chemical industry usually contain different pollutants, which are introduced into the natural waters. This is also the case in the Koper area (Gulf of Trieste, northern Adriatic), where the local chemical industry produces phthalates and different polyacrylates. The results of photocatalyzed degradation of dibutyl phthalate (1), acrylic acid (2) and methyl methacrylate (3) will be presented in this work. Dibutyl phthalate is used as plasticizer in different resins, it has been considered as teratogenic compound to aquatic organisms and is a rather stable compound in the natural environment. The direct photolysis rate in natural waters is very low, since it only absorbs light up to 330 nm. Acrylic acid and methyl methacrylate are used as monomers for polyacrylate production. They don't absorb light at environmentally significant wavelengths and are also stable against other processes of degradation. Thus, an efficient process should be applied to remove these pollutants from the waste waters.



Much research work today is oriented towards the goal of destroying pollutants before they leave industrial plants. Photocatalytic degradation, induced by semiconductors such as TiO_2 and ZnO , has been proposed as an important procedure for reducing the concentrations of organic pollutants in waste and drinking waters. The advantage of these processes is the complete mineralization of organic compounds as the final reaction step.

Solutions of dibutyl phthalate, acrylic acid and methyl methacrylate in distilled water with TiO_2 and ZnO in suspension were irradiated in an immersion well photochemical reactor, equipped with a 125 W medium pressure mercury lamp and a cut off filter at 300 nm. The suspensions were purged with oxygen during the irradiation. Kinetic studies were performed using gas chromatography.

The photocatalyzed degradation of selected organic pollutants was the first order reaction. The kinetic studies revealed rather high degradation rates in comparison with the direct degradation rates in homogenous solutions without semiconductor oxides. The degradation rates were dependent on the semiconductor oxide concentration. The increase in TiO_2 and ZnO concentration resulted in a higher reaction rate. The ZnO exhibited better photocatalyzing properties in comparison with TiO_2 . This is probably due to the higher pH of the ZnO suspensions. At the end of photodegradation (about 3 hours) no organic compounds could be detected in the irradiated solution. This indicates the complete mineralization of studied organic pollutants.

In conclusion, photocatalyzed degradation of selected organic pollutants could be considered as an efficient process for their removal from wastewater.

SPATIAL AND TEMPORAL DISTRIBUTION OF VOLATILE ORGANIC COMPOUNDS IN THE AREA OF MADRID (SPAIN) DURING A YEAR

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The assessment and control of the atmospheric pollutants are directed, according to the last recommendations of the E.U., to measure the ozone precursors, volatile organic compounds (VOC), and between them, benzene, toluene, xylenes, etc. for their participation in the photochemical oxidation and so as for their toxicological power. These subjects are considered in the Daughter Directive (200/69/EC) on limit values for benzene and carbon monoxide, and in the Framework Directive (96/62/EC) on ambient air quality assessment and management, which set up the benzene as a pollutant to determine.

An alternative to the conventional methods in the VOC determination, is the technique of the passive samplers, which is being normalized by the CEN/TC 264 and ISO/TC 146 and developed by many laboratories in the last years, with analytical sensibility for the levels of these compounds in ambient air comparable in precision and accuracy to the other techniques.

The advantage of these samplers is their low cost and easy handling. Therefore they can be used a lot of them in the studied zones allowing to know the VOC levels in larger periods of time with high spatial resolution, obtaining daily, weekly and annually mean values in a lot of points. That is very useful in the control of VOC in these areas.

In this work, passive samplers filled with graphitized carbon sorbent were used to collect the studied compounds. After, samples were analyzed using an automated thermal desorption apparatus coupled to a capillary column gas chromatograph and a flame ionisation detector.

The spatial and temporal distribution of volatile organic compounds (VOC_s) were determined in ambient air samples taken in urban, semiurban and rural areas. For this, 300 radial passive samplers were collected in Madrid city and 40 were taken in surroundings area for 7 days each two months during a year.

Obtained data were successfully used to investigate local emission phenomena and to know the large-scale VOC distribution in these zones during the studied time.

OCCUPATIONAL EXPOSURE TO FORMALDEHYDE: IMMUNOLOGICAL RESPONSE AGAINST THE MOLECULAR ADDUCT F-HSA

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Relevant exposure to Formaldehyde (F) can occur in occupational sites (e.g., hospitals and during manufacture) and in household indoor environments, where products potentially emitting F are common (insulating materials, chipboard and plywood, fabrics and heating and cooking emission). Moreover, tobacco smoke increase exposure to F: a smoker of 20 cigarette/day is exposed to 1mg of F/day (IPCS, 1989). Acute and chronic irritant effects of F are well known (IPCS, 1989) and mutagenic activity was demonstrated in several biological systems. F is classified as a probable human carcinogen (classified by IARC in group 2A and by EPA in group 1B) based on animal studies with neoplastic lesions at the point of contact, the respiratory tract and limited evidence of human respiratory tract carcinogenicity (IARC, 1995).

Formaldehyde binds human serum albumin covalently, giving rise to the molecular adduct F-HSA with formaldehyde as hapten. The aim of this work was to evaluate the exposure to Formaldehyde using the humoral immune response to the adduct F-HSA (Formaldehyde - human serum albumin) as biological marker of F exposure. In addition a part of subjects was selected to cytogenetic analysis of chromosomal aberration (CA) and sister-chromatide exchanges (SCE) to evaluate if F can induce the expression of these cellular modifications.

The population under control was a group of 39 subjects occupationally exposed to F, employed in a pathology department in three different hospitals of northern Italy. To each subject a questionnaire was submitted and the following analysis were carried out: personal exposure to F during working hours, prevalence of IgG against F-HSA adduct (made using an enzyme immunoassays: the Displacement assay) and the application of the E.L.I.S.A. test, Sandwich Enzyme-Linked Immunosorbent Assay, in order to obtain the antibody titre of the subjects examined; a sub population was also tested for cytogenetic damages as SCE and CA. Besides this, to evaluate exposure to tobacco smoke urinary cotinine was measured in the whole population.

Personal exposures to F values were always and largely lower than the TLV - TWA of 0,37 mg/m³ (the mean value in the three hospitals was 48.6 µg/m³). Even if exposures to formaldehyde were low, all subjects developed IgG antibodies against F-HSA and the correlation between these two parameters was statistically significant (p<0.05). The specific marker (F-HSA) was not able to discriminate the subjects exposed to F present in tobacco smoke although the urinary cotinine distinguished smokers and not smokers (p<0.001). The cytogenetic markers, CA and SCE, were not significantly correlated with personal exposure to F and F-HSA probably because they are more influenced by tobacco smoke (respectively r=0.40 and r= 0.34). The ELISA test showed the presence of antibody titre for only 6 subjects because its high specificity. These results confirm the usefulness of this specific biological marker to identify the exposure to formaldehyde, even if, if compared to personal air monitoring, it represents a longer exposure history.

THE REDUCTION OF OCCUPATIONAL AND ENVIRONMENTAL EXPOSURE TO BENZENE, TOLUENE AND XYLENES DUE TO TWO LEGISLATIVE ACTS OF PRIMARY PREVENTION.

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Benzene, toluene and xylenes (BTX) are primary pollutants present in air due to emissions from automobiles, petrochemical industries and combustion processes. These compounds are described by US EPA and IARC as mutagens; in particular benzene is classified as human carcinogen. Some professional activities can increase significantly the human exposure to aromatic hydrocarbons, in particular the delivery of gasoline. Besides, active smoke represents an important source of benzene exposure for humans. Thus, the survey of BTX air pollution in urban air and in occupational sites allows to monitoring the effects of preventive acts enforced to improve air quality and human health.

The purpose of this study was to investigate BTX pollution after the enforcement of laws aiming to limit the potential increase of aromatic hydrocarbons in air. DM n°25, November 94 imposed from 1/1/96 to 31/12/98 an objective of quality of benzene of 15 $\mu\text{g}/\text{m}^3$ and from 1/1/99 of 10 $\mu\text{g}/\text{m}^3$. Several measures were adopted in Italy to obtain this objective: traffic restriction, commercialisation of catalysed new cars, reformulation of gasoline and devices to extract the vapours in gasoline pumps. In particular, the law n. 413 (November 13, 1997) fixed, starting from 1/7/1998, the maximum content of benzene in gasoline at 1% and, for aromatics, at 40%. This law imposed also that, from 1/7/2000, all the gasoline's pumps must be equipped with vapour inspirators. For these reasons we evaluated: urban BTX air level before and after the enforcement of these two laws and the occupational exposure to aromatic hydrocarbons before and after the imposition of vapour inspirators by means of personal-breathing-zone samplers of gasoline vapours in a population of service station attendants.

Results obtained from air monitoring highlight seasonal trends, typically of this kind of pollutants, and an important reduction (from 105.02 $\mu\text{g}/\text{m}^3$ in 1998 to 47.76 $\mu\text{g}/\text{m}^3$ in 1999) of aromatics. In particular, the annual level of benzene in air showed a decrease of mean values from 6.19 $\mu\text{g}/\text{m}^3$ in 1998 to 3.95 $\mu\text{g}/\text{m}^3$ in 1999 largely under the limit imposed by DM n° 25 1994. Occupational benzene exposure of service station attendants drastically decreased from 1997 to 2000 (from 217.57 $\mu\text{g}/\text{m}^3$ in 1997 to 44.59 $\mu\text{g}/\text{m}^3$ in 2000). In 2000 samplings were carried out just four months before July 1, when some gasoline service stations did not installed the vapour inspirators jet. Thus, we were able to distinguish stations with and without these devices. In particular, the group of workers having the vapour inspirators showed a benzene "personal" contamination of 11,89 $\mu\text{g}/\text{m}^3$ while, the other workers showed a medium level of 87,5 $\mu\text{g}/\text{m}^3$. (TLV-TWA = 1600 $\mu\text{g}/\text{m}^3$).

In conclusion results obtained showed the usefulness and the effectiveness of these types of regulatory actions enforced to reduce the environmental and occupational exposure to BTX in particular to benzene.

COTININE AND N-(2-HYDROXYETHYL) VALINE AS MARKERS OF PASSIVE EXPOSURE TO TOBACCO SMOKE IN CHILDREN.

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Large segments of populations are exposed to environmental tobacco smoke (ETS) which is a risk factor for lung cancer and heart, circulatory and respiratory diseases. In 1993, ETS was classified as a class A carcinogen by the US EPA. In fact, ETS is composed of more than 3800 different chemicals and at least 40 known carcinogens. Passive smoking has a harmful effect on the respiratory health of children. This statement reviews the evidence that children exposed to environmental tobacco smoke have higher rates of lower respiratory illness during their first year of life, higher rates of middle ear effusion, and higher rates of sudden infant death syndrome. Furthermore, children with asthma whose parents smoke have more severe symptoms. Biological markers observed in biological fluids of passive smokers, include many metabolites of components of tobacco smoke, increase activation of enzymatic system that metabolise carcinogens, and increase urinary mutagens. Nicotine is also metabolised to cotinine, which is measurable in urine and, also in passive smokers, correlates specifically to exposure to ETS; the half-life of cotinine is 20h. Another marker of tobacco smoke, but aspecific, is the N-(2-hydroxyethyl) valine (HOEtVal) resulting from the reaction between ethylene oxide (EtO) and N-terminal valine in haemoglobin; EtO is one of the ETS known compounds that is considered by IARC carcinogenic to humans (group 1).

The aim of this study was the evaluations of urinary cotinine and HOEtVal in 100 children between 3 and 14 years old, to relate these markers to the passive exposure to ETS. To each subject a questionnaire was submitted obtaining information about sex, age, residence and parents' smoking habit; the urinary cotinine was analysed with a gas chromatograph (GC) equipped with a NP Detector and the prevalence of HOEtVal was measured using the N-alkyl Edman method and analysed by gas chromatography-mass spectrometry (GC-MS). Furthermore, levels of the two biomarkers associated to tobacco smoke were investigated taking into account their different biological role, respectively internal dose marker (cotinine) and early biological effect marker (HOEtVal).

Mean age among the 100 children was 8,4 and there were 42 females and 58 males. *A priori* ETS was broken down into four categories, according to the following smoking habits of individuals who lived in the household: 1) no family member smoked; 2) at least one member of the family smoked; 3) only the mother smoked; and 4) only the father smoked. The other variable considered was the total number of cigarettes smoked daily by the mother and the father. The mean values of the urinary cotinine expressed as ng/ml for the four categories considered were respectively: 1) 12.6; 2) 23.0; 3) 27.2; 4) 23.1 and this biomarker was positively correlated with the total number of passive cigarettes smoked ($r = 0.680$). The same considerations were made for HOEtVal and the results showed mean values, expressed as pmol/g globin, respectively: 1) 2.5; 2) 7.3; 3) 7.7; 4) 7.2 and also this biomarker was positively correlated with the total number of passive cigarettes smoked ($r = 0.417$).

A first comparison between results, relative to both cotinine and HOEtVal in children, was performed and both the two markers sensibly discriminate passive exposures to tobacco smoke.

INFLUENCE OF SAHARIAN EPISODE ON ATMOSPHERIC POLLUTION DURING A SAMPLING CAMPAIGN IN ALPINE VALLEY IN AUGUST 2000

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Ground measurement of volatile organic compounds (VOCs), carbonyls compounds, NO, NO₂, O₃, PM10, particles concentrations were conducted in summer 2000 in an Alpine valley at Orelle and Sollières, France during one week from august 22nd to august 30th. This sampling campaign took place into a larger regional project : Alpine Valley Pollution (POVA).

The aim of POVA project is to determine pollution due to the traffic in Chamonix valley and Maurienne valley, before and after the opening of the Mont Blanc road tunnel ; to evaluate respective parts of different sorts of emission : biogenic and anthropogenic ; to determine their variability, and at last to develop a model of atmospheric pollution dispersion in the complex alpine terrain and realize scenario studies.

During this week an abnormal situation changed compounds evolution between the august 26th and 28th. A wind profiler, installed in Modane (between Orelle and Sollières, in Maurienne valley) has recorded datas during this week, and it appeared that the diurnal variation East-West of the wind changed into a south wind during these two days. In fact, this wind came from Sahara and contains a lot of sand. We have nominated this phenomena “ Saharian episode”.

A lot of changing in the diurnal/nocturnal evolution was able to be observed during this period. First, the particles number considerably increased. The increase of particles was detected the august 26th at 16:00. The concentration of particles in the air has doubled for fine particles (with diameter 0.3 µm , 0.5 µm) and this high concentration decreased the 27th at 07:00 AM. For the large particles, the same peak appeared the 26th at 16:00 but decreased early the 26th at 23:30 PM. This episode corresponded exactly with an increase of PM10. The NO/NO₂/O₃ cycle has been perturbed, too. During the episode, O₃ stayed at relatively high concentration (50 ppbv) , even during the night. Then, NO and NO₂ concentrations were low during this period, without any peak between the 27th at 00:00 AM and the 28th at 00:00 AM. The temperature decreased during all the episode because of this increasing of particles.

For the VOCs measurements, the same observations have been recorded. In fact, sand contains SiO₂, which is an adsorbent for VOCs. When the sand cloud arrived above the valley, firstly the VOCs concentrations increased and decreased few hours later.

All the cycles seemed to return to the initial situation after this episode with a valley wind restoring.

This “Saharian episode”, not predicted, was really interesting for the comprehension of different mechanisms on the transversal alpine pollution dispersion.

THE RISK OF DESERTIFICATION IN ALBANIA

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The Republic of Albania is located in the Balkan Peninsula, between 39° 38' and 4° 39' N latitude, and 19° 16' and 21° 40' E longitude. The maximum dimensions of the country are 355 km from north to south and 150 km from west to east. Total surface area of the country is 28748 km² of which 23.4 % lies between sea level and 200 m in altitude, 48.1 % between 200 and 1000 m, 27.5 % between 1000 and 2000 m. It is very mountainous, with many varied landscapes including bare rock. Because of the differences in climate, natural vegetation, slope, and parents rocks, soils are highly diverse.

The information presented in this paper is based on the data picked up from many approaches undertaken for the degradation of the soil in Albania and the complementary data picked up from the published statistics. For realisation of this paper we have supported the real evaluation of the existing state and then we have analysed some cases of the desertification of the soil in Albania.

Desertification is a new contemporary term which has a wider meaning than the easy natural degradation of the space. It is a process where the fertile areas are changed to dry one, as a result of the poor land administration or climatic changes. It includes the loss of the biological and economical productivity of the agricultural lands, pastures, forests, etc.. Is there desertification in Albania? We don't have desertification in global sizes like Africa etc., but in the sizes of our concrete microecosystems we can say that we have desertification with obvious acceptable risks. The arable land in Albania has been widened 2.4 times from the years 1938 to 1990, or from 292000 ha to 704000 ha, while the surface of pastures and meadows have been reduced to 470900 ha or 2.13 times smaller. Even the forest surface in the same period has been reduced with 262900 ha, or from 1307700 ha to 1044800 ha. After the year 1990 it has been noticed an expansion of pastures and meadows and a reduction of forests. Thus 1997 compared to 1990 the surface of pastures was expanded with 29000 ha, while that of forest was reduced with 18800 ha. Today we are facing the same tendency with a drastic deterioration of forests. Approximately 2/5 of the arable area in Albania is terraced, whose technical conditions have been far from the acceptable level. Actually, 122000 ha land of this surface has been refused to be taken as consequence of its unusually poor quality, which has been brought its almost complete desertion. As a result, in many regions of the country the ecosystem has been seriously damaged and entire unproductive territories have been destroyed. Approximately 11-12 thousand ha of land are in danger of sliding and about 4500 ha are slidden or demolished lands. Littoral erosion of rivers and streams caused each year the loss of more than 100 ha, while the rivers network transports to the sea about 60 million ton of hard materials a years. The excavation from the river beds of inert materials for building purposes, has caused only in 1999 the destruction of 3000 ha of arable land. About 20 % of the Albanian territory is pre-exposed to an erosion reaching a level of more then 50 ton/ha/year, whereas in certain areas erosion intensity reaches up to 120 ton/ha/year. Actually about 10 thousand ha peat soils was damaged by burning and high intensity of mineralization. The same alarming is the chemical degradation of land in almost the entire country.

AMMONIA EMISSIONS FROM VEHICLES AND THE EFFECTS ON AMBIENT AIR CONCENTRATIONS

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It is well established that the major source of ammonia emissions is related to agricultural production systems. Atmospheric ammonia, which can be deposited as ammonium on soil and vegetation, may contribute to undesired changes particularly in oligotrophic ecosystems. Protection of vegetation from adverse effects, as eutrophication and acidification, will only be assured by a drastic reduction of emissions of nitrogen compounds.

Ammonia is emitted in smaller amounts from most combustion processes in industry and traffic. Precatalyst gasoline cars emitted ammonia at a low rate, so in the past the contribution of vehicle emissions had been estimated as negligible. However, there are some indications, that the introduction of catalytic converters may have played an important role in rising ammonia emissions; but there are only two original reports, which describe relevant measurements related to specific engine types. Whereas many uncertainties remain, the tendency of such results apparently are confirmed by ammonia concentration measurements performed near roads. It could be proven that the concentration ranges are similar to those reported from agricultural areas.

Vehicle density was the major parameter influencing the diurnal variation of atmospheric ammonia. The concentrations showed a high dependency from meteorological parameters like humidity (rain) and wind direction. Consequently the position of the mobile measuring station relative to the crossroads ammonia sources exerted an important influence.

As ammonia begin to come under the spotlight of international pollution abatements policies further measurements of emission, atmospheric concentration and deposition are necessary in order to be able to establish NH_x budgets. Since transport NH_3 emissions still provide large uncertainties further investigations under real conditions are required.

We are grateful for the funding of the project from the Bavarian Environmental Protection Agency (LfU), Augsburg.

PHOTOCATALYTIC DEGRADATION OF METHYL-ORANGE AND ORANGE II IN AQUEOUS SUSPENSION OF TITANIUM DIOXIDE UNDER SOLAR IRRADIATION

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Textile wastewater results of hard ambient impact due to the variation in composition and concentration of contaminants. More than 10,000 commercial products are used in textile industry where more than 3,000 are colorants. Industrial processes comprises a few working and dying phases that use a big quantity of water of good quality and product wastewater hardly loaded of contaminants. In this type of wastewater the principal problem is the presence of colorants and surfactants.

Colorants are present in wastewater because the textile baths never finish with the total consumption of colorants so wastewater has the colorants not adsorbed on textile fibbers. A concentration around $1\text{g}\cdot\text{L}^{-1}$ is enough to dye water but wastewater from these industries can have a more concentrated loading. This kind of wastewater is usually treated in a chemical-physical plant or most commonly in an active sludge biochemical plant but in order to obtain water suitable to be recycled in production cycles (especially dyeing processes) further treatments are needed. In fact, water to be recycled must have a better quality than that to be discharged.

The dye abatement, however, still represents one of the main problems in the treatment process. Among all the dyes present in wastewater, azo-dyes are the most common ones.

Among the purification systems, the oxidative process seems to be the most promising one. It is very effective towards the destruction of chromophoric structures of dyes, removing colour that is the main “disturbing” factor for water recycling.

Photocatalysis in the presence of irradiated semiconducting oxides has been successfully used to oxidise many organic pollutants present in aqueous systems [1]. It has been also used to decolorate and mineralize many kinds of azo-dyes on bench scale by using both artificial irradiation and solar technology. In this work the heterogeneous photocatalytic system has been used for performing the oxidation of two common and very stable azo-dyes: methyl-orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{SO}_3\text{Na}$) and orange II ($\text{C}_{16}\text{H}_{11}\text{N}_2\text{SO}_4\text{Na}$). The photocatalytic oxidation was carried out in aqueous suspensions of polycrystalline TiO_2 (anatase) irradiated by sunlight. The abatement of substrate, of total organic carbon content and of colour was monitored. The influence of the presence of strong oxidant (H_2O_2 , $\text{S}_2\text{O}_8^{2-}$) and ionic (Cl^- , SO_4^{2-}) species on the process was studied. The dependence of dye photooxidation rate on the following parameters: (i) substrate concentration; (ii) catalyst amount; and (iii) pH was also investigated. At the used experimental conditions the substrate photooxidation rate follows a pseudo-first order kinetics with respect to the substrate concentration. The presence of $\text{S}_2\text{O}_8^{2-}$ enhances the reaction rate more than that of H_2O_2 .

1. M. Schiavello (Ed.), Heterogeneous Photocatalysis, Vol. 3, Wiley Series in Photoscience and Photoengineering, John Wiley and Sons, Chichester, 1997.

USE OF CDNA-MICROARRAYS METHOD FOR CHARACTERIZING CHANGES IN GENE EXPRESSION LEVEL IN CULTURED HUMAN CELLS AFTER EXPOSURE TO PESTICIDES.

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Wide use of pesticides requires a better understanding of the mechanisms by which they could affect exposed workers. A major problem facing biologists in assessing the effects of exposure to a pesticide or, as it is more often the case, to a mixture of pesticides, is the use of reliable biomarkers.

The DNA microarrays method, which is based on the binding of cDNA from mRNA to complementary single stranded nucleotidic sequences, allows the simultaneous and quantitative detection of expression level for a lot of genes.

Hence, DNA microarrays are expected to be very useful for detecting specific impacts on molecular mechanisms involving a change in genes expression. Besides, this method could help for categorizing pesticides as a function of their chemical structure and their related effects on the gene transcription.

In a first step, A549 cultured cells (from a human lung carcinoma) were submitted to three pesticides frequently used in greenhouses, namely, Abamectine (avermectin), Methomyl (carbamate) and Endosulfan (organochlorinated), for 6 hours at 3 concentrations, then, immediately frozen at - 80°C. Controls cells were sham-treated.

Total RNA was obtained according to the Chomczynski's method (phenol /CHCl₃ extraction) and verified to be DNA- and protein-free by spectrophotometry and separation on agarose gel. RNA samples corresponding to each timepoint were mixed with biotinylated oligo-dT to bind the poly-A⁺ RNA fraction. The obtained complexes were then attached to streptavidin-coated magnetic beads and collected using a magnetic particle separator. ³²P-labeled cDNA probe synthesis was performed directly on the beads using the captured poly A⁺ RNA as the template. To increase the sensitivity of the method, a gene-specific primer mix, which only contains primers for genes that are represented on the microarrays, was used for cDNA labeling, in order to concentrate the radioactive label into probes which are specific for the cDNA printed on the array.

Probes were hybridized in duplicate to the Atlas Human Stress Array (Clontech), which features cDNA fragments from 234 human genes known to be involved in the stress response. After overnight hybridization, the arrays were washed and analyzed by phosphorimaging. Standardization of gene expression level over the membranes was achieved by measuring the total radioactivity. A 2-fold difference or higher was considered as significant. From our results, it appears that some genes were upregulated (e.g., genes coding small heat shock proteins, map-kinase-8, heme-oxygenase-2) whereas genes coding proteins such as DNA-polymerase-alpha, CytP450-1A1 and Proliferating Cell Nuclear Antigen were found to be downregulated.

By using both the microarrays and the immunodetection of inducible stress proteins, it would be possible to assess the effects of acute or chronic exposure to pesticides.

THE EFFECT OF AIR POLLUTION ON CROWN AND FOLIAR NUTRIENT CONDITIONS OF FORESTS IN THE SOUTHERN TURKEY

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Through the 1970's large scale forest decline due to the acidic deposition were found in northern and central Europe. It has been seen from the results of an international survey of tree condition which has been carried out under the Convention of Long Range Transboundary Air Pollution (CLRTAP) and the European Union Scheme on the Protection of Forest against Atmospheric Pollution from 1988 that, the health of forest condition declined also in the Southern Europe. The most sensitive species have been found as conifer forest on the Mediterranean coast and mesophile forest of the Mediterranean–montane plane growing at the edges of the natural ecological distribution.

In order to determine the concentrations and deposition flux of pollutants, wet-only precipitation samples were collected, between 1992 and 1996 at a permanent station established on the Mediterranean coast of Turkey. Besides precipitation samples, in order to evaluate the alterations of the effect of the air pollution on soil and trees, 24 sampling locations were selected on the southern Turkey forest. On these sampling points, at the years 1992, 1993 and 1996, pine needle samples from conifer trees were taken from labelled trees. At the years 1992 and 1996, soil samples from the depths of 0-30 cm, 30-60 cm, 60-90 cm were taken. Collected rain samples were analyzed for major ions and trace elements using a combination of analytical techniques, including ion chromatography, atomic absorption spectrometry. Soil samples were analyzed for pH, major exchangeable cations (Ca, Mg, Na, K), P, S, organic matter, Fe, Mn, Zn, Al, Ni, Cr and Pb. Variability in load of elements in deposition and concentration of elements in soil solution has been observed between sites, years of observation. The annual mean pH of the precipitation was observed around 5.17, with high variability in the observed values due to different source regions. High concentrations of SO₄ and NO₃ measured in samples with high pH indicated extensive neutralization of acidity by alkaline species. Results suggest that more than 70% of the acidity has been neutralized by CaCO₃ which originates both from airborne local soil and dust transported from North Africa.

On the selected sampling points, at the years 1992-1993, 1994-1995 and 1996-1997, foliage samples from conifer trees were taken from the labelled trees, and visual indices of tree conditions, like defoliation and discolouration, dry weight of the canopies, were reported. Between the years 1992 and 1997, the degree of defoliation and discolouration of the canopies according to the damage indexes were changed from 10-25% to 25-60%. By examining the soil and rain water chemical composition, the reason of damage on the trees were tried to be explained.

**AIRBORNE DEPLETED URANIUM PARTICLE DISPERSION AND HAZARD
FROM INTAKE THROUGH INHALATION**

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In this paper we present depleted uranium aerosols dispersion, from cloud generating due DU munitions impact to hard target. For diffusion modeling it is used Gaussian puff trajectory model. It is shown that dispersion depend of meteorological conditions. Regardless to concentration DU distribution, in the worst situation would be people that would be find 200-600 meters far from hard target in the moment of hitting of munitions with DU, during cloudy weather and slow wind. Amount of intake of DU through inhalation, that is the most dangerous route of intake, can varied due to level of physical activity at one side and characteristics of aerosols and assumed meteorological scenario at the other.

CLIMATOLOGICAL CHARACTERISTICS OF RURAL SURFACE OZONE IN THE AREA SURROUNDING THE CITY OF ATHENS, GREECE

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Ozone plays an important role in the physico-chemical processes of the troposphere but it is also important due to its strong oxidant properties, which at certain concentration levels found in many urban areas around the world, may cause damages to humans, animals and vegetation. For this reason atmospheric ozone standards are proposed by various organizations or state authorities. The problem of tropospheric ozone has changed dimensions about a decade ago, when it was realized that during the 20th century an almost global increase of surface rural ozone concentrations has been observed, especially in the northern hemisphere. This increase is attributed primarily to photochemical production. In central and northern Europe there are many rural air pollution stations, providing a satisfactory picture of the spatial distribution of surface ozone concentrations but there are only a few systematic measurements for the Mediterranean basin and especially for its eastern part. The high levels of solar irradiation observed in the Mediterranean, in combination with the emitted anthropogenic and biogenic ozone precursors, favor in principle enhanced photochemical ozone production.

The scope of this paper is to make a detailed examination of the climatology of rural ozone around the city of Athens by examining its seasonal and diurnal variation characteristics as well as its interannual variation. The analysis is mainly based on the continuous 10-year ozone record (1987-1996) of the station of Liossia, located at the northern edge of the urban agglomeration (12 km from the city center). The data of this station were screened for cases of strong airflow from rural areas (only measurements under strong northern winds, bringing rural air masses to the basin were retained for further processing). The continuous data-set of the rural station of Aliartos located about 80 km NW of Athens were also considered for the year 1996, the first common year of operation of both stations.

The diurnal variation at the remote station of Aliartos, is considerably larger than for the rural values at Liossia, reflecting the different site characteristics influencing the nocturnal ozone destruction close to the ground as Liossia is located on a mountain slope and Aliartos in a plain. Despite the lower average ozone values in Aliartos, there is a good agreement between the two stations if the afternoon values (12-18 h, period with the best vertical mixing) are only compared. In both stations there is a clear seasonal variation of the mixing ratios of rural ozone with average summer afternoon values reaching 65 ppb in August and lowest winter afternoon values being about 25 ppb in December-January. It is remarkable that the 55 ppb, 8-hour average ozone standard for human health protection of the European Union, which is also a WHO guideline, is regularly exceeded at noon and afternoon hours during summer at Aliartos as well as at Liossia when rural air masses are examined. There is not a clear interannual trend of the rural ozone levels at Liossia during the examined 10-year period, despite the year-by-year fluctuations. The possible origins of these high rural ozone levels, their variation characteristics as well as some aspects regarding the human and vegetation ozone exposure in the area, in combination with the urban originated ozone, are discussed.

**RECENT PROGRESS CONCERNING
THE DEMOLITION & CONSTRUCTION DEBRIS IN EUROPE**

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Construction and Demolition (C&D) waste is an important part of the waste management sector of most industrialized countries. With an estimated annual production of 300 million tones in the EU countries and more than 3 million tones in Greece, the treatment and the disposal of C&D debris represents a significant factor both in terms of quantity and environmental aspects.

The importance of recycling the C&D wastes is recently mentioned by the E.C. DGIII report, published in July 1998 under the title “The Competitiveness of the Constructive Industry”. According to this report, the building construction sector produces huge quantities of wastes, while in some countries members of the EC (Greece included) the shortage of building materials constitutes a major problem.

On the other side recycled products have to compete with traditional building materials and therefore controlled standard qualities are essential for the products. On top of that a remarkable energy quantity is necessary for recycling the main components of the C&D wastes. However, the most serious obstacle appears to be public perception of these materials as inherently hazardous and as very low quality compared to virgin raw materials.

In the present work, recent data of the C&D debris sector of Europe are analyzed, while special emphasis is laid on the existing situation in Greece. Additionally, the possibilities of energy savings and the investigation of new recovery techniques related to integrated recycling procedure are examined. Finally, the European trends and main policies to support increased recovery of C&D waste are also critically evaluated.

MODELLING BIOAEROSOL TRANSPORT NEAR WASTEWATER TREATMENT FACILITIES

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Bacteria, fungi and viruses are often encountered in aerosols and they can be pathogenic or cause allergies following inhalation. Wastewater treatment facilities have been found to generate bioaerosols, which are transported by the prevailing winds downstream to areas that can be several hundred meters away. Bioaerosol formation has a significant effect on air quality in the vicinity of the treatment plants. The amount and characteristics of the formed bioaerosols depend on the aeration system employed at the aeration tank of the wastewater treatment facility.

In particular, we examined bioaerosol formation at the Herakleion Industrial Park wastewater treatment facility in Crete. Concentrations of airborne bacteria were measured downwind and upwind of the aeration tank and samples were taken by using Merck's MASS-100 bioaerosol collector. The use of different growth media enabled the separation and enumeration of several classes of microorganisms. Bioaerosol formation was quantified near the treatment plant as a function of distance from the aeration tank, wind velocity and direction. In addition daily fluctuations were recorded.

In this study, we modelled the movement of bioaerosol particles near the wastewater treatment facility in an effort to explain several high concentration measurements that were made at specific locations, which are much higher, compared to measurements in other nearby locations. Results of a sensitivity analysis are presented and the conditions under which such high measurements can occur are pointed out.

**CASE STUDIES OF THE ATMOSPHERIC TURBIDITY IN ATHENS, GREECE:
COMPARISON BETWEEN SUMMER AND WINTER**

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This work estimates the Ångström turbidity coefficients, assuming a linear behavior of the natural logarithm of aerosol optical thickness, $\ln\delta_{\alpha}(\lambda)$, versus the natural logarithm of wavelength, $\ln\lambda$, in the urban environment of Athens, Greece. The calculations were based on beam solar irradiance data recorded by a simple pyrheliometer performing spectral measurements in the range 320-575nm with a resolution of about 0.5nm. In addition, the Schüepp's turbidity parameter is considered. Case studies of these parameters were carried out on two distinct cloudless days, one for summer and one for winter atmospheric conditions. The comparison reveals that the atmospheric turbidity is higher during the summer day. Furthermore, the larger values of the Ångström wavelength exponent found during the winter day indicate that smaller atmospheric particles are present in the ambient air of the Athens basin in winter than in the summer. The results are discussed with view to the different air pollution sources and sinks between summer and winter.

**CASE STUDIES OF THE TOTAL NO₂ COLUMN IN THE ATMOSPHERE OF
ATHENS, GREECE: COMPARISON BETWEEN SUMMER AND WINTER**

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During the period 1996-97, total NO₂ column measurements were performed in Athens, Greece. Here, the results of two distinct days are presented, one in the summer and one in winter. The measurements used a solid-state spectrometer and were based on the spectral absorption of beam solar irradiance in the visible region. The total NO₂ column in the atmosphere above Athens is temporarily very variable and exhibits values in the range 10^{-3} - 10^{-1} atm-cm as an order of magnitude. The values are much higher compared to those reported for other cities. The total NO₂ column values calculated during the summer day in Athens exceed those found on the winter day. The above-mentioned observations indicate that the total column of this gas is highly influenced by local pollution sources discharging in the mixing layer.

**N-ALKANES, PAH AND ORGANIC ACIDS IN THE ATMOSPHERE OF
CITY GARDEN IN ROME.
CONCENTRATION LEVELS AND SEASON VARIABILITY**

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Concentrations of *n*-alkanes, polynuclear aromatic hydrocarbons and *n*-alkanoic acids were determined in the atmosphere of Villa Ada, the largest city garden in Rome. Analytes were investigated in both condensed and vapour phase, by sampling size-segregated aerosol fractions (i.e., PM_{2.5}, PM₁₀ and total suspended particles) onto inert filter membranes, as well as semi-volatile species by means of polyurethane foam cartridges, located downstream to them.

Aerosols and organic vapour were enriched from air in field campaigns performed during all year seasons in 2000, while the winter campaign was repeated in 2001. In this way not only qualitative and quantitative variations of contents of all classes of compounds in the atmosphere were investigated, but also the relative impact of emission sources onto the ambient quality was evaluated, based onto the particle-size distribution.

By looking at *n*-alkanes and acids, natural emission released by high vegetation as well as other natural sources, influenced over all the composition of large particles (i.e. those exceeding 10µm). By contrast, anthropic sources characterised the nature of aerosols affecting human health. In particular PAH and Nitrated-PAH were concentrated in the fine fraction of aerosols, comprising particles not exceeding 2µm.

Anthropogenic pollutants followed the usual trend along the year, presenting their maximum concentrations in winter and minimum in summer. Instead, components emitted from natural sources presented maximum concentrations during the mild season (spring and summer). Due to the low levels reached in summer, the average annual concentration of benzo(a)pyrene remained below 1.0 ng m⁻³, which represents the index of quality of the air selected by Italian Ministry of the Environment (Decree November 22, 1994, No. 191) to represent carcinogenicity related to atmospheric aerosols in urban air, although this level was passed in most days in December and January.

INFLUENCE OF TRAFFIC DISTRIBUTION ON SOME METAL CONTENTS IN URBAN SOILS: “URBAN” AND “NATURAL” ELEMENTS

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In contrast with soils in agricultural areas, soils in urban areas (particularly in parks and gardens) have a direct influence on public health not related with production of food. This is due to the fact that it can come easily in contact with humans and be transferred to them, either as suspended dust or by direct contact. Moreover, even though they are rarely used for agronomic activities, they receive higher than normal loads of contaminants from traffic and, in heavily industrialised cities, industrial activity.

This work presents data of a preliminary stage of a wide study to be initiated in several European cities aimed at defining the main parameters for a comprehensive description of urban soil quality. Among such parameters, the metal contents and availability are especially significant from an environmental viewpoint. Data of a pilot study have already been shown before, and some preliminary results for Seville were also presented elsewhere.

Samples of surface and sub-surface soils from about 30 sites in parks and gardens within the urban area of Seville were collected. The metals extracted by several techniques, including the sequential extraction protocol recommended by the European Union, were determined. The various sets of results were related to several soil parameters that can be expected to have any influence upon metal retention, namely carbonates, organic matter and clay contents. The data were also related to the main expected source of metal pollution by using the density of traffic and its distance to each sampling point.

The results suggest that the contents and availability of some of the chosen metals, namely Cu, Zn, and Pb, seem to be strongly related with urban activity, represented by traffic. Other elements do not show such a relationship. This conclusion agrees with previous observations in the literature of the distribution of trace elements in street dust of cities as thoroughly different as Madrid or Oslo.

The carbonate or organic matter contents are only moderately related with either total or available metal contents, and no relationship is found for the clay content. This result, combined with the dependence upon traffic, suggests that the metal loading is likely to be mainly due to simple deposition from atmosphere, rather than to a chemical reaction with soil components. However, the possibility that some soil components make metal mobility more difficult by bonding the added metals to their surfaces cannot be excluded.

APPLICATION OF CANONICAL ANALYSIS TO AIR TEMPERATURE AND PRECIPITATION REGIMES OVER GREECE

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The goal of this study is to estimate the relation between air temperature and precipitation in Greece and thereafter to define the regions of the covariability of the two parameters. For that purpose the air temperature and precipitation mean monthly data of 28 and 20 meteorological stations respectively, for the period 1950-2000, are analyzed. The assessment of the seasonal and annual data from the individual monthly ones was regarded necessary because the seasonality of the relation of air temperature and precipitation is under investigation.

The first step is the application of Principal Component Analysis (PCA) to each of the two variable groups of the seasonal air temperature and precipitation.. The result is to reduce the number of variables in each group and more specific to define the main significant factors for each parameter. The number of factors derived, is according to the Scree Plot criterion and to the rule: eigenvalue ≥ 1 .

The second step is the application of Canonical Correlation Analysis (CCA) to the factor scores derived from the use of PCA, of each parameter. So that, the canonical roots are extracted and the number of the roots will be equal to the minimum number of variables in either set.

In the process, the computed canonical scores are correlated to the respective original data, aiming to define regions of positive and negative correlations between the canonical roots of the air temperature and precipitation.

AIR POLLUTANT EMISSIONS AND CONCENTRATIONS BASED ON URBAN TRAFFIC MODELING

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Traffic is considered to be the major source of air pollution in urban areas. The temporal increase of passenger car ownership, the increased use of passenger cars, the reduction in the use of public transport systems, the renewal of the vehicle fleet by new technology vehicles, and the improvement of the fuel quality produced the following results: a) the temporal decrease of CO, Pb, SO₂, TSP concentration levels, b) the stabilisation or slight increase of NO₂ and O₃ and c) the holding of the suspended particulates and the aromatic hydrocarbons above the air quality standards in urban areas.

In this paper, an environmental evaluation of various traffic scenarios is realised using the Thessaloniki urban area as a case study. Traffic, emissions and air quality data have been studied for the main road network of the urban area. Traffic data include traffic volumes, composition and vehicle speed. Emissions have been calculated for the pollutants: CO, NO_x, SO₂, VOC and TPM. Air quality measurements include CO, NO₂, SO₂ and TSP.

Traffic and emissions data were based on the General Transportation Study initiated by the Organisation for the Master Plan and Environmental Protection of Thessaloniki (OMPEPT). This study started in 1988 and its second phase was conducted in 1997-99 and included -among others- a roadside survey with a sample size of 33.836 drivers and a home based interview survey with a sample size of 3.324 households. The air quality data result from the Ministry of Macedonia-Thrace and the Municipality of Thessaloniki monitoring networks.

All traffic scenarios have been tested and evaluated with the use of the EMME/2 traffic model. Within EMME/2 the geometrical and functional characteristics of the road network of the study area were represented in an adequate way and thus, the analysis of the trip characteristics at strategic level was made feasible. The model supports the four stages of the classical transportation planning process concerning the future traffic forecasts (trip generation and distribution, modal split, traffic assignment). The study area was divided into 316 internal and external traffic zones. The length of the EMME/2 network was 4.357 km.

The evaluation of the scenarios concerning their air pollutant emissions was based on the use of the COPERT II methodology, which was developed within the framework of the EU program CORINAIR.

Within the framework of this paper the evolution of the relationship between traffic - emissions – air quality during the decade 1988-98 is examined at a first level. Furthermore, the relationship between traffic – emissions is examined for the four discrete traffic scenarios, which were developed for the following target years: a) 1998, b) 2004, c) 2014 and d) 2014+. In addition to the above mentioned examination, a qualitative and semi-quantitative prediction is made for the expected air quality levels in the study area.

BIOACCUMULATION OF PAHS ASSOCIATED IN THE LEAVES OF *CUPRESSUS SEMPERVIRENS* L. THE USE OF LEAVES TO VALUE AIR QUALITY IN THE PALERMO (SICILY) AREA

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Results for concentration of total polycyclic aromatic hydrocarbons (22 compounds) and their profile in leaves of *Cupressus sempervirens* L. are presented and discussed with reference to their sources.

In this work, the *Cupressus* leaves have been used as samplers. In particular, this plant was chosen because it is widespread in the Mediterranean area and it is commonly found both in the metropolitan and in the peripheral areas of the city of Palermo.

The results have demonstrated that Palermo, like other cities in the world, is prone to a rather high level of atmospheric pollution, in particular in the zones with heavy traffic.

Chemical analyses were carried out by GCMS technique.

The use of *Cupressus* as samplers, as in the case of other plants, offers the possibility to assess the air quality, in a determined geographical area, without the need for long periods of sampling with complex, difficult to handle instruments and numerous analytical calculations.

SIXTEEN YEAR AIR QUALITY TRENDS ASSOCIATED WITH THE VEHICLE TRAFFIC OF ATHENS CITY CENTRE

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Air quality data obtained by the Athens air pollution-monitoring network, during the period 1984-1999, is analysed. The analysis of the atmospheric pollutants concentration measurements show that, during this period, decreasing trends -observed in all monitoring stations- can be attributed to various pollution-sources improvements, such as vehicle fleet renewal and fuel quality improvement.

The analysis has demonstrated that decreasing trends have been observed for almost all air pollutants investigated. Notwithstanding, smoke and carbon monoxide concentration levels in the centre of Athens respectively remain above the EU and WHO limit values, for the most part of the examined period. Violations of the limits were on the decline during the greater part of the period examined.

The analysis has also illustrated that highest ozone concentrations were observed at the northern suburbs of Athens. In all stations located at the northern part of Greater Athens Area, the percentage of 8-hour daily averages (12:00-20:00) of ozone concentrations, exceeding the EU threshold for human health protection, caused increasing trends during the period examined.

VOLATILE ORGANIC COMPOUNDS CONCENTRATION LEVELS ON A DAY WITHOUT TRAFFIC IN THE CENTRE OF ATHENS

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In the framework of LIFE European project “In town, without my car!” for a healthier and a more friendly city, in the 22th of September 2000, an area in the commercial centre of Athens was reserved for pedestrians, bikes, clean vehicles and public transport.

The main sources of volatile hydrocarbons in the atmosphere are certain industrial processes and human activities, principally motor vehicle exhausts.

Air samples were taken during that day, and also the day before, at the same location, from 8 am to 8 pm, in order to examine the extent in which traffic restriction would affect VOC concentrations.

Concerning the 22nd of September, samples were also taken on a location where vehicle circulation was free.

Air samples were passed through preconditioned glass tubes filled with Tenax TA and the analysis of the VOCs was performed in a thermal desorption unit, coupled to a Gas Chromatograph, using a flame ionization detector.

Nine hydrocarbons (namely, the *aromatic* benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, 1,3,5-trimethylbenzene, and the *aliphatic* hexane, heptane, octane) were selected for measurement.

Analysis of the samples showed that VOC concentrations in air during the day without traffic were reduced by more than 50%.

**PM₁₀ CONCENTRATIONS IN THE URBAN AREA
OF THESSALONIKI, GREECE**

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In the last few years there is a growing concern for the contribution of the PM₁₀ concentrations (breathable particulate matter with an aerodynamic diameter of less than 10 µm) to health effects. This study reports systematic ambient PM₁₀ measurements, at the commercial center monitoring station of the Municipal Air Quality Network of Thessaloniki, from 1994 to 1999. PM₁₀ concentrations were measured with two different methods, the beta-gauge principle and the tapered element oscillating microbalance method. The correlation between the daily PM₁₀ concentrations derived from the above two methods, was very good throughout the referenced period. The daily relative frequency distribution of PM₁₀ concentrations show that the proposed mean daily standard of the European Union is considerably exceeded, in the urban area of the city. The analyzed data show a significant annual variation, while pollution-roses appear to be a factor that helps to explain short-term variables in airborne particulate concentrations.

AIR TEMPERATURE VARIABILITY AND TRENDS OVER GREECE

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In this study, the variability and trends of the mean annual and seasonal surface air temperature in Greek peninsula are examined. The climatic data used, concern mean monthly values of air temperature of 25 meteorological stations of the Hellenic Meteorological Service, for the period 1950-2000.

In the beginning, the Principal Component Analysis (PCA) is applied on the mean annual and seasonal air temperature in order to define the regions within which the air temperature covariates..

In the process, the air temperature timeseries are analysed, so that the variability and trends are described. As the annual timeseries concern, a cooling trend is observed from the early 1960's till the middle of the decade of 1970, when the trend reverses to heating till nowadays. It is remarkable that the today air temperature levels do not exceed the levels of the middle of the century.

During the winter, it is crystal clear that a cooling trend exists from the middle of the decade of 1950 to the end of the decade of 1980, especially in the south region of the country. Afterwards an increasing trend is observed till nowadays. The pattern in spring appears a slight heating trend in the northern region of Greece and a cooling trend in the south. The summer timeseries are similar to the annual ones, so the contribution of summer in annual variability is unquestionable. Generally speaking, the air temperature in autumn follows the same distribution in time.

Finally, spectrum analysis on annual and seasonal air temperature is applied investigating for periodicities in the air temperature.

SPECIATION OF METALS IN EMISSIONS AND WORKING AREAS BY SELECTIVE SEQUENTIAL EXTRACTIONS

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The toxicity of heavy metals is related to their chemical form, physical state and oxidation number: the knowledge of the different chemical species air-dispersed is therefore very important for a correct evaluation of the probable damage to human health caused by their exposure. Due to the different toxicity related to the distinct metal compounds, hygienic level threshold for the individual species should be established by legislation. In Italy are currently used as indicative tolerable concentrations the values fixed by ACGIH (American Conference Governmental Industrial Hygienists). With regard to emissions Italian law establishes tolerable values only for the total metal ignoring the speciation. It is expected that more detailed limits for the different chemical species of every toxic metal will be fixed by law.

Since a few years our group is interested in the problem of speciation of toxic metals in air by studying sequential extraction procedures for separating selectively the different inorganic species that can be present in particular in emissions and working places where these metals are produced or processed (1,2).

The proposed procedures are first tested on synthetic samples prepared in laboratory with the different metals salts in the presence of atmospheric particulate matter, previously checked for the absence of the investigated metal. The speciation is then applied to reference materials (urban particulate matter NIST SRM 1648, Coal fly ash NIST SRM 1633 and 1633a) and real samples. Finally matrix spiking and recovery analyses are evaluated and the repeatability of the speciation is assessed by performing multiple analyses of the spiked samples. Determinations are made by conventional instrumental techniques such as GFAAS and FAAS, ICP, Voltammetry.

Even if the proposed procedures need extractions of the matrix, the reactions that can take place during the different dissolution steps can be reasonably expected, being the scenario of every emission or defined work place a priori foreseeable: the possible interferences can be therefore evaluated and the procedures adapted.

The procedure proposed for the different inorganic species of beryllium and lead that can be found air dispersed in working areas and/or emission will be described.

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DETERMINATION OF HEXAVALENT CHROMIUM IN THE ATMOSPHERE OF THE CITY OF ISFAHAN

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Chromium is released into the atmosphere from both natural and anthropogenic sources. The major sources of this element in urban atmosphere are anthropogenic sources include; production of iron and steel, and a smaller proportion from the combustion of fossil fuels. (1) Chromium exists in the environment predominantly in two oxidation states, Cr (iii) and Cr(vi). The toxicity of these two physicochemical forms are different and Cr (vi) is known as toxic and carcinogenic form.. Determination of atmospheric concentration of Cr(vi) is important because of the continuous nature of exposure and also the size of the general public at risk.(2) In this work, air was passed through an impinger using a low-volume pump. Sampling period was 24 hours and air was drawn through the impinger with a flow rate of 15 l/min. Two impingers were used in this work. The first impinger contained 250 ml of sodium bicarbonate buffer solution, and the second one was empty and used as a guard for pump. The impinger solution was used for the determination of Cr(vi) concentration.

The determination was carried out by ion chromatographic technique. Table 1 shows the concentration of Cr(vi) in several samples.

Table 1: Concentration of Cr(vi) in the atmosphere of the city of Isfahan

Sample	(ng/m ⁻³) Concentration of Cr(vi)
1	6.8
2	7.7
3	4.7
4	3.9

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SEASONAL VARIATION IN ATMOSPHERIC CONCENTRATIONS OF PARTICULATE PHASE PAHS IN ISFAHAN

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Polycyclic aromatic hydrocarbons (PAHs) are by-products from the incomplet combustion or purolysis of organic materials.(1) The sources of PAHs into the atmosphere can be divided into 1) natural sources; such as forest fires and volcanic activities, and 2) anthropogenic sources. The major anthropogenic sources of PAHs include; residential heating systems, coke production, waste incineration, and internal combustion engines.(2) Several of these compounds show carcinogenic and/or mutagenic properties, therefore they may pose a human health threat.(3) Although human exposure to PAHs can occur through several environmental path ways, in recent years there has been considerable concern over the potential human adverse effects of PAHs in the atmosphere. PAHs in the atmosphere are mostly associated with airborne particulate matter. In this work, airborne particulate matter from the atmosphere of the city of Isfahan was collected on quartz fiber filter (QM-A) using a high-volume air sampler with an average flow rate of 1 m³ min⁻¹. The exposed filters were then extracted with soxhlet using dichloromethane for 8 hours. The determination of PAHs was carried out on a Philips gas chromatographic Model PU-4400 equipped with flame ionization detector. A BPX5 cappillary fused silica column and temperature programming were used for separation of PAHs. Table 1 shows the average concentrations of PAHs in the atmosphere of the city of Isfahan in different seasons.

Table1: Mean concentrations of PAHs in the atmosphere of the city of Isfahan in different seasons of the year (ng/m⁻³).

Compound	Spring	Summer	Autumn	Winter
Phenanthrene	2.6	1.7	3.1	3.1
Anthracene	2.3	1.6	2.9	3.0
Fluoranthene	2.0	2.2	2.6	2.5
Pyrene	2.7	2.1	3.2	3.7
Benzo(a)anthracene	3.0	2.6	3.1	3.9
Chrysene	2.4	2.4	2.9	4.2
Benzo(b)fluoranthene	1.6	1.4	2.4	2.8
Benzo(a)pyrene	2.0	2.3	3.4	4.6

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THE EFFECTS OF AIR POLLUTION ON CARBONATE STONE MONUMENTS IN URBAN AREAS (SIVAS, TURKEY)

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In this study, the gypsum formation in carbonate stone by air pollutants has been investigated. The mineralogical compositions, (by using X-RD) and texture investigation, (by optical microscopy research of thin section) of the samples taken from the 13 historical building from various parts of Sivas and which are at different ages, have been examined. The samples have been chosen from the unsheltered surfaces. The gypsum rate that is formatted on polluted surfaces has been explained with the polluted atmosphere of Sivas city, high relative humidity, the age of the buildings and stone characteristics.

**AN ANALYSIS OF WINTER AIR-POLLUTION STUDY IN URBAN AREA IN SIVAS,
TURKEY.**

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In this study air pollution level in the city center of Sivas for a 10 years' period are analyzed. Winter season' and annual averages of sulfur dioxide and particulate matter measurements have been carried out in central area of Sivas by City Health Management. Specifically the winter seasons' concentrations are presented and their causes and their change with respect to meteorological parameters are discussed. The statistical relations between pollutants and meteorological parameters have been found to be significant. Based on the data analysis an attempt is made to provide useful information about the air quality levels taking into account international air quality standards. The determining of air pollution control strategies will be useful. These control strategies consist of supplying quality energy sources, limiting the consumption for various hours during the day and alternative energy sources.

URBAN AIR POLLUTION DUE TO VEHICLES IN GREECE

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It is well established in major and minor urban centers that a major contributor to air pollution is due to the operation of vehicles. A major undertaking has been in evolution by a team of researchers with the help of their students at the Technological Educational Institution of Thessaloniki to measure vehicle emissions at several Greek cities. In this paper the measurements in two cities, Thessaloniki and Katerini will be presented. Thessaloniki is the second in population in Greece with about a million inhabitants, while Katerini is a smaller city of about 65000 inhabitants, but lies on an important crossroads on the way to Athens from Thessaloniki. The atmospheric pollution in an urban environment poses a serious problem, since the joint consequences of vehicle emissions and traffic noise affect dramatically the physical and mental health of the citizens, the quality of life and services. Exhaust gas data from vehicles were taken separately for each season of one year, in particular: carbon monoxide (CO), carbon dioxide (CO₂), oxygen (O₂), and hydrocarbons (HC) at idle and at 2000 RPM. A set of sensory measurements has been also acquired, based on aural, nasal and visual observations on vehicles under test. In the present paper, a novel emission policy is proposed for the detection of gross polluting vehicles in the city, based on sensory observations.

OUTDOOR BENZENE EXPOSURES IN RESIDENCES NEAR A COKE OVEN PLANT

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To measure outdoor benzene exposures of people living near a coke oven plant in Genoa, temporary net-works of passive samplers were used, involving students of local schools. These monitoring campaigns were included in an educational program called “Benzene in Rete” whose aim was to inform teachers about benzene sources, fate, effects and legislation and to actively involve students and their families in the study of this problem in Genoa town. Starting from 1999, three annual sampling campaigns were organised in two Genoa’s districts, Cornigliano and Rivarolo. The Cornigliano district is very close (from 400 to 1110 m.) to a steel factory with a coke oven that daily produces about 860 t of coke coal. The daily emission of benzene from the coke oven was estimated to be 15,4 kg. In each sampling campaign about 60 passive tubes (by Perkin Elmer filled with Chromosorb 106) were simultaneously exposed, in the month of April for seven days, outside the residences of as many as students living in the two districts. Students were selected according to the floor of their residence and to have an uniform distribution of sampling sites. Benzene and toluene were analysed by thermal desorption and GLC with a FID detector. Table shows results obtained in each monitoring campaign. In 1999 and 2000 the coke oven was in full operation (four batteries). In 2001 a battery was closed with a reduction of 30 % of coke production.

TABLE . Mean outdoor benzene concentrations (ug/m³) in Cornigliano and Rivarolo districts

YEAR	(1999-2001)							
	CORNIGLIANO				RIVAROLO			
	high floors	low floors	min	max	high floors	low floors	min	max
1999	10.3 ± 4.8	10.6 ± 5.9	3.8	22.4	4.4 ± 2.2	4.5 ± 1.9	1.8	9.6
2000	6.4 ± 2.8	7.7 ± 3.5	2.8	14.9	5.2 ± 3.4	4.7 ± 2.4	2.4	12.3
2001	7.0 ± 4.4	10.4 ± 6.3	1.0	22.0	2.3 ± 1.0	3.0 ± 1.4	1.0	6.3

In Cornigliano, benzene concentrations were strongly dependent from wind direction and distance from the coke oven. The highest benzene concentrations were found near this plant and with winds from Est South Est. In this anemological condition the Cornigliano district is down wind the coke oven and its emissions. Results demonstrated that even the partial closure of the coke oven was inadequate to respect the benzene air quality standard (10 ug/m³) in residences close to this plant. Different ratio between toluene and benzene (tol/benz) in coke oven and traffic emissions (0.25 and 3.6 respectively) were used to calculate the contribution of these two sources. In 1999, about 70% of the benzene found in the Cornigliano district was estimated as emitted from the coke oven. Our conclusions are that benzene emitted from the Cornigliano coke oven is a relevant contribution to the exposure of population resident near this plant and its complete closure is necessary to respect benzene air quality standard in this area.

MEASUREMENTS OF SULFUR POLLUTANTS AND VOC CONCENTRATIONS IN THE ATMOSPHERE OF A SUBURBAN AREA IN GREECE

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The measurements of Sulfur gases and Volatile Organic Compounds (VOCs) in air are very important. Many of these air pollutants are toxic and notorious for their obnoxious odors even when present at parts per billion levels.

These air pollutants play an important role in air quality for two main reasons:

a) Sulfur species lead to the formation of sulfate aerosol and contribute to the acidity of precipitation and VOCs contribute to the built-up of ground-level ozone, which causes photochemical smog.

b) Some of them (especially Hydrogensulfide and Benzene) are toxic and/or carcinogenic. The air pollutants monitoring campaigns occurred in two periods, August and November of 2000, in a suburban area, near an industrial zone, 70 km away from Athens. The campaign was carried out each six (6) hours during a week. Air samples were collected from five sites by using sampling bags for sulfur compounds and glass tubes filled with Tenax TA for VOCs. The analysis of the pollutants was based on a gas chromatographic separation used a flame photometric detector for the sulfur compounds and a flame ionization detector for the VOCs. The sulfur species investigated include H_2S , CH_3SH , COS , CS_2 in the concentration range of 0.4-37 ppb, while the hydrocarbons were: benzene, toluene, ethylbenzene, m-, p-, o- xylenes, heptane and octane in concentrations from $0.27 \mu g m^{-3}$ to $44.7 \mu g m^{-3}$.

The air pollution station of the NCR “DEMOKRITOS” was installed at the sampling location where meteorological data were recorded from a meteorological sensor 10 meters above the ground.

INVESTIGATION OF LEAD LEVEL IN THE WORKING ENVIRONMENT AND BLOOD SERUMS OF THE WORKERS IN SEVERAL INDUSTRIEL BRANCHES

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In this work, in 34 various work places in Mersin Industry Site, small fan ventilators, which run with alternative current and are equipped with filter paper are set and they are worked 3 days (8 hours a day) , so that the air of the media hit the ventilators. The samples collected, passed through a series of suitable chemical processes in the laboratory and the values are measured in Atomic Absorbtion Apparatus and the amounts for each m³ of air have been calculated. Apart from that, blood samples of 103 workers from various work branches have been taken and lead levels have been investigated on AAS. All of the measurements have been classified according to work branches and both in the work branch and in control group and in blood serum and in the air, the measured values are compared with the standard values.

Maximum lead concentration found in the blood of the egos pipe repairmans.

MODELING TRAFFIC-RELATED AIR POLLUTION IN STREET CANYONS OF THESSALONIKI, GREECE

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A simple microscale dispersion model was used to predict the concentrations of traffic-related air pollutants measured at certain monitoring stations in the Thessaloniki basin. Input is wind speed and direction, atmospheric stability, aerodynamic characteristics of the canyon and total pollution emission at street level. The model results were validated and compared with actual measurements. Comparisons are also presented among carbon monoxide vertical concentrations profile. These findings may have important implications in designing monitoring and theoretical studies to support investigation on the health effects of vehicular pollutant concentrations in urban street canyons.

ENDOCRINE DISRUPTORS IN SEWAGE TREATMENT PLANTS , RECEIVING WATERS AND SEDIMENTS. INTEGRATION OF CHEMICAL ANALYSIS AND BIOLOGICAL EFFECTS ON CARPS

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Occurrence of alkylphenol ethoxylates or their metabolites (alkylphenols and carboxylated derivatives), as well as natural and synthetic steroids in sewage treatment plants (STPs) effluents and in their receiving waters were related to the biological effects, measured as alterations on vitellogenin (VTG) synthesis on natural fish populations. Water composites of STP influents, effluents, sludge, river water, sediment and feral carps (*Cyprinus carpio*) were analyzed over a seven month period in two tributaries of the Llobregat river (NE Spain). Solid phase extraction-liquid chromatography-mass spectrometry (SPE-LC-MS) analysis revealed the presence of concentrations up to 31 µg/L of nonylphenol ethoxylates (NPEOs), 15 µg/L of nonylphenol (NP) and 35 µg/L of nonylphenoxy carboxylate (NP₁EC) in river water downstream of STPs. These compounds were also found to accumulate in river sediment with concentrations ranging from 10 to 820 µg/kg of NPEOs and from 22 to 645 µg/kg of NP. Natural and synthetic estrogens and progestogens also occurred in the water and sediments analysed but in the ng/L range. VTG fluctuated among sites and sampling periods but it was enhanced in the most polluted river downstream the main STP where also some fish intersexuality was observed. However female VTG was mostly depleted downstream the STW plant. High correlation between EDC present in water and sediment and VTG induction in male carp was observed, especially for alkylphenolic compounds in water and in sediment samples ($r = 0.83 - 0.84$, for $n = 24$) and for estriol and estrone in water ($r=0,78$ and $0,94$, for $n=9$ and 8 , respectively).

Acknowledgements

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**THE EFFECT OF AQUEOUS ENVIRONMENTAL CONTAMINATION OF
NONIONIC SURFACTANTS (APEOS) ON THE REPRODUCTION RATE OF
ZEBRAFISH, *DANIO RERIO*.**

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Alkylphenol ethoxylates (APEOs), a second in significance group of surfactants used in detergent formulations, mostly as components of household institutional and industrial cleaning products, are released to the environment, mainly via sewage effluents. These nonionic surfactants and/or their metabolites have been shown to be potential endocrine disruptors for both invertebrates and fish, inducing vitellogenin production in males of rainbow trout (*Oncorhynchus mykiss*), common carp (*Carpio carpio*) and other fish species.

In the present study we have sampled Israel streams/rivers and coastal seawater in the Mediterranean Sea, for APEOs contamination and their homologous distribution and tested the effect of these APEOs on eggs production of the zebrafish, *Danio rerio*. APEOs concentrations have been found to be within the range of 12.5-75.1 ppb and 4.2-25.0 ppb in the rivers and their estuaries respectively.

Fifteen groups of zebrafish were exposed to 5 concentrations within these ranges (0, 5, 10, 25 and 75 ppb) of APEOs and eggs produced were counted every 2 days for 20 days. Exposure to concentrations above 5 ppb affected eggs production in zebrafish after 10-16 days of exposure. The decrease in eggs production was related to the APEO concentrations. Ten days after exposure the decrease reached to 88.8±1.9%, 83.3±3.4% and 77.1±1.3% levels compared with control in 10, 25 and 75 ppb respectively.

The results provide a rough estimation to the degree of potential endocrinic/estrogenic contamination in the coastal water and rivers of Israel and demonstrate the potential damage for the already disrupted ecosystems in these environments. The results will be discussed in terms of APEOs distribution in aqueous environments – health risk potential – regulation relationships.

SUSPENDED MATTER AND PARTICULATE COPPER SPECIATION IN THE POLLUTED ABU-KIR BAY, EGYPT

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Abu-Kir Bay, a shallow semicircular basin at 36 km east of Alexandria receives water from three main sources; highly polluted drainage water via Tabia outfalls at its southwestern side, contaminated brackish water from Lake Edku at its southeastern side via Maadia channel and fresh Nile water from Rosetta Nile branch at its eastern side. Suspended matter (SM), the main pathway by which dissolved ions may be removed from seawater to be incorporated into sediments, is important with regard to distribution of particulate copper (PCu). Several processes including; 1) inputs by land discharges, 2) output to the open sea, 3) regeneration from the bottom sediments and 4) biological activities control the SM budget in the bay. The SM values were high in the nearshore water and decreased seaward. The distinct peak of SM in November at Tabia Sector (TS) reflects the high bottom values.

Because the environmental impact of a particular metal species may be more important than the metal concentration, copper partitioning patterns in Abu-Kir Bay were studied to determine the metal sources, geochemistry, associations and availability for biota. In Maadia Sector (MS), the copper fractions were dominated by F3 (49.0%) > F5 (25.8%) > F4 (16.6%) > F2 (5.0%) > F1 (3.5%) of the total copper. In the TS, the order was F5 (76.0%) > F4 (9.3%) > F3 (6.5%) > F2 (5.8%) > F1 (2.4%) of the total copper. The equations of multiple regression show that pH and dissolved oxygen affected F1 in MS, contrary to TS where the F1 distribution was affected by temperature and SM. In this heavily polluted sector, a higher surface F2 value was found and decreased with depth following the decrease in the untreated industrial wastes with depth. The depth profile of F3 fraction indicates a higher surface value followed by a slight decrease with depth, showing that particles of Fe/Mn oxides are important terminal scavengers in the surface water. The vertical distribution of F4 varied slightly at TS, giving an increase in the surface water from the discharged raw industrial wastes containing high concentrations of organic and inorganic pollutants. Significant positive correlation between F5 and silicate was found in the middle layer of MS and in the surface and middle layers of TS, indicating an enrichment of alumino-silicate material in the SM in these water layers related to wastewater effluents.

**INVESTIGATION OF NATURAL RADIOACTIVITY CONCENTRATION IN
BUILDING MATERIALS FOR INTERIOR AND EXTERIOR ADORNMENTS IN
MODERN GREEK STYLE CONSTRUCTIONS**

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This study focus on the determination of the natural radioactivity concentration of various building materials used for interior and exterior constructions located in Greece. Natural radionuclides (U-238, Th-232 and K-40) concentration in specially prepared samples is measured utilizing the direct gamma-counting method. These values are presented as specific activities (Bq Kg⁻¹) for each radionuclide in every constructing material while the overall results are tabulated, analyzed and compared with similar data from other studies. Additionally, the radiobiological impact to humans exposed to this specific radiation is investigated by estimating the probable radiation dose uptake (in mSv per year) and comparing it with the maximum permissible absorbed dose to humans as given by the world standards.

**EFFECTS OF THE USE OF *FLUMEQUINE* IN AQUACULTURE:
MICROBIAL RESISTANCE AND SEDIMENT CONTAMINATION**

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Intensive farming (including aquaculture) imposes the use of large amounts of antibacterial drugs. These drugs are used to prevent the diffusion of diseases, easily diffused at high breeding densities. Drugs are administered by oral route: they are slowly absorbed and excreted in active form with deject. Waste discharge lead to the introduction of these chemical into the environment.

Flumequine is a Quinolone antibiotic, widely used in intensive acquaculture; in these activities waste discharge is direct, particularly in marine farming. The presence of antibacterial drugs in the marine environmental poses several problems; among them contamination of abiotic compartments (water, sediment, etc.) and induction of microbial resistance are the most common. The aim of this work has been to evaluate the presence of both Flumequine residues and microbial resistant strains in sediment near an aquaculture station at Cala Galera (Orbetello, Tuscany).

Sampling has been performed in January 2001, twenty samples were taken around the cages where sea bass are bred. The entity of the microbial community in both non selective medium (marine agar) and in the presence of 10 µg/ml Flumequine were determined. Microbial strains were divided on the base of morphological differences and biochemical markers. Analysis of Flumequine residues in the sediment were performed in HPLC – Fluorimetric detection.

In the twenty samples the amount of microbes (as CFU, Colony Forming Units) is highly variable; in all samples resistant strains are present, ranging from 30 to 90%. About 70 different groups were identified, 50 of them found resistant.

The relation of resistance with presence/absence of drug residues and with the sampling location are discussed.

MICROSYSTEMS FOR ENVIRONMENTAL SENSING

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Due to massive human activities such as industrial manufacturing, agriculture and transport the natural environment is increasingly contaminated by a broad spectrum of harmful chemicals. This is one source among others of the growing demand for analysis of samples with respect to their chemical composition and its quantification. Whereas excellent laboratory analytical methods exist for the analysis of almost any pollutant in a variety of matrices, only few methods are available for on-line, on-site or in-situ analysis. For these applications new chemical sensor systems have to be developed with improved performance concerning response time, sensitivity, selectivity, stability, and lifetime.

The application of microsystem technology to these problems has proven extremely successful. Microsystem technology integrates signal processing with miniaturized sensors and actuators. It makes use predominantly of microtechniques derived from semiconductor technology, but it extends considerably the range of materials and technologies available for the realisation of electrical, mechanical, optical, chemical and biological functions. Stand-alone micromachined sensors, as well as miniaturized chemical analysis systems which perform several steps automatically (such as sampling, sample transport, separation, and detection) have begun to influence the field of environmental sensing to a great extent.

Environmental applications of microsystems could range from industrial process control to workplace monitoring for specific pollutants, and from the detection of oil contaminations in soil, surface water and groundwater to the sensing of motor vehicle exhaust emissions. Three examples for microsystem applications will be described in detail in order to give a general idea of what is feasible with this technology.

The first example is an automatic sensor system with chemical sensors for water analysis. It is part of a groundwater monitoring network which allows frequent measurements at low cost. The sensor system has an active fluidic system which combines micromachined and non-micromachined components to take water samples automatically. Different types of sensors are included into the system: two ion selective sensors and an optofluidic microsystem which works as a microphotometer. Furthermore, the possible application of a multisensor system based on an array of non-specific potentiometric chemical sensors with data processing by an artificial neural network to groundwater monitoring will be discussed.

The second example deals with an enzyme-based microanalysis system for the determination of gas-phase ethanol. It is based on a new method of valveless sample introduction in flow analysis systems, the so-called flow-diffusion analysis. Such systems consist of microchannels, micropumps, bioreactors and amperometric sensors and can be applied to the detection of many classes of hazardous chemicals.

The third example describes a novel oil condition sensor system which can be used to individually determine the oil change intervals for automotive engines or for hydraulic circuits. It is therefore an example of how microsystems can be utilized for the reduction of waste. The system is based on microacoustic sensors particularly suited for operation in liquids. Using at least two indicator quantities for the oil quality different oil strain scenarios can be distinguished.

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**THE WATER FRAMEWORK DIRECTIVE:
THE CHALLENGES OF IMPLEMENTATION FOR RIVER BASIN-COASTAL ZONE
RESEARCH**

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On the 23rd October 2000 the European Parliament and Council passed a Directive establishing a framework of community action in the field of water policy (Water Framework Directive- FWD). The implementation of this Directive will have very considerable long-term implications on information needs and research objectives covering all European river basin and coastal zones.

Waters in the European Community are under increasing pressure from the continuous growth in demand for sufficient quantities of good water quality for all purposes. The objective of Community policy on the environment is to contribute to pursuit of preserving, protecting and improving the quality of the environment, in prudent and rational utilisation of natural resources, and to be based on the precautionary principle and on the principles that preventive action should be taken, where necessary, to ensure good water status. Environmental damage should, as a priority, be rectified at source and that the polluter should pay.

An effective and coherent water policy must take account of the vulnerability of all surface and ground waters, including aquatic ecosystems located near the coast and estuaries or in gulfs or related closed seas, as their equilibrium is strongly influenced by the quality of inland waters flowing into them.

There are diverse conditions and needs in the community which require different specific solutions. This diversity should be taken into account in the planning and execution of measures to ensure protection and sustainable use of water in the framework of river basins. Decisions should be taken as close as possible to the locations where water is effected or used. Priority should be given to action within the responsibility of Member States through drawing up of programmes of measures adjusted to regional and local conditions.

The implementation of the Water Framework Directive thus raises major challenges, these include an extremely demanding timetable, in particular in the nine preparatory years; the complexity of the text and the diversity of possible solutions to scientific, technical and practical questions; the problem of capacity building and an incomplete technical and scientific basis with a large number of fundamental issues in Annex II and V, which need further elaboration and substantiation to make the transition from principles and general definitions to practical implementation successful. A strict limitation of human and financial resources in Member States further adds to the challenge.

IMPACT OF MAN'S ACTIVITIES ON SEDIMENTS OF A FISHING LAKE IN ALEXANDRIA, EGYPT. (METALS)

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Lake Maryout is a fishing lake lining Alexandria at its southern side. Most of the landed fish comes from its Main Basin (one of the lake's four sub-basins). This basin, area 6000 acres, since the sixties of the last century is polluted as it used to receive raw sewage and industrial effluents from Alexandria City at four hot spots, distributed along the coasts of its eastern half. This has led to a noticeable decline with time in the quantity and quality of the fish catch and to subsequent social and economic problems to the fishermen. In a solution for these problems the government has erected two treatment plants in July 1993 to primary treat these waste effluents before discharging into this main basin at only two sites. One via an agricultural drain opens at a (an old) site lies at its southeast side while the other is at a new site at its northwest side.

Surface sediment samples were collected from this polluted basin in 1992 and in 1996 i.e. before and after the erection of the two treatment plants respectively and analyzed for the priority metal pollutants Ag, As, Sb, Cr, Hg, Ni, Pb, Cd, Zn and Cu in addition to organic carbon (org-C). Sediment samples were also collected from the other lake basins far away from the sewage discharge for comparison. The data reveal that the sediments of the Lake Main Basin are remarkably enriched with all the studied elements with respect to those of the other basins of the lake. The enrichment was more noticeable for the (spoiled) sediments in front of all the old hot spots in addition to those off the new source. The elevated concentrations particularly for the last six studied metals are found to be at levels comparable to their corresponding of the Median Effect-Range of Long and Morgan recommended by EPA, that may have possible effect on bottom fauna and other organisms (including edible fish) live in this polluted basin. This situation makes this important lake basin as a dangerous source for health-hazard fish. Suggested solutions are presented here for rehabilitation of the lake and its sediments. The most accepted ones by the government include diversion of the sources simultaneously with dredging of the spoiled sediments and advanced treatments of the effluents and reuse the water for irrigation.

ADSORPTION AND DESORPTION OF ENDOCRINE DISRUPTOR COMPOUNDS ONTO/FROM SOILS AND SLUDGES

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Several xenobiotic compounds including various pesticides and industrial chemicals have proven to act as “endocrine disruptors” (EDs). These are compounds able to cause alteration, i.e., disruption, of the normal endocrine functions of organisms by direct or indirect interference with their hormonal systems acting as hormone-like substances. Assessment of potential environmental hazards associated with ED compounds involves the evaluation of the most important processes such as adsorption and desorption that may affect and control their behavior and fate in soil.

The objective of this work was to investigate adsorption and desorption processes of four ED compounds, bisphenol A (BPA), octylphenol (OP), ethynil estradiol (EED) and 17 β estradiol (17ED), onto/from four soil samples collected from the surface (0-30 cm) and deep (30-90 cm) horizons of two sandy soils originating from Portugal (P30, P90) and Germany (G30, G90) and containing different amounts of organic carbon (OC), and two sewage sludges (PS and GS) used as amendment for these soils. Adsorption kinetics and adsorption/desorption isotherms and coefficients, K and $1/n$, of each ED and each soil and sludge were measured using the slurry-type method, HPLC technique and data fitting in linear and nonlinear Freundlich and Langmuir equations. In addition, the distribution coefficient, K_d , and the organic carbon partition coefficient, K_{oc} , were calculated.

Adsorption kinetics experiments showed that adsorption of EDs onto all substrates examined occurred in two phases, a rapid one occurring generally in less than 10 h of contact and corresponding to more than 90% of total adsorption, and a slow one that might need several hours until attainment of equilibrium. Experimental adsorption data of BPA onto all substrates were better described by a linear isotherm, those of OP by either a linear or a nonlinear Freundlich isotherm, those of EED by a nonlinear, L-shaped ($1/n < 1$) Freundlich isotherm and those of 17ED by a Langmuir-type isotherm. In general, the K and K_d values of the four EDs followed the same trend for all samples, that is $GS \geq PS \gg G30 > P30 > P90 \geq G90$. The four EDs were adsorbed much more extensively (between one and three orders of magnitude) onto sludges than onto soils, among which surface horizon samples were able to adsorb more than deep horizon samples. The adsorption capacity of substrates for EDs was directly correlated to the OC content of sludges and soils. The small differences of K_{oc} values measured among the various soils suggested that not only the content but also the nature and properties of OC affect the extent of adsorption, and that other soil components, e.g., clay minerals, might be involved in the adsorption process of EDs. Among the various EDs, OP appears to be the most adsorbed, and EED and 17ED showed a similar extent of adsorption onto any substrate. Adsorption of BPA was generally reversible and its desorption occurred fastly, and was completed after few desorption steps. On the contrary, adsorption of OP and EED was mostly irreversible, partial desorption occurred slowly, and most substrates retained high amounts of adsorbate at the end of the experiments.

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SURFACTANTS IN SURFACE AND GROUND WATER IN THE MEDITERRANEAN REGION: IS THERE A PROBLEM?

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Sustainable development is a key demand in our world of finite resources and endangered ecosystems. Given the environmental imperatives, the potential ecotoxicological risk of anthropogenic chemicals and the limited economic feasibility of many of even the most advanced treatment and remediation technologies, the switch from the currently dominant corrective paradigm to the emerging preventive practice in production, development, consumption and disposal is unavoidable. Surfactants, the dominant components in detergent formulations, constitute a particular issue of concern since they enter the aqueous and terrestrial compartments of the environment as such or as (bio-)degradation products. A research-based systemic understanding of the distribution, pathways, biodegradation, survival and effects/consequences of these surfactants is the key for appropriate integrated *relevant* environmental policy, regulation and education – to be implemented regionally and worldwide.

Israel, as a country with a high standard of living and, hence, typified by high consumption of detergents, will be here used as an illustrative case study. It is located in a semi-arid region, thus experiencing an extreme shortage of water supplies. Of about 5×10^8 m³ of the annually produced sewage – containing ca. 9-12 ppm of anionic (mainly LABS) and 1-3 ppm of nonionic (mainly APEOs) surfactants – about 27% and 45% of the total quantity are used, following secondary treatment, or directly, for aquifer recharge and agricultural irrigation, respectively. Since (i) only secondary treatment is available for sewage effluents in the country; (ii) APEOs are quite biodegradation-resistant due to their branched-carbon alkyl chain; and (iii) about 2/3 of the nonionic surfactants used in Israel are of the ‘hard’ APEO type, these nonionic surfactants and/or their metabolites reach surface and groundwater. The nonionic surfactant concentration profiles of the country’s rivers, ground waters and coastal water of the eastern Mediterranean Sea were found to be within the range of 12.5-74.6, trace – 20.2 and 4.2 – 25.0, respectively. The Israel nonionic surfactants case may be considered as a well investigated example, typical of other countries which are confronted with (superficially) conflicting interests in the socio-techno-environmental context, requiring sustainable solutions. Hard nonionic surfactants and/or their metabolites, the origin of which are either domestic, institutional, industrial, or agricultural wastewater, and/or surface streams polluted by municipal sewage, reach both groundwater and the Mediterranean Sea. Neither the existing sewage treatment facilities, nor naturally occurring biodegradation processes in the receiving surface water systems, or physical soil adsorption appear to be capable of avoiding this pollution.

In view of (i) the estrogenic/endocrinic potential of these anthropogenic nonionic surfactants; and (ii) the recently reported findings of estrogenic activity of domestic sewage treatment wastewater effluents in European countries (e.g., UK), it is clear that there is a problem. The continuing use of APEOs in detergents will be discussed and conclusions will be drawn in terms of production-consumption-management of water resources-sewage treatment-regulation-environmental impact-to be implemented environmental policy relationships.

EFFECT OF CHROMIUM ACTION ON THE PROTEIN COMPOSITION OF *ARTHROBACTER OXYDANS*

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The possibility of using intrinsic microorganisms to transform toxic heavy metal Cr(VI) ions to their less mobile and less harmful Cr(III) forms has stimulated intensive interests in studying of the mechanisms of metal-organic reactions at the microbial-mineral surfaces. Using bacterial capability to remediate metal contamination in geologic environments is especially important for Georgia - where heavy metals are major components of the pollutants.

The effectiveness of biotransformation often depends on the genetically regulated mechanisms of microbial resistance to metal toxicity that dictate the mode of metal-organic reactions. The goal of our study was to ultimately establish an understanding of the molecular basis bacterial detoxification of Cr(VI). As a first step toward this novel goal, we investigate the influence of Cr(VI) action on the protein composition of bacterial cells. We are reporting our results using *Arthrobacter oxydans* as our bacteria model. *A. oxydans* is known for its ability to reduce Cr(VI) under aerobic conditions. It is isolated from a site in the United States that has been polluted with mixtures of heavy metals, radionuclides and organic compounds due to nuclear production activity.

The effect of concentration of chromium on the protein composition of cells grown in the culture medium was studied by adding Cr(VI) (as potassium chromate) at the beginning of the stationary phase of growth. The range of concentrations studied was from 3.5 ppm to 210 ppm. The effect of Cr(VI) exposure time was investigated by adding 35 ppm Cr(VI) in the culture medium. The time-course of chromium action considered was from 1 hr to 72 hrs (without subculture). The protein concentrations were measured with Roche Protein Assay ESL kit. The protein compositions of the whole cell extract and the cell wall were characterized by sodium dodecylsulfate polyacrylamide gel electrophoresis (SDS-PAGE) on 10% (w/w) acrylamide gel. The cell wall protein was investigated by capillary electrophoresis too.

It was observed that the protein composition of the bacterial extract begins to change at 28 ppm chromium in the culture medium. Similar changes were observed in the whole protein extract composition after a 40 - hour exposure to chromate at 35 ppm. In all cases, the relative quantity of proteins of different molecular weight changed. Those that are mostly affected are the protein with a molecular weight about 80 kDa, the protein fraction with molecular weight about 45 kDa and the cell wall protein with a molecular weight 60 kDa. The observed increase of the quantity of some protein fraction component, including the cell wall protein component, at the initial contact to Cr(VI), can be considered as the initial step of Cr(VI) reducing by *A. oxydans*. Such a suggestion was confirmed by Electron Spin Resonance, Atomic Absorption and microcalorimetry measurements.

EFFECTS OF TBT ON COELOMOCYTES OF THE MARINE WORM *SIPUNCULUS NUDUS*

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Tributyltin (TBT) has been widely used as effective biocide in antifouling paint formulations. As a consequence, TBT was introduced into the aquatic environments, where it shows a variable persistence in water column, depending on the environmental conditions. In sediments, TBT is more persistent, with a half-life from few months to several years. Moreover, as this compound is highly lipophilic, contaminated sediments represent a risk for benthic organisms which can accumulate it.

In the present study, we investigated the effects of various concentrations of TBT on some functional responses of short-term cultures of coelomocytes from the marine worm *Sipunculus nudus*, a sediment-feeding sipunculan common in the littoral zone of the North Adriatic Sea (Italy), in order to evaluate the possibility to use these animals as sentinel organism in biomonitoring studies. At the end of the treatments, the viability of coelomocytes, as monitored by Trypan Blue dye exclusion test, was 70% at 10 μM TBT, so that used concentrations (0.01 to 1 μM) were considered to be sublethal. At 10 μM TBT, cytolysis of haemerythrocytes was also observed.

In the presence of TBT, the *amoebocytic index*, i.e., the percentage of coelomocytes with amoeboid shape, and the *endocytotic index*, i.e., the percentage of coelomocytes containing Neutral Red dye, were significantly ($p < 0.001$) inhibited at 1 μM . *Lysosomal activity index*, i.e., lysozyme activity measured spectrophotometrically on coelomocytic lysate, was reduced at 0.05 μM ($p < 0.05$) and 0.1 μM ($p < 0.01$). The *apoptotic index*, i.e., the percentage of coelomocytes with chromatin condensation detected with Acridine Orange, showed a significant ($p < 0.001$) increase at 1 μM after 1 h.

All these indexes can be proposed as biomarkers being sensitive, rapid and reproducible and can be considered as useful tools for monitoring TBT contamination in marine sediments.

REMOVAL OF NITRATES IN TREATMENT OF WELL WATER

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One of the most important parameters of impurity of the groundwater, which is caused by the result of the agricultural activities, is the nitrate. The amount of the nitrates above a certain level in drinking water brings dangerous results. Nitrate causes the formation the carcinogen nitroamines in adults and also causes the infant fatality because of the methaemoglomineamie. In general, maximum 50 mg/L nitrate concentration level is allowed in drinking water by the World Health Organisation (WHO). Limits of allowable levels by WHO is 25 mg/L for adults and 10 mg/L for babies.

In this study, the answers to the problems encountered in the preparation of bottle washing water obtained from wells are investigated. In this industry, well water (Plant I : 40 m³/h and nitrate level : 65 mg/L; Plant II : 80 m³/h and nitrate level : 57 mg/L) was first flocculated and then was passed through sand filter and active carbon filter respectively. Although the other parameters were within the allowable limits but the nitrate levels were above the given limit values.

In the laboratory studies using anionic ion exchangers, it was aimed to lower the nitrate levels below the limit values in the pretermitted water. According to results obtained from these studies, capacity of the ion exchangers was calculated for both plants. In the plant I, nitrate level was kept at the desired level first utilising anionic ion exchanger in a by-stream and then raw water added to the water passed through exchanger. In the plant II, since TDS values 600-700 mg/L, nitrate removal project was abandoned a by-stream was demineralised and mixed with raw water. In doing so, nitrate level was brought to the 45 mg/L and TDS level to the 400 mg/L.

EDTA AMENDMENT TO ENHANCE LEAD PHYTOACCUMULATION IN CONTAMINATED SOILS

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One of the main environmental problems in industrial areas is the high accumulation of contaminants in soils, which limits land uses. Phytoremediation is emerging as a cost-effective and environmentally sound alternative for metal-contaminated soils and is based on the ability of certain plants to extract metals from the soils with their roots and to concentrate high amounts of these metals in the aerial biomass. Although these plants, called hyperaccumulators, may accumulate high metal amounts, one limiting factor is the relatively low solubility of certain metals in the soil solution. As far as Pb is concerned, this metal accumulation in plants depends on the soil characteristics controlling the solubility and mobility of Pb. One method to increase the solubility of lead in soils consists of the application of chelating agents (such as ethylenediaminetetraacetic acid, EDTA), that bind with the free Pb^{2+} cation and form a complex that becomes less prone to cation exchange and sorption phenomena in soils.

The objective of this research is to study the enhanced accumulation of Pb in the *Zea mays* (corn) after chelate addition to soils. One selected soil was contaminated with $Pb(NO_3)_2$ so that the final Pb content was 500, 1000, 1500 and 2000 mg/kg soil DW. Corn seeds were germinated in a greenhouse (equipped with supplementary lighting) in plastic pots which were filled with the original soil (control case) and the artificially contaminated soil. EDTA solutions were added to the soil at a rate of 1, 5 and 10 mmol/kg EDTA 4 weeks after seed germination. Then, the plants were harvested 7 days after the chelate addition. The same experimental procedure was carried out with the *Brassica juncea* (indian mustard) in order to use the results as a comparative case. Roots and leaves of plants were washed, dried and ashed in a muffle furnace. The ash samples were dissolved in an acid mixture in order to determine Pb content in the extracts by atomic absorption spectrophotometry.

Corn grown in Pb-contaminated soil treated with EDTA significantly increased leaf and root Pb uptake compared to those without EDTA treatment, although the enhanced Pb accumulation increase was highly affected by the rate of the chelate addition. Anyhow, the enhanced increase was higher in roots than in leaves. The highest Pb amount accumulated in the leaves was 9 and 11 $\mu\text{g/g}$ for 1 and 5 mmol/kg EDTA addition respectively. However, the metal amounts in roots were 50 and 90 $\mu\text{g/g}$ for the same chelate addition.

Although Pb-EDTA is highly water-soluble and poses potential risks to groundwater in its application, it is very efficient in increasing soluble Pb concentration and phytoextraction. In order for phytoremediation to be efficient and safe, further research about in-situ application rate, weather conditions and other parameters is necessary.

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**PLASTICITY OF GENOME IN REPLY TO PB AND CD STRESSES
IN *FUNARIA HYGROMETRICA***

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Researches of last years have shown that plant genome, and in particular the repetitive/non coding fraction of it, can be “modulated” in reply to the action of environmental stresses, that seem to cause quantitative variations of specific families of DNA (see Bassi, 1991, Biol. Zentralb. 10: 1-13). To this regard, it has also been suggested that repeated/non coding DNA could act as a mediator between environmental stimuli and gene expression, receiving messages from the environment, modifying itself accordingly, thereby influencing, in conformity with the message, the gene expression itself (Bassi P., 1990, Biol. Rev., 65: 185-225).

One of external factors able to cause the above phenomenon are heavy metals. Moreover, both in animals and in plants, it has been observed that one of the targets of such elements is repetitive DNA (Sissöeff et al., 1976, Prog. Diff. Res., 197-204).

The aim of the present research is to investigate how heavy metals may influence repetitive DNA in Bryophytes: these organisms, in fact, are particularly suitable for such a kind of studies. In particular, we observed the genome behaviour in front of the stress caused by Pb, Cd and Zn in *Funaria hygrometrica*: in fact, in this moss previous data have offered evidences that lead is able to induce modifications not only at morphological level (Basile et al., 1995, Ann. of Bot., 76: 597-606), but also at the genomic one (Bassi et al., 1995, Protoplasma, 188: 104-108). The research has been done both, in individuals grown in *in vitro* controlled systems, as well in individuals grown in Sardinia metal mines.

All our results, obtained by different experimental approaches, seem to agree in the fact that heavy metals in *F. hygrometrica* can influence the repetitive DNA behaviour. Particularly: a) the X-ray TEM microanalysis showed that the metals are able to reach the nuclear chromatin; b) cyto-molecular investigation of the nuclear genome carried out with A+T and G+C specific fluorochromes showed that metals are able to induce selective amplification of G+C rich repetitive DNA sequences belonging to peculiar agglomerates that in presence of metals increase both in size and number; c) *in situ* DNA hybridization (FISH) with total rDNA showed that the metal susceptible repetitive DNA is owned, at least in part, by ribosomal DNA.

BIOACCUMULATION AND LOCALISATION OF HEAVY METALS IN MEDITERRANEAN AQUATIC PLANTS

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Phytoremediation is an emerging technology that uses selected and engineered metal-accumulating plants for environmental clean-up. In the ambit of a program financed by Campania Region on phytoremediation of polluted sites, we prepared *in vitro* culture systems to assess the capacity of bioaccumulation and phytodepuration of three species of aquatic plants, the monocotyledons *Lemna minor* and *Elodea canadensis*, and the moss *Leptodictyum riparium*. The plants were exposed to increasing concentrations (from 10^{-7} to 10^{-3} M) of cadmium, lead, chromium, zinc and copper salts for several days. Of the three plants examined, *L. riparium* appeared to be the most resistant ($EC_{50} = 10^{-4}$ M for Cu, Cr and Zn, 10^{-5} M for Pb and 0.5×10^{-5} M for Cd). This species remained viable and capable of regenerating damaged tissues for more than 1 month at heavy metal concentrations corresponding to EC_{50} , and up to 6 months at lower metal concentrations. For all the species examined, the concentration of 10^{-3} M was lethal for all the metals tested. Damages regarding chloroplasts were observed at morphological level, and ultrastructural analyses revealed visible effects at the level of vacuolar and thylacoidal organisation. Moreover, the cytochemical analyses of the nucleus showed a rearrangement of heterochromatin. X-ray SEM microanalysis revealed localisation of heavy metals mainly on the cell wall and in other cytoplasmic compartments.

Bioaccumulation of heavy metals was evaluated by Atomic Absorption Spectrometry. A statistical analysis (ANOVA and PRINCIPAL COMPONENTS analysis) of the data obtained show that: **i)** *L. minor* accumulated less Cu than the other two species. In addition, Cu accumulation was not dose-dependent, maximal accumulation having been reached at the lowest dose applied (10^{-6} M). In *L. minor* Cd accumulation was linearly dependent on external metal concentration. The amount of Pb accumulated in *L. minor* was higher than in *E. canadensis* but lower than in *L. riparium*. The more effective concentration of Pb used was 10^{-4} M. *L. minor* did not accumulate Cr. **ii)** *L. riparium* was the most effective in accumulating Cu and Pb at all the concentrations tested; at variance with *L. minor*, it accumulated Cd in a non-linear manner. Cr was barely detected at the highest concentration applied (10^{-4} M) **iii)** *E. canadensis* accumulated less Cu than *L. riparium*. However, at variance with the other two species, Cu accumulation linearly increased with the Cu concentration, thus suggesting a lower uptake rate of Cu than in other two species. Cd accumulation was dose-dependent as in *L. minor*, whereas the only effective concentration of Pb was 10^{-4} M. Cr accumulation was as in *L. riparium*.

QUALITY ASSESSMENT OF MARINE SEDIMENTS FROM THE COASTAL AREA OF LIGURIA (ITALY)

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The aim of this study was to evaluate the quality of marine sediments collected at sites along the coastal area of Liguria (Italy) by establishing their chemical/physical and eco-toxicological characteristics. Fifteen sediment samples were studied, granulometric fractions were obtained and the concentration of heavy metals and of the main organic pollutants was determined. A battery of bioassays was also conducted on the same sediment samples. The battery included three organism tests: the bacterium *Vibrio fischeri*, the amphipod *Corophium orientale* and the echinoderm *Paracentrotus lividus*.

Physical/chemical and eco-toxicological results showed widespread contamination, mainly by Chromium, and toxicity.

In a second phase of the study, in order to understand whether Cr is bio-available to the organisms the concentration of Chromium was established in a number of samples after extraction with HCl and total mineralization. Extraction with HCl reduced Chromium levels by approximately 50 %, suggesting that the metal is rather weakly bonded by the matrix.

Some bioassays and a bioaccumulation test were also performed on these samples. Results of the bioassay on *Corophium orientale*, which evaluated the entire sediment (solid matrix + pore water) showed toxic levels, while the tests on elutriate with *Vibrio fischeri* and *Paracentrotus lividus* found no evidence of hydrophilic toxic compounds. A further bio-accumulation test with *H. diversicolor* showed no significant bio-accumulation of Chromium.

INFLUENCE OF TBT ON THE ACTIVITY OF THE DETOXICANT ENZYMES, GST AND GPX, FROM HAEMOCYTES OF THE COLONIAL ASCIDIAN *BOTRYLLUS SCHLOSSERI*

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In the last decade, some authors have hypothesised that a considerable part of the immunotoxic effects described for tributyltin (TBT) in mammals was due to Ca²⁺-independent mechanisms involving changes in sulphhydryl groups of both proteins and reduced glutathione (GSH). Among the detoxicant enzymes, which play a multiple role in the metabolism of many xenobiotics of invertebrates and vertebrates, there are glutathione-transferase (GST) and glutathione-peroxidase (GPX).

GST catalyses the conjugation reactions of GSH with electrophilic xenobiotics or their derivatives. It has been described in the antioxidant defence systems mainly of the gill of bivalves and as a mediator of xenobiotic detoxication in the liver and kidney of marine fish. In mammals, the activation of GST has been proposed to occur after TBT treatment and the presence of mercapturic acid supports this hypothesis. However, this derivative was never found in molluscs, suggesting that invertebrates possess a different detoxicant system of organotins.

GPX is an antioxidant enzyme, which protects from the effects of reactive oxygen species production, requiring GSH consumption. In marine fish, since the inhibition of GPX by various organotin compounds had been recently described, this enzyme can be used as an effective biomarker of these pollutants. High concentrations of GPX were found in the blood of many invertebrates. The GPX activity detected inside the gill of bivalves is associated with GST and is catalysed by this enzyme.

In cultured haemocytes of the colonial ascidian *Botryllus schlosseri*, we have observed by immunocytochemistry that positivity to both GST and Se-dependent GPX antibodies disappeared after incubation, for 60 min at 25 °C, in the presence of 0.1 µM and 1 µM TBT, respectively. This suggests that conformational changes occur probably due to direct interaction of the xenobiotic with these antioxidant enzymes. Moreover, the spectrophotometric assays on the haemocytic lysate have shown that TBT was able to significantly inhibit the GST activity (µmoles/min/mg protein) 2.6 times at 0.01 µM and 4.8 times at 0.1 µM, whereas the Se-dependent GPX activity was inhibited 1.5 times at 0.05 µM TBT. Our data suggest that even in the ascidian blood cells, enzymes involved in detoxication metabolic processes are present and that GST is the most important and sensitive among them.

MAPPING OF RADIONUCLIDES IN SOILS OF CYPRUS TO DEVELOP THE FIRST BACKGROUND DATABASE

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In Cyprus, during 1998, in the field of radioactivity, research was carried out to evaluate the levels and distribution of both technical and natural radionuclides in soils. The aim was to establish background data and create capabilities for early identification of trends or increase due to the use of nuclear weapons or accidents.

The program was planned in cooperation with the NCSR -Dimokritos Institute in Athens and the analysis was carried out at the Radioactivity Laboratory of the State General Laboratory in cooperation with NCSR- Dimokritos Institute.

87 samples were taken from the non occupied area of Cyprus. First a chart was prepared and the whole area was divided into 87 sampling points (1 point per 64 km²). These sampling points were then arranged according to the 5 districts of Cyprus.

All the samples collected were analyzed for Caesium (Cs) and natural radionuclides using high resolution gamma spectrometry (HP-Ge detector).

The measured activity of Caesium (Cs) was found to vary from district to district. The higher values for Cs were measured in Larnaca area.

The distribution of natural radionuclides over the investigated area will also be presented.

EVALUATION OF THE METAL – FIXING CAPACITY OF A SARDINIAN ZEOLITE AND COMPOST IN REMEDIATION OF HEAVY METALS CONTAMINATED SOILS

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The south-west Sardinia has been the most important mining region of Italy for a long time. Lead, copper and zinc were the minerals extracted.

The mines abandonment and the absence of effective interventions of remediation in these areas, have caused the spreading of steriles and flotation sludge through wind erosion and rain-fall and, consequently, the heavy metals pollution in large areas of the surface and the ground-water.

Currently the most widely accepted method for remediation of heavy metals contaminated soils, is altering the chemical composition of these compounds through the addition of various admixtures.

This process is commonly known as stabilisation.

Since several years we have been carrying out a wide scientific research in order to settle remediation techniques for heavy metals contaminated soils, which do not involve strong modifications in the physical and chemical characteristics of the treated soils. In this research we show the preliminary results which describe the metal-fixing capacity of a local zeolite compared with a compost.

The chemical analysis of steriles has shown high concentrations of heavy metals: Pb 0,2, Zn 0,4, Mn 0,3, Fe 7, Cu 140, Cd 30 mg Kg⁻¹ d.m.. The polluted soils collected at several kilometres below the mines, show variable concentrations in relation to the distance from the polluting source and soil depth. Particularly Pb and Zn respectively reach, in the soil superficial horizons, total concentrations of 1 and 1,5 %. The mobile fraction is included between 40 and 80% of the total concentration.

Zeolite and compost were artificially polluted at controlled pH and temperature with increasing concentrations of three heavy metals (Pb, Zn and Cd) in order to obtain the absorption isotherms. The results show a good fixing capacity of zeolite in comparison with the following metals: Zn, that presents a L-TYPE isotherm, Pb and Cd, that present a S-TYPE isotherms. The Pb – compost isotherm curve is characteristic of materials showing an affinity proportional to the concentration of the contaminant. The Zn - compost and Cd - compost isotherm curves are S shaped.

After contamination the samples were treated with extracting agents of different strength (H₂O, Ca(NO₃)₂ 0,1N, EDTA 0,05N) to study the contribution of the different interaction mechanisms.

Most of Pb and Zn are fixed by zeolite with strong bonds, instead most part of Cd is absorbed with an electrostatic bond.

Analysis of the Pb fractions extracted from the compost show that all the lead adsorbed is strongly retained. The Ca(NO₃)₂ extracts almost no Pb, but 60% of it can be extracted by EDTA. The fractions of Zn and Cd also follow a similar trend. The Ca(NO₃)₂ extracts, on average, less than 10% of both heavy metals. The EDTA can extract 60% of the total amount of pollutant adsorbed.

PERSISTENCE OF CHLORPYRIFOS AND ENDOSULFAN IN SOIL

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Horticultural crops may be affected by different pests causing serious damages to plants and consequently important yield reduction. Several insecticides are applied to tomato crops to control pests in Spain, the third country producing tomato for preserved food in Europe, being chlorpyrifos and endosulfan widely used. Chlorpyrifos is a broad-spectrum organophosphorus insecticide controlling a wide range of insect and arthropod soil pests, while endosulfan, a mixture of α - and β -isomers, is an organochlorine insecticide used for the control of sucking and chewing insects on fruits and vegetables. In the application of endosulfan to tomato plants one part of the insecticide reaches the target while other part is deposited on the soil. Therefore both pesticides are found in the soil where they are subjected to different processes that will determine the fate of these agrochemicals.

The aim of this work was to study the effect of different factors such as, temperature and soil moisture content, in the degradation of these chemicals in soil under laboratory conditions. The influence of rhizosphere soils in the degradation of these pesticides was also studied. Plant used in this assay were weeds usually found in tomato crops (*Amaranthus retroflexus*, *Chenopodium album* and *Solanum nigrum*). In addition, field experiments were conducted in the Spanish region of Badajoz to determine the levels of chlorpyrifos and endosulfan throughout the growth season of tomato and the residual levels of these chemicals after harvest. Soil from the top layer (10 cm) was sampled, extracted with ethyl acetate in small columns and insecticide residues were analysed by gas chromatography with electron-capture detector.

Results obtained under laboratory conditions showed that the degradation of chlorpyrifos and endosulfan in soil followed first-order kinetics. The effect of temperature on the rate of insecticide degradation was studied using the Arrhenius equation ($k=A_0 e^{-E_a/RT}$). An increase of pesticide degradation with temperature was observed. Half-lives, in the range of temperatures studied, varied from 85 to 25 days for chlorpyrifos, from 40 to 27 days for α -endosulfan and from 513 to 89 days for the β -isomer. The influence of the soil moisture content in the degradation of these compounds was studied using the empirical equation $H = AM^{-B}$. Results obtained with chlorpyrifos and α -endosulfan fitted well that equation, while no correlation with soil moisture content was observed with β -endosulfan. The different kind of rhizosphere soils studied did not affect the degradation (at 25 °C and 8 % of soil moisture content) of pesticides, being the half-lives obtained around 21, 32 and 80 days for chlorpyrifos, α -endosulfan and the β -isomer respectively.

The levels of these chemicals in the soil throughout the season, obtained in two tomato fields, varied from 0.155 ± 0.045 to 0.008 ± 0.002 $\mu\text{g/g}$ for chlorpyrifos, from 0.074 ± 0.043 to 0.008 ± 0.002 for α -endosulfan and from 0.146 ± 0.077 to 0.011 ± 0.005 for β -endosulfan. A study of residual insecticide levels two months after harvest was carried out in 18 commercial fields. No chlorpyrifos residues were detected, while residual levels of α -endosulfan varied from 0.032 ± 0.020 to 0.0014 ± 0.0007 and from 0.178 ± 0.064 to 0.009 ± 0.006 for β -endosulfan.

INDICES FOR SURFACE WATER QUALITY AND IMPACT ASSESSMENT: FROM DATA TO CONCRETE INFORMATION

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The development of an innovative monitoring and evaluation scheme for surface waters is presented. This is based on integration of chemical, ecotoxicological and microbiological/ virological parameters and criteria. To bridge the gap between research and decision-making and to provide more concrete information, monitoring results from 226 parameters, were integrated and expressed by nine quality or effect indices: The Industrial pollution, the Pesticide pollution, the Nutrient Pollution, Organic Pollution, the Bacteriological, the Toxicity, the Biodiversity, the Benthic Saprobity and the Irrigation Quality Index. Each index reflects a different type of pollution or effect. Target values were developed for each index based on available limits of the individual parameters included in each index. For compounds for which limits do not exist, information from international literature and data bases of ecotoxicological data were used to develop target values. Expert judgment and socioeconomic factors are considered in developing these technical and political oriented targets. All indices are integrated in one yardstick (the Amoeba) by which the status of water resources, degree of deviation from targets and priorities for policy measures are clearly described. This Amoeba evaluation based on holistic evaluation of interrelated parameters (indices) clearly provides management oriented information and is complimented by the traditional evaluation. The latter based on individual parameters judged against legal limits, identifies specific parameters for which deviation from limits occurs and provides technical/legal oriented information. This integrated evaluation scheme can also provide information for Environmental Impact Assessment studies in catchement zones. The main elements of the system design and development of Amoeba, as well as potentials to support informed decision making will be discussed. This work was done within the EC funded, Life Project 95/CY/B2/CT/868 MED.

SORPTION-DESORPTION OF Pb(II) BY MODEL ASSOCIATIONS OF SOIL COLLOIDS

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Natural colloids are organomineral associations of multiple soil constituents, which are the main contributors to sorption and transport processes affecting contaminants in soil and water. The importance of individual soil constituents on contaminants sorption is usually evaluated by studying the sorption behaviour on selected soil fractions or by investigating changes in sorption after removing soil constituents, such as Fe oxides or organic matter. An alternative approach is the use of model sorbents.

In this work, we have studied the sorption of Pb(II) by binary and ternary sorbents containing montmorillonite (SWy), ferrihydrite (Ferrih) and humic acid (HA), and the results were compared with the sorption behaviour of the individual model sorbents. The model particles were prepared in the laboratory and characterised by elemental analysis, X-ray diffraction, infrared spectroscopy and specific surface area measurements. Pb(II) adsorption isotherms were obtained using the batch equilibration technique and fitted to the Langmuir equation. The corresponding Langmuir parameters, C_m and L , were calculated. Results obtained were discussed to establish the interaction mechanism.

With regard to single sorbents, sorption of Pb(II) was high on humic acid, moderate on montmorillonite, and zero on ferrihydrite. Accordingly, ferrihydrite coatings on SWy reduced the sorption of lead by the resulting SW-Ferrih systems. HA coatings on SW increased the sorption of lead, whereas this effect was not observed for the Ferrih-HA systems. This was attributed to blockage of the functional groups of HA responsible for Pb(II) sorption (carboxylates and phenolates) as a result of their interaction with the ferrihydrite surface. A similar behaviour was observed when HA was associated with Ferrih-coated montmorillonite.

Pb(II) desorption isotherms showed that sorption by the model associations was reversible. Spectroscopic studies revealed the role of carboxylate groups in the retention of lead and the presence of Pb(II) in the clay interlayers.

The results of this study confirmed that the sorptive behaviour of colloidal particles is not the simple sum of the sorption on single components, illustrating the usefulness of considering the behaviour of binary and ternary model systems as sorbents in order to give a more realistic interpretation of the adsorption process in soil.

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**STUDIES ON THE ADSORPTION OF CAESIUM, COBALT AND EUROPIUM
RADIONUCLIDES ON AGRO-RESIDUES FROM AQUEOUS SOLUTIONS**

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Individual adsorption studies of Cs^+ , Co^{2+} and Eu^{3+} on agro-residues (rice husk and bagasse pith) from aqueous solutions are reported. Optimal conditions for the adsorption of the metal ions have been identified. The variation of the amount sorbed of the isotope per gram adsorbent with concentration of the relevant element was determined. The adsorption of these cations by rice husk and bagasse pith was also determined in the presence of interfering ions. The desorption tests from aqueous and acidic medium were examined. The data suggest the possible use of the two agro-residues for the preconcentration of these cations.

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KINETIC BEHAVIOUR AND DEGRADATIVE CAPABILITY OF *LENTINULA EDODES* LACCASE ISOENZYMES ON DIFFERENTLY-SUBSTITUTED CHLORINATED SUBSTRATES

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Laccase (E.C. 1.10.3.2 benzenediol:oxygen oxidoreductase) is a copper oxidase able to bring about the oxygen-dependent oxidation of a wide array of substrates including substituted phenols, anilines, benzidines and benzenethiols. Laccase acts on phenolic substrates by a one-electron abstraction from the hydroxyl group giving rise to aryloxyradicals and quinones, which, in turn, undergo non-enzymatic reactions. Due to their poor solubility in water systems, reaction products can be removed from solution by centrifugation or simple filtration. Therefore, the enzyme could be a suitable candidate for the removal of targeted compounds from several industrial and agroindustrial effluents. Among these compounds, chlorophenols constitute a major class of priority pollutants. In fact, they are produced as precursors of chlorophenoxyacetate herbicides, as wood preservatives and broad-spectrum biocides. In addition, they are present in effluents from chlorine-based bleaching processes.

In the present study, extracellular laccase isoenzymes were isolated from solid-state cultures of the fungus *Lentinula edodes* Berk Pegler (strain SC-495) and partially purified by ammonium sulfate precipitation, affinity chromatography (Concanavalline A-Sepharose) and anion-exchange chromatography (Mono-Q). The purification scheme yielded a preparation containing three protein bands with laccase activity as assessed by staining with phenolic substrates after partially denaturing SDS-polyacrylamide gel electrophoresis. Initial reaction velocity measurements were performed with differently-substituted chlorinated substrates using a Clark oxygen electrode. In addition, the kinetics of laccase-catalysed removal of these substrates from synthetic effluents was studied by reversed-phase chromatography.

These experiments showed that both the initial reaction rate and the removal yields, regardless the incubation time, greatly varied depending on the nature of substituents and their reciprocal positions on the aromatic ring. As expected, the initial rates of laccase-catalyzed oxidation of the chloro-substituted benzenediols were higher by more than one order of magnitude than the major part of the other chlorinated phenols under study. In addition, the halogenation pattern appeared to heavily affect the initial oxidation velocities of dichlorinated and trichlorinated isomers. In particular, 2,4- and 2,6-dichlorophenol were oxidized at a higher rate than the other isomers. This was also observed by comparing the initial velocities of laccase-catalysed oxidation of 2,4,6-trichlorophenol, 2,4,5- and 2,3,6-trichlorophenol, the former compound being oxidized at a higher rate than the latter phenols. The enzyme failed to oxidise nitro-substituted chlorophenols in accordance with previous studies reporting that compounds bearing electron-withdrawing functional groups were not prone to oxidation by phenoloxidizing enzymes.

UPTAKE AND DISTRIBUTION OF AS IN *AMARANTHUS BLITOIDES* GROWING ON CONTAMINATED SOILS

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Previous results obtained by our group have demonstrated the high potential of *Amaranthus blitoides* to be used in phytoremediation of contaminated soils with heavy metals and arsenic (De Haro et al., 2000). A pot experiment was conducted to investigate the efficiency of this species to extract and accumulate As gradually added to soil, and therefore to establish the suitability of *Amaranthus blitoides* for remediation of polluted soils by As.

The experiment was performed at three levels of As: 1, 3 and 10 mg As Kg⁻¹ [added as sodium hydrogen arsenate (Na₂HAsO₄ · 7H₂O)] to the surface of soil, together with the corresponding control plants. Arsenate significantly increased total dry biomass production compared to control plants at the highest level of As after six weeks of growth in contaminated soil. The As concentration in root and shoot were significantly increased by increasing As levels and time of exposure in the contaminated soil. The *A. blitoides* plants accumulate higher levels of As in the roots than in the shoots. The results of this experiment confirm that *A. blitoides* is a promising species for phytoremediation of As by its potential for uptaking this pollutant and to produce high biomass.

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GEOLOGICAL HISTORY AND GEOTHERMAL POTENTIAL AS PRIMARY FACTORS AFFECTING DIVERSITY AND ABUNDANCE OF PHYTOBENTHIC COMMUNITIES IN COASTAL ZONE OF GREEK ISLANDS.

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The coastal phytobenthos of Greece is constantly researched and evaluated in terms of abundance, distribution and diversity through national and international research projects. The results obtained so far clearly indicate that the geological history and geothermal potential of the islands (i.e. volcanic or not) are factors that affect significantly the physical and chemical quality of the water in the coastal zones of these islands and thus, the distribution, abundance and diversity of the benthic community profiles.

The main results from the existing data are the following ,

a. Volcanic Islands

- the number of species and coverage is almost stable throughout the year
- Phaeophyceae show the highest coverage
- phytobenthos community structure remains almost identical throughout the year
- low number of species (below 120) with small range (100-120)

b. Other non volcanic areas

- the number of species and coverage show significant differences throughout the year
- Chlorophyceae exhibit the smallest number of species and coverage, while Rhodophyceae the highest phytobenthos community structure exhibits changes
- higher number of species (above 120) with higher range (70 - 120)

ENVIRONMENTAL BEHAVIOUR OF MONOCHLOROBENZENE IN AN ARABLE LOAMY SOIL

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The intensive use of monochlorobenzene (MCB) as solvent, degreaser and intermediate in chemical synthesis resulted in its widespread occurrence in the environment. Pollution of groundwater by this organic compound is becoming an important problem in some areas. To understand the fate and behaviour of monochlorobenzene in the environment the biodegradation and volatilization processes in an arable loamy soil was investigated. In a closed aerated laboratory system ^{14}C -monochlorobenzene was incubated with sieved (<2mm) soil material, amended with different substrates. Wheat straw was used as a slowly available C source and N, P fertilisers as an easily available additional nutrition source for the soil microorganisms. The evolved $^{14}\text{CO}_2$ and volatilised ^{14}C -compounds were trapped separately and quantified by liquid scintillation counting. At the end of experimentation ^{14}C -mass balance was established. The results show clearly, that volatilization is the main loss mechanism of MCB from soil whereas mineralisation is of minor importance. Additional nutrition sources cannot increase the mineralisation process considerably.

**AN ENVIRONMENTAL EVALUATION OF METALS RELEASE FROM PESTICIDES
AND ITS IMPACT ON WATER AND
SOILS POLLUTION IN EGYPT**

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Remarkable increase in the use of pesticides and fertilizers in terms of quantities and qualities is recently observed which can seriously threaten our environment. Some of pesticides contain certain heavy metals such as As, Hg, Cu, Zn, and many other associated metals. The present study was designed to investigate the level of heavy metals in some pesticides and to study the fate of these metals in drainage water. A field study was carried out in an Egyptian village named Qutta. The studied pesticides are Mancopper, Diathen M-45, Trimelitox Phorte and zinc phosphide. The investigated metals are Cd, Pb, Cu, Zn, Fe and Mn. Results obtained revealed that there is a slight increase in the level of metals in the drainage water in comparison with the irrigated water. Meanwhile, a noticeable building up of metals in plant and soil was also recorded.

CHEMICAL CHARACTERISTICS OF SEAWATER AND SURFACE SEDIMENTS OF THE AEGEAN SEA (FEBRUARY 1999)

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The present work contains the results of the investigation on the nutrient content of the water column and on the carbon and nitrogen of the surface sediments, sampled at six stations in the Aegean Sea during February 1999. The nutrients analysis was carried out by means of a Bran-Luebbe Autoanalyser while carbon and nitrogen in the sediments were determined on a Fisons CHN elemental analyser.

Variations of temperature and salinity are essentially restricted to the upper layer (0-100m). The range of the physical parameters for all depths were the following: temperature ranged between 9.38 and 15.39 °C and salinity between 32.32 and 39.07 psu. The lowest values of temperature and salinity, observed at the northeastern part of the study area, are probably attributed to the freshwater inputs originated from the Evros river, as well as to the inflow of the less saline surface water coming from the Black Sea. These values are lower than those recorded during previous sampling cruises in May 1997 and September 1998 and it is evident that they are affected by the greater river discharge and the lower atmospheric temperatures occurring during winter. Rather high oxygen concentrations (attaining ~6.3 ml/l) were observed in the surface layer of the northern part coinciding with the low salinity and temperature values. The vertical distribution of dissolved oxygen revealed that the maximum variations of the parameter were recorded in the layer from 0 to 100m depth; the concentration gradient was very small from 100m to the bottom. Since the greater part of organic material has been oxidized in the upper layer (50-100m), oxygen depletion diminishes with depth and consequently in the deeper part of the water column a smaller negative gradient of oxygen concentration is observed.

In the euphotic zone, nutrients are practically depleted by the phytoplankton uptake. However, extremely high nutrient concentrations were observed at the surface of the area which is under the influence of the Evros river discharge. The oxidation of organic matter induces a rapid increase in the nutrient concentration below 200 m, and the enrichment in reactive phosphate, nitrate and silica rises progressively in deeper waters. The range, the mean and the standard deviations of the nutrients concentrations, in $\mu\text{mol/l}$, for all the stations and depths are the following: nitrite+nitrate: 0.25-13.8, 1.97 ± 2.09 ; phosphate: 0.008-0.420, 0.067 ± 0.064 and silicate 1.45-16.48, 2.84 ± 2.18). Attention is drawn to the N:P and Si:P ratios and their possible deviation from the theoretical values. From the regression analysis the following equations were found: $\text{NO}_3 = 29.9 \text{ PO}_4 - 0.07$ ($n=51$, $r^2=0.84$), $\text{N:P}=29.3$; $\text{SiO}_4 = 32.1 \text{ PO}_4 + 0.68$ ($n=52$, $r^2= 0.88$), $\text{Si:P}=42.3$.

The percentage of organic carbon by weight at the sediment surface was 0.20-0.80%, while the percentage of total nitrogen was 0.02-0.11%. The organic carbon concentrations obtained in this study are of the same order of magnitude with sedimentary organic carbon data from other offshore waters in the eastern Mediterranean and the Aegean Sea. The ratio of organic carbon to nitrogen ranged between 7 and 9 and is similar to the Redfield value of 6.6.

ATRAZINE RESIDUES IN SOIL, SURFACE AND GROUNDWATER IN AGRICULTURES AREAS OF SERBIA

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Atrazine is a triazine herbicide, used worldwide since 1952 to control annual weeds in different crops. In Yugoslavia atrazine is one of the most commonly used herbicides. Subsequent to its extensive use, numerous reports on soil, surface and groundwater contaminations have been documented.

Because of that, atrazine was monitored in a typical crop growing area in Serbia, and in this paper we report the results of four years investigation of soil, surface and groundwater pollution by atrazine.

The soil samples were collected from different localities, from the tilage level, on two depths (0-15 and 15-30 cm) during the period September-November from 1995 to 1999. Surface and groundwater samples were taken from the same localities at the same period. The residues were detected by gas chromatography and ELISA tests.

The results have shown that almost all analysed soil samples contained residues of atrazine. These quantities varied from 0.02 to 0.10 mg/kg (0-15 cm), and up to the 0.05 mg/kg (15-30 cm), depending on the locality, soil type and the year of investigation.

Concerning the residues in surface and groundwater it was found out that most of the analysed samples contained atrazine residues. So, in the case of surface water quantities of residues ranged from 1.0 to 4.13 µg/L, while groundwater contained residues up to 0.1 µg/L, depending on the locality and the year of investigation.

EROD ACTIVITY INDUCTION IN AQUATIC ANIMALS

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The aim of this study was to evaluate the sensitivity of ethoxyresorufin-O-deethylase (EROD) activity in the crab *Carcinus maenas* hepatopancreas and in the juvenile *Dicentrarchus labrax* (sea bass) liver, under laboratory conditions, as well as, to study the enzymatic induction profile in male and female crabs.

In this perspective, sea bass and crabs were exposed during 3 days to the concentration range of 0, 0.1, 0.3, 0.9 and 2.7 μM β -naphthoflavone (BNF), a standard and potent liver EROD inducer.

Sea bass liver EROD activity was significantly increased at 3 days exposure to 0.9 ($p < 0.01$) and 2.7 μM ($p < 0.001$) BNF, when compared to control. The no-observed effect concentration (NOEC) after 3 days sea bass exposure was defined at 0.3 μM BNF. Maximal liver EROD activity increase was observed at 2.7 μM BNF (4.4-fold increase over control). Therefore, sea bass liver EROD results revealed a dose-related response from 0.3 up to 2.7 μM BNF.

The crab EROD activity was significantly increased after 3 days exposure to BNF, showing a NOEC at 0.3 μM BNF. Male crabs exhibited a significant EROD activity at 0.9 ($p < 0.02$) and 2.7 μM ($p < 0.02$) BNF, when compared to control. In males, this activity reaches a maximal value at 0.9 μM BNF (4.1-fold increase over control) and it was slightly decreased at 2.7 μM (2.8-fold increase over control). In females, the EROD activity was significantly increased (4.4-fold over control) at 3 days exposure only to 0.9 μM ($p < 0.01$) BNF, when compared to control. However, it was increased in females at 2.7 μM BNF (5-fold over control), although not significantly.

The main results reveal that control sea bass exhibit higher liver EROD activity, when compared to the activity of crabs hepatopancreas. However, both species can be used as bioindicators to assess aquatic contamination, since a similar EROD activity increase was observed after BNF exposure, a PAH-like EROD inducer. Furthermore, it was observed the same NOEC, suggesting similar sensitivities. The use of crabs as environmental bioindicators also gives the advantage to easily distinguish contamination effects on males and females, due to their phenotype differences. However, further studies at different maturation stages are required to understand it.

ASSESSMENT OF LIVER BIOTRANSFORMATION AND GENOTOXICITY INDUCTION IN SEA BASS AFTER SHORT-TERM EXPOSURE TO RESIN ACIDS

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Resin acids (RAs), a group of diterpene organic compounds, are discharged with the effluents of pulp and paper mills. During pulping and bleaching processes, RAs are extracted from trees cellulose fibres and discharged with the effluents of pulp and paper mills. Among the dominant RAs, abietic acid (AA) and dehydroabietic acid (DHAA) are the most abundant in effluents. Cacia pulp and paper mill effluent, one of the major polluting sources of the River Vouga and Aveiro Lagoon, is presently discharged into the Aveiro coastal area. Therefore, there is a particular interest in the validation of genotoxicity tests and liver responses as biomarkers for pulp and paper mill contaminants environmental monitoring.

In this perspective, juvenile *Dicentrarchus labrax* L. (sea bass) was exposed during 0, 2, 4, 6 and 8 hours to the concentration range of 0, 0.0125, 0.025, 0.05, 0.1, 0.3, 0.9 and 2.7 μM abietic acid (AA) or dehydroabietic acid (DHAA). Liver cytochrome P450 (P450) and liver ethoxyresorufin-*O*-deethylase (EROD) were determined as biotransformation biomarkers. Genotoxicity was measured as erythrocytic micronuclei (EMN) and nuclear abnormalities (ENA).

AA inhibited EROD at 2 hours exposure to 0.05 μM . A significant P450 increase was observed at 2 hours exposure to 0.05 (2.3-fold) and 2.7 μM (6.3-fold), as well as, 6 and 8 hours exposure respectively to 0.0125 (3.4-fold) and 0.025 μM (4.9-fold) AA. EMN and ENA frequency were significantly increased at 2 hours exposure to 0.9 μM AA. A significant EMN and ENA increase was observed with an increased exposure length up to 8 hours.

DHAA induced a significant EROD increase (3.2-fold) at 2 hours exposure to the lowest concentration tested. Liver P450 was significantly increased at 2 hours exposure to 0.025 (1.8-fold) and 0.3 (2.5-fold), at 4 hours exposure to 0.1 (3.6-fold), and at 6 hours exposure to 0.1 (3.2-fold) and 0.3 μM (2.8-fold), whereas it was significantly decreased (30% of control value) at 4 hours exposure to 0.9 μM . EMN and ENA frequency were significantly increased from 0 up to 2 hours exposure to all DHAA concentrations tested and kept high from 2 up to 8 hours.

The comparative analysis of the two resin acids genotoxic effects showed that DHAA is more genotoxic than AA, since 0.0125 μM promoted at 2 hours a 20- and 3-fold EMN and ENA respectively increase, against a maximal induction of 13- and 3-fold increase for 2.7 μM AA at 4 hours exposure. However, RAs genotoxicity is not directly associated with high levels of liver EROD activity and liver P450 content, in the sea bass. Therefore, several biomarkers as well as bioindicators are requested to assess the effects of aquatic contaminants, since the absence of a specific effect does not always reflect the absence of contamination and toxicity.

TRACE METALS (CD, CU, CR, PB, ZN) IN THE BLUE MUSSEL FROM THE EASTERN ADRIATIC

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This paper presents the results of the first two years of monitoring of trace metals using mussels, as a part of the National Monitoring Program of the Adriatic Sea supported by MEDPOL. This project was designed to determine the status and trends of trace metal contamination in the coastal and estuarine waters of the Croatian coastal region.

The levels of essential (Cu, Zn) and non-essential (Cd, Pb, Cr) metals were determined in a whole soft tissue of the Mediterranean blue mussels (*Mytilus galloprovincialis*) collected at a grid of sampling stations (30 locations) along the eastern Adriatic coast. The mussels from natural populations were collected annually, at the same sites and times, with an intention to establish temporal changes of trace metal concentrations in the marine environment. Special attention has been paid to shellfish breeding farms in the Mali Ston Bay, where samples were collected seasonally (4 samples per year). The analyses of trace metals were performed by a GF-AAS. All results were determined on dry-weight basis (mean water content: 38 ± 13 %).

Although a wide range of concentrations was observed for lead (0.4 – 10.9 mg kg⁻¹ d.wt.) and zinc (49 – 836 mg kg⁻¹ d.wt.), most of the values were lower than 3.0 mg kg⁻¹ d.wt. and 250 mg kg⁻¹ d.wt., respectively. Higher lead concentrations were recorded in the areas with input of industrial and urban wastes. Mean copper concentrations (10.1 ± 6.3 mg kg⁻¹ d.wt.) were several times higher in comparison to mean values reported for the Mediterranean, but only 1.2 – 1.8 times higher in comparison to the reference station in the Mali Ston Bay. Values for cadmium (0.92 ± 0.33 mg kg⁻¹ d.wt.) and chromium (1.76 ± 0.61 mg kg⁻¹ d.wt.) were within the range of values reported for coastal areas of the Mediterranean.

It was difficult to perform comparison of obtained results with published data for Adriatic and Mediterranean due to variations in both the quality of analytical data and in sampling procedures. Especially high differences exist between wet weight/dry weight ratios reported by different authors. Generally, presented data on trace metal content in mussels provide no proof of the general pollution of the Croatian coastal area as compared with reference station, but some evidence of locally increased levels was found, especially for Pb and Zn.

No statistically based conclusions could be drawn in relation to annual trends in trace metal body content, since the power of tests for trends is limited by the number of years for which data are available. However, there is indication that concentrations of lead, chromium, copper and zinc in mussels from highly urbanized areas are decreasing, while no significant difference was observed for cadmium.

A comparison of contaminant concentrations in the edible tissue of mussels from shellfish breeding farms with the Croatian legislation shows that the consumption of their meat is not harmful for humans.

DYNAMICS OF ANTROPOGENIC INFLUENCE TO PLANT COMMUNITIES OF ABRAU PENINSULA OF CAUCASUS BLACK SEA COAST

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The plants of Abrau peninsula are rich and original. There are more 180 rare and disappeared species. 40 species of them are classified as protected. 18 species of them are in Red Book of USSR. Group of relict and endemic plants have particular interest. Common number of relict species is 49, endemic species is 31 (23% of them are the local endemic species).

However my research shows that man activity strong influences on the state of plant communities of Abrau peninsula. Cutting forest, herds of cattle, ploughing fields, gardens and vineyards, building the settlements, tourbases, rest houses and many unorganised tourists lead to degradation and destruction of peninsula plant communities. It leads to the substitution one communities by others.

In process of my work the standart methods of plant geobotany description and decode of air photographs in 1948, 1986 and cartographic methods are used.

Comparative analysis of air photographs shows that in various years the different kind of man influence on nature took place. In period of Grate Patriotic War 1941-1945 and after it the cutting oak and hornbeam forest from *Quercus petraea* and *Carpinus caucasica* had occurred to restore economy. In the flood plains where large settlements of Abrau peninsula were located the 60%-70% place with forest was cutted.

Communities of *Juniperus excelsa*, *Pistacia mutica* and *Pinus pithyusa* are growing on the steep south slopes near Black sea. Namely here the main quantity of rare species of plant communities, endemic and relict species of Abrau peninsula are located. Because of road absence in 1948 this plant communities have been influenced by people in less degree than on other plants. It is known that junipers are growing very slowly and only after 120-150 years old they reach 4-6 m height. In present time the junipers in majority plant communities have 4-6 m height. Therefore preserved juniper communities of Abrau peninsula probably are not less than 120-150 years old.

After it the common picture was changed. By 1986 recreation and tourism owing to good natural condition and building roads along Black sea had played big role. Namely relict communities of *Juniperus excelsa*, *Pistacia mutica* and *Pinus pithyusa* near shore have been influenced by people because there was built many tourbases and rest houses. For last 20 years in Novorossiysk region the 538 hectares of juniper forest was cutted to organize the holiday area. Also in present time unorganised tourists play big role to depress the coast plant communities. Tourists cut trees, bush, trample grass and make fires. Often they are reason of forest fire. For example in 1993 near one of tourbase the fire have burned 1,5 hectar of juniper communities and in 2000 - 3 hectar.

To protect relict plants of Abrau peninsula the state reserve must be organised in this region urgently. Research, restore and health-improving measures must be conducted here. Moreover it is necessary to estimate the acceptable recreation pressure on the plants of Abrau peninsula.

CHEMICAL AND PHYSICAL ALUMINIUM SPECIATION IN SOIL SOLUTIONS

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Aluminium in its various species buffers protons in soils and natural surface waters and play an important role in the cycling of other elements. Its toxic effects on organisms are well known. However, aluminium occurs in various chemical species, of which free Al^{3+} , AlOH^{2+} , and $\text{Al}(\text{OH})_2^+$, were found to be the most crucial to evaluate its toxicity and in the predict the impact of proton inputs on soils and surface waters. The concentration these reactive Al species may be difficult to determine directly because the interaction of them with, for example, a complexing agent, leads rapidly to rearrangement amongst labile aluminium complexes. A very large number of methods exist for the fractionation of aluminium but only a few interlaboratory comparisons are reviewed in the literature. The lack of conformity or specificity of the analytical procedures for Al speciation is not the greatest hindrance for achieving verification and quality control. The main reported drawback of all these method performance programs is the instability of any standard samples provided for the testing program.

The aim of the work was to investigate relatively simple methods for determining of reactive Al species in soil solutions. Two ion exchangers (Iontosorb-Oxin and Iontosorb-Salicyl, fy Iontosorb, Ústí nad Labem, Czech Republic), and two chelating exchangers (Spheron-Oxin and Spheron-Salicyl, fy Lachema Brno, Czech Republic) were used for the separation of individual Al species over a wide pH range (2.0 – 8.0) with ICP–AES and ETAAS detection. The efficiency and selectivity of chromatographic Al species separation were investigated in model systems consisting with various inorganic and organic Al compounds as well as in the real soil solutions. The determination of reactive Al species was performed using spectrophotometry method based on the reaction time long enough only for substantial reaction with free and “labile” forms of Al too. In unfiltered and filtered (0.1 and 0.4 μm) model and real soil solutions were determined the amounts of reactive Al species by chromatography and spectrophotometry methods. Moreover a modified “Driscoll” method was used as a “standard” method of analysis for the determination of several aluminium speciation fractions. Results of analytical procedures are compared with distributions calculated using chemical equilibrium models. The soil solutions were collected from locations where the high aluminium activities are the most hazardous factor for terrestrial ecosystems. The practical outcome of the work is the utilization of proposed Al speciation procedures for calculation of Al toxicity indexes which allow more objective assessment of Al toxicity in soils in comparison with informations about so called “active Al” contents or $\text{Ca}^{2+}/\text{Al}^{3+}$ ratios.

AN OVERVIEW OF THE METHODS USED TO EVALUATE THE INTERACTIVE EFFECTS OF CHEMICALS

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Increased heavy metal and organic pollutants contamination in aquatic ecosystems has become a major concern. Furthermore, it has become an accepted fact that, since chemicals never occur alone in nature, it is most important to investigate the combined effects of chemicals on aquatic organisms. There are quite some studies that investigate the interactive effect of chemicals on aquatic organisms. On the other hand, not all of these studies use the same method in order to predict the theoretically expected effect when two or more chemicals are applied on an organism. The interactive effect is called additive, if the experimental results are not significantly different from the theoretically predicted ones, otherwise it is either synergistic or antagonistic. It is often possible that the interactive effect of two chemicals may be characterized as “additive” based on one method and “synergistic” or “antagonistic” based on another one. The purpose of this study is to present different methods that have been used for evaluating the interactive effect of chemicals, to compare these methods and to show studies where these methods have been used.

The first models dealing with interaction or joined action of chemicals were used mainly for predicting effects of drugs and herbicides. One of the oldest and most widely used model was described by Gowing in 1960. Tammes published a model based on isoboles in 1964. Rumens criticized Gowing’s model and published his own in 1974. Another very popular model is the model of toxic units. Koenemann (1981) has suggested the use of Mixture Toxicity Index for predicting the interactive effects of chemicals. Kungolos et al. in 1997 suggested a model for evaluating the interactive effects of chemicals, using a method based on the theory of probabilities. The final equation that was used by Kungolos et al. was essentially the same with another equation, which had been used by Colby (1967) and others based on the model first developed by Gowing (1960). Still the reasoning was different. The explanation for the model developed by Gowing (1960) and Colby (1967) was based on the assumption that the chemicals acted consecutively on the organism. The model which was used by Kungolos et al. was based on the assumption that the chemicals acted simultaneously and not consecutively on the affected organism.

ORGAN DISTRIBUTION OF RESIDUES OF A BRANCHED NONYL PHENOL ISOMER IN *LYMNAEA STAGNALIS L.*

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Branched isomers of p-nonyl phenol (NP) are perceived to be more resistant to biodegradation in aquatic environments as well as to have more estrogen-like toxicity behaviour than the straight chain isomers. By use of GC-MS, some of them have also been identified to exist in higher concentrations in the isomeric compound mixture than the straight chain isomers. The investigations of the distribution and metabolism of branched isomers in aquatic organisms are therefore important in understanding the mechanisms of toxicity of NP. A single branched isomer of NP, 4(3',6'-dimethyl-3'-heptyl)-phenol, was synthesized in the laboratory and used in *in vivo* studies of its organ distribution and metabolism in *Lymnaea stagnalis L.*, following constant exposure to ¹⁴C-NP isomer in water over a period of 8 days at an average exposure concentration of 5.7 ppb (range: 4.9-5.9 ppb). The results obtained clearly showed the transfer of the isomer residues in various internal organs of the organism following uptake in water and food. The bioaccumulation factor in specific organs, especially in the heart and in the digestive gland/albumen gland, was very high, reaching BAF_w values of 1106 and 637, respectively, compared to a BAF_w value of 72 obtained previously by whole tissue analysis. The high concentrations of this toxicant in the digestive gland and in the heart shows that their cell membranes are capable of absorbing and retaining it more than the other organs. The accumulation of the residues was also relatively higher in the stomach/intestines (BAF_w 133) and in the gonads (BAF_w 294) than in muscle (foot) (BAF_w 50). The digestive gland which is the major site of digestive activity responsible for processing, storage and excretion of fine particulate materials absorbs the fine particulates (< 4µm) and any adsorbed toxicants from circulating blood whereas the high bioaccumulation factor in the heart may correspond to its central function which involves very rapid filtration and circulation of nutrients and excretory material in the blood.

Analysis of extracts of organ tissues by HPLC and GC-MS after digestion with Pankreatin and nitric acid, showed one more polar hydroxylated metabolite in the digestive gland/albumen gland, heart, stomach and in the gonads, in addition to the original isomer. A similar metabolite with the same HPLC retention time was also detected in faeces. Further *in vitro* metabolism studies of this isomer would be useful in understanding its biotransformation and toxicity in aquatic organisms.

INFLUENCE OF ORGANIC AMENDMENTS ON METAL RETENTION BY A SANDY SOIL

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The disposal of many organic wastes on agricultural lands is a widely used practice. The wastes frequently contain substances which improve soil fertility, however other components can have undesired consequences for crops. Agricultural applications of these residues is important for both environmental and economic reasons.

The purpose of this study was to evaluate the effect of the addition of two residues used as amendment on the retention of copper and zinc on a sandy soil.

The soil was sampled from the surface horizon of a soil classified as Hydromorphic Regosol. The soil was amended with urban waste compost or compost manufactured from olive mill wastewater and other plant residues.

The results of the present study showed that the addition of the residues increased the retention of both heavy metals. The proportion of added Cu retained is considerably higher than that of Zn, suggesting a higher affinity of the soil for the former. The desorption of the sorbed metal by dilution is always negligible, regardless of whether the soil has been amended or not.

The addition of the waste amendments increases the pH and organic matter content of the soil. The result strongly supports that pH is the main driving “force” for retention of the metal.

The application of wastes to soils must be studied carefully, because in some cases can contribute to immobilise metal, but pH changes that may eventually take place (through fertilisation, acid rain, etc) may easily reverse the process toward the undesired release of significant amounts of metals in soluble forms.

EVALUATION OF A FRESHWATER ENVIRONMENT QUALITY USING A BATTERY OF ECOTOXICOLOGICAL TEST

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Ecotoxicological tests are an indispensable tool in the evaluation the environmental quality, in fact chemical analysis alone could not give direct informations about the synergistic, additive or antagonistic effects of contaminants on biota. Moreover environmental toxicity test (on receiving waters and sediments) may reveal or confirm the existence of toxic conditions in the receiving water, and may demonstrate the location of unknown toxic point-source or diffuse discharges.

The Sabato river, located in Southern Italy, represent a really interesting case-study: it borns in a uncontaminated area and then crosses different potential contamination sources: highly industrialised zone, densely populated areas, and agricultural ones. Its waters, therefore, contain a complex mixture of different effluents. Moreover ours previous screening ecotoxicological study shown an unexpected ecotoxic zone in the surroundings of springs.

The aim of this work is to evaluate the Sabato river environmental quality by means of a battery of ecotoxicological tests during a year period. Water and sediment samples from 10 sites (disposed in according to the different potential source of contamination) were collected.

A battery of toxicity test were conducted on river water: acute toxicity test with *Vibrio fisheri* (Microtox), *Daphnia magna*, *Thamnocephalus platyurus*, *Brachionus calyciflorus*; chronic toxicity test with *Selenastrum capricornutum*. The same acute and chronic toxicity test were conducted also on sediment elutriates; moreover *Daphnia magna* sediment toxicity test was conducted too. It's really important utilising a battery of toxicity test to show species-specific answers. The chronic test (algae test), moreover, let to investigate the long term toxicity effects, probably different from acute ones.

The result obtained in all tests, for the first six months of biomonitoring, suggest a compromised situation in the terminal part of the river. Moreover, the waters near the head of the river (about 3 Km) show an continuos ecotoxic character mainly marked with algae toxicity test. This result, in according with our previous data, is probably due to the polluted waters coming from Dragone Valley by underground circulation (karst).

EFFECT OF AN ORGANIC AMENDMENT ON NUTRIENT AVAILABILITY AND PLANT CONTENT

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Interest in organic agriculture has been increasingly growing in the last few years due to environmental problems related to conventional farming, as well as to the economical support given by the European Union. Conventional farming causes organic matter depletion, one of the more important characteristics of the degradation of cultivated land.

Application of organic matter has long been known to improve physical properties of soils in addition to providing some nutrients. However, as far as the use of organic matter is concerned, more information is needed on the effect of application of organic matter on crop production.

The purpose of this study was to evaluate the effect of organic versus mineral farming on the availability of nutrients and their content in different plants.

The soil used in this study was a calcareous loamy soil, classified as Xerofluvent. The pH is 7.6 and has 23 per cent of carbonate content. The organic matter amendment was a composted vegetal residue with a high C/N ratio.

Field as well as green-house experiments were carried out. Four replicates per treatment were randomly established in a complete block design. During five years and before each crop the soil received 30000 kg ha⁻¹ of the compost, or a conventional mineral fertilizer. The plots were planted with three rotation crops. Samples of both types of fertilized soils were taken at the end of each cropping. At the end of each growing period the plants were randomly collected for each plot to estimate the nutrient content. Micro and macro nutrients were determined in the plants.

Available micronutrients were estimated with 2 extracting solutions, DTPA in presence of CaCl₂ and TEA at pH 7.3 and EDTA at pH 7. Available P, K, Ca and Mg were also determined. The preliminary results obtained show that for string beans, and for the leaf and stem of leaf-beet, the K content corresponding to the plant from organic plots are greater than the content from plants in mineral plots. However the calcium content has the opposite behavior. On the other hand the data corresponding to carrot plants do not show differences between organic and mineral plots

DTPA-extractable micro nutrients were scarcely affected by both types of farming, while EDTA-extractable Fe, Mn and Zn were somewhat higher in organic than in mineral plots. However higher differences were found in the contents of macronutrients elements.

SIGNIFICANT PRESENCE OF LEAD AND OTHER ENVIRONMENTAL POLLUTANTS ON CHAMELEON EGGS IN SOUTHERN SPAIN

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Females of oviparous species that inhabit polluted environments can acquire and accumulate pollutants and transport them to their eggs. Also reptile eggs with permeable shells could absorb pollutants from the soil where they develop. Pollutants can produce severe impacts on eggs leading to embryo death or abnormal embryonic development. We have analysed the presence of chemical toxicants inside chameleon eggs from southern Spain. In this area, chameleon (*Chamaeleo chamaeleon*) is considered an endangered species that usually inhabits highly humanised areas. Previous studies have shown high embryo mortality rates under natural incubation conditions. Low concentrations of nine of ten analysed organochlorine pesticides appeared in all the studied clutches. Only DDT and DDE were found at concentrations above 1 ppb. Total PCBs were present at higher concentrations, with an average value of 17 ppb. Residues of Cu, Pb and Zn were found in the clutches. Lead concentration was especially significant with an average of 14.2 ppm. Zn concentration averaged 11.05 ppm. Cd was not found in any egg. The lead concentration found in chameleon eggs has been found toxic for other species and tissues. The main source of Pb in the area is probably related with the combustion of leaded fuel in vehicles. Traffic is very intense in the area and chameleons use to live very close to motorways. Lead could be ingested in the diet or breath by females, and also could be absorbed by eggs from the first soil layers where they are laid.

SUBLETHAL EFFECTS OF LOW LEVELS OF SOIL POLLUTION ON PERMEABLE-SHELL LIZARD EGGS

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Many reptile species lay eggs with soft-shells that are permeable to soil water. In fact, eggs usually absorb water from the soil increasing their weight and volume up to three or four times from egg laying. We hypothesised that eggs may also absorb other chemical substances from the soil, including some pollutants. Absorption of pollutants could negatively affect embryonic development and survival.

To test whether pollutants can cross through the egg membrane and affect embryos we exposed eggs of two Iberian lizard species from unpolluted areas to acidic water and to chemical fertilisers. In all cases, pH of 4 or ammonium nitrate concentrations of 200 mg of nitrate per litre had no effect on incubation duration and embryo survival. Ammonium nitrate had sublethal effects on hatchling size and juvenile performance. These effects may influence the success or the survival of juveniles during or after their first wintering. Also, the sublethal effects indicate that pollutants can cross through the membrane and enter inside the egg, affecting the embryo. We also have evaluated the impact of low Ph and ammonium nitrate on the morfology of the egg membrane after incubation.

DOSE-EFFECT RELATIONSHIP BETWEEN UV-B RADIATION AND AMPHIBIAN EMBRYO MORTALITY

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The embryonic stage of some amphibian species is very sensitive to ambient levels of UVB radiation. Many amphibians lay their eggs in clear and shallow water and eggs are fully exposed to solar radiation. Egg masses have a transparent gelatinous matrix and egg membranes are also permeable to UV radiation. In field studies we have studied the sensitivity of eggs of different amphibian species to ambient levels of UVR. We tested eggs of several species at different locations and years. Some species were always sensitive and others were always tolerant, but for some species results varied among experiments. Environmental variability of UVR dose could explain this apparent contradiction. To know the dose-effect relationship, we conducted in the laboratory several experiments where we exposed eggs of different species to realistic and controlled increasing levels of artificial UVB radiation. Embryos of all studied species showed a positive relationship between UVR intensity and mortality rate. Moreover, and for a given UVR intensity, there was a positive relationship between dose and mortality. We found significant differences in sensitivity among species. The spadefoot toad was the most sensitive species and showed high mortality after three days of exposure. The rest of species showed significant embryo mortality after at least five days of exposure. Weather conditions and air and water quality affect UVR exposure and could significantly influence the impact of UVR on amphibian embryos in the field. Moreover, the duration of the embryonic development, strongly related with water temperature and the oviposition site characteristics, may be also related to the impact of UVR on amphibian embryos in the field.

EVALUATION OF NONYLPHENOL TOXICITY IN THE CLAM TAPES PHILIPPINARUM

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Nonylphenol (NP) is widely used in nonionic surfactant formulation, especially in producing nonylphenol ethoxylates (NPEs). NPEs are commonly employed in plastics, latex paints, lubricating oils, emulsifiers, pesticides, paper and textile industries, and both household and industrial detergents. As a consequence of their wide use, high levels of NPEs are discharged in the aquatic environment, either directly from untreated effluents or indirectly from sewage treatment plants, where they are biologically degraded to de-ethoxylated intermediates, of which NP is the final product. In water, NP is more persistent than NPEs; moreover, because of its high lipophilicity NP can rapidly be accumulated by aquatic organisms, especially by bivalve molluscs.

In the present study, we evaluated lethal and sublethal effects of NP on the clam *Tapes philippinarum*, ecologically and commercially important in the lagoon of Venice. In 96 hour lethality test, animals were exposed to 0, 0 plus acetone, 0.19, 0.38, 0.75, 1.5, 3 mg NP l⁻¹. The 96-h LC₅₀ was 1.12 mg l⁻¹.

To evaluate alterations of physiological responses (filtration rate, respiration rate, scope for growth and survival in air) clams were exposed to various sublethal NP concentrations (0, 0 plus acetone, 0.025, 0.05, 0.1, 0.2 mg NP l⁻¹) for seven days. Adverse effects of NP were observed on physiological parameters of clams. Filtration rate significantly decreased at 0.1 and 0.2 mg NP l⁻¹ (p<0.001 and p<0.01, respectively). A significant decrease in respiration rate was also observed at all tested NP concentrations. Moreover, scope for growth, which represents the difference between the energy absorbed from food and the energy lost via respiration processes, was significantly reduced at 0.1 and 0.2 mg NP l⁻¹ (p<0.01 and p<0.05, respectively). Finally, the highest tested NP concentrations significantly decreased the resistance of clams to air exposure and enhanced the mortality rate (P<0.01 at 0.1 mg NP l⁻¹ and P<0.001 0.2 mg NP l⁻¹).

The results of this study demonstrate that the analysed physiological parameters are responsive to NP short-term exposure. Moreover, as tested NP concentrations are similar to environmentally realistic levels, a condition of potential risk for the preservation of coastal biocenoses is highlighted.

VALUATION OF THE CHELATING ABILITY OF SOIL MICRO-ORGANISMS USING AUTOMATED POTENTIOMETRIC TITRATION

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The importance of soil micro-organisms depends on their ability to transform animal and vegetable remains into simpler compounds that enter again into the ecosystem life cycle. Furthermore, they are the main responsible for the mobilisation, bio-transformation and bio-accumulation processes of micronutrient and/or pollutant metals present in traces in the soil. It is long-time known the micro-organism ability, in particular bacteria and fungi, to interact with metals by means of adsorption phenomena.

In this paper the binding ability of functional groups present in the cell walls of an ubiquitous soil fungus, *Trichoderma viride* Pers.: Fr., towards some heavy divalent metals, Cd, Co, Cu, Pb and Zn, was studied.

Processing the data from potentiometric titration of *T. viride* by the McCallum, Midgley and Gran's combined methods, the surface of the cell wall was characterised in terms of functional group total acidity, distinguishing among strong, weak and very weak acidity.

Using Henderson Hasselbalch equation the dissociation constant values of weak and very weak acid, pK_{a1} e pK_{a2} respectively, were graphically determined. Titration data of *T. viride* in the presence of metal were instead processed with the Bjerrum's method adapted by Gregor for determining the conditional stability constants of metal complexes with synthetic polyelectrolytes in terms of $\log K_1$ and $\log K_2$. Here has been used for 1:1 and 1:2 metal-*T. viride* complexes, respectively.

No simple equilibrium can adequately describe the complexation process of metals with complicated absorbent systems like the one we have studied. Among the different methods till now used for the study of complex natural systems, the potentiometric method, modified according to Irving and Rossotti, allows a good evaluation of the ligand dissociated form, a feature that deeply affects the results validity. This approach does not require the determination of free metal in solution, not an easy parameter to evaluate during the potentiometric titration.

FLUMEQUINE TOXIC AND TERATOGENIC EFFECTS ON EMBRYONIC DEVELOPMENT OF *BRACHYDANIO RERIO*

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Intensive aquaculture imposes the use of antibacterial drugs. As a general rule drugs administered by oral route are slowly absorbed and excreted with deject (Alderman and Michel, 1992). As a consequence, animal waste from intensive aquaculture contains antibiotics and other drugs in active form. Flumequine is a Quinolone antibiotic, widely used in intensive aquaculture (Quevauviller and Maier, 1994). It is quite persistent and has been found in the wastewater of a sea bass intensive aquaculture station, during a treatment period up to a level of 50 μL^{-1} (Migliore et al. 2000). To assess the risk of flumequine environmental contamination several tests can be utilised: embryotoxicity could be useful.

The use of early life stages of *Brachydanio rerio* in toxicity testing has several advantages. Zebra fish are relatively easy to breed in the laboratory, eggs available all year round; embryonic and larval development can be continuously checked and malformations observed by microscopy, because of the transparency of eggs and post-hatch larvae.

The aim of this study has been to evaluate toxic and teratogenic effects of flumequine on embryonic development of *Brachydanio rerio*. Different Flumequine concentrations were used (77 mg/L, 50 mg/L, 38.5 mg/L, 25 mg/L, 19.2 mg/L, 12.5 mg/L, 9.6 mg/L, 4.8 mg/L) to assess mortality in 24h old embryos: mortality was directly related to dose, reaching 74% at the highest concentration (2% in controls). Experiments were performed in triplicate; 30 animals per group were used.

Teratogenic effects were studied on survived individuals, at all doses. No alterations were found at concentrations lower than 25 mg/L and higher than 50 mg/L. At intermediate concentrations a distinctive phenotypic feature has been observed: malformation of the caudal portion of the embryo, with an evident folding of the body, along both the antero-posterior and lateral (right-left) axes. In particular, a significant alteration of the muscular apparatus were observed. The myosepta are often interrupted while the fibrillae showed a poor development with large empty areas in the embryo. Alterations are most often unilateral. Significant alterations were also found in the cephalic region: disorganisation and poor development of the basicranial, oral and branchial cartilage were observed. The central nervous system was usually well developed but in few cases eyes were unilaterally deformed. In these individuals the layering of the nervous portion got lost and lenses, not differentiated, were like buds.

In conclusion, Flumequine caused toxic and teratogenic effects on *Brachydanio rerio*. Experiments must be performed to assess the chronic toxicity of Flumequine, more representative of the concentrations found in environmental compartments.

PHOTOLYSIS IN WATER OF SELECTED HERBICIDE (TERBUTHYLAZINE AND IMAZETHAPYR)

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Terbuthylazine and Imazethapyr are s-triazine and imidazoline herbicides active against annual and perennial grass and broad-leaved weeds, useful when applied either pre or post-emergence. In Morocco are recommended for weed control in cereals and sugar beet.

We investigated the phototransformation of these herbicides in aqueous solution tampered to pH 7. Experiments were conducted using a suntest (Heraeus) apparatus, which provides a good simulation of solar light.

The concentration of remaining herbicides was followed using a high- pressure liquid chromatograph (HPLC) equipped with UV detector at 230 nm for the both herbicides terbuthylazine and Imazethapyr.

Kinetic parameters of photoreaction show a first order dependence of concentration of herbicide versus time. The order of susceptibility to photolysis was imazethapyr followed by terbuthylazine.

A BIOGEOCHEMICAL MODEL OF A MEDITERRANEAN LAGOON (SACCA DI GORO, 1989-1998)

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A model of the Sacca di Goro ecosystem has been developed and partially validated with field data from 1989 to 1998. The model considers the nutrient cycles in the water column as well as in the sediments. Furthermore, phytoplankton, zooplankton, and *Ulva rigida* dynamics, as well as shellfish farming, are taken into account. Due to the recent anoxic crises in the Lagoon, the dynamic of oxygen has been also simulated. The actual version of the model is a 0D with input fluxes from the watershed and exchange with the Northern Adriatic Sea. Nutrients from the watershed, wet and dry deposition, temperature, light intensity and wind speed are considered as forcing functions. The results show that the model is able to capture the essential dynamics of the lagoon, with values in the same order of magnitude with the measurements from experimental campaigns. The coupling with a 3D hydrodynamical model of the Sacca di Goro, as well as with the watershed model of Burana-Volano is presently under development.

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MARINE OUTFALL LIFETIME IMPROVEMENT BY CHANGING PORT TYPE OF DIFFUSER PIPE IN THE BLACK SEA EXAMPLE

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Marine outfalls are commonly used for disposal of domestic wastewater in many of Mediterranean Countries. Outfall systems are sensitive hydraulic performance. Both system lifetime and environmental efficiency depend on hydraulic performance of outfall. Many of outfall systems were designed with diffuser pipe including simply opened holes (sharp edged port) sides of pipe. Many of outfalls have sharp edged ports in wide pipe wall thickness (SEWWT). However it could be encountered at low hydraulic performance especially in some of this type outfall systems that were designed as sharp edged ports diffuser pipes. When these sharp edged systems converted to the bell mouthed ports their hydraulic performance could be increased more than their initial service lives. In this study, considering old style outfall, some sharp edged ports outfall systems were designed using Black Sea's characteristics according to various flow rates then the same systems were converted to the bell mouthed ports systems and differences in flow rates of the systems were studied theoretically. The results of changing the shape of the ports were analyzed according to the increase in outfall systems.

A MULTIDISCIPLINARY INVESTIGATION OF A PERTURBATED AREA ALONG THE LIGURIAN COAST

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From 1995 to 1997 an integrated approach to study the environmental health of marine coastal area near a treatment plant in Ligurian Sea (Italy), was applied. Physical, chemical, biological and ecotoxicological characteristics of sediment were determined and the results were evaluated with multivariate analysis, to find relations among the physical-chemical and biological parameters and among sample sites. Furthermore the results were compared with previous integrated studies in the same area in order to evaluate spatial and temporal alterations of the sediment quality.

The relatively high levels of two trace metals (Cr and Cu), pointed out also in previous study (1987), is mainly due to the presence of basic rocks, belonged to local river basins. Whereas the concentration of Zn, Hg, PAHs and PCBs, although were lower than in 1987, highlighted a persistent environmental impact, confirmed also by the bioassays.

In spite of the evident contamination, the macrozoobenthic community showed a natural gradient with a high specific diversity and richness in the coastal zone and a progressive decrease of the structural parameters in the open sea.

CHARACTERISATION OF SEDIMENT POLLUTION AND TOXICITY IN THE FUSARO COASTAL LAKE, CAMPANIA, SOUTHERN ITALY

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This report is a part of a study aimed at evaluating the status of sediment pollution and toxicity in a set of coastal lakes in the Campania region, approximately 30 km NW from Naples, Italy. The Fusaro Lake has been affected for decades by domestic and industrial wastewater effluents. These were from an electronics plant, that has disposed of a number of inorganics into the Fusaro Lake.

In the prospect of a remediation plan, it was necessary to evaluate the effects of multiple pollution on sediment composition and toxicity. Sediment samples from Fusaro Lake were analysed for the levels of a series of inorganic and organic contaminants, and tested for a set toxicity endpoints in sea urchin (*Paracentrotus lividus*) embryos and sperm affecting early life stages. A total of 21 sampling sites were defined, aiming at the most even distribution of sampling sites, except for a higher site concentration in proximity of the plant effluent outlet. The following endpoints were evaluated both including lethal and sublethal effects: a) acute embryotoxicity, i.e. early (pre-hatch) embryonic mortality; b) developmental defects, consisting in retarded or malformed pluteus larvae, or arrest in larval differentiation, e.g. at gastrula stage; c) changes in sperm fertilization success, and d) transmissible damage from sperm to the offspring.

The major goals of this bioassay series consisted of: a) defining the localisation and comparing the toxicity outcomes of sediment samples; b) referring sediment toxicity to contaminant levels. Namely, inorganics were either measured following strong-acid extraction or by seawater extraction under stirring for 24 hrs; organics were measured by HPLC.

The results provided the following evidence: a) the topographic pattern of inorganics levels consistently showed a set of sampling sites with highest contaminant levels, with a maximum concentration near the lake outlet; b) an analogous and consistent pattern was shown by PAH levels; c) toxicity outcomes suggested an association with the topographic distribution of pollutants, although regression analysis failed to provide a significant relation with either inorganics or PAH levels. Regarding inorganics, a non-significant, yet suggestive correspondence was observed between toxicity outcomes and the cumulative levels of Cu, Ni and Zn, measured following seawater extraction. When inorganic levels were measured following strong-acid extraction, regression analysis led to the lack of any association towards toxicity data. This was consistent with our previous study pointing to the relevance of inorganic analyses based on seawater extraction, whereas strong-acid extraction failed to lead to any association with toxicity data.

Altogether, the present results provide further evidence for the applicability of sea urchin bioassays in evaluating sediment toxicity. The results suggest the opportunity of analysing inorganics by a mild (e.g. seawater) extraction for a realistic evaluation of inorganic levels in polluted sediment.

EFFECTS OF COPPER (II) EXPOSURE ON DNA, RNA AND PROTEIN CONTENT IN THE VENUS CLAM *CHAMELEA GALLINA*

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After an *in vivo* exposure, the effects of copper on DNA, RNA, protein contents and their relative ratios were investigated in the venus clam *Chamelea gallina*, aiming to evaluate the use of these biochemical parameters as stress biomarkers in future research.

Clams were exposed for 1, 4 and 7 days to various concentrations of Cu^{2+} (0, 10, 60 and 110 $\mu\text{g/l}$). Small pieces of gill and mantle were dissected and immediately frozen with liquid nitrogen. Nucleic acid and protein contents were measured according to the methods of Caldarone and Buckley (1991) and Bradford (1976), respectively.

In gill and mantle DNA and RNA contents present the same course. The relative DNA content (DNA/dry weight) significantly decreases with respect to controls at the highest tested Cu^{2+} concentrations ($p < 0.001$ at 60 $\mu\text{g/l}$ and $p < 0.01$ at 100 $\mu\text{g/l}$) in 1 day-exposed clams, whereas exposure causes a significant increase at 10 $\mu\text{g/l}$ after 7 days. The relative RNA content shows a significant decrease at the highest tested concentrations in 1 day-exposed clams; a slight decrease is observed after 4 days of exposure at 10 and 60 $\mu\text{g/l}$, while a highly significant increase is found at 110 $\mu\text{g/l}$. A significant difference in RNA level, compared to controls, is observed in 7 day-exposed clams at all assayed Cu^{2+} concentrations, although the highest RNA value is detected at 10 $\mu\text{g/l}$. Gill exhibits higher values of nucleic acids in comparison with mantle. In gill RNA/DNA ratio significantly increases with increasing heavy metal concentration only in clams exposed for 7 days. In mantle RNA/DNA ratio does not show a significant variation during the exposure. Gill protein level shows a trend similar to those observed in nucleic acid contents. Moreover, the protein synthesis is highly depressed after 4 and 7 days of exposure as revealed by protein/DNA ratio values. In the present work copper affects biochemical parameters after 1 day of exposure, whereas a longer exposure time causes a different metabolic response of clams to toxicant.

The RNA/DNA ratio and the other related parameters are usually considered ecophysiological indexes, which summarise the physiological activity of animals under given environmental conditions. They may help to explain chronic effects of contaminants and can also be used for the assessment of the wellbeing of bivalves in the field. As growth is closely related to protein biosynthesis which is controlled by RNA, the level of RNA will vary according to metabolic needs, whereas DNA quantity is constant in somatic cells, so that the DNA content represents an index of the number of cells and can also give an estimate of the cell size. A deep alteration in parameter values occurs in clams exposed. Both tissues respond in a similar way to copper-exposure, even though gill is more responsive. The effects observed could be attributed to an inhibition of energy-yielding processes, channeling of energy for maintenance of homeostasis, or interference with feeding.

The comparison of nucleic acid and protein contents and their relative ratios can represent an integrated approach in stress assessment.

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THE MICROBIOLOGICAL QUALITY OF SURFACE WATER IN CYPRUS

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During the period July 1996 - March 2000, 167 water samples from the seven main dams of Cyprus and their contributing rivers were tested as part of the EU LIFE project 95/CY/B2/CT/868 MED. The bacteriological examination of the samples included detection and enumeration of total coliforms, faecal coliforms, faecal streptococci and *Salmonella* spp. The virological parameters tested were F-specific RNA bacteriophages and culturable enteroviruses.

According to the EU Directive 75/440/EEC for water intended for the production of drinking water, 90% of the samples must comply with the limits set for the category concerned. The Lefkara, Kalavassos, Dhypotamos and Polemidhia Dams fell into the A2 category (Normal physical treatment, chemical treatment and disinfection). The Yermasoyia and Evretou Dams only just failed (>85% of the samples complied with the A2 limits). The Kourris and Asprokremmos Dams, which are Cyprus' two largest reservoirs, complied with the A3 category (Intensive physical and chemical treatment, extended treatment and disinfection). It should be noted that, of the 11 times that the samples were outside (over) the A2 limits, 8 cases involved only high total coliform numbers. This can possibly be explained by the fact that most of these cases coincided with long drought periods with low water level and high temperatures in the dams. Since the drought period seems to be getting longer every year, frequent monitoring of the water of the dams and rivers is essential, in order to ensure that its use is safe for the health of the consumer.

In addition, the Polemidhia Dam was used as a polluted reference point, as it is contaminated by a nearby sewage stabilisation pond. Although the water of its contributing river, Garyllis, was found to be significantly contaminated, the water of the dam itself was of good bacteriological and virological quality and could be classified under category A2. However, the water of this dam can only be used for irrigation since it receives treated sewage effluent.

Analysis for salmonellae was performed only for the last 3 sampling sessions of the programme, hence, no significant conclusions could be deduced, although their presence in a few samples is of concern. F-specific RNA bacteriophages were only sporadically detected (except, again, for River Garyllis, which was consistently contaminated). Enteroviruses were absent from 10 L samples.

The rivers gave, generally, higher bacterial counts than the dams they contributed to. This could be mainly attributed to the high dilution factor and/or the high retention time of the water in the dams.

HEAVY METALS IN LAKE PAMVOTIS' (NW. GREECE) ECOSYSTEM.

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Rock weathering, soil erosion and leaching continuously transfer metal-species into freshwaters, in cooperation to agricultural, industrial, recreational and various other human – originated discharges. Metals, consequently, enter the water-based trophic chains affecting the physiology and biodiversity of the water fauna.

Lake Pamvotis, situated in North – West Greece is a shallow eutrophic lake exposed, for decades, both to natural processes and human activities.

The aim of the present work was to evaluate the degree of metal's bioaccumulation in lake Pamvotis ecosystem.

For this purpose, water, surface and near-bottom samples, as well as sediments were collected every month over a year, from 2 different lake sites, one near the city and the other near the island of the lake.

Tissue samples (muscle and liver) were also collected from different fish species (Cyprinus Carpio, Carassius auratus gibelio)

Solid samples (total suspended solids (TSS), sediments, tissues) were subjected to acid digestion in microwave oven. Metals in water and solid samples were consequently measured by means of flame and flameless AAS.

Our results show that metals (Mn, Fe, Ni, Pb, Cu, and Cr) present significant accumulation in the lake sediments indicating ecosystems' chronic insult by metals. In water samples the particulate matter (TSS) consists the water fraction bearing the main metal burden, while the soluble metal fraction ranges, more or less, within permitted limits for freshwaters. In both fractions near bottom samples are significantly higher in metal levels, ($p < 0.0001$) compared to surface ones, implying metal redistribution due to sediments' pollution.

In fish samples metals exceed permitted limits for consumers in certain species. *C. auratus gibelio* presents the highest Pb and Cu concentrations in liver and muscle samples. ($Pb_{liver}: 5,812 \mu\text{g/g}$, $Pb_{muscle}: 3,858 \mu\text{g/g}$).

In conclusion, bioaccumulation of metals occurs in Lake Pamvotis ecosystem indicating the need for integrated management of the lakes' basin.

BUTYLTIN AND PHENYLTIN COMPOUNDS IN SEDIMENTS AND BIOTA OF THE LAGOON OF VENICE (ITALY)

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Since the 1950s, organotin compounds have been widely used as pesticides and in different industrial processes (e.g as stabilizers in PVC, wood preservatives and catalyzers). More recently, they have been used as the active biocide in the antifouling paints (Tributyltin) applied on the aquaculture cages, on the hulls of the boats and released by shipyard activities.

Their relatively high toxicity, at the beginning mostly underestimated, was extensively investigated since the '80s, when lots of oysters died in Archacon Bay, France (Alzieu et al., 1986), and male sexual characters became superimposed in female gastropods (Imposex), causing sterility (Brian et al., 1986).

The environmental fate of these compounds, their bio-availability and toxicity towards organisms depend on the chemical structure of each compound. For this reason, it is very important to determine the speciation, i.e. the concentration of each congener.

The more important compounds are those with three butyl or phenyl groups (TBT and TPhT) and their breakdown products with two or one organic group (DBT, MBT, DPhT and MPhT).

This work presents the result of a research aiming at developing an analytical procedure for organotin compounds speciation and determining their concentrations in sediment and biota samples from the Lagoon of Venice.

The analytical procedure, adapted from Morabito et al., 1995, enables the determination of the named organotin congeners even at very low concentrations (d.l. = 0.2 ng g⁻¹, d.w.) and in presence of many interferences. The procedure was validated by optimizing the following steps: extraction, derivatization with pentylmagnesiumbromide, preconcentration, clean-up and determination by GC-MS. Procedure accuracy and precision were determined by using certified materials and participating to inter-laboratory exercises.

Sediments and organisms, belonging to different trophic levels, were sampled in 12 locations in the Lagoon of Venice, characterized by varying contamination impact. The results have pointed out that organotin compound contamination is at considerable levels both in sediments (Σ TBs (ng g⁻¹, w.w.): from 1.44±0.05 to 1287±6; Σ PHTs: from 1.08±0.02 to 689±29), and in organisms, with the highest concentrations found in filter feeders like mussels (Σ TBs (ng g⁻¹, w.w.): from 12±1 to 1616±104; Σ PHTs: from 4±1 to 759±61). Organisms were detected to concentrate differently the single congeners.

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ACCUMULATION AND DISTRIBUTION OF SLUDGE-BORNE TRACE ELEMENTS IN A SILT LOAM SOIL FOLLOWING TEN YEARS OF SLUDGE ADMINISTRATION.

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Most of municipal and industrial sludges contain plenty of nutrients such as nitrogen, phosphorous and organic matter and they can therefore contribute to the mineral nutrition of plants and to the soil fertility. However the use of sludge in agriculture could result, on long term, in severe drawbacks, given the potential of the biosolids to contain trace elements (heavy metals) at hazardous concentrations. The mobility of trace elements is responsible for the accumulation and distribution in soil and it is determined both by the intrinsic properties of each metal species and by the soil chemical, physical and biological characteristics.

The study focuses on the accumulation and leaching of heavy metals in a silty-loam agricultural soil, disposed of dehydrated and composted sewage sludge for ten years. Total and bioavailable soil metal contents from the soil surface to a depth of 100-cm, were investigated. The experiment has been set up as a complete randomised block design; every year the sludge was applied at rates of 5 and 10 t/ha and soil was ploughed at 30 cm of depth. At the tenth year soil samples were collected at 25, 50, 75 and 100 cm of depth, to analyse total and bioavailable contents of Cu, Ni, Pb and Zn.

The statistical analysis was performed on any metal species regarding total and bioavailable concentrations. Firstly, ANOVA was carried out by treatments and by depths and, where significant differences occurred, multiple comparisons for both treatment and layer means were performed. Secondly ANOVA was carried out for any single treatment to detect differences at various depths. In the case of significant F values layer means were subjected to multiple comparisons. At third, ANOVA was carried out to detect significant differences among concentrations of all treatments occurring on the same layer. As above, in the case of significant F values, treatment means were subjected to multiple comparisons. Finally, metal concentrations of every treatment from surface down to 100 cm were plotted against the corresponding values of Control and analysed as linear regressions. The aim was to assess whether sewage sludge could alter the way metals distribute “naturally” into the soil profile, meaning the distribution pattern of Control “unaffected by sludge” rather than natural.

The concentration of all metals (total form) increased for sludge disposal whilst, regarding DTPA-extractable fractions, only zinc and nickel gave significant differences in comparison to the control. The sludge besides to increase the concentrations of heavy metals, affected the distribution of total Zn, Ni, Pb and available Ni in the soil profile, since they strongly diverged from the distribution of control plots (N3). DTPA-extracted Cu and Zn instead, followed the natural distribution pattern more than the other elements. They in fact are known to be easily complexed and it is presumable that the enrichments of such elements in soil, was sorted into the soil fractions at the same ratios of control soil.

As a general view results indicated that, at the experimental conditions, the increasing of heavy metal concentrations, due to sludge provision, does not necessarily enhance their bioavailability.

ECOLOGICAL RESEARCH OF LANDSCAPES OF THE RUSSIAN BLACK SEA COAST

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The problem of management and the natural resources protection of the Black Sea coastal zone of Russia, characterized by unique subtropical landscapes, where various anthropogenic transformations undergo, has vital importance. Some nature reserves should be established in this region. The aim of this investigation is to study the structure, the evolution and modern ecological state of Abrau Peninsula landscapes. It's suggested as one of main conservation site due to the relatively low anthropogenic transformation and ancient history. One can find here natural and differently modified landscapes. Nowadays, the ecological situation is aggravated due to the construction of pine-line and oil terminal near Novorossiysk and increasing of uncontrolled recreation within the narrow coastal zone.

On the basis of fieldwork (mapping and profiling with regular step of investigation of 20-25), remote (space and aerophoto) sensing the large-scale landscape scheme (1:50 000) of the southern part of Abrau Peninsula and more detailed maps (1: 25000) on some areas within this region have been compiled. Some landscapes with different spatial organization belonging to two types were revealed. The coastal landscapes are characterized by complex landscape structure due to abundance of seismoslides and by Mediterranean vegetation with rare, relict and endemic species. Particular attention was paid to the study of functionality and ecological state of unique Mediterranean ecosystems – pine-tree forests, pistacio-juniperous and juniperous open-lands.

Collected data are being analyzed by methods of multivariate analyses. On the basis of landscape map a special maps of chemical element migration conditions, humidity and pH of soils, vegetation transformation and complex landscape-ecological map have been done for the model areas. It was ascertained that the study landscapes undergo both direct impact of human activity and indirect, mainly by chemical pollution. Direct impact causes the reduction of the biological diversity, including ecosystems with relict and endemic species and expansion of shrubs, the decrease of biomass, the increase of soil disturbances and formation of new landforms, the appearance of new dumps and so on. The appearance of pollutants, including toxic ones in vegetation, soils and water can be marked out as a result of the second type of pressure. The concentration variability of elements in natural landscapes is lower in comparison with anthropogenic ones, especially for Pb, Cu and some others. Our recent study confirmed the high concentration of Cu in the soils of former vineyards, which had been found some years ago, as well as high concentration of Cd and Pb in water.

Landscapes of the study region were divided into several groups – practically unchanged, with low, moderate and high transformation, according to the different types of changes under the anthropogenic pressure.

The region can be regarded as natural and cultural heritage of Russia and Mediterranean region and as a standard background for ecological monitoring of Mediterranean landscapes.

EFFECTS OF THE ENDOCRINE DISRUPTOR 4-NONYLPHENOL ON THE ZOOPLANKTON OF FRESHWATER MODEL ECOSYSTEMS

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Introduction

Endocrine disruptors in the environment interfere with the hormone system of a wide range of organisms. Many of them have estrogenic character. Technical 4-nonylphenol (NP) is one of the chemicals with the potential to affect hormone pathways. It occurs in the environment as a biodegradation product of alkylphenol polyethoxylates and is found in surface waters as well as in sewage treatment effluents and sediments in $\mu\text{g/L}$ -concentrations. The estrogenic property of NP was shown for vertebrates, especially for fish in earlier studies. The results for invertebrates are controversially discussed. Effects of NP on the zooplankton community were shown in only one field study with littoral enclosures where NP was added directly to the medium. Our microcosm study was conducted to assess the hazardous potential of NP on the natural biocenosis under realistic exposure conditions.

Methods and Materials

Microcosms constructed of cylindrical, bottom-closed stainless steel containers (\varnothing 80 cm, height 60 cm) were filled with sediment (10 cm) and water (230 L) including the natural plankton community from an oligo-mesotrophic littoral area of a nearby lake (Lake Ammersee, Bavaria, Germany). The microcosms were surrounded by water in an artificial outdoor pond, to stabilize temperature. Technical NP was applied during seven weeks in seven different concentrations ranging from 10 $\mu\text{g/L}$ to 120 $\mu\text{g/L}$ (max. concs.) using a controlled release system made from semi-permeable LDPE tubes. Nine microcosms served as controls. The physical and chemical parameters were measured and plankton samples were taken in weekly intervals from May to September. Multivariate statistical methods (CANOCO) were applied to detect effects of NP on the zooplankton as well as toxic effects on the phytoplankton.

Results and Discussion

The nonylphenol concentrations increased during the first 2.5 weeks, remained constant until the reservoirs were removed, and dropped below the limit of determination in the first two weeks of the six-week-post-application phase. The values for oxygen saturation, pH, conductivity as well as $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ of the microcosms exposed were on the whole within the range of the controls. The total abundance of the rotifers increased before the nonylphenol dosing and even during and after the application their population dynamic did not show any dependence on the concentration of NP. In contrast to that, the variation within the organism densities of the cladocerans and copepods seemed to be more moderate in the polluted microcosms than in the controls. Likewise the total abundances of the cladocerans in the two and the copepods in the four highest NP-concentrations were lower during the exposition. Whether the observed effects result from the endocrine disrupting or the toxic properties of NP could be verified by an experiment with a positive control, e.g. ethinylestradiol.

EFFECTS OF THE ENDOCRINE DISRUPTOR 4-NONYLPHENOL ON THE PHYTOPLANKTON OF FRESHWATER MODEL ECOSYSTEMS

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Introduction

For a comprehensive protection of aquatic ecosystems from endocrine disruptors all parts have to be considered, including possible (indirect) effects on primary producers. For this an outdoor microcosms study was conducted with 4-nonylphenol (NP), one of the most discussed endocrine disruptors in the environment. A method of continuous exposition was developed and applied to meet the conditions in natural systems.

Methods and Material

Microcosms constructed of cylindrical, bottom-closed stainless steel containers (Ø 80 cm, height 60 cm) were filled with sediment (10 cm) and water (230 L) including the natural plankton community from an oligo-mesotrophic littoral area of a nearby lake (Lake Ammersee, Bavaria, Germany). Four microcosms were continuously exposed to different concentrations of technical NP by controlled release through a semipermeable LPDE-tube for seven weeks. 2 microcosms served as control. Phytoplankton samples were taken before, during and for six weeks after exposure. The samples were fixed and prepared for microscopic investigation. To detect changes in the community composition, the Principal Response Curve (PRC) method was applied among other characterization methods.

Results and Discussion

The nonylphenol concentrations increased during the first weeks of dosing. Maximum concentrations reached were 30, 60, 90, and 120 µg/l, respectively, for the four exposed microcosms. After the end of exposition concentrations declined to the detection threshold within 2 weeks. The identified species of different algal classes revealed a considerable diversity in the microcosms. The number of species did not decrease significantly during the experiment in the control microcosms. At the beginning of the exposition the microcosms did not vary much, regarding the composition of the species. This indicates the usefulness of the testdesign in order to obtain relevant results. There was no evident concentration dependent effect of nonylphenol on the species number. In accordance with this diversity and evenness show no shifts due to the exposition to nonylphenol. Whereas the cell density of the phytoplankton also did not indicate clear effects during the period of dosing, it seemed to be affected within the first week after its end, when the total cell density increased in the control microcosms. In contrast, it decreased dose dependent in the exposed microcosms. The differences did not appear during the following weeks. The total biomass showed no changes which correlate unambiguously with the exposition to nonylphenol. The biomass was highly variable, both over time as well as between microcosms, which made it difficult to detect effects. It tended to be dominated by one or a few large species, obscuring biomass changes of many of the small species. This might be a reason for the contrary findings of cell density and total biomass. This explanation is supported by indications of concentration dependent biomass shifts on class level, a more detailed parameter.

IMPLEMENTATION OF LAKE OHRID MONITORING PROGRAMME

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The Lake Ohrid, the oldest one in Europe and one of the oldest in the world, represents a refuge for numerous freshwater organisms from the tertiary period whose close relatives can be found only as fossils. It is inhabited with numerous endemic and relict forms or organisms.

Lake Ohrid (max. length 30,4 km; max. width 14,8 km) is situated in the SW part of FYR of Macedonia in the Ohrid valley, on the border with Republic of Albania at 639,2 m above sea level. Around 2/3 of the lake surface area belongs to FYR of Macedonia and 1/3 belongs to Albania. It has a surface area 358,2 km², maximum depth of 288,7 m, mean depth 163,7m, shoreline length 87,53 km (56,02 km Macedonian and 31,51 km Albanian). It has a drainage area of 1042,25 km² and 40 tributaries most of which are temporary flowing creeks and rivers especially during heavy rains and melting of snow from the surrounding high mountains.

A Lake Ohrid Conservation Project supported by the World Bank, has been established with joint efforts from both countries sharing the lake FYR Macedonia and Albania. It consists of four components:

1 Institutional strengthening, 2 Monitoring programme, 3 Watershed management and 4 Public awareness.

This project is aimed at improvement in restoration and future conservation of the lake.

On November 1999 started the implementation of Lake Ohrid Monitoring Programme. The sampling was realised at three stations in Lake Ohrid and one station in Lake Prespa. At the same time is done the sampling at the tributaries. The water samples are taken at 0, 10, 20, 30, 40, 50, 75, 100, 125, 150 m.

From the experiences with implementation of Lake Ohrid Monitoring Programme, we learned that it is not an easy task we have set ourselves. Ample experience in tuning the objectives of our monitoring programme towards water management needs is not yet present.

We did not want to be over ambitious and we focused on the upper part on the monitoring cycle: water management, monitoring strategy and further assessment, information utilisation and water management, to complete the cycle. The cycle represents the repeating evaluation and adaptation of the monitoring network. Lake Ohrid Monitoring Programme is the most effective when it is tailor-made. As the body of the information need grows, or loses weight, the monitoring programme should regularly be tailored to keep a perfect fit.

Another conclusion is that monitoring and assessment becomes increasingly complex. It is not enough anymore that the specialists in different disciplines, chemists, biologists and physicists, collect enormous amount of data and report these separately. Increasingly, water is being viewed in an integrated manner. A systemic analysis and assessment of water quality, habitats, biological communities, sources and fate of pollutants, as well as mass balances, should be conducted in order to provide reliable and useful information. Only with this integrated information a good understanding of the situation of the Lake Ohrid ecosystem at hand will be possible.

As the borders of the ecosystem are independent of national administrative borders, international co-operation becomes increasingly important.

Finally it was concluded that there is a growing public consciousness of environmental issues. This leads to the demand for more and better information and it is up to us to provide this in a comprehensible way.

HEAVY METALS MONITORING IN SOIL AND SUBSOIL WITH CHEMICAL AND GEOPHYSICAL TECHNIQUES.

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Geophysical methods are widely used in many different fields such as groundwater resources evaluation, hydrogeology, natural hazards assessment and mining engineering. All these techniques are based on the measurement of some electrical and magnetic properties of soil and subsoil. As an example, ground penetrating radar is a high resolution technique of imaging shallow soil and ground structures obtained measuring variations in dielectric constant ϵ . High-resolution tomographies, instead, are based on measures of electrical resistivity ρ : this parameter gives many information about subsoil geological structure and about the presence of groundwater. Magnetic surveying is based on observations of variations in magnetic permeability μ and in magnetic susceptibility χ ; this technique is very useful to map cavities, structural trends and basement feature.

Nowadays these methods, mainly used for analysing geological structures of the subsurface soil, are been used also for monitoring soil contaminants. In particular they seem to be very successful for evaluating hydrocarbons presence and their profile in subsoil after acute episodes of contamination. These applications point out that the geophysical techniques have many advantages in comparison with chemical techniques, commonly used for evaluating soil contaminants level. In fact they give information in real time, give 3-D imaging of subsurface soil, are not invasive and are cheaper than other techniques. So it is very interesting to investigate the possibility for applying these techniques in monitoring surveys aimed to evaluate soil contamination.

Here we present a preliminary study to compare chemical and geophysical techniques for monitoring heavy metals content in soil. In particular we focus our attention in an area of Basilicata Region, the Agri valley (Southern Italy) in which agricultural activities are prevalent. During the last years in this area there was a rapid increase of oil extraction activities. At present crude oil production is 7000 barrels per day but it was estimated the future production would increase to about 80.000 barrels per day. Furthermore many infrastructures are going to be built up (oil treatment plant, oil pipeline, etc.).

At the first we are performing laboratory tests with metals-contaminated soils for evaluating the variations of magnetic susceptibility. Contemporaneously we are investigating, with different geophysical techniques, some test sites in which phenomena of soil contamination are limited in a well defined area in order to point out different behaviours between polluted and unpolluted soils. In Agri valley, we have georeferenced a transect in which we will collect soil samples for heavy metals chemical analysis and in which we will perform some field campaigns for determining high-resolution tomographies and magnetic properties patterns.

THE ROLE OF BIOINDICATION IN THE WATER QUALITY IMPACT ASSESSMENT

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The process of environmental impact assessment involves the major elements of identification, measurement, interpretation and communication of impact. Ecotoxicological assessment of hazardous chemicals is an essential element in determining overall risk and protecting public health, welfare and the environment. Therefore in recent years ecotoxicological methods became an essential part of any EIA.

Since aquatic ecosystems are among the most productive and diverse habitats, it is not surprising that they are easily upset by a variety of perturbations caused by human beings. The impact of chemicals on aquatic ecosystems can be evaluated by several ways: laboratory bioassays, bioindication or biomonitoring programmes.

Traditionally, environmental risk has been assessed by chemical residue determination in samples from the affected site. This approach has several limitations. The most important factor is the availability of the chemicals from the environmental compartments to the biological receptors, defined as bioavailability. A bioindication approach resolves many of the difficulties by providing a direct measure of toxicant effects in the affected species.

In our practice we have been using a number of bioindicators in specific environments like lake Balaton and river Tisza, as well as in some other wetlands. The main pollutants assessed were heavy metals, various pesticides and toxic components of effluent discharges. Some of the standard test protocols (like *Daphnia* immobilisation test) were compared to new methods under standardisation. According to the results with *Lemna minor*, *Daphnia* heart rate and Microtox tests a multispecies approach is suggested. On the other side the test methods will give us the possibility for a habitat-specific indication of the pollution. In this respect the various indices of biodiversity may also be useful for environmental assessment.

PHYTOEXTRACTION OF CADMIUM AND ZINC BY *BRASSICA NAPUS* L. AT THREE RELEVANT GROWTH STAGES. A POT EXPERIENCE.

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Phytoextraction of heavy metals by no food crops could be a practicable mean to control the heavy metal levels in agricultural soils administrated with refuse biomasses (e.g. urban or industrial sewage sludge), provided that the process is competitive with respect to other applicable technologies.

The aim of this research was to investigate the capability of *Brassica napus* to extract, at different growth stages, Cd and Zn from an artificially contaminated soil in order to optimise its use.

The experiment was carried out in controlled conditions (pots). The soil was administered with MSW “low metals” compost enriched with cadmium (50 and 100 mg/kg of soil) and zinc (300 and 600 mg/kg of soil). The experimental design included: control soil (T); control soil + not enriched compost (T+C); control soil + cadmium enriched compost (Cd 50; Cd 100); control soil + zinc enriched compost (Zn 300; Zn 600); control soil + cadmium and zinc enriched compost (Cd 100+Zn 600). Plants were collected at three growth stages: emergence, flowering and harvesting. Roots, stems and leaves (roots, straw and seeds after the harvesting) were sampled for biomass measurements. Plant heavy metal concentrations were determined after acid digestion by Inductively Coupled Plasma (ICP). Metal removals were calculated for each growth stage multiplying metal concentrations by biomass.

Roots morphological parameters (total length and mean diameter) were also obtained by Computerized Image Analysis.

The results showed that the *B. napus* accumulated cadmium and zinc during the whole life cycle, in all thesis. Maximum accumulation activity was at the emergence. This did not strongly affect biomass production but did modify morphological parameters of roots such as length, mean diameter and their ratio.

At the emergence and flowering, cadmium and zinc removals by harvestable parts (stems+leaves or straw+seeds) were higher than removals by roots. Heavy metal contents in shoots seemed to be influenced by the levels of soil pollution and sampling time. Soil heavy metal concentrations and cadmium and zinc removals by shoots were positively correlated. Higher heavy metal removals were found at flowering for both, cadmium and zinc.

In presence of Zn, removal of Cd was reduced.

IDENTIFICATION OF TWO *HSP90* GENES IN CARP

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Two *hsp90* cDNA isoforms (*hsp90 α* and *hsp90 β*) were isolated from the common carp (*Cyprinus carpio*). Gene-specific probes and primers were selected and used in Northern blot hybridization and RT-PCR reactions to measure the basal *hsp90* mRNA levels and to follow the inducer-specific expression of the *hsp90* genes in different tissues during *in vivo* studies. The *hsp90 β* gene is largely constitutively expressed at a fairly high level in all the examined tissues (brain, liver and kidney) and is slightly inducible by an elevated temperature. *Hsp90 α* mRNA is present in the brain, but is hardly detectable in the kidney and liver of unstressed animals. In the brain, this gene is greatly upregulated following thermal stress, whereas in the liver and kidney heat shock has only minor effects on its expression. *Hsp90 α* , but not *hsp90 β* , responds to an elevated level of Cd in a dose-, time- and tissue-dependent manner.

AQUATIC PHOTOLYSIS OF ANTIFOULING PAINT BOOSTER BIOCIDES UNDER ENVIRONMENTAL CONDITIONS

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The International Maritime Organization (IMO), Marine Environment Protection Committee (MEPC), have recently announced a proposed ban on the use of TBT as an antifouling agent due to its severe impact on the aquatic ecosystem. This ban is likely to be introduced in 2003 and will lead to an increase in vessels using alternative "TBT free" coatings containing copper combined with organic booster biocides.

Currently, nine booster biocides are approved for use in amateur and professional antifouling products: chlorothalonil, dichlofluanid, diuron, irgarol 1051, sea-nine 211, TCMS pyridine, TCMTB, zinc pyrithione and zineb. These coatings are already used and applied to the hulls of ships and boats to prevent the growth of bacteria, macroalgae, mussels and other invertebrates. As a result important coastal concentrations of these biocides have been found in areas of high yachting activity, particularly in marinas and sportive harbors in the Mediterranean region. Among the different transformation processes (biotic and abiotic), photodegradation is an important factor influencing the fate of organic micropollutants in the environment.

The aquatic photochemical behavior of the biocides chlorothalonil, dichlofluanid, irgarol 1051 and sea-nine 211 has been studied under natural sunlight conditions in different types of natural waters (sea, river and lake water) as well as in distilled water. The photolysis experiments were performed in May through July 2000. It was found that the photodegradation rates proceeds via first-order reaction. The half-lives of the selected biocides ranged from 1 to 59 calendar days showing a dependence on the constitution of the irradiated media. Kinetic experiments are monitored with gas chromatography techniques GC-ECD and GC-FTD, while the major photodecomposition products were identified with GC-MS techniques.

DETERMINATION OF RADON CONCENTRATION IN CYPRUS WATERS

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The objective of this work is the accurate measurement of radon concentration in Cyprus water samples. The attempt was to collect the most of the samples from springs in the vicinity of known faults.

For the analyses, a liquid scintillation counting system, using the Packard protocol for measuring radon in water, was employed.

INDUCTION OF PHYTOCHELATIN SYNTHESIS BY HEAVY METALS IN MARINE MACROALGAE FROM THESSALONIKI BAY, N. GREECE

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Thioles are sulfuric analogous of alcohols and include phytochelatins (PT) with cystein and glutathione (GSH) being the most common peptides in plants. In the presence of metals (Hg, Pb, Cu) thioles form chelating complexes. Phytochelatins are polypeptides different from metallothioneins (MT) of mammals and their presence is linked to the presence of metals. Photoautotrophs are the main entrance for heavy metals in the trophic chain with humans and animals as the final receivers.

Reduced glutathione, GSH (γ -glu-cys-gly) exists interchangeably with the oxidised form, GSSG. In plants, its physiological importance is expressed as sulphur metabolism and defence. It is the precursor of the phytochelatins, which are essential in sequestering heavy metals. Heavy metal toxicity poses major environmental and health problem. Cadmium is a non-essential heavy metal, toxic to cells at very low concentrations. Cadmium ions displace Ca^{++} or Zn^{++} in proteins and may cause oxidative stress. Furthermore the concentration of essential, but at high concentrations toxic, metals such as Cu^{++} , Zn^{++} , Fe^{++} is strongly controlled. We present data on phytochelatin concentrations in natural samples of dominant species from Thessaloniki Bay that exhibits an increasing pollution level. An HPLC innovative method was applied for measuring micromoles of the peptides.

CHEMICAL COMPOSITION OF LAKE MAGGIORE SEDIMENTS

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Lake sediments, acting as a sort of “memory” of all the phenomena that affect the lake and its drainage basin, have been often used to trace the role of human influence in determining the final chemical composition, as opposed to the “natural” contribution deriving from rock erosion.

This approach has been used to study the evolution of Lake Maggiore, the second largest Italian lake (212 km²), which has a fairly large watershed (6.599 km²) and a heterogeneous mineralogical composition. Moreover, this area is well developed as regards industry, commerce and tourism. A number of papers have documented the presence of point sources for nutrients, pesticides, surfactants and toxicants such as As, Cd, Cr, Hg, Se, and Zn.

This research offers an unusually long record since the first campaign started in 1962-63, when 174 grab samples were collected from the Southern basin of Lake Maggiore; afterwards, in 1975 40 samples were collected from the same basin. In 1986, 214 samples were taken from the whole lake; and finally, in 1999, 121 samples were again collected from the whole lake.

All samples have been analysed by X-ray fluorescence (Si, Al, Ca, K, Fe, Mg, Ti, S, P, Pb, Zn, Cu, Ni, Mn, and Cr) and by atomic absorption spectrometry (Cd, Hg). Detailed distribution maps for macro- and microelements have been drawn on the base of these analyses.

Moreover, in the last campaign, the sediment samples have been analysed by inductively coupled plasma - mass spectrometry to provide further information on Sc, Co, As, and V, which can be used to trace both natural and anthropogenic inputs.

Since the maps of distribution of the different elements mark the changes in chemical composition over four decades, they can easily point out the anthropogenic influences on the geochemical cycling of elements in this environment.

TRACE ELEMENTS IN SEDIMENT CORES OF LAKE ALIMINI (LECCE ITALY)

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The study of lake sediments allows us to reconstruct the history of populations who lived, in the past and at present, in a drainage basin. Transport of sediments by wind, rainfall and rivers bring to the lake water the “prints” of both anthropogenic and natural origin.

In order to correctly manage the quality of hydrological resources, it is of great importance to understand what happened in the past in areas, such as the Mediterranean region where the lack of fresh water is a real problem.

Three sediment core samples from the large Alimini Lake (near Lecce, with an area of about 3.2 km²) were collected and studied. These cores allowed us to reconstruct the history of the lake over the last hundred years (the period of time has been evaluated by analysis of Cs¹³⁷).

Sediment core samples were separated every 1 cm and analysed by AAS. In this way it was possible to observe the temporal distribution of the concentration of Cu, Cr, Hg, Mn, Ni, Pb and Zn. Moreover, concentration of C, N and H has been evaluated by combustion analysis.

For all the elements, with the exception of Mn and C a decreasing of the concentration has been noticed at a depth of 24-25 cm. This layer has probably been formed during the 1950s. Mn and C instead have a different distribution: lower concentration values are found in the central part, while upper and lower layers of the probe have higher concentration.

Increasing concentrations for all elements apart of Mn and C is mainly due to the introduction in those years of more intensive and mechanised agricultural practices, together with a massive use of chemical products containing trace metal elements. However, concentrations of all the elements investigated do not appear to be a problem in the Alimini Lake and they are below the limits imposed for good quality lake sediment.

EVALUATION OF CADMIUM DETERMINATION IN SOIL EXTRACTS BY HG AAS

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Cadmium is one of the most hazardous of elements to human health. In general, most soils can be expected to contain $< 1 \text{ mg.kg}^{-1}$, except those contaminated from discrete sources or developed on parent materials with anomalously high Cd contents. It is important to be able to identify the various forms of Cd in soil, especially in the soil solution, in order to more fully understand the properties of this metal in natural systems. The toxic effect of a metal is determined more by its form than by its total concentration.

For this reason, the determination of this element in very low concentration is very important. Direct determination of Cd in soils and soils extracts by atomic absorption spectrometry is difficult because the high salt concentration, arising from the original extract and major elements extracted from soil, leads to spectral and chemical interferences that are difficult to remove.

A very sensitive method, hydride generation AAS, was evaluated for the determination of cadmium in soil extracts. A continuous-flow system with 3% (m/v) solution of sodium tetrahydroborate(III) as the reductant in 1.5 % (m/v) solution of NaOH was used for generation of volatile species of Cd from the sample solutions containing 0.3 mol.l^{-1} HCl. A heated quartz absorption cell (800°C) was used for the atomisation of CdH_2 . The effect of concentration of NaOH, NaBH_4 and HCl on the absorbance of Cd were examined. The ratio of BH_4^-/H^+ in the reacting mixture was found as the parameter which predominantly affects the efficiency of cadmium hydride generation. The potential interference from cations and anions common in soil solutions and other hydride-forming elements, respectively, were tested and their elimination by adding KCN to the NaBH_4 solution is discussed. Cobalt ions and thiourea were investigated as the possible catalysts for Cd species generation. The method was utilised for the determination of Cd in soil extracts obtained by treating of soil by different extractive reagents.

The comparison of described method with the conventional electrothermal AAS was performed. The detection limit (3*standard deviation of 10 determinations of blank) was 0.02 ng.ml^{-1} for HGAAS and 0.1 ng.ml^{-1} for the ETAAS, respectively. The precision (relative standard deviation for ten replicate analyses of 1 ng.ml^{-1} solution of Cd) was $\pm 4\%$ for HGAAS.

The method was verified using certified reference materials of water SMI 12-3-10 “Trace Elements in Water” (Slovakia) containing $5 \pm 0.5 \text{ ng.ml}^{-1}$ Cd, NIST SRM 1643c “Trace Elements in Water” (USA) containing $12.2 \pm 1.0 \text{ ng.ml}^{-1}$ Cd, and CRM 283 „Sewage sludge amended soil“ (Belgium) containing $24.3 \pm 1.3 \text{ mg.kg}^{-1}$ Cd in EDTA extract and $18.3 \pm 0.6 \text{ mg.kg}^{-1}$ Cd in acetic acid extract, respectively. The results obtained were in good agreement with the certified values.

The proposed procedure was used for Cd determination in different type of soils from contaminated and uncontaminated regions of Slovakia.

RECOVERY OF PHOSPHATES FROM CHEMICAL PRECIPITATES

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Phosphates present in municipal sewage in the main stream as well as in the side stream (sludge processing stream) are often removed by precipitation with ferrous sulphates. This results in sulphates increase in treated sewage on one hand, and production of sludge of limited agricultural use. Investigations on biological reduction of sulphates under anaerobic conditions have been carried out on a relatively large laboratory scale model. An anaerobic fixed bed filter of a volume of 12 litres was used. With a hydraulic load of $0.013 \text{ m}^3/\text{m}^2 \cdot \text{h}$ the hydraulic retention time (HRT) was 5 days. The filter was thermostated at a constant temperature of $30 \text{ }^\circ\text{C}$. Phosphates present in treated waste water haven been precipitated out with ferrous sulphate $[\text{Fe}_2(\text{SO}_4)_3]$ The molar and mass ratio of $\text{SO}_4^{2-} : \text{PO}_4^{3-}$ was 1.5 :1. With the increase of the amount of ferrous sulphates added, a decrease in pH was observed. In the range of pH 4 to 6, phosphates were precipitated as FePO_4 , while at pH above 7 in the form of $\text{Fe}_3(\text{PO}_4)_2$. Under anaerobic conditions ferrous sulphides are produced but no free hydrogen sulphide was not detected. In parallel to sulphates reduction an increase in phosphates in the solution was measured. Increase in sulphates reduction could be correlated to the increase in the COD : S rate. The activity of sulphate reduction bacteria was assessed on the base of microbiological investigations and the effects of sulphates. The carried out investigations have shown the feasibility of biological phosphates recovery. It has to stressed that there was an increase of pH from about 7,0 to 7,3, and thus there was no simple chemical resolubilization of phosphates.

POLYCYCLIC AROMATIC HYDROCARBONS IN MARINE SEDIMENTS OF MOROCCAN ATLANTIC COASTAL

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A total of 10 surficial sediment samples obtained from Moroccan Atlantic Coastal -Casablanca-Safi- area, were analysed of a suite of 15 polycyclic aromatic hydrocarbons (PAHs).

PAH levels in polluted sediments are similar to those of polluted areas of Japan, North America and Europe.

However, PAH sources cannot be identified from the information available.

The analysis are conducted by U.V. fluorescence (synchronous excitation) method and confirmed by capillary gas chromatography/mass spectrometry.

BIOMONITORING OF COASTAL WATERS BY USING MICROALGAL TESTS

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Growth tests upon marine microalgae can provide important information about factors limiting algal growth, bioavailability of nutrients, and also be used as indicators of the water trophic state and toxicity levels.

This study was aimed at assessing the quality of the Regione Campania (Italy) coastal waters through algal bioassays with the marine chlorophyta *Dunaliella tertiolecta*. Superficial waters were sampled monthly, from October to December 2000, in 22 stations along the Campania shoreline, with the objective to evaluate the environmental trophic state and likely chronic toxicity.

Campania is the Italian region characterized by the highest demographic pressure and the adjacent marine area receives large amounts of contaminants from a variety of sources (industrial, domestic and agricultural effluents), which reach the marine environment mainly through rivers.

Experimental results show high toxicity effects in the Northern part of the study area, particularly near the Garigliano River, and also highlight high trophic levels in the zone between the outlets of the Garigliano and Sarno rivers.

Microalgal growth limiting factors are represented by phosphorus in proximity to river mouths, and both phosphorus and nitrogen in all other stations.

In our study microalgal test cultures have proven to be a sensitive chronic toxicity assay and a useful tool to evaluate the “health” of marine coastal waters, by allowing their classification into quality categories.

**TOXICITY OF A COMPLEX MIXTURE ON SEA URCHINS
P. LIVIDUS AND S GRANULARIS EMBRYOS.**

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Use of sea urchins embryos and gametes in testing developmental, reproductive and cytogenetic of chemicals and complex mixtures has been successfully developed by a number of laboratories worldwide.

Chemicals in the environment rarely occur alone; however 95% of all toxicological studies evaluate the effects of single chemicals. Where chemical mixture interaction studies have been conducted, most have focused primarily on chemicals that are similar in either structure and/or mechanism, concluding that these environmental toxicants act mainly through additive interaction.

Aim of these work is the study of toxicity effects of dissimilar chemicals mixture on the embryos of the Mediterranean sea urchins *P. lividus* and *S granularis*. First we investigated the toxicology of the individual chemicals evaluating NOEC and LOEC values: Then we mix the different substances at these levels in attempt to test the eventual effects due to their interaction. We use three heavy metals: Pb, Cr and Cd, three pesticides Clorpyrifos, Pentaclorophenol, Azinphos-methyl and three PAH : Fenantrene, Antracene, Pirene.

The mixture of metals at NOEC value produce no effects on sea urchin embryos; we obtain the same no effects results also for pesticides and PAH mixture respectively. these environmental toxicants, therefore, don't seem to act through an additive interaction. Moreover the complex mixture of all toxicants at NOEC levels, doesn't show any embryotoxicity effect.

Complex mixture of the three classes of chemicals at LOEC and NOEC levels produce very interesting data.

SOIL SILVER CONTENT OF AGRICULTURAL AREAS SUBJECTED TO CLOUD SEEDING WITH AgI

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Cloud seeding with AgI has been carried out by the Greek Organization of Agricultural Insurance (ELGA) over two agricultural areas of Northern Greece (Hemathia-Pella and Serres) for a 12-year timespan in order to suppress the hailstone formation, thus protecting crops from damage.

To examine the possibility of soil pollution due to Ag used, 2.500 representative soil samples were systematically taken from 200.000 (Hemathia-Pella) and 100.000 (Serres) ha. Since the total quantity of AgI used in cloud seeding of the two areas was small (469 and 361 Kg, respectively) a spectrophotometric Ag-detection method sensitive to ppb quantities had to be developed.

Soil samples were originated from undisturbed surface soil. In order for Ag elution to be examined, soil samples were taken from three different soil depths as well.

Silver concentration detected in either surveyed area, ranged from 15 to 510 ppb. Average concentrations in soils of Hemathia-Pella (45 ppb) and Serres (37 ppb) were not statistically different from those of control areas (Tyrnavos, Ormylia and Halkidiki) not subjected to AgI cloud seeding. In addition, all measured Ag concentrations were comparable to those reported in the literature for unpolluted soils. As for Ag elution in the field, an average concentration of 87, 51, 44ppb was measured in soil depths 0-10, 10-20, 20-30 cm, respectively.

To further obtain information on Ag mobilization through different soil substrates and/or into plants, a 2-year pot experiment was followed. Silver iodide and/or AgNO₃ were applied on the soil surface and grass species seeded there where periodically irrigated, mimicking a natural rainfall pattern. Silver was quantitated in water leachates and in grass species subsequent to application of various AgI quantities. While Ag was not detected in water leachates and exhibited a very slow motion through the soil columns, comparable to that recorded in the field, it was absorbed by grass species though in minute (0,35 ppb) quantities.

**ASSESSMENT OF ENVIRONMENTAL CONDITIONS AND THEIR TIME
VARIABILITY IN PAPPAS LAGOON NW PELOPONNESE, GREECE.**

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Pappas Lagoon situated at the northwestern coast of Peloponnese, Greece, has been the subject of considerable discussions mainly among local authorities and the local people during the last years due to the specific environmental problems encountered there. The main and severe problem is the intermittent release of large amounts of H₂S from the lagoon seafloor.

As a result of this phenomenon toxic conditions were formed leading to fish death.

This phenomenon was investigated on the basis of in situ measurements in the water mass and the seafloor as well as laboratory experiments carried out on the collected sediments and particulate matter.

Salinity, temperature, dissolved oxygen, pH measurements and the determinations of Cl, SO₄, Ca, in the water column were carried out. In addition their time variability was determined. The geographic variability of carbonates, silicates, organic carbon and metals such as Fe, Mn, Pb, Zn, Cu in the sediments and in particulate matter was determined.

All data are interpreted in combination with the geological geomorphological regime.

LONG-TERM TRENDS OF SECCHI DEPTH AS A INDICATOR OF EUTROPHICATION IN COASTAL AREAS OF THE MIDDLE ADRIATIC SEA

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Since 1976 the IOF Split, has been collecting oceanographic, nutrient and biological data from several stations near bigger towns along eastern Adriatic coast and open sea stations as well. The long-term studies of chemical and biological parameters point to the fact that, during past decade, there is a continuous increase in the eutrophication level in all studied areas. Eutrophication has become an acute environmental problem especially in semi-enclosed areas and gulfs with limited exchange of water with surrounded sea. Changes in biological production are estimated by indirect measurement. For example, Secchi depth measurement, procedures that indicate the amount of particulate material in surface water. The primary advantage of this method is simplicity. A white disk, 0.30 m in diameter, is lowered into water and depth at which the disk disappears from view is recorded.

Our study focused on Secchi depth measurement in coastal areas of the middle Adriatic. In the Table 1. we give a range (R), long-term averages (ξ) with standard deviation (sd) and number of analysed data (n) with trends in Secchi depth on period 1978-98.

Stations	Zadar, Z-1	Šibenik, Š-1	Split, S-1	Ploče, P-1	Dubrovnik, D-1
R (m)	8 - 12	1 - 8	3 - 21	4 - 18	8 - 26
$\xi \pm sd$	13.9±3.0	4.0±1.5	11.8±4.1	9.8±3.8	16.2±4.2
n	48	56	59	55	54
Trend, m yr ⁻¹	-0.06	-0.08	-0.02	-0.06	-0.07

Many factors cause observed changes. The time of day, local wind speed and cloudiness can cause systematic shifts in the reading of Secchi depth. Amount of attenuating (suspended) material in the seawater is the main factor that directly affects the measurement. Light attenuation in water is attributable to four factors: water molecules; dissolved yellow pigments; photosynthesising biota and inanimate particulate matter.

Our study has shown a significant decrease in Secchi depth in the all-coastal areas, for 10 to 15 m that comparing with values found for station at the open Adriatic Sea. The decrease could have been attributed to higher concentration of suspended and particulate matter originating from the surrounding land areas. The lowest values were recorded at the stations Š-1 and P-1, presumably due to effects of fresh water input by rivers Krka and Neretva.

We also analysed the variation changes between seasons. The lowest values were recorded in the springtime, at almost all stations, (excepting at the station Š-1), what could be attributed to higher biological productivity.

Relationships between Secchi depth and chlorophyll concentration have been reported as a power function with relation: $Z = 10.86 * chl a^{-0.48}$ ($R^2 = 0.98$). The analysis show that at least part of change in Secchi depth is due to an increase in chlorophyll concentration.

As a conclusion, we want to emphasise that trend of changes Secchi depth have had a negative sign, at the all investigated areas, that means Secchi depth decreased from 0.02 to 0.08 m yr⁻¹ during that period (see table 1).

THE ROLE OF RESIDUE ANALYSIS IN EXPORT-IMPORT RELATIONS

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Export and import of food from the Mediterranean countries to the EC is a politically sensitive area with regard to possible residues and hygienics. Especially the first of these points mainly influences the marketability of food products, but microbiological contamination also is often the cause for objections. The problems of the Mediterranean can be described as interface between permissible levels for the application of pesticides, waiting times, tolerances, residue data, and restrictions. Many charges of food, especially fish, meat, and spices, are rejected resulting in high financial losses. In this paper, an overview of the problems with food contamination and main causes are presented. It will be shown by means of several examples how contaminations may be minimized or even eliminated at the interface between quality control and export-import business.

CONDITIONS FOR ESTABLISHING AND RUNNING A SUCCESSFUL ENVIRONMENTAL SPECIMEN BANK

(based on experience with the German Environmental Specimen Bank)

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An environmental specimen bank consists of three main components:

- i Sampling and preparing the specimen,
- ii medium and long term storage of samples without any contamination or any kind of change of chemical composition,
- iii the analytical characterization of the samples.

An environmental specimen bank has short term, medium and long term uses. With recent analytical characterization, the resulting data can be considered as monitoring data.

Much more important, however, is long term observation, which gives some information on tendencies. In this case, the most important aspect is observing minute changes. This means that the complete process from taking samples over storage to analysis has to conform to the highest standards of precision and accuracy by using standard operating procedures (SOP).

Standard operating procedures have to ensure that every sample undergoes the same treatment, through all procedures. Especially the not rectifiable processes like sampling and preparing the sample material are to be executed with highest precision.

The selection of matrices (bioindicators), and sampling sites as well as the scope of analytic characterisation is of crucial importance and must initially be made very carefully; later, after checking their relevance according to the experience made, they must possibly be altered. Here, the experience of the German environmental specimen bank can help avoid faulty developments and reduce the financial needs.

Examples show how the Environmental Specimen Banking system is applied (used), based on real samples taken in several sites of Germany. The data are examined for patterns in time and sampling sites.

In order to obtain reliable results, the use of reference materials is an absolute must. Internal reference materials must be established to ensure comparable (adequate) analytical results.

Analytical characterization has, for practical reasons, to be limited to a certain number of pollutants. This should not lead to a narrow view of the information potential contained in the samples.

AN ENVIRONMENTAL RISK ASSESSMENT TOOL - A DATABASE FOR DANGEROUS SUBSTANCES AND PREPARATIONS

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The environmental policy of the European Union as formulated in the Fifth Environmental Action Program aims at the sustainable development of the environment as a whole. One of the main priorities of this policy is the chemical risk control and management.

Within this context, the National Technical University of Athens - Greece in cooperation with the Ministry of Labor and Social Insurance of Cyprus carried out a project under the title `Integrated Control of Industrial Pollution and Chemical Substances in Cyprus`.

As part of the obligations arising from task 1.1 of the aforementioned project the two partners collected the necessary information and data concerning the existing situation related to the management of the chemical substances and preparations in Cyprus. In addition, they designed, developed and implemented a detailed inventory for these substances in Cyprus.

The methodology and the various tools developed order to establish an integrated chemical control system in Cyprus included the following:

- Determination of the chemical substances and preparations of interest according to EU`s Directives , Regulations and EINECS
- Registration of all activities related to these chemicals
- Development of a questionnaire that was sent to the private and public sector the aim being the collection of data concerning the production, consumption and storage of chemical substances and preparations
- Design, development and implementation of database for the management of all the data collected for the inventory

The database includes information collected from various enterprises all around the island by distribution of a specially designed questionnaire. The database can provide important information on the quantity of chemicals for each enterprise of Cyprus giving at the same time the necessary details of the identity of the chemical substance or preparation as well as information on the enterprise itself and its owner.

This database is considered to be a valuable and powerful tool in the effort of implementing new legislation and the fulfillment requirements for assessing the impact of chemicals and their risk on the environment at national level.

OPTIMIZATION OF HEADSPACE SOLID PHASE MICROEXTRACTION CONDITIONS FOR THE DETERMINATION OF ORGANOPHOSPHORUS INSECTICIDES IN NATURAL WATERS

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Headspace solid phase microextraction (HS-SPME) has been developed for the analysis of seven organophosphorus insecticides i.e. diazinon, fenitrothion, fenthion, ethyl parathion, methyl bromophos, ethyl bromophos and ethion in natural waters. Their determination was carried out using gas chromatography with flame thermionic and mass spectrometric detection. To perform the HS-SPME, two types of fibre have been assayed and compared: Polyacrylate (PA 85 μm), and polydimethylsiloxane (PDMS 100 μm). The main parameters affecting the HS-SPME process such as temperature, salt additives, memory effect, stirring rate and adsorption-time profile were studied. The method was developed using spiked natural waters such as ground, sea, river and lake water in a concentration range of 0.05 to 1 $\mu\text{g/L}$. The HS-SPME conditions were optimized in order to obtain the maximum sensitivity. Detection limits varied from 0.01 to 0.04 $\mu\text{g/L}$ and relative standard deviations (%R.S.D <17) were obtained showing that the precision of the method is reliable. The method showed also good linearity for the tested concentration range with regression coefficients ranging between 0.985 and 0.999. Recoveries were in relatively high levels for all the analytes and ranged from 80 to 120%. Water samples collected from different stations along the flow of Kalamas river (N.W. Greece) were analyzed using the optimized conditions in order to evaluate the potential of the proposed method to the trace- level screening determination of organophosphorus insecticides. The analysis with HS- SPME has less background interference and the advantage of its non – destructive nature reveal the possibility of the repetitive use of the SPME fibre.

INTEGRATED CONTROL OF INDUSTRIAL POLLUTION AND CHEMICAL SUBSTANCES IN CYPRUS

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The European Union's environmental policy, as set out in the Treaty on European Union, aims to achieve sustainability by including environmental protection in EU sectoral policies, preventive measures, the 'polluter pays' principle, combating environmental pollution at source and shared responsibility. The development of an integrated system for control of industrial pollution at a national level is of vital importance for every country according to the targets of the European Union Fifth Environmental Action Program.

One of the main priorities is the Integrated Pollution Prevention and Control and the minimization of the environmental impacts of the industrial activities on atmosphere, water and soil as much as possible. Pollution prevention is based on the promotion of environmental friendly technologies and the implementation of Best Available Techniques (BATs), while pollution control is achieved by data collection concerning the emissions from certain activities, assurance of the compliance with the EU directives and implementation of the regulations.

Cyprus as an accession country is taking the necessary measures to harmonize its legislation, administrative and other procedures to the Acquis Communautaire. Cyprus places very high on the priority list the development of a comprehensive system for the control of industrial pollution.

The main scope of the present paper is to present the activities carried out within the framework of the LIFE project TCY98/CY/167 that was carried out by the National Technical University of Athens – Greece and the Department of Labor of the Ministry of Labor and Social Insurance of Cyprus. The overall objectives of the project were the following:

- Establishment of integrated systems for chemical substances control and risk management, for industrial emissions and emissions of volatile organic compounds
- Implementation of these systems in Cyprus aiming at a detailed assessment of the situation concerning the chemical substances and preparations, industrial VOCs emissions and industrial emissions (gaseous and liquid).
- Development of Best Available Techniques guidelines for the implementation of the EU directive for Integrated Pollution Prevention and Control (IPPC).
- Development of a new legislative framework for industrial pollution control the aim being the harmonization with the EU Directives.

The paper focuses on the description of all actions carried out in order to meet the aforementioned objectives as well as on the methodology that was developed for the inventory of industrial emissions, VOCs and chemical substances.

**TOXICITY ASSESSMENT OF INDUSTRIAL WASTEWATERS
BY AN ON-LINE RESPIROGRAPHIC BIOSENSOR**

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The objectives of this work were to evaluate the toxic properties of industrial wastewater by using an online biosensor, to assess their effect on activated sludge microorganisms, to correlate toxicity properties with organic loading and to monitor weekly and daily variations of toxicity characteristics. The results of this study are very helpful in estimating the potential toxicity of industrial influents and their effect on a municipal wastewater treatment plant, since co-treatment of industrial - municipal wastewaters is currently applied or planned in several existing treatment plants.

An on-line respirographic biosensor, RODTOX (KELMA, Belgium), was used in this work in order to characterize the toxicity properties of wastewaters from the Thessaloniki industrial area, for a period of about 4 months. The operation of this biosensor was based on the inhibition of respiration activity of activated sludge microorganisms due to the addition of samples with toxic properties. Toxicity of industrial wastewaters reached up to 80%, during the monitoring period. Samples with high toxicity properties presented various short term BOD values. Evaluation of weekly and daily variations showed that peak inhibition values, exceeding 35% inhibition in microorganisms respiration activity, were usually appearing during weekends and evening hours, indicating the reduced quality of incoming wastewaters at that time period.

IMPROVED ENVIRONMENTAL MONITORING - MANUAL OF BEST PRACTICE FOR THE DESIGN OF WATER QUALITY MONITORING PROGRAMMES

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The Environment Agency (England and Wales) has undertaken a major collaboration programme in the UK (in collaboration with the Scotland and Northern Ireland Forum for Environmental Research (SNIFFER)) and the Po River Authority in Italy (with scientific support of National Research Council - Water Research Institute). This has resulted in the development of a common Manual of Best Practice for the design of water quality monitoring programmes. The Manual provides guidance for any organisations undertaking monitoring activities in the aquatic environment. Different versions of the manual have been produced for use in the UK and Italy, but both are based on common principles, while allowing different approaches to the implementation of monitoring programmes in each country.

For a given monitoring objective, the Manual gives the user step-by-step guidance through the choice of an appropriate monitoring strategy, deciding what to measure and how and when to measure it, as well as how to analyse the resulting data and generate management information. The guidance covers the use of both chemical and biological monitoring methods, for rivers, estuaries and coastal waters. The user will therefore be able to design a monitoring programme that will be most appropriate for the set of problems and circumstances encountered.

The UK version of the Manual of Best Practice consists of the manual itself and nine associated software tools. Through the use of the software tools, the principles of the Manual are put into practice when planning a monitoring programme.

The Manual itself is split into four parts. Part A, Concepts, lists the acknowledged business needs for water quality monitoring. Part B then supplies a more detailed treatment of the planning and analysis activities. Part C of the Manual presents the results of a series of case studies undertaken in the UK during the development of the Manual. The case studies are examples of the various Monitoring Strategies, illustrating the application of the Manual itself and then use of the nine software tools. The final part of the Manual comprises a series of Appendices comprising a Glossary of statistical terms, an explanation of the need for the “Statistical Approach” to monitoring programme design, background to designing monitoring programmes, typical chemical and biological methods, estimation of mixing zones in rivers, tables of typical variations for selected determinands at some continuously monitored sites, statistical tables, technical details for planning procedures, summary of available software; and user guides to the nine software tools for use in association with the Manual. The nine software tools produced in support of the methodology are set out in the Manual. Four of the tools deal with the planning aspects of a programme, the other five are to help with generating management information through the statistical analysis of the data gathered.

EU REGULATORY RISK ASSESSMENT: SCIENCE AND POLICY

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The EU chemicals legislation has been under review since 1998. The main obstacle identified in this review has been the slow progress in risk assessing the EU existing substances. The EU Environment Council concluded in June 1999 that a new EU Chemicals Policy is needed and outlined a number of recommendations for the Commission to consider in shaping the future chemicals policy. In February 2001, the Commission produced a White Paper on the Future Chemicals Policy. The over-riding aim of the new policy is sustainable development.

The presentation will give an overview of the main challenges faced by the EU in implementing the new policy. New risk assessment methodology will need to be developed and the concept of targeted risk assessment will need to be made operational. A methodology is needed to assess the risks to humans from persistent, bio-accumulative and toxic substances, which poses challenges both for exposure assessment methodologies and for hazard assessment methodologies. The presentation will emphasise the policy needs and articulate the current state of play in the EU regulatory fora where the current risk assessments methodology is under revision, thus giving an overview of where the major knowledge gaps are.

ENVIRONMENTAL LEVELS AND RISK ASSESSMENT OF CHLORINATED PARAFFINS

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Polychloro-*n*-alkanes (PCAs), also known as chlorinated paraffins (CPs), are a family of complex mixtures representing more than 200 commercial products, that have been widely used in industry throughout the world since their introduction nearly 50 years ago. Use applications for chlorinated paraffins range from extreme pressure additives in lubricants, to secondary plasticizers in paints and plastics, to flame retardants in various plastics and textiles, as well as fat liquoring agents in leather finishing. Because of their high production volume, their widespread and unrestricted use in the open systems, they are already present in a range of environmental compartments. Due to the complex composition of the CP mixtures and the difficulties involved in the work-up, identification and quantification of their components, compared to the other anthropogenic compounds, world wide relatively little useful data are available on CP concentrations in the ecosphere.

Commercially available products are classified according to their carbon-chain length into short chain CPs (C₁₀-C₁₃ – SCCPs), medium chain (C₁₄-C₁₇ – MCCPs) and long chain (C_{>17} – LCCPs) compounds with a chlorination degree ranging from approximately 35 % to greater than 70 % by weight. This distinction is important when considering environmental levels and effects or toxicity as it has been found that these can vary depending on both the chain length and to lesser extent the chlorine content of the product, e.g. SCCPs have been placed on the United States Environmental Protection Agency (EPA) Toxic Release Inventory and in Canada are classified as Priority Toxic Substances under the Canadian Environmental Protection Act (CEPA). In Germany, the Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area has classified virtually all chlorinated paraffins as Category III B (i.e. suspected carcinogens). In the beginning 2001 the EU has published a proposal to ban SCCPs from being marketed and used in the Member States, as a result of significant environmental risks.

Here, a multitude of CPs measurements in different environmental compartments will be reviewed and details of the risk assessment of CPs in different countries will be discussed.

EVALUATION OF ACUTE TOXICITY AND GENOTOXICITY IN SURFACE WATERS IN CYPRUS WITH AN INTEGRATED APPROACH.

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Effective pollution prevention and protection of waterbodies are becoming essential goals for monitoring. To achieve these goals it is essential to apply both chemical and biological methods in an integrated way. Bioassays are indispensable cost-effective tools, to signal, predict and control chemical pollution in the aquatic environment at early stages of their development. In order to address effects of pollution on different organizational structures and sensitivities a battery of microbiotests was selected, consisting of Microtox™ test, Algaltokit F™, Daphtokit F™ magna and Mutatox™ test (the direct and the after S9 activation). Validation and evaluation was done according to ISO.

In the present work, the results of acute toxicity and genotoxicity in surface waters in Cyprus will be presented and discussed within the context of an integrated chemical and biological approach.

In the direct Mutatox test no one sample was found definitely “positive” genotoxic and only exceptionally suspect samples were found. In the Mutatox test after activation with S9, no sample was found to be definitely “positive” genotoxic but in all dams samples classified as “suspect genotoxics” indicating that the genotoxic response can be attributed to a rather stabilized bulk of compounds which are present in the water bodies, whilst these were not detected chemically. The least sensitive test was Daphtox, with only the 4% of dam samples was found toxic to this test, while the almost perfect complementarity of Microtox test to the other two test is clearly shown.

From the experience of the 4 years monitoring and research under an EU funded Life Project, it was clearly shown that the application of battery of complementary approaches is essential prerequisite for cost effective monitoring, early identification of emerging pollution and optimization of monitoring schemes. For example Toxicity testing signaled the presence of potential genotoxic compounds whilst these were not detected chemically, either due to low concentration i.e. below detection limits, or limitations of the implemented investigation scheme.

TRACE ELEMENT BIOMONITORING WITH MOSS AND LICHEN BAGS IN THE CITY OF NAPLES (SOUTHERN ITALY)

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Mosses and lichens because of their high surface/volume ratio, the simple anatomy and the absence of cuticle, quantitatively accumulate heavy metals in their tissues. For this peculiarity, they may show an elemental composition which reflects, in an integrated way, particulate matter and metal ions present in the atmosphere, and may be considered biomonitors of environmental pollution (Bargagli, 1998, Berlin: Springer). Since mosses and lichens are often scarce or even absent in urban areas, different transplant techniques have been developed.

In this study moss and lichen bags were used to define the status of air quality in Naples urban area. The species employed were the moss *Sphagnum capillifolium* and the lichen *Pseudevernia furfuracea*. To study differences in metal uptake by two different cryptogams, at the beginning of July 1999 bags were settled in 23 sites of the study area across gradients of suspected pollution. The bags were gathered after 10 e 17 weeks of exposition (at the end of the dry and during the wet season, respectively). This procedure allowed to evaluate: i) possible washing away of elements; ii) influence of humidity in moss and lichen metals uptake. After exposure period, specimens were processed according to the method indicated in the guidelines published by ANPA (Cenci, 1999, Nimis and Bargagli 1999, Atti del Workshop “Biomonitoraggio della qualità dell’aria sul territorio nazionale”. Roma, 26-27 Novembre 1998, ANPA). Al, As, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Ti, V, Zn were determined by ICP-MS (inductively coupled plasma/mass spectrometry). The reliability of results was checked analysing Standard Reference Material (CRM 482 and CTA-OTL-1, CTA-VTL-2).

Metal concentrations in *S. capillifolium* and *P. furfuracea* were submitted to descriptive statistical and multivariate analysis (hierarchical clustering), using the program Syntax 5.0 (Podani, 1993, Syn-Tax. Scientia Publishing. Budapest). Significant differences were found between metal uptake in *S. capillifolium* and *P. furfuracea*. In particular, during the dry period there was a higher accumulation in the moss than in the lichen. The uptake appeared to be similar during the wet period. Correlations among metals evidenced particular associations for Fe- Cu- Cr , Cd – Co, Ni- Al- Fe. Pb did not show significant correlation with any other metal. The high levels of Cu, Fe, Pb, Zn, Cd, essential components of alloys wires and tyres of motor vehicles and fuel, released into the atmosphere as fine aerosol emission, suggested the main source of pollution was vehicular traffic.

This study was co-financed by M.U.R.S.T. funds (PRIN 1998) project “Cryptogams as biomonitors in terrestrial ecosystems”.

PHOTODEGRADATION OF THE PESTICIDES TRIFLURALIN AND CHLORPYRIFOS IN NATURAL WATERS

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Pesticide contamination of surface and ground waters from agricultural uses has been well documented around the world. Herbicides are widely used as pre- and post-emergent weed control agents for a wide variety of crops while insecticides are applied in different types of cultivation for the elimination of crustaceans, fruit flies and mosquitoes. The potential of contamination of water and sediment is high due to their physico-chemical properties such as water solubility, adsorptivity (K_{oc}), and hydrolysis half-lives. As a consequence they are found in various natural waters and soils in European countries. Therefore, information related to possible degradation mechanisms is of environmental interest in order to estimate their fate in aqueous and soil media. The photochemical degradation of the herbicide trifluralin (2,6-dinitro-N,N-dipropyl-4-trifluoromethylaniline) and the insecticide chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) has been investigated in different types of natural waters (ground, river lake, sea) and in distilled water. The photolysis experiments were conducted under simulated solar irradiation using a xenon arc lamp as the light source (suntest instrument). Photodegradation rates followed first order kinetics and natural occurring dissolved organic matter (DOM) inhibited the photolysis reaction in all cases. Half-lives of the studied pesticides ranged from 11 to 840 min depending on the constitution of the irradiated media. Kinetic experiments were monitored with gas chromatography (GC) and flame thermoionic detector (FTD) while the major photodecomposition products were identified with GC-MS techniques.

THE TOXICOLOGICAL ANALYSIS IN THE MONITORING OF THE LANDFILL IMPACT ON THE TERRITORY

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The authors have monitored five landfills of various capacity placed on Campania territory. Experimental measures of inorganic and organic chemical parameters on leachate and inspection's wells water have been carried out. In addition the ecotoxicological analysis have been effected on *Daphnia magna*, *Selenastrum capricornutum* and *Vibrio fischeri* (Microtox®).

The results obtained from the toxicological examination, introduced in laboratory routine accomplishing the last rule in the management of the waters, have been compared with chemical parameters. According to the results of water analysis it isn't possible to deduce a meaningful correlation between chemical and toxicological analysis, therefore the environmental impact of the considered landfill is negligible.

The leachate examination doesn't allow to establish precise correlations too, nevertheless a bland toxicity is noticed in water of different inspection's wells on *D. magna*, without chemical analysis identified probable causes.

The Authors conclude reaffirming toxicological examinations validity as preliminary moment, important, even if not exhaustive, to the analytical approach in the study of MSW leachate and inspection's wells landfill.

MONITORING OF POPS IN RUSSIA

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Research of pollution caused by POPs in Russia has been carried out in compliance with federal and regional programs and also with support of international environmental funds. In 1994-2000 a program called “Dioxin” has been carried out in Bashkortostan, one of the regions in Russia. So far this is the only experience of a complex and completed research program in Russia. Over 2500 analyses of isomer-specific PCDD/Fs determination in all environments were made: in the air, soil, bottom sediment, snow, surface and waste waters, water supply sources, emissions of industrial enterprises, biological tissues of animals and human beings (blood, breast milk, fat), in food stuff (meat, milk, fish). In order to evaluate PCBs pollution, determination of 12 DLPCBs was carried out. There are dumps of herbicides with expired date of use to be disposed of. In this connection experimental results of determining the POPs in the environmental objects were obtained (Aldrin, Dieldrin, DDT, DDE, Endrin, hexachlorbenzene, chlordane, heptachlor). Mirex and toxaphene have never been used in the region.

Determination of 17 toxic PCDD/Fs and 12 toxic DLPCBs was performed in compliance with the USEPA methods 1613 B and 1668 A (HRGC/HRMS). The Centre was certified within the framework of Gosstandart of Russia and participates in international intercalibrations.

As it has been shown by the results of 6-year PCDD/Fs monitoring the area of industrial centres in Bashkortostan is an area of industrial risk of dioxin pollution. The territory of the chemical plant producing phenoxyherbicides and the old landfill site of industrial waste is a zone of extreme pollution demanding remediation. PCDD/Fs content in slit and sludge is up to 200 ppb TEQ-WHO, in soil and in the material of which industrial buildings are made – over 10 ppb. Soil, grass and snow within the radius of 200 m around the plant are polluted with PCDD/Fs emitted by incinerators of toxic chlororganic waste up to 0.2 ppb. Background monitoring has shown that urban soil in case there is no PCDD/Fs emission source is polluted within the range of 1-3 pg/g. Treated drinking water normally does not contain any detected PCDD/Fs concentrations. Among PCBs the highest concentrations have been detected for PCB IUPAC # 118, 105, 156. Food pollution with PCDD/Fs and PCBs does not exceed sanitary norms for Russia and more often it is lower than the respective levels reported for Western Europe and North America, especially in terms of high-chlorinated hydrocarbons. The daily PCDD/Fs intake by humans corresponds to WHO recommendations and makes 1-3 pg/kg of body weight per day. However as a result of phenoxyherbicide production during the 60-80s there is a cohort of dioxin affected workers (about 300 people) in Ufa. PCDD/Fs content in their blood is now from 150 up to 8000 pg/g lipids (TEQ-WHO). After-effects of so high pollution consist in the increased risk of mortality caused by cardiovascular and oncology diseases but not diabetes.

The revealed environmental problems of the region demand to solve the tasks of landfill site areas and industrial sites remediation, disposal of toxic sludge, reduction of PCDD/Fs and PCBs emissions from incinerators. Though for the last 3 years some reduction of the background PCDD/Fs level in blood of the population has taken place but still this level is by 30% higher than that on the average in Russia and it testifies to continuing PCDD/Fs and PCBs emission. Finding and rehabilitation of dioxin exposure cohorts, reduction of toxic load on the population requires continuation of POPs monitoring in the environment of the region.

***IN VITRO* EVALUATION OF THE POTENTIAL HAZARDOUS EFFECTS OF WIDELY USED AGRICULTURAL CHEMICALS ON THE EXPRESSION OF THE TUMOUR SUPPRESSOR GENE P53.**

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The p53 tumor suppressor gene encodes for a protein, which has an important role in controlling oncogenic development. Alterations of p53 gene and its protein have been found to be associated with genetic events in human malignancies. Wild type p53 protein, which is a nuclear phosphoprotein, has been characterized as an essential regulator of cell growth arrest and apoptosis when DNA damage occurs due to genome damaging agents. Several studies have shown that an increase in cellular p53 following treatment with potential genotoxic chemicals can be taken as an evidence for DNA damage. Moreover, p53 has been shown to be deregulated by several environmental agents such as benzene and phorbol esters and agricultural chemicals.

In animal studies several pesticides have been proven to be carcinogenic or tumor promoters. Mice exposed to atrazine showed an important increase of the levels of the p53 protein produced from the peripheral blood lymphocytes. Moreover, a significant increase of the protein was observed in the brain of mice that have been exposed to deltamethrin. Many types of human neoplasias occurring in rural populations, such as lung and breast cancer, leukemia and non-Hodgkin's lymphomas, have been associated by demographic studies with the exposure to different agricultural chemicals and their combinations, which probably have highly genotoxic effect.

The purpose of the present study was to detect the *in vitro* effects of widely used, by Greek farmers, agricultural chemicals on the expression of the p53 gene.

TK6 cultured cells were treated with various doses of several agricultural chemicals (paraquat, linuron, atrazine, deltamethrin, mancozeb, methidathio, bromopropylate and quizalofop ethyl D) and combinations of the above. After 24 hours the cells were lysed and the lysates were analysed for p53 expression by ELISA analysis. In parallel cells were treated with mitomycin C, which is known to produce significant increase of the p53 protein levels and served as a positive control of the experiments.

None of the chemicals tested had any effect on the expression of the protein. However, two of the chemicals (paraquat and quizalofop ethyl D) tested at concentration 50µM, produced a significant increase of the p53 protein levels, giving an evidence of their possible genotoxic effect when exposure at high doses occurs. The results showed a dose-dependent increase in the p53 protein production of cells treated with mitomycin C as expected.

THE SOIL POLLUTION WITH HEAVY METALS IN ROSTOV-ON-DON

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Introduction. Soil cover is the area of transit and final accumulation of pollutants, including heavy metals. Soils sorb all possible products of technogenesis as a result of the high active surface of colloids, becoming the “depot” of toxic substances and the major sorption-chemical barrier for their migration from the city’s atmosphere into underground water and river network.

Materials and methods. The investigation was carried out in the recreational zone (i.e., in parks, squares, shelter belts, etc.) and also in the downtown and the industrial part of the city, including the soils under asphalt. The native soil cover was presented by ordinary chernozems. The total content of heavy metals and their forms dissolved in hydrochloric acid and acetate-ammoniac buffer was determined by spectral method for estimation of the soil cover pollution. Further the content of heavy metals in the urban soils and in the background analogues was compared. For this purpose the factor of technogenic concentration or abnormality (K_C) was counted. This coefficient shows the excess of the heavy metals’ content in urban soils in comparison with their content in background ones.

Results and discussion. In the city’s recreational zone the maximum values of K_C are registered for Zn and Cu. For Zn this coefficient changed from 1.6 up to 12.9; for Cu - from 2.0 up to 5.0. The variation of this parameter for other elements is much weaker. In the forest-park zone the increased content of V and Zn, close or a little bit exceeding values of maximum permissible concentration (MPC), are marked.

Other data were obtained during the soil-geochemical investigation around industrial enterprises and in the central part of Rostov-on-Don. All urbanozems and ecranozems are characterized by the high pollution levels not only in covered layers, but in buried soils as well. In the anthropozems the pollution of practically all layers by mobile forms of Mn, Ni, Co, Pb, Cd (acetate-ammoniac extract) was determined, and the excess of MPC was significant. Thus, for Mn this index was varying from 2.5 up to 5 MPC in different soil layers, for Co - from 1.1 up to 2 MPC, for Pb - from 2.8 up to 4.5 MPC and for Cd was reaching 36 MPC. The total content of Pb in superficial soil layer was exceeding MPC in 2-5 times almost on 50 % of the city’s territory. But we have faced the phenomenon which it is difficult to explain by simple pollution with toxicants carrying by air. For instance, in park soils covered by the asphalt almost 50 years ago the increased content of heavy metals was fixed, particularly, the content of Co, Ni, Mn and, especially, Cd. These facts, probably, deny the well-known opinion that covered soils cease to play the role of filter and protector in the relation to other natural environments, and, in particular, to hydrosphere.

Conclusion. In urban conditions the significant contrast of the soil cover pollution is observed. Heavy metals (e.g., Hg, Cd, Pb, Zn, Cu, etc.), being as highly toxic pollutants even in the case of minimal excess of the maximum permissible concentration, may be used as technogenic pollution indicators.

USE OF NEAR-INFRARED SPECTROSCOPY TO EVALUATE HEAVY METAL CONTENT IN BRASSICA JUNCEA CULTIVATED ON THE POLLUTED SOILS OF THE GUADAMAR RIVER AREA

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Phytoremediation is considered as a potential solution for the remediation of contaminated soils. The success of phytoremediation technology is dependant of several factors such as the ability of accumulating high concentrations of metal in the shoots and to produce high biomass. Previous works have shown the possibilities of using *Brassica juncea* in the phytoremediation of contaminated soils, particularly those affected by the toxic spill of the Aznalcollar mine (Southern Spain) (Del Rio et al., 2000).

A rapid screening method of analysis of heavy metals (Pb, Zn and Cu) in plants have been developed by using Near Infrared Reflectance Spectroscopy (NIRS) previously calibrated with samples analysed with classical chemical methods. We have used this technique to evaluate the heavy metal content of 123 accessions of *Brassica juncea* cultivated on the contaminated soils of the Aznalcollar area. Other characteristics such as shoot and root dry weight and density of plant have been studied to determinate the most tolerant accessions.

The results of this study indicate that several accessions of *Brassica juncea* display high tolerance and ability for uptaking heavy metals, and could be used with phytoremediation purposes.

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THE MICRONUCLEUS TEST AS A NONDESTRUCTIVE BIOMARKER IN THE ASSESSMENT OF BIRD POPULATIONS

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A new approach in biological monitoring is the use of biomarkers. In the last twenty years ecotoxicology has been increasingly concerned with the use of biomarkers to evaluate the biological hazard of toxic chemicals and, as part of an integrated approach, in the assessment of environmental health. In fact the concept of biomarkers for the evaluation of environmental risk has captured the attention of control agencies and is currently being assessed by several research commissions. A biomarker is generally defined as “change in a biological response that can be related to an exposure to, or toxic effect of, an environmental chemical or chemicals». The term “biological response” ranges from molecular, biochemical and physiological responses, to behavioral changes and even changes in species composition (Fossi, 1994).

Pollution monitoring is limited by the sensitivity of method utilized. Test in whole animals offer advantages, since an organism can process or metabolize component to its toxic form (Rodryguez-Ariza, Nieves et al., 1992).

The micronucleus test was first developed to detect structural chromosome damage induced by chemicals, it detects the effect of mutagenic agents on chromosomes by the identification of acentric fragments and/or lagging chromosomes, those remaining separate from the nucleus (Schmid, 1975). Later on it has been shown that micronucleus can be a consequence of spindle dysfunctions (Yamamoto, Kikuchi, 1980) as well. Finally, it has been generally assumed that detects both structural and numerical chromosome aberrations (Pavlica, et al., 2000).

Some of the advantages of the micronucleus test are its simplicity, reliability and sensitivity; at present it has been validated as in situ biomarker in different species, including birds (Minissi, et al., 1996; Hose et al., 1987; Zuniga-Gonzales et al., 2000).

We obtained peripheral blood samples from 13 bird species, from three different areas of Russia: north of the Kola peninsula (settl. Dalnye Zelentsy), Azov environs and Taman peninsula. Slides were dried, fixed and stained by May-Grunwald-Giemsa. The frequency of micronucleated erythrocytes was manually scored through an oil immersion objective. For each individual, 3000 erythrocytes were scored.

In bird peripheral blood of each area the micro-nucleated erythrocytes were detected. Our results have shown the tendency of increasing a number of micro-nucleated erythrocytes in birds from Azov environs.

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DETERMINATION OF TRACE ELEMENTS AND EVALUATION OF THEIR ENRICHMENT FACTORS IN LICHENS OF DIFFERENT ALPINE AREAS OF NORTHERN ITALY.

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Since many years the lichens have been proposed as biomonitors in studies related to the atmospheric pollution of metals and trace elements. The specific capability of absorbing and accumulating this type of pollutants from the air associated to their longevity and resistance to the environmental stresses, make lichens suitable for studies on air quality assessment.

In this work, a study for trace elements characterization and analysis in epiphytic lichens collected in different areas of three alpine regions in north Italy is presented. The results furnish a preliminary data bank of the elemental concentrations and gives information for the assessment of TE distribution present in different areas. In addition, the evaluation of the concentrations of TE of anthropogenic origin may provide indications about the long-distance atmospheric transport phenomena.

To this purpose, samples of superficial soils were also collected and analyzed to obtain the trace element enrichment factors (EF). The EF have been calculated according the following equation:

$$EF = C_x/C_n \text{ (ambient)} : C_x/C_n \text{ (background)}$$

where C_x is the concentration of the X element whose enrichment is to be determined and C_n is the concentration of the N normalizing element assumed to be uniquely characteristic of the background. In our case the ambient consists of samples of lichens thallus while the background consists of samples of the surrounding soils. Using scandium as normalizing reference crustal element and the data obtained from the analysis of the lichens and the soil samples the EFs values of more than 20 elements have been determined. Element related to anthropic activity such as W, Zn, Co, Cu, Cr, V, Cd, As, Pb, Ni, Sb and Br present, in almost all samples, EFs values significantly greater than 1, therefore they may be considered associated to non local natural and/or anthropogenic sources.

Most of the trace elements were determined by instrumental neutron activation analysis (INAA), while lead and cadmium measurements were carried out with electrothermal atomic absorption spectroscopy (ET-AAS). The three areas object of study were: a region of northern pre-Alps (500 m s. l.) located in the of the province of Biella (Piedmont); selected sites at different altitudes in the Valsavaranche of the National Park of the Gran Paradiso (north-east Alps) and the small town of Livigno (2000m s.l.) in the north Alps of Lombardy. In each locality more than 24 trace elements were studied. The elemental concentrations as well as the corresponding Enrichment Factors have been evaluated and compared.

**THE BIOASSAY WITH THE SEA URCHIN *PARACENTROTUS LIVIDUS*: THE
CHOOSE OF DIFFERENT END-POINTS FOR DIFFERENT ENVIRONMENTAL
MONITORING**

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The negative interferences which pollutants contained in the marine sediments can exercise on organisms, can be put into evidence through the integration of ecotoxicological analysis in the common chemical-physical analysis. The ecotoxicological approach, in particular, provides some important information about pollutants bioavailability, as well as synergical and antagonistical effects of toxicants and, in the last years, many bioassays are being employed in Italy in the environmental monitoring of coastal areas.

In this work the toxicity of some harbour and coastal sediments is investigated by a bioassay with the Mediterranean sea urchin *Paracentrotus lividus*.

The aim of this study was to examine different end-points for sediments at presumable different pollutant levels (low, medium or high level of contamination) and the possibility to choose the appropriate assay for different environmental monitoring.

The experiment was performed evaluating the spermiotoxicity inducted from sediments elutriates. The end-points considered was the fertilization-rate in order to evaluate the short-term toxicity, and the larval development to assay the longer term toxicity. The way of working is referred to international protocols opportunely changed for *P. lividus*.

The results of this preliminary study suggest that for coastal areas, presumably not much polluted, the study of longer term toxicity could be enough; while in case of harbour and some others polluted areas (dredged material dumping site, petroleum extraction areas, and so on) the evaluation of both, short and longer term toxicity, is preferred.

Methodological investigations and standard procedure studies about sea urchin bioassay are desirable; a future international protocol can be an important support for the management of harbour and coastal sediments monitoring plans.

ATMOSPHERIC MONITORING, TOXICOLOGY AND QSAR MODELLING OF NITROPHENOLS

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Nitrophenols and nitrocresols are widespread toxic compounds generated in the tropospheric aqueous phase by the nitration of aromatics. Organic analysis of urban rainwater has indicated how antropogenic activity influences the chemical composition of the atmosphere. Aromatics with polar substituents, such as phenol, benzoic acid etc., have been found in appreciable concentrations in many areas.

Liquid chromatography coupled to a photodiode array detector and atmospheric-pressure chemical ionization ion sources were used for the determination of a variety of nitrophenols in air and rain samples after solid phase extraction using silica gel and XAD-7 resin-adsorbents (rainwater). Nitration of phenols in the troposphere appears to act in both the gas- and the aqueous phase, leading to dinitrophenols. The first nitration most likely occurs in the gas phase, then transfer to the aqueous phase and a second nitration results in the dinitrophenols.

These compounds are toxic in all organisms as they interfere with a basic cell function, namely energy transduction. The phytotoxicity of nitrophenols and nitrocresols was studied by determining the reduction in soya seed germination, measuring root length after 5 days of exposure and then calculating the germination index as IC_{50} (mmol/L). The results of this study indicate that phenol and cresols have no effect at the tested doses, whereas the nitration products always show some effect, the activity of the dinitroderivates being higher than the corresponding mononitroderivates. In order to predict the toxicity of these relevant compounds on animals both the uncoupling activity of the oxidative phosphorylation and the inhibitory effect of oxygen consumption in mammalian mitochondria were determined *in vitro* for 18 available phenol derivatives. Measurements of the activity on the respiratory function and of the uncoupling activity were made using the oxygen electrode. The inhibitory effect of the oxygen consumption was calculated as Respiratory Control Index (RCI) inhibition, while the uncoupling activity was measured as ADP/O ratio reduction.

The experimental data have been modelled in a QSAR approach using a wide set of theoretical molecular descriptors, selected by the Genetic Algorithm procedure: OLS models with satisfactory predictive power were obtained for all the responses. The models were validated by the *leave-one-out* and *leave-more-out* procedure (Q^2_{LOO} =85-93% Q^2_{LMO} =82-93%). Using these models it is easy to predict good IC_{20} or IC_{50} values for all the toxicity responses, also for not experimentally tested compounds. The predicted values for all the mononitro-, dinitro-phenols and -cresols were checked for reliability by the *leverage* approach. The diversity of the structural descriptors selected for the modelling of the various responses allows the highlighting of the different modes of action.

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RANKING OF “EEC PRIORITY LIST 1” CHEMICALS FOR STRUCTURAL SIMILARITY AND MODELLING OF ALGAL TOXICITY

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Environmental exposure situations are often characterized by the simultaneous presence of a multitude of heterogeneous chemicals that vary in structure as well as in their modes of action. In order to predict and assess mixture toxicity from existing knowledge about the toxicity of the single compounds two different concepts are available: *Concentration Addition* for mixtures of substances with similar mode of action, and *Independent Action* in the opposite case of mixture components with dissimilar modes of action. Mixture studies on specifically acting chemicals evidenced the predictive capabilities of the concepts in principle, but furthermore demonstrated the need to prior grouping of the chemicals into classes of similar and dissimilar action. However, for the majority of chemicals knowledge on their toxic mode of action is either inadequate or not available. To indicate that groups of chemicals possess similar modes of action, QSAR studies can be applied: the general hypothesis hereby is that chemicals with similar structure patterns in structure would have a similar mode of action.

Studies on mixture toxicity and the application of QSARs and chemometric techniques are object of two EEC Projects (*PREDICT: Prediction and Assessment of the Aquatic Toxicity of Mixtures of Chemicals* and the following *BEAM: Bridging Effect Assessment of Mixture to Ecosystem Situations and Regulation*), in which the authors were and presently are involved.

In both of these projects, the EEC priority List 1 (Council Directive 76/464/EEC), consisting of heterogeneous environmental chemicals of mostly unknown or unspecific modes of action, built the base to select the components used in the mixture experiments. To that end, a data set of 202 compounds was studied and classified according to structural similarity which finally allowed the identification of the most representative and dissimilar chemicals. A wide set of molecular descriptors (counts, topological and 3D-WHIM) was used to describe the chemical structure of the compounds with the final aim to find an objective method to group the compounds on the basis of their structural features. Different chemometric approaches (Hierarchical Cluster Analysis, Principal Components Analysis, Kohonen maps) were applied to highlight the 11 structurally most dissimilar compounds.

These chemicals were then tested to assess their algal toxicity on *Scenedesmus vacuolatus* and the experimental results were modelled by the above cited molecular descriptors. On this highly heterogeneous data set we obtained satisfactory and cross-validated OLS regression models, by applying Genetic Algorithm for the variable subset selection. In addition, it was verified that the concept of *Independent Action* should be applied to predict the toxicity of this mixture of structurally dissimilar compounds, thus demonstrating that the structural dissimilarity of the selected compounds is correlated to a dissimilarity in their mode of action. The comparison with QSAR models obtained on congeneric environmental chemicals, which mixture toxicity was well predictable with *Concentration Addition*, will be discussed.

QSAR AND CHEMOMETRIC APPROACHES TO THE SCREENING OF POPS FOR ENVIRONMENTAL PERSISTENCE AND LONG RANGE TRANSPORT

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Several pollutants of concern, including pesticides, PAHs, PCBs etc. have a Long Range Transport (LRT) potential due to the combination of their persistence in the environment and their inherent tendency towards mobility. These pollutants have been found not only in polar ice but also in high European mountains (for instance in the Italian and Swiss Alps).

Half-life data are commonly used as persistence indicators, but are available only for a few organic compounds, vary greatly for the various compartments, depend on laboratory tests and are reported in the literature mainly as a range of values. The reported average and max values have been used as the input data in our QSPR studies. Validated OLS regression models have been realised by using different theoretical molecular descriptors to predict half-life values in the atmosphere, soil, surface water and groundwater for 130 organic pollutants of different chemical classes (PAH, PCB, some pesticides, etc). All the regression models have been strongly validated for their prediction power by the *leave-one-out* and *leave-more-out* procedure ($Q^2 = 70-90\%$) and the predicted data have been checked for reliability by the *leverage* procedure. These predicted values are obviously not the real half-life, but are reasonable estimates that can be combined simultaneously by Principal Component Analysis to produce a useful index for global persistence.

Different physico-chemical properties are important in determining LRT, for instance, volatility, solubility in water, different sorption coefficients and half-life in the different compartments. The finding of the best combination of chemical properties minimizing LRT is a multi-criteria problem and this can be approached by MultiCriteria Decision-Making (MCDM) techniques. In this case utility functions are applied to the most relevant properties determining LRT, allowing a ranking of the studied chemicals according to their LRT potential.

Finally the application of QSPR regression models and classification models (CART) to the obtained MCDM scores allows a fast screening and ranking of existing chemicals for their inherent tendency towards LRT. This approach could also be applied usefully to new chemicals, even those not yet synthesized, as only the knowledge of molecular structure is needed.

MONITORING OF PHYTOPLANKTON AND SUSPENDED PARTICULATE CONCENTRATIONS AT SHALLOW WATERS ALONG THE MEDITERRANEAN COAST OF ISRAEL USING GEOCHEMICAL AND HYPER-SPECTRAL REMOTE SENSING METHODS

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The quality of marine waters depends to a large extent on the density of phytoplankton and suspended particulate matter (SPM), and their composition. The water quality along the Mediterranean coast of Israel was mapped with the hyper-spectral Compact Airborne Spectrographic Imager (CASI) sensor during two airborne campaigns (April 1997 and October 1999). The aim of the study was to: a) implement the use of hyper-spectral remote sensing methodology as a rapid synoptic monitoring tool in a transitional zone from polluted point sources to clean seawater and b) to present the first comprehensive distribution of chlorophyll-a (chl-a) and SPM concentrations at the shallow water belt (<30m depth) along the coast.

In such relatively small size areas, where high spectral and spatial resolution is required, the use of CASI is particularly attractive. The present study demonstrates the advantage of hyper-spectral remote sensing techniques as a monitoring tool in coastal sites characterized with patchy distribution and sharp concentration changes of SPM and chl-a.

RISK COMPARISON OF ANTIFOULING BIOCIDES

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The amount and quality of available risk relevant data for different antifouling agents used as alternatives for tributyltin is very diverse. In order to gain a reliable impression of the comparative risk of using tributyltin, copper, Irgarol (R) 1051, Sea-Nine (R) 211 and zinc pyrithione, a method to characterize this risk by five independent indicators has been previously described. In this presentation, new estimations of the release from commercial ship hulls, of their range in space and time, of their bioaccumulation and of their biological activities are presented, each in combination with the uncertainty of the respective estimations. The estimated copper inputs from antifouling paints only make up less than 10 % of the total copper inputs into the marine biosphere. However, the risk analysis suggests, that the accumulation of copper in deep sea sediments might be a significant problem. The risk profiles resulting from the five indicators only convey an impression of the relative risks, and each indicator value should be disputed in the public.

MONITORING OF WATER QUALITY OF KALAMAS RIVER, EPIRUS GREECE: A MULTIVARIATE ANALYSIS

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River basins are the natural environmental units integrating the effects of all human activities and resource units.

Kalamas River is situated in the Northwestern part of Greece and flows into the Ionian Sea. The river's main length is about 113 Km and its catchment's area about 1831 Km². It receives agricultural, domestic and industrial sewages from the catchment's area.

An integrated monitoring system was applied during the low flowing season, in order to estimate the pollution level and to evaluate biotic community.

In the present study, an attempt was made to estimate the water quality of Kalamas river using physicochemical variables, aquatic macrophytes, and multivariate data analyses. Samples were obtained from two selected stations at bi-monthly intervals, during April to September 2000. The following parameters were examined: water temperature, pH, Dissolved Oxygen, PO₄-P, NH₄-N, NO₃-N, NO₂-N, Chlorophyll-a.

The multivariate analysis techniques (CANOCO, Discriminant SPSS), were applied to data. Correlations were sought between the environmental factors and the abundance of the different species using canonical analysis.

Kalamas river appeared to have poorer water quality during the low flow season than during the high flow season as determined by comparison with a previous survey undertaken in winter 1999. Also the upstream sites had better water quality than the down stream areas.

Multivariate analyses, which consider the abundance of different species and the structure of biocommunities appeared to be more appropriate for the evaluation of water quality.

THE BIRD SPECIES OF THE MEDITERRANEAN REGION AND THE DANGERS THAT FACE THEM

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The Mediterranean Region is geographically divided into four parts and has a variety of ecosystems thanks to the suitability of ecological conditions. Therefore, it also has a rich variety of bird species because of rich vegetations and aquatic areas. 348 (81.7%) of 426 bird species which have been recorded in Turkey exist in the Mediterranean Region. 202 (58.0%) of the regional bird species belong to *Nonpasseres*, and 146 (42.0%) to *Passeres*. Of these bird species, *African Darter*, *Anhinga rufa*, left the region due to the drainage in the Amik Lake, and it has become extinct since 1970. The number of bird species recorded only in the Mediterranean Region is 11, and of these *Bulbul*, *Pycnonotus barbatus*, is likely to become endemic.

According to the status of the *nonpassares* bird species identified in the region and Red Data Book (=IUCN) criteria, the distribution of them is as follows: A.1.2 (= threatened with extinction): as winter visitors (=KZ): 1 species; As breeding species (=G): 4 species; As years birds (Y):19; In the status of A.2 (=severely endangered): KZ=7 species; G= 30 species; Y=26 species; in the groups of A.3 (=endangered): KZ = 1 species; G= 19 species; Y= 20 species; in the groups of A.4 (=potentially endangered): KZ=1 species; G= 10 species; Y = 16 species; All the species above breed in Turkey. Nonbreeding species in the group of B.2 and B3 are 45. As is seen, almost all of the *nonpassares* bird species are endangered.

The most important dangers which face the bird species are as follows: (a) extensive use of pesticides in agriculture and forestry, (b) the drying of aquatic areas, (c) forest fires, (d) the transfer of the natural areas to housing and industry, (e) destruction of coasts, (f) contamination of aquatic areas, and (g) hunting.

COMPOSITION AND TOXICITY OF BAUXITE SOLID RESIDUES: RISK ASSESSMENT AND PROSPECTS FOR SITE REMEDIATION

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Bauxite manufacturing by-products may represent a subject of environmental concern, as far as bauxite by-products may affect marine, freshwater or terrestrial biota in the vicinity of plant facilities or in sludge disposal sites. By-products of bauxite manufacturing include: i. process sludge, whose disposal is either carried out in marine coastal sites or in inland sites, and ii. solid residues, that occur from sludge drying and from other process materials, spreading from bauxite plant facilities to the surrounding areas.

Previous investigations have provided evidence for bauxite sludge-associated toxicity to sea urchin and mussel embryogenesis and fertilisation success. Aluminium bioaccumulation occurs in marine plants collected nearby a coastal bauxite sludge disposal site, and adverse effects on a benthic macroinvertebrate community were also reported in a study of a bauxite sludge-polluted lake.

We have investigated whether solid residues released by some bauxite manufacturing plants could be associated with any comparable toxicity as was detected for bauxite sludge. A series of studies was carried out on solid residues collected in areas close to four bauxite manufacturing facilities located in Gardanne (Southern France), Portovesme (Sardinia, Italy), Aghios Nikolaos (Greece), and Seydi ehir (Turkey). The overall results provided evidence for bauxite residues toxicity to sea urchin early development, resulting in embryonic mortality, developmental arrest and larval malformations, with different topographic and analytical patterns in the different areas investigated. The analytical data pointed to the possible roles of both the major bauxite components (Al and Fe), and/or of the “minor” components, such as Zn, Mn and Pb. The observed differences in bauxite residues composition may be related to differences in ore mineralogical features and, possibly, to manufacturing process(es) in the different facilities. A major outcome of these studies is related to the extraction procedures carried out prior to inorganic analysis, in that strong-acid extraction failed to result in any correlation with toxicity data, whereas a “mild” extraction procedure, by soaking bauxite residues in seawater for 24 hrs provided analytical data that were compatible with the environmental availability of the metals analysed for, and that showed significant correlation results with the outcomes of toxicity bioassays. Thus, the present experience points to the need to evaluate inorganic contaminant levels following a realistic extraction procedure as, e.g., seawater extraction.

The perspectives of interventions for site remediation should take into account the following, multi-faceted aspects of soil pollution as related to bauxite residues: a) an accurate topographic survey of the affected sites should provide an adequate dataset of toxic metal levels as released from residues, as nominally high (acid-extractable) levels of inorganics may fail to result in realistic information on environmental availability; b) in those sites where environmental release of toxic inorganics is verified, the most appropriate and cost-effective devices should be proposed in order to remove the main sources of environmental hazard (e.g., inertisation by concrete immobilisation), and c) bauxite ore should be chosen, as for origin and composition, in order to optimise solid residue disposal from bauxite manufacturing.

THE MAN , THE ECOSYSTEM AND THE TOXIC CHEMICALS - RISKS AND POTENTIAL FOR PREVENTION AND PROTECTION

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It is well understood today that Man is part of the Ecosystem and its survival and future depends directly on the health of his surrounding environment. The sustainability of our environment is dependent on the preservation of the biological chain and consequently on the effective prognosis and prevention of the impacts of chemicals. Pollution is mainly related to the use of Chemicals which have become “essential” in our modern world. Over 100,000 chemicals are registered and at least one thousand of new ones are introduced every year in the market. The problem of chemical pollution is becoming very serious threatening on a global scale the survival of our planet.

How this cocktail of chemicals can affect human health and the Ecosystem? Which are the main toxic effects? What about combine exposure to a number of chemicals ? What are the mechanisms for protection and prevention? This presentation will focus on these concerns and will try to provide some answers on how as individuals and as a society can be protected from these risks. Particular emphasis will be put on risks from chemicals with long term effects like mutagens, carcinogens and endocrine disrupting chemicals (i.e. chemicals that affect the genetic material, growth, reproduction and the endocrine system). Reference will be also made on possible increased risks for oncogenesis due to exposure during childhood.

To cope with the complex problem of chemicals, the policy of sustainable development, calls for effective mechanism of prognosis and prevention of the impacts of chemicals and reduction of their uses. To this effect two principles have to be applied :

- **the principle of holistic approach** by which Ecological and the Human risk identification, management and reduction, is dealt with and
- **the precautionary principle** according to which when a reasonable evidence of hazard exists, actions to eliminate pollution causes could be taken without waiting for absolute proof.

In the second part of the presentation reference will be made on the application of these principles and policies to reduce chemical risks at National and EU level.

NONYLPHENOL ETHOXYLATES AS POSSIBLE TRACERS OF RECENT INDUSTRIAL CONTAMINATION OF PO RIVER SEDIMENTS

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The releases of many organic chemicals from industrial, urban and agricultural activities have lead to widespread contamination of aquatic environments. Since many of these compounds are likely to be associated with settling particles, aquatic sediments tend to become contaminated by a complex mixture of organic chemicals.

The inability to predict the toxic potential of trace amounts of mixed chemicals makes toxicity bioassays essential tools to define the integrated effects of contaminated sediments upon organisms and aquatic ecosystems. While chemical analyses can help to provide qualitative and quantitative evaluation of the anthropogenic contamination but cannot provide information on the risk associated with the sediment-borne toxicants, biological tests evaluating the potential sediment toxicity are still unable to discriminate between the role of the different compounds or the contamination sources. Therefore, the combined use of chemical and ecotoxicological analyses of sediments is the most effective approach for the assessment of hazardous sites and contamination causes. Particularly, the use of sediment solvent extracts for both, chemical analysis of organics and toxicity biotesting, provides a good opportunity to evaluate the relationships linking toxic effects to chemical concentrations. However, apart from few studies where a special TIE procedure was used, chemical characterization of sediments usually consist of analyzing some classes of hydrophobic organic compounds, which may be poor indicators of extract toxicity. The selection of reliable indicators is thus important for the identification of the toxic contamination sources.

Because of the surfactant properties of NPEs, NPE-containing compounds have many uses in a variety of industrial activities. Despite the known environmental hazard, their production, as well as their entry into the environment increased in EU during recent years. In this study, the use of NPEs as chemical tracers of industrial contamination was evaluated on Po River sediments. The river drains the most economically important area of Northern Italy, where both industrial and agricultural activities are possible sources of contamination. A total of 20 sediment samples were collected downstream of the confluences of the main tributaries of the river, during two sampling seasons. The toxic potential of river sediments have been recently investigated using solvent extracts for toxicity tests on *S.capricornutum*, and for PCBs, PAHs, DDTs and herbicide analyses. NPEs analysis, although performed later with a separate extraction procedure, was made on the same sediment samples. The NPEs concentrations detected over the river course were compared with the toxicity trends observed during both samplings. Relationships between ecotoxicological and analytical data were also compared for the different classes of organics.

A good agreement was found between NPEs and some more traditional classes of contaminants, suggesting the primary role of industrial sources for sediment contamination. Relationships between toxicity and chemical data also support the possible use of NPEs as reliable indicators of sediment toxicity.

ENVIRONMENTAL IMPACT ASSESSMENT OF MAJOR PEDESTRIANIZATION SCHEMES THROUGH THE USE OF MODELING TECHNIQUES

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The excessive use of private cars during the last decades lead to the creation of major traffic and associated environmental problems in urban areas and especially in their centers. The confrontation of these problems include, among others, the improvement of the level of service offered by the Public Transport systems, the construction of the necessary infrastructure for the pedestrians, and the implementation of demand management measures. Especially the implementation of pedestrianization schemes in city centers aims not just to the provision of a safe environment for the pedestrians, but also to the resolvment of traffic and environmental problems and to the overall improvement of the quality of life for residents, employees and visitors of an area. Therefore, the ex-ante evaluation of such measures is a difficult task due to the large number of the parameters involved.

Within the framework of this paper, the environmental impact from the implementation of major pedestrianization schemes introduced in central areas is evaluated through the use of a traffic simulation model. The model used in the research was the SATURN (Simulation and Assignment of Traffic to Urban Road Networks). The road network used in the model consisted from 44 nodes and 110 links. The following environmental parameters are examined through the use of the model : CO, CO₂, NO_x, HC, Pb and energy consumption.

The extent to which the road network is used is also examined, as expressed in travel distance (pcu*kms) and in travel time (pcu*hrs) where pcu is passenger car unit. Various alternative scenarios were developed, tested and assessed concerning their environmental impacts, and the results are presented and discussed within this paper. In addition to the model results, qualitative criteria were used, where appropriate, to assist the evaluation procedure.

The case study for which this research takes place is the city of Komotini, which is found in Northern Greece and has a population of 50.000 inhabitants. The city faces severe environmental and traffic problems due to the fact that the road network is insufficient to serve existing traffic, the use of Public Transport is limited, no environment friendly vehicles exist, and finally pedestrian trips are also limited since no adequate infrastructure exists and thus the environmental and safety conditions do not promote such trips. In order to implement demand management measures, an extensive pedestrianization scheme is examined including main streets passing nowadays through the city centre.

Since the case study is representative of medium size cities with similar environmental and traffic problems, the results are of general interest and applicability, and the same applies to the evaluation methodology which was followed.

MODELLING THERMAIKOS GULF'S DIATOMS GROWTH RATE AS A FUNCTION OF TEMPERATURE, LIGHT AND NUTRIENTS

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A deterministic model is developed to form the influence of nutrients (Silicon, nitrates and phosphates), light and temperature on spatial and temporal changes of the diatoms growth rate (μ_{\max}) from the surface of Thermaikos Gulf.

Temperature was considered to influence diatoms growth rate based on Eppley's equation (1972). The mean daily temperature, $T(t)$, of the surface water was computed as a one-year period *cos*-function with max. 27 °C and min. 6.6 °C. Light intensity, $I(t)$, was considered to influence μ_{\max} according to Steele's equation (1962), while the mean daily light intensity was calculated as a function of the maximum daily light intensity (at noon) and sunshine duration. Nutrients were considered to influence μ_{\max} according to Michaelis-Menten's equation. The daily values of nutrients' concentration, for a one year period, were estimated using cubic splines. Field data show that the daily values of temperature, light and silicon have no significant differences among stations while nitrates and phosphates have. The above model runs using three different I_{opt} for diatoms growth and data from four stations of Thermaikos Gulf.

Model's results show that during the year diatoms' μ_{\max} has three peaks and appears spatial variability. Temporal changes may be correlated with temperature, light and silicon while spatial variations with the heterogeneity of nitrates and phosphates concentration. Changes of the maximum growth rate cause continuous changes of phytoplankton composition, since different species dominate each time. Therefore, in the beginning of spring diatoms with small I_{opt} seem to be dominant, while at the end of spring and in autumn co-exist diatoms with relative higher I_{opt} . Apart of light, the concentration of nitrates seems to play an important role during these periods. The growth rate takes its minimum value between July and August where the values of nutrients are minimum, temperature is maximum and the values of light intensity are significant higher comparing with the optimum values. So, the limiting factors are temperature and light during winter and nutrients and photoinhibition in summer.

4-AMINOANTIPYRENE SPECTROPHOTOMETRIC METHOD OF PHENOL ANALYSIS. STUDY OF THE REACTION PRODUCTS VIA LIQUID CHROMATOGRAPHY- DAD – MS

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Phenol analysis by liquid and gas chromatography is sensitive and selective. In a previous paper published by our group, the sensitivity and selectivity of the spectrophotometric method assay with respect to AAP, were studied.

Six 4-aminopyrazolone compounds were synthesized and their complex products with phenols were monitored by color intensity.

In the present work the quinonoid products formed by the reaction of the six newly synthesized 4-aminopyrazolones with phenols were studied in order to find out the relation between color intensity and structure as well as the interference from other colored by-products in the spectrophotometric analysis. The products formed in this reaction were analogues to those between 4-AAP and phenols. The condensed reaction products are analyzed by liquid chromatography-diode array detection (DAD) – Thermal Beam Mass Spectrometry (TB-EI/MS) and Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI/MS). In all cases these products were analogous to the ones formed by the respective reaction between 4-AAP and phenols.

Diaminopyrazolones (DAP, DADP) do not form diquinone-imide structures. The amine group in 4 position of the pyrazolone ring seems to react more readily with phenols without allowing the formation of other quinonoid by-products.

Theoretically, the 4-amino group is more reactive due its participation in a conjugated system present in the pyrazolone ring, which stabilizes intermediate cationic forms or radicals.

All 4-aminopyrazolones form dimers and numerous other by-products. None of them absorbs in the critical spectrophotometric range 420-500 nm and therefore they do not interfere in the implementation of the method.

ANGUILLA ANGUILLA L. BIOCHEMICAL AND GENOTOXIC RESPONSES TO BENZO(A)PYRENE

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Anguilla anguilla L (eels) were exposed during 3, 6 and 9 days to 0 (control), 0.3, 0.9 and 2.7 μ M benzo(a)pyrene (BaP).

Liver biotransformation induction, was measured as liver ethoxyresorufin *O*-deethylase (EROD) activity and cytochrome P450, compared with the genotoxic effects, measured as erythrocytic nuclear abnormalities (ENA) and blood and liver DNA strand breaks, induced by BaP.

The eel's liver exhibited a highly significant EROD activity increase at 3 and 6 days exposure to 0.3 μ M BaP and at 3, 6 and 9 days exposure to 0.9 and 2.7 μ M BaP. Liver P450 did not suffer any significant increase during the experimental exposure for any BaP concentration. However, a significant increase in liver ALT activity at 9 days exposure to 2.7 μ M BaP was observed.

The liver DNA integrity measured as DNA strand breaks was significantly decreased at 3 and 6 days exposure to 0.9 and it was significantly decreased at 3 days exposure to 2.7 μ M BaP.

Blood DNA integrity was significantly decreased at 3 and 6 days exposure to 0.3 μ M BaP and at 3 days to 0.9 and 2.7 μ M BaP. Furthermore, the ENA frequency was significantly increased at 6 and 9 days exposure to 0.3 μ M BaP. However, ENA increased at 3 days to 0.9 μ M BaP and at 3, 6 and 9 days exposure to 2.7 μ M BaP.

From the above results we may conclude that the blood DNA is more susceptible than liver DNA. to genotoxic substances namely to the liver BaP metabolites.

Our experimental, results demonstrate that an increase in the eel's blood and liver DNA integrity corresponds either to a DNA repairing process and/or decreased genotoxic potential of BaP. Whereas an increased ENA frequency may correspond to a cell repairing process similar to healing wound process where the cell spits off the damaged DNA. The previously proposed experiments allowed us to relate Phase I biotransformation enzymes with different levels of genotoxicity biomarkers such as DNA strand-breakage and ENA frequency.

NAPHTHALENE AND B-NAPHTHOFLLAVONE TOXICITY TO *ANGUILLA* *ANGUILLA* L.: EFFECTS ON HEPATIC METABOLISM AND GENOTOXICITY

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A battery of biomarkers was adopted to evaluate naphthalene (N) and β -naphthoflavone (BNF) effects in European eel (*Anguilla anguilla* L.). The assayed biomarkers include liver cytochrome P450 content (P450) and ethoxyresorufin *O*-deethylase (EROD) activity as indicators of biotransformation activation, liver alanine transaminase (ALT) activity as indicator of the hepatic health condition, erythrocytic nuclear abnormalities (ENA) and immature erythrocytes (IE) frequencies as indicators of genotoxicity and haematological dynamics disturbances, respectively. Eels were exposed to an N or BNF concentration range (0, 0.1, 0.3, 0.9, and 2.7 μ M) over 3, 6, and 9 days.

Both xenobiotics revealed to be strong biotransformation inducers. After 3 days exposure, liver EROD activity was significantly increased by all N and BNF tested concentrations, exhibiting a similar dose-response dependency, i. e., a progressive increase up to 0.9 μ M and a less accentuated increase for 2.7 μ M. This pattern of response was also observed for 6 and 9 days N exposure. P450 was significantly induced after 3 and 6 days exposure, respectively for BNF and N. Liver damage, expressed as liver ALT activity decrease, was observed after 6 days exposure to 0.9 μ M BNF. Oppositely, the lowest BNF concentration increased ALT activity after 3 days exposure.

In terms of genotoxicity, only BNF displayed a significant ENA induction. This response was measurable in a well-defined point in time. Thus, ENA frequency kept similar to the control at 3 days exposure, exhibiting a significant increase only on day 6, where a dose-response relationship was clearly observed. At day 9, ENA frequencies returned to the control levels, showing inclusively a significant decrease for 0.9 μ M BNF. Concomitantly with this ENA response, IE frequency demonstrated a general decrease along all the experiment, indicating haematological disturbances able to impair the ENA expression. Despite the absence of a statistically significant ENA induction in N-treated groups, seems to be evident an ENA increase tendency, suggesting that this PAH cannot be conclusively assumed as a non-genotoxic compound.

The present results elect EROD activity, carried out in *A. anguilla*, as a useful short to medium-term biomarker of exposure to both PAH and flavonoid substances. However, some problems can emerge in the presence of high doses of xenobiotics. Concerning genotoxicity, it is hypothesized that ENA response depends on the exhaustion of the detoxification process and/or on the balance between erythropoiesis and erythrocytic catabolism, as well as on the fish DNA repairing capacity.

THE EVALUATION OF ATTENUATION PROCESS USING RISK ASSESSMENT METHOD

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The attenuation process is one of the ways how the natural decontamination of soil can be achieved. During this process the degradation of contaminants can be seen by the dechlorination of the polychlorinated hydrocarbons. During the process typical sequence of chlorination is detected. The composition of the mixture is developing during time and space as the „contamination cloud“ moves downstream the groundwater flow. On this way the composition of the mixture predictably changes. The change of the risk of this mixture during the attenuation process is evaluated by Risk Assessment Method in the contribution.

INFLUENCE OF NATURAL AND ANTHROPOGENIC SOURCES ON HEAVY METAL DISTRIBUTION IN URBAN SOILS – A CASE STUDY FROM NAPLES (CAMPANIA), SOUTHERN ITALY

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In the last decades, because of the recognition of potential health risks associated with heavy metal pollution, many scientists involved in environmental studies have focused their interest on levels and behaviour of these elements both in natural and contaminated environments. The role of the soil processes in accumulating or mobilising metals is very important in environmental science due to the central position of the soil in the hydrological cycle and ecosystem.

The metropolitan area of Naples due to intense human activities is an emblematic area affected by various environmental pollution of soils and waters in addition to hydrogeological volcanic, seismic and bradyseismic hazards. The geology of the area is prevalently represented by volcanics, erupted from the Upper Pleistocene to Recent by Mt. Somma-Vesuvius on the east and the Campi Flegrei fields on the west. The morphology of the metropolitan area of Naples city can be subdivided in flat areas, constituted by reworked pyroclastic terrains, and by hills originated by the overlapping of different welded pyroclastic flows (i.e.: Campanian Ignimbrite and Neapolitan Yellow Tuff) intercalated with pyroclastic deposits of different origins and ages (i.e.: Campi Flegrei, Mt. Somma-Vesuvius, Ischia).

In order to compile a multi-element baseline geochemical of the metropolitan area of the Napoli we have sampled for this study, in situ top soil and imported filling material (mainly soil, volcanic ash, pumice and scoriae). The sampling, pH and radioactivity surveys have been carried out on about 200 sampling sites covering an area of about 120 Km², with a grid of 0.5 x 0.5 km in the urbanised downtown and 1 km x 1 km in the sub urban areas. In each site has been determined the pH and radioactivity of each soil sample. The pH values range from 5.93. to 8.21. Pb isotope compositions, for a selected number of samples, will be determined to discriminate the natural (geogenic) from the anthropogenic components in the soils. All the geochemical data set for the top soils of Naples metropolitan area, so far investigated, have been processed to compile geochemical single element distribution, R-mode factor analysis element associations and risk maps by means of a Geographical Information System (GIS). These maps will be a useful tool for land use planning; in particular, areas potentially dangerous for residential/recreational and commercial/industrial activities will be enhanced.

GENOTOXICITY OF THE EXTRACTS FROM COMPOSTS OF DIFFERENT ORIGIN

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The ever increasing population growth, industrialization processes and development of new chemical substances have caused a drastic increase in the presence of harmful pollutants in the environment. About one-third of these chemicals showed significant genotoxic activity in different organisms. Consequently, it is not surprising that in recent years there has been concern regarding the genotoxic hazards linked to the accumulation of mutagenic substances in the different environmental compartments, through the release of both industrial and domestic wastes.

Among the different ways of treating these wastes, compost production is an ever increasing practice because of its importance from both the economic and environmental point of view. Unfortunately, very little information is available on the possible genotoxic effects of complex mixtures, such as compost, on the different biological systems, while the genotoxic properties of some organic and inorganic substances present in the compost are well known (e.g. some heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls).

In the present study, the micronuclei test in *Vicia faba* seedlings has been used in order to assess the genotoxicity of both aqueous and organic (DMSO 5%) extracts from six composts coming from different starting materials: organic fraction of solid urban wastes, rumen waste sludge, source separated municipal solid waste, high quality municipal solid waste, olive mill pomace and pig slurries.

The evaluation of the genotoxic effects of the extracts was carried out by studying the frequency of Micronucleated cells (MC) in root meristems of *Vicia faba*. Micronuclei are Feulgen positive corpuscles, localized within the cell wall in the cytoplasmic area surrounding the main nucleus and formed by chromosome or chromosome fragments that are not incorporated into daughter nuclei at the time of cell division. Micronucleated cells frequencies were scored from 15,000 cells (15 root tips, 1,000 cells for tip) for each experimental group. Means and standard errors were obtained and Student's t test, at 0.01 level, has been used for analyzing the significant differences among the treated groups and one untreated sample (Control).

The results from this study showed different behaviour of the compost studied, depending on the starting-material features: no genotoxic damage was induced by compost from olive mill pomace, source separated municipal solid wastes and high quality municipal solid wastes, whereas a significant increase in MC frequency was observed when *Vicia faba* seedlings were treated with organic fraction of solid urban wastes, rumen waste sludge and pig slurries.

Finally, preliminar results seem to suggest that composting process could be able to reduce the genotoxic activity present in some starting-materials considered in this study.

THE USE OF BIODIESEL AS ALTERNATIVE FUEL - ENVIRONMENTAL AND HEALTH EFFECTS -

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In Germany 360.000 tons of biodiesel (mainly rape seed oil methylester) were sold in the year 2000. More than 500.000 tons are expected in 2001. Besides the benefit of the CO₂-reduction from regenerative fuels it is necessary to judge the environmental and health effects that derive from the use of biodiesel in combustion engines.

Therefore, regulated and some important non-regulated emissions from neat fuels and from blends of biodiesel and fossil diesel fuel (DF) were determined. With regard to the current discussion about emissions of particles, measurements of particle size distributions, analyses of particulate matter, and determinations of its mutagenic effects were carried out. Moreover, the emissions of ozone precursors were compared for both fuels.

Biodiesel differs in its physical properties slightly from DF. This enables the engine adaptation on biodiesel by software optimization for an improved combustion. For this purpose a biodiesel sensor was developed. Preliminary modifications of injection settings like injection time and pressure indicate the opportunity of a biodiesel optimized engine.

In all, biodiesel leads, compared to DF, to positive and negative effects. However, the main positive aspects are the significant soot and PAH reductions. Moreover, the mutagenic potency of its exhaust particulate matter is much lower than that originating from DF.

On the other hand at some engines NO_x, aldehyde, and other ozone precursors like alkenes increase by use of the alternative fuel. Therefore a higher ozone forming potential was observed during some investigations.

In course of the engine tests an oxidising catalytic converter (OCC) was used, too. It was found that this OCC increases the mutagenic potency of both DF and biodiesel particulate matter emissions. With regard to this effect the use of this OCC cannot be recommended. Current tests shall reveal, whether this is a singular or a general trend.

INDUSTRIAL HAZARDOUS WASTE MANAGEMENT IN GREECE

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Every year in Greece more than 300.000 tn industrial hazardous wastes (IHW) are generated. Main sources of IHW are a small number of large and major industrial plants such as metal, chemical, refinery, cement and fertilizer industries. Those industries generate about 90% of IHW in Greece. About 600 small and medium size industries such as tanneries, textile dyeing plants, galvanizing and agricultural industries are considered to be minor sources of IHW. IHW are also produced by shipyards, petroleum transportation and storage activities. Generation of IHW in Greece is characterized by the production of small quantities and reduction of those quantities during last decade.

The first EC Directive on hazardous and toxic wastes (78/319/EOK) was enforced in 1978 and became also Greek law by the Ministerial Decision (Y.A. 72751/3054/85). This Directive lays down the general rules for the management of toxic and hazardous wastes. According to that, waste generators must ensure that the wastes they produce are properly transported and disposed off in a site or facility approved by a competent governmental authority. Storage, treatment and disposal of hazardous wastes can be carried out only by companies that have been granted a relevant permit and that holders of those wastes assign storage, treatment and disposal of hazardous wastes only to those companies. A series of EC Directives followed the first one in order to prevent environmental degradation. These Directives refer to transboundary shipments, specifications for temporary storage, collection, transportation, recovery/reuse, thermal treatment and sanitary landfill, elimination of dangerous gas emissions from incineration of hazardous wastes, elimination of PCB's PCT's and batteries containing dangerous substances.

Currently in Greece there are not any disposal facilities for IHW. The applied principal IHW management methods include:

- Temporary storage.
- Transportation and treatment abroad.
- Reuse, recycle, regeneration.

Until today, the majority of the produced quantities of IHW are temporary stored in their production sites, creating problems both for the industry and the environment.

This study presents the production processes and types of IHW produced in Greece, reviews the current European Union and Greek legislation and evaluates and suggests potential treatment methods and disposal alternatives.

INTEGRAL SYSTEMS AND WASTE MANAGEMENT IN THE AGRO-INDUSTRIAL SECTOR

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By O.M.W. (olive mill wastewater) we mean, in general, the watery residual waste coming from the transformation processes of the olive into oil. It contains the own olive water and the water from its washing and processing. The O.M.W. causes serious problems when it is poured into the rivers and soil. It represents an enormous organic matter addition, (COD between 40.000 and 210.000 ppm and BOD between 10.000 and 150.000 ppm). It generates a superficial film in the waterways and soil due to the oil content and its toxicity for the flora is remarkable. Other environmental problems that the O.M.W. produces are its phytotoxic effects, especially for the plants germination, the premature fall of the fruit and the vegetables senescence. To have a rough idea of the high pollutant power of the O.M.W., it can be said that the processing of 1.000 kg of olive it causes an equivalent contamination as a population of 300-500 inhabitants. An additional problem in the O.M.W. purification is its seasonal production. It is only generated for a period of five months per year (from November to March) that is the time that lasts the picking up and mill process of the olive. Its degradation in the nature is quite difficult basically because it contains products with high antibacterial power.

All these characteristics have motivated the total prohibition in Spain of O.M.W. pouring to the public network since 1983, encouraging ponds and lagoons construction for its elimination by natural evaporation.

Since 1993, several researchers of Valladolid University and CARTIF Technology Centre have studied the serious problem of the olive mill wastewater purification, their possible elimination and use, to avoid their poured to the annoying and problematic evaporation pools. Fruit of this research is the development of industrial plants' family based on a physico-chemical process. This has resulted in a spin-off company, which has already built some industrial plants, as follows:

- Mobile plant for the treatment of the OMW produced by a three-phase system mill. It has been shown and operated at various industry sector exhibitions.
- In Sotoserrano (Salamanca) for the treatment of the OMW generated by a mill equipped with a three-phase olive milling facility of 50 tonnes/day.
- In Jimena (Jaén) for the treatment of the OMW produced by a mill equipped with a two-phase capacity of 100 tonnes/day.
- In Atarfe (Granada) for the treatment of the OMW produced by a mill equipped with a two-phase capacity of 300 tonnes/day

The paper discusses the preliminary work made with the aim to design this innovative purification Plant. The main characteristics of this plant are:

- ✓ total elimination of the liquid effluent and of the evaporation ponds, with the resulting clearing of space in the mill;
- ✓ water recovery from the effluent and its recycling;
- ✓ energy savings derived from the use of the olive stones as fuel in the purification process, and recovery of the waste heat from water evaporation for internal use;
- ✓ total independence from fossil fuels;
- ✓ valorization of the residual cake as organic fertilizer (composting)
- ✓ use of ashes from the combustion chamber as mineral fertilizer;

NECESSITY OF TOXICITY TESTS TO THE LEATHER INDUSTRY EFFLUENTS

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Throughout the world, the assessment of wastewater discharges or effluents is focused on the precautionary principle i.e. the reduction of specific pollutants or substances in the framework of their emission policies. Chemical procedure alone can not provide sufficient information on the potential harmful effects of chemicals on the aquatic environment. In other words, the toxicity could not be explained totally by using physical and chemical information. A toxicity evaluation is an important parameter in wastewater quality and in the monitoring of discharged effluents. Many effluents are of a complex nature. This complexity limits a complete assessment with chemical analysis because of lack of analytical technologies. The toxic effects of unknown and often undetermined substances in complex mixture or with possible synergistic effects among compounds to wastewaters can be detected only by toxicity testing. In addition to these, although in some cases the effluent quality of wastewater is not violating the discharge limits, the wastewater could show toxicity.

Acute and conventional bioassays were done in the effluent samples of current leather industry treatment plant. The enrichment toxicity tests are novel applications and give an idea whether there is potential toxicity or growth limiting and stimulation conditions. Different organisms were used such as bacteria (Floc and Coliform bacteria) algae (Chlorella sp.), fish (Lepistes sp.) and protozoan (Vorticella sp.) to represent four trophic levels. Furthermore, the COD fractionation tests were done and the results were compared to these tests for assess the effect of COD subcategories such as soluble inert COD, soluble slowly and readily biodegradable COD on possible toxicity for leather industry. While the COD in effluent not exceed the discharge limits (COD= 260 mg l⁻¹), toxicity was determined in leather industry effluents on day 100. This result was explained by high soluble inert COD level (145 mg l⁻¹). On the other hand, while the COD was exceed the discharge limits, toxicity was not determined on day 1. This could be attributed to high slowly degradable COD ratio in wastewater (50% of the total soluble COD consisted of slowly hydrolyzable COD). The leather industry results showed acute toxicity for at least two organism in 7 out of 20 effluent samples. The toxicity test results were assessed with chemical analyses such as COD, BOD, phenol, sulfur and chromium.

AN EUROPEAN REGULATION ABOUT OLIVEMILL WASTE INDUSTRY.

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In the Mediterranean Area, the olive mill industry produces a huge quantity of wastes that can be considered either as a polluting stream or a resource to be recycled. If considered as a polluting wastes, they must undergo depuration before their release in the environment; if considered as a resource, they can be utilised as a soil conditioner, and/or as a starting material to obtain high value products. A wide body of literature confirms these possibility. However, due to the huge quantity of waste produced yearly, land application and composting are the technologies which can mainly be proposed to solve the problem.

The double aspect of olive wastes generates antagonism among various political groups, mainly agriculture and environment ones, because of their different point of view on this topic. Every Country has its own regulation that often vary greatly among them with a consequent non-uniform application of generally accepted guidelines. Due to the insufficient regulation, there is a need of a normative that impose a common behaviour among the UE Countries. The preliminary points to propose suitable laws are:

1. The knowledge of the state of the olive mill industry.
 - Olivemill industry dislocation;
 - Working potentiality;
 - Oil extraction technologies;
 - Waste production and management
2. Environmental Knowledge
 - Pedomorphological, hydrological and climatic situation;
 - Agricultural practices.
3. Knowledge of technologies proposed to face waste disposal and possibility of using them in efficient and economic way
4. National regulations and ecopolicy
 - Protection of resources
 - Re-utilisation of olive mill wastes;
 - Avoidance of waste
 - Environmentally compatible disposal of wastes
5. Economic valuation

The paper discusses the preliminary work made with the aim to:

- ✧ compare the regulation of the main oil producers (Spain, Italy, Greece and Portugal), taking into consideration the applicability of technologies in the environmental situation of every country ,
- ✧ elaborate common rules about the management of olivemill waste industry to propose few, clear and efficient laws.

DEVELOPMENT OF AN INTEGRATED PLAN FOR SOLID WASTE MANAGEMENT IN CYPRUS

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Cyprus is at the European Union pre-accession stage, therefore it needs to satisfy all requirements that E.U. sets in the European Environmental Policy, in order to achieve protection of the environment and public health. The management of solid waste is among the priorities of the European environmental policy, hence Cyprus it is currently developing the necessary legislative framework to address this issue. The project aimed at developing an integrated action plan for the management of solid waste in Cyprus (hazardous and non-hazardous) taking into account the special features of the island. After careful consideration of the current European and Cypriot legislation as well as the present situation, a strategic plan of targets and actions is proposed for the effective and integrated management of solid waste. The main effort should focus on the prevention and reduction of the quantity and volume of waste, promotion of reuse and recycle over energy recovery and final disposal. In cases where final disposal is unavoidable, this should be made in an environmentally friendly way. A legal gap analysis between the Cypriot and E.U. legislation concerning waste management was carried out. The basic E.C. Directives as well as the main Cypriot laws were described. A specific legislative framework referring to solid waste management, which shall govern all the targets and actions, needs to be implemented.

The categories of solid waste that were examined are the following: (i) non-hazardous solid waste (household waste, packaging waste, waste from electrological and electronic equipment, end of life vehicles) and (ii) hazardous solid waste (industrial waste, PCBs, waste oils, batteries, infectious wastes).

IMMOBILIZED NATIVE BACTERIA AS A TOOL FOR BIOREMEDIATION OF SOILS AND WATERS : IMPLEMENTATION AND MODELING

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Water and soil contamination by chlorinated and recalcitrant compounds has recently become of increasing concern. The relatively new concept of bioremediation provides a potentially cheap alternative to traditional disposal techniques in addition to representing a genuine removal of contaminants by microbial degradation as compared with the relocation of contaminants in such processes as land filling. The efficient application of bioremediation projects remains to understand the behaviors of microorganisms involved in the degradation or removal of the target pollutants at the remediation sites.

The aim of this study was to perform bioremediation systems, using isolated soil bacteria able to degrade different herbicides: Propachlor, Simazine or Oxadiazon. Toward this goal, molecular biology technology and bacteria adaptation modeling and simulation, were applied.

- We have developed molecular techniques as potential tools for efficient remediation of xenobiotics pollutants by natural microbial communities: a) ERIC primers were used in amplification by PCR assays, for the general detection of bacteria used in bioremediation processes. b) oligonucleotide probes were designed from DNA homologous regions of genes involved in aromatic ring-cleavage, and specific Fluorescence In situ Hybridization (FISH) protocol was implemented.

To understand and predict the behavior of bacteria and pollutants in the system, three modeling approaches were discussed:

- Modification of the Chemostat Model (CM): in order to give account of the observed phenomena in the lag phase, poisoning and adaptation to a new substrate. In our version of CM, a maximum (poisoning) concentration of substrate is introduced, featuring the chemical effects of cellular membrane damaging. Also, our equations reproduce the increasing ability of microorganisms to get energy from a new substrate, allowing an increasing maximum concentration.
- Introduction a model of nutrient- adsorption in different media. The porosity of the matrix medium is shown to be crucial for substrate distribution and biofilm formation.

Simulation with a cellular automaton, at the level of a single cell, is presented to describe the process of membrane permeability, considering: substrate liposolubility, adaptation and cell immobilization.

COMPOSTING OLIVEMILL INDUSTRY WASTES : FROM LAB PRACTICE TO REAL APPLICATION

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Olive tree cultivation has been an established feature for a very long time in the Mediterranean areas where the oil production industry yearly produces huge quantities of effluents that can be either considered as a polluting waste or as a resource. If considered as polluting wastes, they must undergo depuration before their release in the environment; if considered as a resource, they can be utilised as a soil conditioner, and/or as a starting material to obtain high value products. In spite of the efforts aimed at facing pollution and protecting the environment, deterioration is still occurring often due to the increase of wastes, poor use of recycling and re-use options. An integrated approach to prevent waste production through new milling low water consuming technologies and transformation of olive wastes into a “quality soil conditioner” could be an efficient management of a resource coming from olive mills. In fact the use of low water consuming technologies could reduce waste production of about 40 %. Furthermore, the waste produced can be easily bioremediated into a “quality” soil conditioner. The improvement of soil characteristics and the beneficial effects on plant growth recorded after compost supply to cropland have been object of a consistent body of investigation.

Composting and co-composting of olive mill wastes have been deeply studied from the theoretical point of view and many pilot plants demonstrated the feasibility of the process. Nowadays, building composting plants in real scale is not anymore a perspective, but a suitable possibility. The results obtained in the Italian Research Project: “Recycle of agro-industrial wastes- Sub-project: Olive oil industry wastes”, a project mainly aimed at transferring technologies to industry, confirm the feasibility of composting processes to be applied to bioremediated olivemill industry wastes in the optic of both a sustainable agriculture and environment protection.

The paper discusses some solution proposed for composting olive by-products either near olive mills or on social platforms. The first data about the economical aspects will also be presented.

REMOVAL OF COLOR FROM TEXTILE WASTEWATER CONTAINING AZODYES BY FENTON'S REAGENT

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Textile wastewater contains many harmful substance such as suspended solids, organic matter and heavy metals. It's known there is a color problem in wastewater of textile industry. Wastewater from dyeing is a dangerous source of environmental contamination. Because color is visible to the public even if the dye concentration is lower than other pollutants and need therefore to be removed from the wastewater before it is discharged

Dyeing which is using in textile industry is getting extremely color character to wastewater. Lots of textile industry use pigments and dyes to its products. Wastewater that occurs in textile industry, generally COD, has content of solid and high amount color characteristics. Dyeing of dyehome wastewater is molecular characteristic and because of carrying environmental importances, this wastewater's treatability researches and exposing the subject of treatment alternatives are very important in textile industries.

In this study, the oxidation processes were carried out using Fenton reagent (Fe^{2+} / H_2O_2). $FeSO_4$, H_2O_2 was used as material in experiment. During the study low pH range (2-3) and different Fe^{2+} / H_2O_2 molar ratios were used. The aim of study is to present result concerning the optimization of azodyes removal of color by Fenton's reagent. The synthetic wastewater was prepared by dissolving Remazol Blue RR gran, Remazol Red RR gran, Remazol Yellow RR gran in distilled water. Since azodyes are widely application area in textile industry, It was preferred in this study. Color measurement have been made using values of indexes of transparency parameter. Values of indexes of transparency = DFZ (Durchsichtsfarbzahl) in accordance to the EN ISO 7887 standards were measured by taking absorbances in 436, 525 and 620 nm. DFZ values were calculated from these measurement.

Fenton's reagent reactions were conducted in a 1000 mL round-bottom flask. The flask was maintained at 25°C with a recirculating about and shielded from light with aluminium foil.

Consequently, the method of Fenton is predicted to be succesful in removal of color.

**THE MATHEMATICAL MODELLING OF ORGANIC LOADING
ON BIODEGRADATION KINETICS AND RESIDUAL PRODUCT FORMATION IN
GLUCOSE FED BATCH REACTORS**

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Most of substances causing water pollution are organic in nature. These substances are biologically reduced, stabilized by microorganisms and become harmless for environment. Organics are converted into inorganic food elements, as a result of biological activities. Activated sludge system is a process whose aim is to remove organic matters in aerobic conditions.

The most important parameter affecting on system performance and activity is the ratio between S substrate concentration and X microorganism concentration, that is S/X (or Food/Microorganism = F/M) .While microorganisms decomposing organic substances, and synthesizing new cells they produce new products that can not be completely decomposed (inert).

The aim of this paper is to investigate whether it is possible or not to develop a mathematical model that can be used for estimation of inert product formation in the activate sludge system with the aid of experimental studies depending on different S_0/X_0 ratios of initial substrate and biomass concentrations.

Experimental studies were carried out in twenty five reactors consisting of a set of five reactors fed with glucose; each containing 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L and 500 mg/L initial Chemical Oxygen Demand (COD) concentrations respectively for each of 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L and 500 mg/L initial microorganisms concentrations. The experimentation programme went on almost two years.

The results of S (COD), X(Biomass), C(Glucose) and S_R (Residual Product) values, from each reactors, together with the F/M ratio are given. It is observed that generally whole parameters affected by F/M ratios. The kinetic coefficients like K_s , μ_m , Y and S_R parameters, which were found by the solution of equation using of least squares method were expressed in terms of F/M ratio. Equation were fitted to experimental data using MATHCAD programme, it was observed that there was a good correlation.

ENVIRONMENTAL CHARACTERISATION OF MIXED ORGANIC/INORGANIC WASTES: LEACHING BEHAVIOR

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Characterisation of industrial wastes containing inorganic/organic contaminants is a complex task, where the normalisation of environmental assessment procedures show many technical and scientific problems to be solved. From the extensive group of industrial wastes with complex composition, foundry sludges is an interesting example. They are one of the most important wastes from foundry activities. The foundry sludges, are generated from gas wet cleaning treatment, which are characterised as hazardous wastes by the European waste catalogue, 2000 that assigns them the code 100213*. Furthermore, in previous works, taking into account the Spanish regulation, the foundry sludges were found to be ecotoxic wastes, due to organic compounds such as phenol and organic carbon, and inorganic compounds such as Zn and other metallic elements.

Environmental assessment regulatory procedures based on leaching tests, which allow to characterise the environmental behaviour of the waste, have been typically the TCLP and DIN 38414-S4. Taking into account the classification of tests has been adopted recently by the CEN (European Committee for Standardisation), the leaching tests can be classified in relation to practise as “characterisation tests” aimed at understanding the leaching behaviour of materials, “compliance tests”, which are generally of much shorter duration that are aimed at a direct comparison with regulatory threshold, and finally “on site verification” tests are used as a rapid check. In this context, the leaching test for granular material and sludges, prEN 12457, at compliance level has been proposed, it is now publicly available for comment. This standard is based on different liquid to solid (L/S) ratios and distilled water as extractor fluid. The driving force behind this standard was the European Directive on the landfill of waste.

Leaching test results can be expressed either as leachate concentration (mg/l) or a constituent release (mg/kg of solid material). The basis selected for expressing leaching results should be based on the type of data comparison, which is desired. Regulatory test results are expressed most often as leachate concentrations for comparison with limit values but do not always take into account the underlying basis for the release phenomena which are observed. Results expressed as leachate concentrations permit, when the phenomenon that controls the leaching is the solubility, the comparison with the legislated limit. But, when the availability controls the leaching and for comparison of the data obtained at different liquid-to-solid ratios, it is necessary to outline a transformation of measured concentrations into mass release (mg/kg).

In this work, leaching behaviour of the foundry sludges using the compliance test prEN 12457 have been studied. Results show the solubility versus availability control of leaching. Data expressed in mg/kg reflect availability control, when data for different L/S ratios coincide (organic compounds). Data expressed in mg/l reflect solubility control when data for different L/S ratios coincide (metallic compounds). It can be concluded that it should be discussed (e.g. as waste acceptance criteria for landfills) what the appropriate limit values should be set.

TREATMENT OF MIXED ORGANIC/INORGANIC WASTES USING CEMENT/ SILICEOUS ADDITIVES BASED STABILIZATION/SOLIDIFICATION

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An environmental problem of the foundry activities is the management of industrial wastes from different processes. The foundry sludges from gas wet cleaning treatment, containing organic and inorganic compounds and, a high content of water (50%) are characterised as hazardous wastes by the European Waste Catalogue, 2000 (1), assigning them the code 10 02 13*. Due to their characteristics, they can be managed using different Stabilisation/Solidification (S/S) technologies prior to land disposal. Different mixtures of cement (or lime) and siliceous additives (silica fume, sodium silicate, silicic acid and siliceous resin sand) were used as binders. The purpose of their use is to acidify the S/S products, and at the same time, to promote the formation of metallic silicates. Acidifying the mixtures, it is expected to achieve a range of pH where, hydroxides from amphoteric metals exhibit a minimum solubility. It is known from the literature that the addition of suitable amounts of siliceous materials drives to the formation of metallic silicates instead of the corresponding hydroxides. The solubility of these species is minimum in a wider range of pH. To check if metallic silicates were formed, the Acid Neutralisation Capacity test, standardised by the Wastewater Technology Centre (WTC) was carried out. This test allows to know the metal concentration in the leachate vs pH. Besides, with the purpose of achieving a low cost process, siliceous resin sand was used.

The purpose of the present work was to develop new S/S formulations based on the use of mixtures of cement (or lime) and several siliceous materials as additives. This is to control the mobility of amphoteric metals, mainly Zn, in both leaching tests using distillate water (DIN 38414-S4 and prEN 12457), and acidic solutions (TCLP), at the same time, to keep the rest of the parameters below the European suggested regulations. Consequently, the S/S products were characterised by the determination of ecotoxicity, EC_{50} , of the TCLP leachates and the chemical characterisation of TCLP and DIN-38414-S4 leachates.

It is concluded that the best results were obtained using mixtures of cement and sodium silicate as binding material. In this system, a silicate amount range of 6 to 10 percent (in the total mixture) gives optimum leachability. It reduces the mobility of the amphoteric, mainly metal Zn in both types of tests, and also of the TOC (Total Organic Carbon), another parameter to be controlled in the sludge. Therefore, it is relevant to indicate that landfilling of S/S products is allowed for several field conditions.

POLLUTANTS AND THEIR REDUCTION IN SMALL SCALE WOOD INCINERATORS

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In the wood-processing industry huge amounts of wood residues arise. These untreated or treated wood residues and chipboards have to be disposed of. In the past a great part of them was deposited on landfills. But it is more advisable to utilize the thermal energy by incineration of this material. When combusted in small-scale wood kilns up to 1 MW only the emission of CO and NO_x are regulated after the *German Immission Prevention Act (BImSchG)*. As filter systems to remove emissions from such wood kilns would not be economic we tested the effects of primary technical measures on the reduction of pollutants formed.

Two different kilns were under investigation: An *underfeed stoker* with a power output of 250 kW of which the geometry of the furnace chamber and the boiler were altered, and a *pre-oven system* with a power output of 65 kW in which the full and partial load operations were tested. Different types of wood residues were burned and CO, NO_x, PCDD/F, and PAH were analyzed in flue gases. After cooling down the systems ashes from several parts of the kilns were collected and also analyzed for the semivolatile pollutants PCDD/F and PAH as well as for macro and trace elements in the fractioned ash particles. The latter were performed to look for the influence of inorganic wood preservatives on the basis of chromium, copper, and boron (CKB) as catalysts on the formation of PCDD/F and PAH.

Results obtained indicated a complex relation between the incineration parameters, emission of CO and NO_x, and the formation of PCDD/F and PAH, as well. Whereas the limit value of 500 mg/m³ for NO_x after *German Clean Air Act (TA Luft)* could be met in the 250 kW kiln 0.1 ng/m³ I-TEQ for PCDD/F in flue gases of waste incinerators (17. BImSchV) was exceeded in all experiments. CO concentrations were in the range of 30-134 mg/m³. Boiler ashes were contaminated up to 5,000 ng/kg I-TEQ PCDD/F. These were lower in ashes of the *pre-oven system* (1,000 ng/kg I-TEQ PCDD/F at maximum) and exceeded the limit value in flue gases just in one experiment. Concentrations of CO (88-771 mg/m³) and NO_x increased synchronously, compared with the 250 kW kiln. It could be shown that an optimization of the combustion parameters for low emissions of CO and NO_x did not necessarily result in the reduction of PCDD/F and PAH, and vice versa.

Analyses of sieve fractions (< 20 – 500 μm) of chipboard ashes for TOC, PAH, macro, and trace elements showed that concentrations of PAH and trace elements increased with decreasing particle sizes. TOC content was higher in the larger particles indicating that the latter were mainly formed of unburned wood constituents.

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REMOVAL OF SULPHUR DIOXIDE IN FLUE-GAS BY SEPIOLITE MINERAL

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Aqueous processes containing lime are commonly used in desulphurization applications. However, problems in aqueous processes force us to study this desulphurization further. To remove SO₂ from flue gas better besides lime containing aqueous processes, there is continuing need for processes which is not effected from CO₂ in the flue gas.

In this study, Sepiolite mineral, a natural adsorbent found in rich deposits around Eskisehir-Sivrihisar region of Turkey, is used to adsorb SO₂ from flue gas. For this purpose, a 40 liters premixed gas mixture containing 2000 ppm SO₂, %10 CO₂, %10 O₂ and %80 N₂ and laboratory scale adsorption column was used in this study. Relation ship between the particle size of adsorbent (<38μ, 38-53μ, >53μ) and activation temperature with respect to SO₂ hold-up capacity was investigated. Changes in the states of adsorbent after SO₂ adsorption and in their natural state were studied by means of an IR spectrometry. It was found that SO₂ adsorption capacity increases as the particle size decrease and also adsorption capacity increased on the temperature of activation increased, and adsorption capacity reached the maximum around 200°C then after capacity decreased. At 200°C, highest adsorption was 2.996 mg SO₂/g sepiolite.

ECOTOXICOLOGICAL DETERMINATION OF ESTROGENIC ACTIVITY AND TOXICITY IN A SMALL WASTEWATER TREATMENT PLANT IN NORTHERN ITALY

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Many xenobiotics, widely diffused in the environment, have the potential to disrupt the delicate balance of the endocrine system of wildlife and humans. Substances showing hormone-like actions in the living organisms are defined EDCs and may mimic, block or interfere with the synthesis, release, transport, elimination and binding of natural hormones. Since the normal functions of all organ systems are regulated by endocrine factors, small disturbances in endocrine functions, in particular during certain stages of the life cycle such as development, pregnancy, and lactation, can lead to profound and long-lasting effects. Various investigations have shown that endocrine disruptors are products of industry and may get into human body through-out the water supplies.

Two different ecotoxicological studies have been developed and applied to screen for the discharge of toxic and estrogenic substances in aquatic environment from a small industrial wastewater treatment plant in Northern Italy. 24h samples of wastewater were taken in parallel from different points of the plant: influent, 3 stages of the treatment and effluent.

Untreated samples, collected in the same point, were assayed with two toxicity test: the Microtox™ and *Daphnia magna*, recently approved by Italian regulatory laws for testing wastewater effluent limits. After solid phase extraction of 1 l sewage samples on 1g C18 (ENV+), simplified proliferation test with human estrogen receptor-positive MCF-7 breast cancer cells (E-screen assay) was performed for the sensitive quantitative determination of total estrogenic activity.

In the E-screen assay the growth of the MCF-7 cells is strictly dependent on the concentration of estrogens in the culture medium, so that the presence of estrogenic substances can be evaluated by measuring the proliferation rate in cells exposed to environment samples. Cells are plated into 24-well plates, after 24hr the seeding medium was removed and replaced by experimental medium with different dilution of the sample extracts. This quantitative assay compares the cells number achieved, after six days, by similar inocula of MCF-7 cells in the absence of estrogens (negative control) and in the presence of 17β-estradiol at different concentration: 10⁻⁸, 10⁻¹⁰, 10⁻¹² M (positive control). The bioassay was terminated by removing the media from the wells and then the proliferation was estimated by the absorbance at 595nm after crystal violet coloration. A blank sample was prepared and it did not induce cell proliferation. As additive behaviour of the estrogenic response 4-nonylphenol, DSE and benzylbutylphthalato (suspected to be estrogenic, 5μM) were proven.

The relative sensitivity of the Microtox assay, employing the marine bacterium *Vibrio fischeri*, was evaluated for its applicability in monitoring wastewater for toxicity. The results of the Microtox assay after 5, 15, and 30 min of exposure, were compared with data obtained from whole effluent toxicity testing (WET) methods that employed *Daphnia magna*.

All samples induced cell proliferation in a dose-dependent manner. The proliferative effect of the five points, relative to the positive control 17β-estradiol (RPE) was between 2 and 65% while that of the substances (4-nonylphenol, DSE and benzylbutylphthalato) between 30 and 85%. The Microtox assay results showed a toxicity only for the influent point.

A first comparison between results from estrogenic activity and toxicity load was performed.

THE USING OF MULTICOMPONENT ACTIVATED SLUDGE MODELS IN THE SERIES WITH RECYCLE SYSTEMS

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In recent years, multicomponent activated sludge models have been used instead of conventional activated sludge models containing both substrate and biomass. The importance of the using of multicomponent models have increased due to either explanation of activated sludge systems or determination of wastewater characterization.

Studies done in recent years showed that most of the concentration of soluble organic matter in the effluent of treatment systems contained soluble microbial products which occurred during biological treatment. In addition to the experimental studies, mathematical models were developed to explain product formation. For the developing of model, equation of reaction rate representing better the present situation in the system were selected.

In connection with the approaches in literature, a mathematical model that is used for estimating effluent COD concentration in dispersed media has been developed in this study. The death-regeneration approach, an approach of multicomponent activated sludge models that contain the formation of soluble inert organic matter in activated sludge systems with which carbon oxidized, was used. Because the differential equations developed for dispersed media were insolvable, the system represented with in-series reactor approach, death-regeneration and hydrolysis concepts advised in IAWPRC Task Group Model were employed.

TREATABILITY AND RECYLING STUDIES ON THE WASTEWATER OF THE TEXTILE DYEING FACTORIES IN BURSA

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Textile industry, one of the most rapidly developing industrial branch in Turkey, plays an important role because of large amount of wastewater consuming and pollutants parameters. The main pollution source of wastewater comes from the dyeing and finishing processes. The dye-stuff and polyvinyl alcohol (PVA) are the main refractory organics of concern in terms of meeting more stringent effluent standards of COD and color.

In this study, textile dyeing factories wastewaters were characterized in Bursa. Parallel to this characterization studies physical, chemical, biological and advanced treatability studies were carried out in wastewater. In physical and chemical treatability studies, %60-80 COD, %80 SS and %70-90 color removal efficiencies were obtained. In biological treatability studies, %90 COD, %40 SS and %80 color removal were obtained. The initial soluble inert COD of wastewater was determined by using the comparison methods. Color removal studies were carried out on effluent for recycling by different chemicals such as hydrogen peroxide, sodium hypochloride and activated carbon. %50-90 color removal efficiencies were obtained.

ENVIRONMENTAL PROBLEMS FROM THE USE OF SMALL RIVERS FOR THE DISPOSAL OF INDUSTRIAL EFFLUENTS.

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The use of small rivers and streams for the disposal of partly treated or untreated urban or industrial effluents is a common practice in many Mediterranean and Black Sea countries. This practice causes a lot of significant environmental problems in the area of disposal but also in the downstream-located areas. In this study, based on projects sponsored by INTAS organization and Greek Secretary for Research and Technology we tried to compare two cases of such rivers as it concerns the effects of the disposal of pollutants to their estuaries

Asopos River, near Athens is the first case. Its length is about 50km and it outflows to the south Euboikos gulf where there are a lot of touristic places and also some aquacultures. It receives the liquid effluents (about 10000 m³/day) from about 80 industries, like metallurgies, food industries, chemical industries, tanneries, poultry and cattle farms, piggeries, textile and paint factories etc. Increased problems are observed during summer when the natural flow of the river is minimised.

A similar case, as it concerns the industrial pollution is the one of river Kubitskali in Georgia. It is also a small river (mean flow about 1.5m³/sec) which flows through the city of Batumi and its estuary is in the Black Sea. Its length is about 6.5Km. The effluents of some industries pollute it and mainly the effluents of one big refinery, which is located near its estuary into the city of Batumi, which is the main port of Georgia. The effluents of the river affect the coastal environment of the city, which is also used for swimming and fishing.

During 1999-2000 period two samplings took place in every river, one in the, low flow and one high flow period. Water and sediment samples were collected and analysed for metals, nutrients, hydrocarbons and organic load. Parameters like pH, temperature, dissolved oxygen, and conductivity were measured in situ. The results of the measurements in combination with the information that we have collected about the main polluting sources in the studied rivers have given very useful information about the environmental problems of both rivers.

Although some treatment plants have been established in industries near Asopos river the polluting load that is transferred through the river to the coastal area of Oropos is still high. A significant percentage of the pollutants are in particulate form and are settled to coastal sediments. The concentration of dissolved oxygen is low and there is apparent danger for the estuarine ecosystems. In the Georgian river also, an increased polluting load has been determined, although the most industries in the area are out of work.. The percentage of particulate pollutants was lower than in Asopos, the dissolved oxygen higher. It is clear that in both cases a different management is needed in order to achieve both better environmental quality and economic development. The data of our study indicate some urgent actions in order to prevent further environmental deterioration.

CATALYTIC EFFECTS OF FE(III) DURING IN THE OXYGENATION OF FE(II) IN CONTINUOUS FLOW IRON REMOVAL SYSTEMS

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It is known that the oxygenation of ferrous iron is catalyzed by the reaction product, ferric hydroxide. Catalytic action of the ferric iron sludges on the oxidation of ferrous iron by aeration has been identified and the kinetics of this catalytic reaction has been formulated by the authors. The oxidation of Fe(II) was studied in batch reactors in which the concentration of Fe(III) was in the range of 0-600 mg/l. It has been experimentally demonstrated that there is no significant effect of Fe(III) on the ferrous iron oxidation at Fe(III) concentrations beyond 600 mg/l.

However, in natural waters Fe(II) is found commonly to be in the range of 0.01-10 mg/l. These ferrous iron concentrations are not high enough to maintain the high levels of ferric iron in the aeration tank. Therefore, similar to the activated sludge processes used in wastewater treatment, it is suggested that the required Fe(III) concentrations can be maintained by recycling Fe(OH)₃ sludge back to the aeration tank.

In this study, an iron removal process which makes the use of the catalytic effect of ferric iron is proposed. For this purpose, a lab scale continuous flow aeration/sedimentation unit with or without recycle was built. The aim of the study was to verify the validity of the findings of the batch type oxidation experiments for also continuous flow conditions. The efficiency of oxidation was about 57-79% when the system was operated without recycle. Fe(II) removal efficiencies were increased to 80-89 %, 90-97 % and 98-99.6%, for the recycle ratios of 50 %, 80% and 100% respectively. The increase of the Fe(II) removals were explained by an increase of ferric concentration in the aeration tank as a result of recycling. The higher the Fe(III) concentration in the aeration tank the better was the Fe(II) removal efficiency upto to the Fe(III) concentration of 300mg/l. Beyond this level, no significant increase in removal efficiency of ferrous iron was observed with increasing ferric iron concentration.

INVESTIGATION OF THE CATALYTIC REACTION KINETICS OF Fe(III) ON Fe(II) OXIDATION AT VARIOUS PH VALUES

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One of the methods for removing Fe(II) from drinking water is the oxidation of Fe(II) by atmospheric oxygen and precipitating in the Fe(OH)₃ form. Catalytic effect of Fe(OH)₃ on the oxidation of Fe(II) has been investigated by several researchers (Tamura, 1976; Sarikaya, 1990; Tüfekci, 1996). In this work, the catalytic effect of Fe(OH)₃ slurries on the oxidation of Fe(II) was studied at various pH values using a batch reactor. Reaction kinetics was studied at three different pH values (pH= 6.2, 6.5, 6.7) and Fe(OH)₃ concentrations ranging from 0 to 1000 mg/l. Reaction rate constant (k_{cat}) was found to increase linearly with increasing Fe(III) concentrations up to 500 - 600 mg/l and decreased with further increases. The model developed for batch system was applied to a continuous system. The results have shown that smaller reactors can be used due to catalytic effect of Fe(OH)₃ on Fe(II) oxidation.

THE EFFECT OF ORGANIC MATTERS ON MANGANESE OXIDATION

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In oxygen-free aquatic environments, such as groundwaters and hypolimnetic waters of eutrophic lakes, manganese exists predominantly in the manganese state Mn(II). In these waters, certain natural organic compounds like humic material also exist. The aim of this study is to find out the effect of tannic acid and acetic acid on the stabilizing Mn(II) to Mn(IV). Experimental studies have been carried out in two stages in a batch system. In the first stage, the catalytic effect of Mn(IV) on manganese oxidation by atmospheric oxygen is studied for the range of 0-300 mg/l Mn(IV) concentrations, keeping Mn(II)=25 mg/l. It has been found that k_{cat} increases linearly with increasing Mn(IV) concentration up to about 300 mg/l. In the second stage, it has been studied how oxidation of Mn(II) and catalytic effect of Mn(IV) are effected from tannic acid and acetic acid. The results of this stage are tannic acid completely inhibited the oxidation of manganese, acetic acid had no observable effect on the oxidation reaction.

**THE TOXIC EFFECT OF SOLVENT ON THE BIOLOGICAL DEGRADATION OF
PENTACHLOROPHENOL AND PENTACHLORONITROBENZENE
BY WHITE ROT FUNGUS**

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PCP (Pentachlorophenol) and PCNB (Pentachloronitrobenzene) are included among potential environmental pollutant due to their strongly durable aromatic structures with chlorine groups. In order to minimize negative effects of these material used in large quantities as fungicide, a study was made on determination of their biological break-down rates and respective conditions thereof. White rot fungi (*Phanerochaete chrysosporium*) is used in determination of biological breakdown. Culture medium containing basic nutrients and tracing items are utilized at the experimental work performed. pH rating of culture medium adjusted to 5. PCP, PCNB and fungi were added to the culture medium of 50 ml volume in separate containers with desired consistency. PCP and PCNB are added to culture medium by solving in acetone. These erlenmeyer flasks were left to incubation at 35 °C for measurement at specific times. In order to investigate the effect of the utilized solvent to the efficiency of the biological degradation, 10 times more solvent was used while PCP and PCNB were added to the culture medium. Results were compared with the trials in which the solvents were utilized as minimum.

By the end of 21 day incubation, It was observed that the used solvent inhibited the biological degradation of PCP and PCNB dramatically and accordingly decreased the amount of the formation of biomass.

METAL LEACHING FROM AGRICULTURAL WASTES USED IN THE DEGRADATION OF H₂S BY BIOFILTRATION

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Biofiltration is a promising technology involving the passage of a polluted air stream through a packed-bed containing micro-organisms that are able to degrade pollutants into harmless products. This technology has significant economic advantages over other air pollution control technologies. The operating/energy costs and the relative capital cost are low, the removal efficiencies exceed 90%, the system operates at ambient temperature and the by-products are harmless or even reusable. The “heart” of a biofiltration system is the filter bed or packing material, which provides a nutrient source, a method of attachment for micro-organisms and, frequently, its own microbial population. This material should have the following characteristics: (1) high moisture retention capacity, (2) high porosity and high buffer capacity, (3) high available nutrient content, (4) a diverse and adaptable microbial population, (5) low cost, (6) and long life (mechanically resistant and chemically inert and stable). The effects of continuous biofilter operation on the physical and chemical properties of the packing material are poorly described in literature. Furthermore, the changes involved in the system should be carefully studied as this information will determine the lifespan and suitability of the packing bed and the possible final use of this material after biofiltration.

The main objective of this work was to study the composition of the leaching solution obtained from a selected support material after different periods of operation in a biofilter used for H₂S degradation. The support material used in this study consisted of a compost made of pig manure and sawdust and extruded into pellets in order to reduce pressure drop. This material was packed into a plastic material bioreactor, with an inner diameter of 0.1 m and height of 1 m divided into three sections of 0.33 m each. At the laboratory, we used a synthetic raw gas stream which was generated by mixing H₂S pure gas (Liquid Air, purity 99%) with prehumidified air. The in-flow H₂S concentration varied from 50 to 250 ppmv.

In order to study leaching problems from the support material, the metal content in the pellets was measured before their use in the biofilter and after continuous operation for several weeks. The content of non-essential metals such as lead, cobalt and nickel in the original pellets was 21, 11 and 22 µg per gram of dry material. These values were low enough so as not to inhibit biological activity. Other essential elements for wildlife like copper and zinc, were present in important amounts (156 and 506 µg/g dry compost respectively) which, although necessary for microbial development, could leach from the reactor. Elements like iron (6294 µg/g), sodium (5647 µg/g), potassium (22692 µg/g), calcium (60074 µg/g) and magnesium (7552 µg/g) were the main ones in the original support and their leaching could cause relevant pH changes in the system.

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AS(III) REMOVAL DURING BIOLOGICAL OXIDATION OF IRON FROM GROUNDWATER

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The use of biological treatment as a potential method for the simultaneous arsenic and iron removal from contaminated groundwater was investigated. The method was based on the growth of certain species of indigenous bacteria, belonging to the *Gallionella* and *Leptothrix* genus, which are capable of oxidizing iron cations. Iron was completely oxidized by the bacteria and removed from the aqueous stream by 99%, through its transformation to insoluble oxides and its removal by a suitable filtering device (polystyrene beads). Arsenic was found to be removed by 99%, depending on the applied conditions of redox potential and dissolved oxygen.

The above treatment method offers several advantages towards conventional physicochemical treatment techniques, as it is more economic and environmental friendly, due to the simultaneous removal of iron and arsenic and to the fact that any additional use of chemical reagents can be avoided, while there is no need for monitoring of a breakthrough point.

EFFECTS OF FOULING WITH IRON IONS ON THE CAPACITY OF DEMINERALIZER ION EXCHANGE PROCESS

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Ion exchange process technologies have commonly been used in some applications i.e. demineralization, softening and dealkalization as standard water treatment processes. Demineralization is the process of removing dissolved ionic impurities from water. Basically, demineralization is a two-step process treatment with both cation and anion resins. The influent water is passed through a column of strong-acid cation exchange resin in the hydrogen form to exchange the influent salts. The corresponding acids are then removed by passing the cation effluent through a column of anion exchange resin in the hydroxide form to replace the anions in solution.

Certain changes appear in the ion exchange material during its lifetime, as it cycles from regenerated to exhausted form. These changes frequently due to by fouling of ion exchange resins. When water containing objectionable substances comes into contact with resin, impurities could clog pores and coat resin surface. In that case, the ion exchange mechanism can become inhibited, producing poor water quality and quantity and decreasing the resin's operating life span.

Almost all water supplies contain iron. This metal precipitate may be created by corrosion and picked up from piping, tanks, regenerating vessels and other equipments. Iron fouling of demineralizer ion exchange process results in an increase in the effluent level of iron, reduction in operating capacity, or possibly a reduction in backwash efficiency under identical operating conditions. Because of pore clogging and the degradation of functional groups, particularly iron fouling of anion resins must be prevented.

In this study, the changes on the operating capacity of demineralizer ion exchange process in the presence of iron ions were investigated.

**THE REMOVAL EFFECIENCY OF THE EXPERIMENTAL WASTEWATER
TREATMENT PLANT IN THESSALONIKI - GREECE.**

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The present investigation was planed to gain information about the removal efficiency of an experimental wastewater treatment plant (Wastewater Stabilization Ponds), designed by N.AG.RE.F. (National Agriculture Research Foundation). The system comprised of three independent triplet-lines of W.S.P. (A, B, C) through which the sewage was sequentially transferred with total retention time 60-75 days. The first pond of each line has a depth of 1.75m and a volume of 1380m³ and the second and third ponds have a depth of 1.25m and a volume of 900m³. The A-line receives preprocessed wastewater from the Municipal wastewater treatment plant, which first goes to an anaerobic pond. C-line receives wastewater after undergoing primary treatment. Biological, physical and chemical parameters were studied on ponds of triplet lines A and C during September 1999 – April 2000. Temperature, phytoplankton biomass, pH and dissolved oxygen concentration seemed to have a significant influence in removal efficiency for both lines. According to these conditions, PO₄ removal in A and C line varied from 20-86% and 9.7-80% respectively. Ammonia removal ranged from 9-86% (A) and 19-89% (C). COD and TSS acquired negatives values when phytoplankton biomass was increasing in the ponds. Finally, the H₂S removal ranged from 50-89% (A) and 40-92% (C) according to the Purple-sulfur bacteria biomass that was dominant when anoxic and sulfide-rich conditions prevailed in the ponds.

AN INVESTIGATION OF CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY IRON IN WATER TREATMENT

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Catalytic oxidation processes have been demonstrated to be quite effective for the removal of various synthetic and natural organic compounds (trihalomethane precursors) in water. The effectiveness of these processes are attributed to the generation of highly reactive and non-selective hydroxyl radicals by the catalytic decomposition of the common oxidants. Among these catalytic oxidation processes, the combination of hydrogen peroxide in the presence of iron oxide has been under investigation in recent years, for the removal of synthetic organics in water. The previous results indicated that the process could remove synthetic organics from water. On the other hand, its treatment potential for the removal of trihalomethane precursors has not been investigated yet. Upon chlorination, humic substances have been indicated to be the trihalomethane producers in natural water.

In this research, catalytic reactions of hydrogen peroxide with iron oxide particles in the presence of humic substances was examined in order to provide an insight to the treatment potential of the process for the trihalomethane precursors. For this purpose, catalytic decomposition characteristics of hydrogen peroxide and the corresponding changes in the UV absorbances related to the concentration of humic substances was investigated at various operational conditions and water quality characteristics. The experiments were conducted in the solutions at various dosages of hydrogen peroxide and iron oxide and concentrations humic acid and inorganic carbon and pH values. Granular goethite, (α -FeOOH) with a size range of 30 to 80 mesh was used in the study. Commercial humic acid was purchased from Aldrich Chemical Company. Experiments were conducted in batch reactors containing 500 ml of synthetic solutions that was mixed thoroughly for uniform distribution. Samples were withdrawn from the solutions at specific time intervals and filtered through Whatman No.1 size filter paper to separate the iron oxide particles from the solution. Then, filtrate was analyzed for the hydrogen peroxide and dissolved iron concentrations, and UV absorbances. Based on the experimental observations, decomposition kinetics were determined and the reactions in the process have been evaluated.

The results indicated that hydrogen peroxide was decomposed on iron oxide in the presence of humic acid. Compared to the decomposition characteristics in the absence of humics (based on the previous studies of other researchers), decomposition rate of hydrogen peroxide was observed to be decreased in the presence of humic substances. The application of various dosages of hydrogen peroxide did not affect the decomposition rate significantly. On the other hand, increase in iron oxide dosages increased the decomposition rate of hydrogen peroxide. The effect of pH, inorganic carbon and humic substance concentrations was observed not to be substantial on the rate of decomposition. The UV light absorbances of the solutions were observed to be slightly affected during the experiments.

OPERATING EXPERIENCES WITH A CIRCULATING FLUIDIZED BED WITH SEPERATING BARS

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For the production of particle boards and MDF-boards used in the furniture industry the company Egger in Brilon needs steam and electricity. This steam and electricity is produced in a power plant consisting among other plants of two 100 t/h steamgenerators with circulating fluidized beds combusting waste wood derived from waste furniture and production waste like wood dust from grinding the boards.

For start up oil or gas can be used.

The special design of the fluidized bed are the separation bars instead of cyclones, which are now installed after the combustion chamber before the convective superheater and economiser tube banks and the multiple cyclone before the gilled tube economiser.

In the paper the problems of the initially not cooled separation bars are described, which led via several design stages to the totally cooled design, which is now in satisfactory operation since more than two years.

Also other changes like a cooled ash recirculation pipe with a siphon from the separation bars to the bottom of the combustion chamber, evaporator panels in the combustion chamber and a so called open nozzle bottom are described.

The non symmetric arrangement of the ash recirculation led to some problems concerning the emission limits, which could initially not be kept all at once. After some changes in the overfire air also these problems could be solved, so that the steam generators are now operating satisfactorily since more than one year.

**INVESTIGATING THE SPECTRAL SIGNATURE OF UNCONTROLLED
LANDFILL SITES IN LESVOS ISLAND, GREECE**

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Any material sited on the earth surface has a specific spectral response as result of the reaction between the object and the incident electromagnetic energy. Until recently, not many results have been published concerning the spectral response of uncontrolled landfill sites and its relationship with electromagnetic energy. The way in which satellite detectors register emitted radiation from waste has not been well known to scientists.

In order to find out and finally register the spectral response of solid wastes not covered with soil we worked on field research and selected as a case study area Lesvos island, Greece.

The disposed satellite image was taken on 26 August 1999 by satellite Landsat TM covering the whole island of Lesvos. We worked on 13 uncontrolled landfill sites.

The field and computer analysis showed that waste reaches a spectral response different from the neighboring land covers. In addition, supervised classification procedure, using specific remote sensing software, incorporates all the uncontrolled landfills in one class.

EVALUATION OF COAGULATION/FLOCCULATION PROCESS FOR S.GIOVANNI A TEDUCCIO MUNICIPAL WASTEWATER TREATMENT PLANT

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The coagulation process is a versatile method used in: i) drinking water production, ii) industrial and domestic wastewater treatment, iii) sludge conditioning, iv) hazardous wastewater treatment. Coagulation is mainly based on the use of Al(III) or Fe(III) metal salts alone or with the combination of calcium salts and the use of polyelectrolyte as flocculants. Coagulant and flocculant dosages vary in a wide range aiming at maximum removal efficiency of pollutants using minimum (optimum) dosages at optimum pH.

S. Giovanni a Teduccio wastewater treatment plant was initially designed in 1960 as a classical biological treatment plant, in 1970's the necessity of the enlargement of the system upon the inflow increase was implemented by changing system to chemical treatment process considering the lack of space. The present system includes screen, sand grinder, oil removal, coagulation/flocculation /sedimentation units, disinfection using hypochlorite, mechanical dewatering, thermal sludge conditioning following a disposal to the landfill area.

Influent chemical characteristics of the plant, representing a medium-sized municipal wastewater including industrial and urban drainage wastewater, are calculated on the basis of mean and standard deviations of 34 measurements as: inflow rate=198±89 m³/h; pH=8±0.2 ; COD=448±170 mg/l; TSS=153 ±75 mg/l; BOD₅=139±69 mg/l; T-P=4±1,5 mg/l; NO₃⁻=30±6.3 mg/l; NH₄⁺=32±12 mg/l; Org-N=7±7 mg/l; Fe=1±0.7 mg/l, Cd=0.3±0.5 mg/l; Ni=0.4±0.3 mg/l; and Pb=2±0.2 mg/l. On the other hand, effluent chemical characteristics are obtained as: pH=8; COD=211±61 mg/l; TSS=69±26 mg/l; BOD₅=87±17 mg/l; T-P=3±3 mg/l; NO₃⁻=22±6 mg/l; NH₄⁺=24±10 mg/l; Org-N=4±2 mg/l; Fe=1±1 mg/l, Cd=0.2±0 mg/l; Ni=0.4±0.3 mg/l; and Pb=2±1 mg/l. Frequency analysis COD measurements were 680 mg/l and 280 mg/l at a 90 % of time in influent and effluent, respectively. Besides, microbiological parameters were measured in influent as: 10.7*10⁶; 5.5*10⁶; 1,7*10⁶ and effluent wastewater after disinfection as, 8.2*10⁶; 4.3*10⁶; 0.7*10⁶ of total coliforms, fecal coli and *Streptococcus faecalis*.

Italian water quality control discharge limits allow to have 160 mg/l of COD and 80 mg/l of TSS before discharging to the receiving water. Thus, this study was designed to improve the removal efficiency of the system. A series of Jar-test experiments with 1 min for rapid mixing, 20 min for slow mixing and 30 min for sedimentation, was conducted on 15 samples having COD and TSS contents varying between 215-380 mg/l and 100-150 mg/l, respectively. Al and Fe salts were tested at different pH values varying between 4-10 for Al and 5-8 for Fe salts and coagulant dosages were chosen as 150 and 450 mg/l considering proper COD/coagulant ratios. Although each coagulant provided high COD and TSS removal efficiencies between 45-90 % in accordance with the literature, it is concluded that the maximum removal efficiency providing discharge limits is obtained for the combination of FeSO₄·7H₂O + Ca(OH)₂ even at a concentration of (150 + 50) mg/l using the same polyelectrolyte at a concentration of 12 mg/l at pH 8. Meanwhile, in the plant 200 mg/l of FeSO₄·7H₂O is being used with the addition of 60 mg/l Ca(OH)₂ at pH 8-9, the required efficiencies are not obtained upon the technical application problems including non existency of an automated system.

OPERATIONAL PROBLEMS IN SMALL WASTEWATER TREATMENT PLANTS: A CASE STUDY

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Small wastewater treatment plants are designed to serve for 1000-10000 population equivalent and a basic characteristic of them, many operational problems, including bulking and foaming, occur because of the inflow fluctuations.

The plant is located in Silivri which is a town of Istanbul at a distance about 65 km in the SW direction for serving around 7 thousands population equivalent living in an apartment block district. In fact, Silivri maintown has a physical treatment following a deep sea discharge line. But, the future capacity for the year 2020, has been already reached by unexpected population increase because of a huge amount of imigration. So, the apartments had to solve their wastewater problem locally. During the EIA phase, the best ultimate disposal alternative was considered to be the disposal to the river flowing nearby as far as the effluent characteristics of the biological treatment plant which are the following: COD=170 mg/l, BOD₅ = 50 mg/l, SS = 200 mg/l, oil and grease= 30 mg/l, NO₃⁻= 5 mg/l, Total phosphorous (T-P) = 1 mg/l and NH₃-N=0.2 mg/l meet the receiving water standards. The plant was designed as activated sludge system assuming 10 days of sludge age and 8 hrs of hydraulic retention time. Influent BOD₅ was also assumed as 240 mg/l while effluent characteristics would be COD=100 mg/l, BOD₅=50 mg/l, SS=15 mg/l, TKN=10 mg/l which would be lower than limits. In five years of total operational period, especially in summer season odour problem, sludge bulking, aeration capacity decrease resulting in a decrease of sludge activity with respect to low system performance obtained were observed.

Including April- June, 2001, a wastewater characterisation study was realized parallel with microbial population examinations, and fluctuations in inflow. Chemical analysis showed that inflow was presenting a strong domestic wastewater character as refereed by Metcalf&Eddy (1995) in tems of COD, BOD₅, SS, TKN and T-P parameters which were measured in a range of 500-700 mg/l, 250-400 mg/l, 190-220 mg/l, 70-85 mg/l, and 9-15 mg/l respectively. The inflow rate was changing daily and also hourly which was tried to compensatsate by a balancing tank of 12 hrs retention time. Moreover, the inflow ratio was higher than expected which means that system was under overloading. Although system performance is still high in terms of carbon-based substrate removal (> 90 %), discharge limits were not provided especially for N and P parameters related to the microbiological examinations showing us there was a high density of *Nocardia* bacteria which is the most significant evidence of foaming and bulking and an occurance of low or high SVI and low MLVSS/MLSS ratio. For the improvement of the system effiency and to solve the other operational problems, different approaches were applied including increasing of return sludge ratio, incresing of oxygen concentration in the aeration basins which provided an increse in removal efficiency parallely to a better microbial population.

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EFFECT OF THREE ORGANIC WASTES ON THE ADSORPTION BEHAVIOUR OF NORFLURAZON IN SOILS

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Norflurazon is a selective herbicide effective against many annual broad-leaved weeds. Its retention in soils is related to the organic matter, being subject to considerable leaching in sandy soils with low organic matter content.

Application of organic wastes to soils can be a good method to reduce pesticide losses due to leaching processes, and also has been generally accepted as a disposal practice that recycles beneficial plant nutrients. However, a wide diversity of organic wastes can be applied on soils of very different characteristics, and the behaviour of these systems with respect to pesticides adsorption can be also very different. For this reason, the aim of this study was to assess the influence of three organic waste amendments on norflurazon adsorption-desorption processes in several soils with very different properties, as a first step to evaluate the potential leaching of this pesticide through organic fertilised soils.

Three organic amendments were used: a commercial product manufactured from olive mill wastewater and other plant residues, an urban waste compost, and wastes from paper industry. The organic carbon amendment of the soils was carried out by mixing thoroughly, during 24 hours, 300 g of the original soil with 20 g of the three amendments. The amended soils were used immediately after preparation and also after aging during two months at 37°C, adding water periodically.

Quadruplicate adsorption experiments were done by mixing 10 g of the native and amended soils with 20 mL of 0.01 M $\text{Ca}(\text{NO}_3)_2$ solutions, containing various concentrations (4, 8, 12, 16, 20 mg L⁻¹) of norflurazon. After shaking for 24 h at 20 ± 1 °C, the suspensions were centrifuged and the concentration of norflurazon in the supernatant was determined. Desorption experiments were performed after adsorption equilibrium was reached, by removing half of the supernatant after centrifugation, replacing it by 10 mL of 0.01 M $\text{Ca}(\text{NO}_3)_2$ solution, allowing equilibration for an additional 24-h period, and after that operating as in the adsorption experiment. This process was repeated twice more.

As a consequence of the basic pH of the residues, the soil pH was higher after the addition of the waste fertilisers. The OM content of the soils also increased after fertilisation, but decreases a little after ageing.

Norflurazon adsorption increases in some of the fertilised soils, specially in those soils with a very low OM content, but decreases in those soils that adsorbed a high amount of pesticide before fertiliser addition. The effect of the different waste fertilisers added on norflurazon adsorption depends on the properties of the soil in which it is applied.

Norflurazon desorption increases in all cases in fertilised soils in comparison to pesticide desorption from native soils, even in those fertilised soils in which the pesticide adsorption was very high. The waste fertiliser that gave a higher norflurazon desorption was the urban waste compost.

CHEMICAL ANALYSIS OF SEDIMENTS OF THE WASTEWATER TREATMENT PLANT IN MOBARAKEH STEEL COMPANY

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A huge amounts of sediments are producing in wastewater plants in Mobarakeh steel factory every year. In order to investigate reusing and adverse environmental effects of these sludges, a chemical analysis and determination of heavy metals was performed.⁽¹⁾

In this work, several samples from the sediments of wastewater treatment plant of the factory were collected. A mechanical sedimentation was performed for fractionation separation. Several samples were digested with a mixture of HNO₃ and HF. The extracts were analysed for Pb, Cd, Cr, Ni, Zn, Mo, and Al.⁽²⁾ The determination were carried out on a Varian-Techtron, Model A-1000 atomic absorption spectrometer. Table 1 indicates the results of this determination.

Table 1: Concentrations of heavy metals in wastewater treatment plant sludge (µg/g).

Element	Concentration
Pb	33
Cd	3.8
Cr	37.8
Ni	79
Zn	300
Mo	--
Al	540

Identification of different phases in the sediments were also performed by using SEM and EDX techniques. As a result the sediments can not be used in agricultural any more and these sediments should be disposal in a suitable manner.

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LANDFILL GAS EMISSIONS IN ISTANBUL-KEMERBURGAZ SOLID WASTE DISPOSAL SITE

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Istanbul is one of the biggest cities in Mediterranean Region. Because of huge number of its population there are massive amount of solid waste in Istanbul. Major portion of this solid waste contains organic substances. Because of this phenomenon vast amount of landfill gas is produced by solid waste in Istanbul. For example Kemerburgaz that is a major solid waste disposal site in Istanbul there are some important landfill gas emissions. In this study some of landfill gas emission data were given and evaluated on environmental impacts.

TECHNICAL ASPECTS AND REGULATIONS RELATED TO SAFETY OF WORKERS IN BUILDINGS FIELD

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The buildings field, for his particular nature, represents one of the most dangerous activity for the worker's health and safety.

The present research showed that most labour accidents happen both for initial choices carried out before the beginning of works – it is necessary, for this reason, to carry out the survey about safety and health already in the first phase of the project – and the extremely variety of duties of workers which is frequently the cause of a dangerous and irrational works.

It was noticed that the italian situation related to the accidents, even lethal, in this field – although the current regulations about prevention and safety – is however worrying.

Often the firms consider the safety as an added cost or a mass of bonds and so they don't respect the law.

The general factors of risk are related to the necessity to guarantee the safety of workers and the hygiene of work sites. The most frequent risk are mechanic, electric, biological, microclimatic, fire and exposure to chemical products (with corrosive, toxic, harmful, irritating, properties, etc.) and to pollutants substances (for instance the Persistent Organic Pollutans –POP), etc.

The fundamental aspects related to “diseconomies” and “disaffections” are neglected – more than primary aspects related to human safeguard which proceed from a default of a “safety culture”.

An other cause of accidents, sometimes even lethal, is related to imprudence or distraction. Besides the “habit” stands in the way of workers to choose a safe behaviour.

To reach an opportune knowledge in this field it is necessary to involve political and managerial forces.

Particularly the aim of the present research, starting form a thorough examination of national and european regulations about the legal-institutional and technical-environmental aspects of the “building site-directive”, is to set up the necessary conditions in order to interpret the D.Lgs. 494/96 – awaiting a supplementary and corrective legal intervention – considering the purpose of the directive and getting the planned result, following the constant leanings of the Court of Justice of the European Union.

INDUSTRIAL WASTES OF THESSALONIKI, GREECE

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The present study is addressed to depict the present state of the industrial waste management in the greater area of Thessaloniki and to suggest methods for their treatment. It presents the Greek and European legislation. The main industrial wastes were estimated and the state of the art regarding the production and disposal of the industrial wastes in Thessaloniki is presented. It was resulted that the major quantities of waste concern phosphogypsum, anhydrous gypsum, used catalysts, olive ginning waste, and acid alkali sludge. Methods for their treatment are recommended.

LAGOONING OF WASTES FROM IRON ACTIVITIES: CHARACTERISATION AND EVALUATION

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Landfilling has been a common practice of management of wastes. However, this provokes an important environmental impact when technical considerations are not taken into account.

In this work is assessed the environmental impact that an iron activity from Northern Spain causes when wastes from its process are disposed into lagoons. Several areas adjacent to the plant were excavated and sludges and waste water were transported into the excavation. Little attention was paid originally to the characteristics of deposited wastes and the technical conditions of soil.

A preliminary research was performed to characterise the wastes originated at the factory. Subsequently, the environmental effect of these wastes deposited in the lagoons was evaluated. The methodology of characterisation has been performed following the criteria of Spanish and UE regulations. Physical and chemical parameters (moisture, heavy metals, Total Organic Carbon, phenolic compounds and cyanides) have been analysed. Besides, the ecotoxicity of samples has also been determined.

It is important to note the sampling methodology made on the lagoons in order to obtain a reliable information. Techniques used in sampling of soils and sediments have been applied.

OLIVE MILL WASTEWATER TREATMENT BY MICROORGANISM ISOLATION

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Olive mill wastewater (OMW), a toxic effluent from the olive oil production, constitutes a major environmental problem, especially in the Mediterranean countries. OMW is a mixture of oily compounds, inorganic salts and water, containing large amounts of sugars, phenolic compounds, tannins, polyalcohols, fatty acids and lipids. As a result, OMW are highly toxic towards microorganisms and plants and several studies have been performed in order to develop an efficient method for their treatment. However, until now, no economically acceptable method for OMW treatment has been found. The aim of this study is to determine an effective biological method for the treatment of OMW by developing specific aerobic and anaerobic microorganisms, to study their optimum growth conditions and to investigate a number of solid natural materials acting as supports for the biodegradation of toxic substances.

OWM samples were collected from an olive oil mill located in Thessaloniki, Northern Greece. From these samples several microorganisms were isolated, including 19 aerobic and 3 anaerobic species and their growth was observed in contact with wastewater samples for 1-2 months. Among the aerobic microorganisms, 11 of them were able to grow up in the presence of OMW. However, different growth patterns were observed for these microorganisms, ranging from very fast values (4 hours) to slower ones due to differences in the acclimatization period. In addition, the use of cellulose rich materials as microorganisms support, resulted in the enhancement of toxic substances biodegradation and in an efficient OMW treatment.

THE INVESTIGATION OF OUR AND NUR EXPERIMENTS IN NITROGEN PHOSPHORUS REMOVAL ACTIVATED SLUDGE LAB -SCALE STUDY

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Activated sludge systems are widely used in wastewater treatments currently. Considering water quality management, not only organic carbon removal, but also nutrient removal are important for stringent water discharge standarts. Therefore, the activated sludge systems are widely used both carbon and nitrogen and phosphorus removal in new wastewater treatment systems or upgrading of existed systems. The determination of system compounds and kinetic parameters for modeling of these systems are important. For this purpose, the respirometric measurements are used in order to show electron consumption rate of biomass.

In order to determinete OUR (oxygen utilization rate) and NUR (nitrate utilization rate) parameters, the lab-scale activated sludge including anaerobic anoxic and aerobic zones was used. Firstly, the performance of the system was continously controlled from influent and effluent samples. OUR and NUR measurements gave an idea about the this kind of nitrogen-phosphorus removal systems. Moreover, P uptake in the anoxic zone was investigated. It was found that phosphorus uptake in the anaerobic zone was related to substrat type consumed biologically. OUR and NUR measurement were observed lower compered to continous activated sludge measurements. This could be considered that mix culture of the system affected the system performance, due to competition of denitrification bacteria and poly-P bacteria.

NITROGEN AND PHOSPHORUS REMOVAL IN LAB-SCALE ACTIVATED SLUDGE SYSTEMS

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The phenomenon of anoxic phosphate uptake with simultaneous denitrification was studied. Experiments have been carried out with biological nutrient removal in a single sludge systems by using the activated sludge samples from the modifications of nutrient removal activated sludge systems. The lab-scale reactor allows nitrification, denitrification and phosphorus removal after alternatively by adding anaerobic, anoxic zone prior to activated sludge system. The aim of the study was to evaluate the denitrification behaviour in biological excess phosphorus removal (BEPR) activated sludge systems. Based on experimental study, the performance of the system for the KOI, NH₄ and phosphorus parameters was reported. The study indicate that a significant fraction of the poly-P organisms can use as an electron acceptor in the absence of oxygen for oxidation of stored PHB and simultaneous uptake of phosphorus.

THE INVESTIGATION OF NITRATE REMOVAL IN FIXED-FILM COLUMN REACTOR BY USING *PARACOCCLUS DENITRIFICANS* UNDER THE EFFECT OF DIFFERENT CARBON SOURCES

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Conventional systems used wastewater treatments are based on the use of the activities of the both immobilized and suspended systems in order to remove of carbonaceous and nitrogenous compounds. The immobilized cells act important factor for removing of the organic and inorganic compounds from domestic and industrial plants. The biofilm or fixed film reactors are widespread form of immobilized cells for wastewater treatment. They are known with high specific surface area since they have high level of liquid flow and partly easy of operating skills. In this paper, the fixed film column reactor was used with the *Paracoccus denitrificans* (heterotrophic microorganism) pure culture for the nitrate included wastewater denitrification. Microorganism was immobilized by using support material as pumice filling materials.

Pumice was used as filter material and artificial components were used for the preparation of feeding solution and the effect different carbon sources (ethanol, methanol, acetate acid, glucose), process and nitrate removal rate were examined. The best nitrate removal rate and optimum C/N ratio was observed with methanol and 3, respectively.

LEACHING BEHAVIOUR OF STEEL FOUNDRY DUST IN DIFFERENT ACIDIC MEDIA

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Industrial wastes are able to transfer pollutants to the Environment. The waste contact with surface and ground water allows the toxic components of the waste to leach out at finite rate. In order to predict the migration of pollutants, leaching tests have been developed to study the environmental risks and to set standard values for the management of wastes. However, a leaching test cannot provide information about the complexity of the interactions between the waste, the liquid phase and the type of soil, but it provides a characterisation of the wastes in terms of solubility and an evaluation of the soluble fraction of the main pollutants. Nowadays, the development of leaching tests in EU is one of the main tasks in the characterisation of wastes. There are three areas under current research: basic characterisation tests, compliance tests and on-site verification tests.

It has been carried out a comparative study on the characterisation of Electric Arc Furnace Dust (EAFD) following four different acidic leaching tests. As leaching agents have been used HCl, H₂SO₄, HNO₃ and acetic acid, the parameters evaluated on Leachates were: pH, conductivity, potential redox and concentration of 11 metals: Cd, Cr, Pb, Cu, Ni, Zn, Al, Ca, Fe, Mn and Si.

Results allow a better understanding of the heavy metals mobility from EAFD, industrial waste.

MONITORING OF TOXICITY IN KRAFT BLEACHING INDUSTRY DISCHARGES

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Some organic and inorganics at toxic levels have been detected in industrial discharges resulting in plant upsets and discharge permit violations. In addition to this, even though in some cases the effluent wastewater does not exceed the discharge limits, the results of toxicity tests show potential toxicity. The chlorinated organics present in effluent from kraft mills employing either chlorine or chlorine dioxide in the bleaching process has become a matter of concern due to its recalcitrance to biological degradation, toxicity to aquatic species, genotoxicity and potential to accumulate in the body of a variety of organisms. The environmental effect of halogenated organic pollutants have long been the subject of vigorous legislative control and research. They are not only poorly destroyed by conventional biological treatment but also reduce the effectiveness of the process. AOX removal has been reported as 30-35% in the aerobic treatment and 40-45% in the anaerobic treatment systems. Chlorine bleaching effluent are considered toxic to the environment owing their highly structured formation under chlorinated phenolic contents.

In this study, it was aimed to investigate the acute toxicity of kraft bleaching industry wastewaters by traditional and enrichment toxicity tests and emphasize the importance of toxicity tests in wastewater discharge regulations. The enrichment toxicity tests are novel applications and give an idea whether there is potential toxicity or growth limiting and stimulation conditions. Different organisms were used such as bacteria (*Floc* and *Coliform* bacteria) algae (*Chlorella sp.*), fish (*Lepistes sp.*) and protozoan (*Vorticella sp.*) to represent four trophic levels. The toxicity test results of kraft bleaching industry showed acute toxicity for at least one organism in 7 out of 20 effluent samples. The toxicity test results were assessed with chemical analyses such as COD, BOD, color and AOX. It was observed that the toxicity of the effluents could not be explained by using physicochemical analyses in 4 cases for kraft bleaching industry. The results clearly showed that the use of bioassay tests produce additional information about the toxicity potential of industrial discharges and effluents.

AEROBIC TREATMENT OF OLIVE-MILL WASTEWATER BY THE WHITE-ROT FUNGUS *PANUS TIGRINUS*

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The mechanical olive oil extraction process generates huge amounts (3.0×10^7 m³ per year) of an effluent, usually termed olive mill wastewater (OMW). Currently, seasonal land-spreading of this effluent represents the major tendency in several Mediterranean countries. The main environmental risks associated to this disposal practice are due to the high organic load and the significant presence of phenolic components of OMW. The concentration of the phenolic fraction may widely range from 1 to 10 g L⁻¹, depending on the cultivar, the harvesting season and the extraction process. Phytotoxic effects as well as antibacterial activity have been associated with the phenolic fraction. Consequently, the fate of phenols is one of the main informing criteria to evaluate the efficacy of a OMW disposal treatment. Therefore, the choice of appropriate biological agents to perform OMW treatment has to take into account the intrinsic capability of the selected microorganism to degrade aromatics.

Fungi belonging to the ecological group of white-rot basidiomycetes have developed a non-specific radical-based degradation mechanism of aromatics based on extracellular enzymes and low-molecular weight agents. In fact, several white-rot species and/or their oxidative enzymes proved to be capable of degrading OMW phenols and to efficiently decolourise the effluent (Pérez, et al., 1987; Sayadi & Ellouz, 1995; D'Annibale et al., 1998; 2000).

In the present study, the degradative capability of the white-rot basidiomycete *Panus tigrinus* CBS 577-79 in the aerobic treatment of OMW was assessed under different submerged bioprocess conditions (shaken flasks, stirred-tank and air-lift bioreactors) and the kinetics of phenols and COD removal, decolorization were investigated. In particular, when using a 2-l stirred tank reactor, the effect of different regimes of agitation (250, 500 and 750 rpm at 1.0 vvm) and aeration (0.5, 1 and 1.5 vvm at 500 rpm) on the depolluting capability of the fungus was investigated.

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**AIR QUALITY ASSESSMENT IN AN INDUSTRIAL AREA
BY USING ENVIRONMENTAL INDICATORS**

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In this study, the concentration measurements of atmospheric pollutants for a thirteen year period, in a industrial area in north western Greece, are analyzed. The analysis of the measurements is focused on the assessment of air quality levels by using environmental indicators. The Pollutant Standards Index (PSI) is calculated and the spatial and temporal variation of the PSI is studied for this particular location. From the analysis an attempt is made in order to provide information about air quality levels, which are identified by descriptors relevant to the health of the population.

INVESTIGATION OF OIL SOURCED PROBLEMS IN WATER TREATMENT BY ION EXCHANGERS

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Ion exchange resins have been used to treat and improve the quality of water and wastewater throughout the world for well over 40 years. Ion exchange resins are not only used to improve the quality of potable waters, which affects our daily lives, but their use is critical in the development of new technologies, such as the nuclear power and semiconductor industries, where high purity water is an essential part of the process.

Ion exchange resin can be contaminated because the ion exchange process depends upon ions transferring from an aqueous solution to the insoluble ion exchange resin and upon the subsequent elution (removal) of these ions from the resin with the regenerant solution. This exchange takes place not only on the surface of the resin particle, but also within the interior of the resin. If the pores are clogged by deposits, or if the resin surface is coated by inert matter, ion exchange capacity is reduced and water quality from the ion exchange unit is impaired. In some cases, the ion exchange resins become so fouled or deteriorated that replacement with new resin is necessary. Therefore it causes economical losses.

In this study, the changes on the capacity of ion exchangers because of oil fouling were investigated. Oil very rarely reaches to the ion exchangers via water continuously. More often, oil trickles from pumps or mixing into water by accident bring about oil fouling. In the case of oil fouling, whatever the source is, pores can be filled up and plugged by the oil and, during regeneration, this plugging can not be reserved. Since the ion exchange centres inside the ion exchange beads were blocked this blockage causes a drop in the capacity. Fouling of strong acidic ion exchangers with oil (0.5, 1.0 and 2.0 mL) results in a decrease in operating capacity of 11%. This means that even at low concentrations oil fouling leads to loss in the operating capacities. Fouling of strong basic ion exchangers results in a decrease in operating capacity of 31 – 32%. The high capacity loss by strong basic exchangers is an expected result, because it is known that generally basic ion exchangers are less stable than strong ion exchangers.

SUCROSE-ENHANCED TNT REMOVAL IN CONSTRUCTED WETLAND

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Phytoremediation is gaining increased attention for treatment of organic wastewater. Constructed wetland is one of the techniques, which practice phytoremediation to remedy polluted ecosystems. The effectiveness of the constructed wetland in treating an artificial 2,4,6-trinitrotoluene (TNT) contaminated wastewater was examined in this study under the addition of sucrose as cosubstrate and aeration.

TNT contaminated wastewater was treated in a surface flow constructed wetland. The constructed wetland consists of a cascade, which contains four steel tanks filled with lava and planted with *Typha spp.* and *Scirpus lacustris*. Sucrose was used as cosubstrate to stimulate the removal of TNT with constructed wetland. Results showed that only 91% of the TNT was decreased after passage of the first tank under the conditions of without sucrose as cosubstrate. In contrast, with the addition of sucrose as cosubstrate, more than 99.8% of the TNT was removed after passage of the first tank, which achieved by passage of two tanks under the conditions of without sucrose. In the viewpoint of practical applicant, the use of sucrose as cosubstrate can reduce treatment facilities and save the constructed area and provide a cost-effective wastewater treatment technology.

The effect of aeration on TNT removal with constructed wetland was also examined, no significant difference was found between the experiment with aeration and without aeration. The main extractable metabolites were Aminodinitrotoluenes (4A2,6-DNT and 2A4,6-DNT). In addition, Dinitrotoluenes (2,6-DNT and 2,4-DNT) were detected as metabolites of TNT.

The adsorption of TNT and its metabolites on Lava can be neglected. The highest level of TNT and its metabolites in plant materials was found in stems.

It is determined that it is necessary and effective to introduce co-substrate into phytoremediation of TNT wastewater treatment. Further investigations should be performed to study other cheaper external carbon sources such as molasses as cosubstrate.

TOXICITY REDUCTION OF A CHEMICAL PLANT EFFLUENT – RESULT OF EFFECTIVE LAB-SCALE WASTEWATER TREATMENT

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Industrial activities consume a huge amount of resources and energy, and discharge enormous emissions to the environment. Those emissions are causing various local and global environmental pollution problems. It is needless to say that minimization of pollutants from industrial activities is of great importance in the future. From this recognition the idea of sustainable development has arisen. The chemical industry can contribute decisively to this guiding principle.

The harmful effects of wastewaters on receiving streams, caused by insufficient quality of effluents, inadequate dimensioning and overloading of present treatment plants, as well as the trends of science and technology call for improvement of the treatment technologies, development of advanced treatment processes and above all for waste minimization in industrial processes to meet the increasing water quality standards.

The organic chemicals and synthetic fibres industry is of importance in terms of its impact to the environment. Wastewaters are generally strong and may contain toxic parameters. Treatment of these wastewaters requires combination of several stages of conventional as well as advanced methods of treatment. In-plant controls and recoveries are important for pollution control. Other alternative of wastewater management such as transfer to a central plant is also possible.

We were faced with wastewater from a chemical factory that produces raw materials for various industries: high pressure and technical laminates, different melamine- and urea-formaldehyde resins, impregnated textile materials and foils. The wastewater (of maximum flow rate 40 m³/day) is discharged into the sewerage system and treated in a municipal wastewater treatment plant. The effluent was highly polluted with organic substances, was toxic to aquatic organisms and therefore did not meet the prescribed criteria for its discharge into the sewerage system. Consequently, the factory was facing a requirement to reduce pollution, especially of toxic components, and to determine actions necessary to achieve compliance with effluent limits. The purpose of this research was to evaluate the effect of lab-scale effluent pretreatment including different stages: physico-chemical treatment (precipitation and flocculation with FeCl₃ and organic polyelectrolyte) and biological batch reactor treatment with adapted activated sludge. As characterization of the harmful properties of effluent was a critical element in our assessment and a key element of strategy, it was necessary to rely on a specific chemical characterisation and whole effluent toxicity tests with *Daphnia magna*, bacteria *Vibrio fischeri* and activated sludge organisms. Comparative results showed the reduction of pollution in physico-chemical treated effluent due to removal of inert waste resins, while evident reduction of toxicity in biologically treated effluent was attributed to decrease of priority pollutants formaldehyde, methanol and butanol. The final quality of effluent met standards for discharge into the sewerage system.

IMPACT OF INDUSTRIAL WASTEWATERS ON TREATMENT EFFICIENCY OF AEROBIC BIOLOGICAL WASTEWATER TREATMENT PLANT

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In many developed countries, toxicity and biodegradability tests on an industrial effluent are required to ensure that the discharge will not have adverse impacts on the aquatic organisms in the receiving water. Because majority of the wastewaters pass through some kind of a treatment before entering the surface waters, a reliable wastewater characterization is a prerequisite for an acceptable treatment strategy. The widely used biological treatment could be drastically affected by changes in wastewater composition and properties, which in spite of an equalisation basins could fluctuate due to the batch processes in the industry. The aim of our work was to determine the impact of two different industrial wastewaters to the municipal wastewater treatment plant. We selected two wastewaters: wastewater from the pig farm and wastewaters from metals industry. Both effluents are treated in municipal wastewater treatment plant (6000 m³ of aeration basin with activated sludge, hydraulic retention time (HRT) = 6-7 hours) which treats 58 % of municipal wastewater and 42 % of industrial one (annual average volumetric load). Besides wastewater from the pig farm (2 %) and metals industry (9.9 %), there is also a significant load of the wastewater from textile, pharmaceutical and variety of other industries.

The impact of both wastewaters on biological treatment plant was evaluated on the basis of whole effluents. Random grab samples of both wastewaters were analysed, TOC, COD, BOD₅, concentrations of nitrogen, phosphorous and suspended solids were determined, using standardized methods. We performed toxicity studies with mixed culture of microorganisms, collected in the aeration basin of the plant (activated sludge) and determined toxicity of wastewaters with measurement of inhibition of oxygen consumption after addition of different concentration of the wastewater (ISO 8192, 1986) and we measured growth inhibition after 3 hours exposure of microorganisms to wastewater (ISO 15522, 1998). Biodegradability was determined in a closed respirometer, where oxygen uptake and carbon dioxide release were simultaneously measured 28 days. Experiment was accomplished according to demands on assessment of ready biodegradability to demonstrate potential for degradation in common environmental conditions. Wastewater from the pig farm inhibited oxygen consumption less than growth. According to measurement of oxygen consumption 180minEC₅₀ was 35.4 vol.%, while it was 15.4 vol. % on the basis of growth inhibition after the same exposure period. The EC₅₀ increased within next two hours (to 21.1 vol.%), indicating adaptation of microorganisms to the wastewater. It degraded readily (83 %, lag phase was 3 days, biodegradation rate was 0.07 day⁻¹ (r² = 0.99) with presumption of the first order kinetics) on the basis of O₂ measurements. The biodegradation, calculated from the CO₂ measurements was comparable. Abiotic degradation was less than 5 %. Wastewater from metals industry was non-toxic to activated sludge. It degraded less than 25 % in 28 days, after significant lag phase (8 days). Abiotic degradation was 15 %. In spite of toxicity of wastewater from the pig farm and low biodegradability of the wastewater from metals industry, efficiency of the treatment plant was not reduced. Optimization of biological treatment should be considered using different recovery methods or pretreatment of persistent wastewater from metals industry, due to high load of this wastewater (9.9 %).