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Environment Institute

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Map of the Joint Research Centre - Ispra Site - showing the location of the Environment Institute premises (in green colour)

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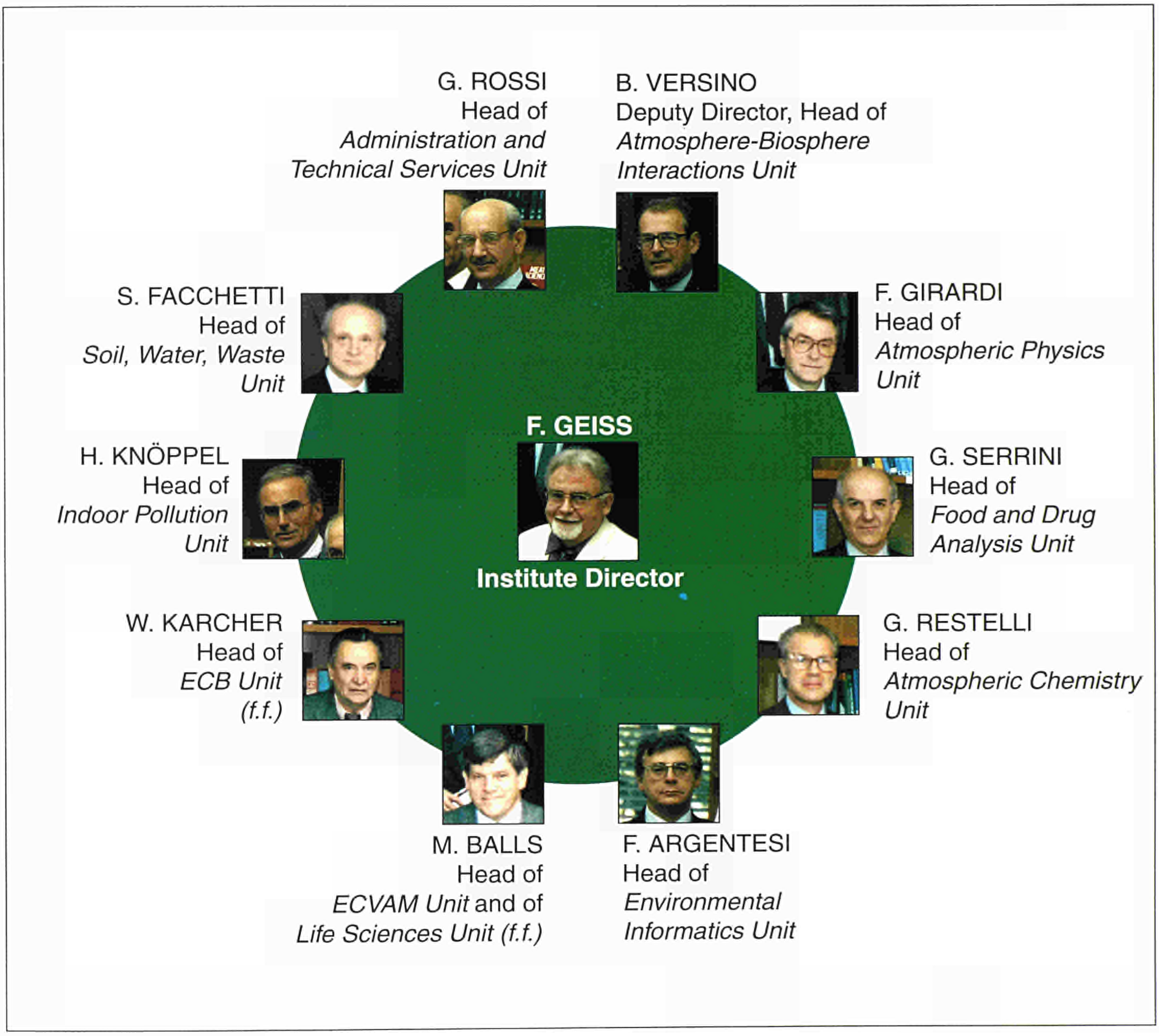
THE ENVIRONMENT INSTITUTE

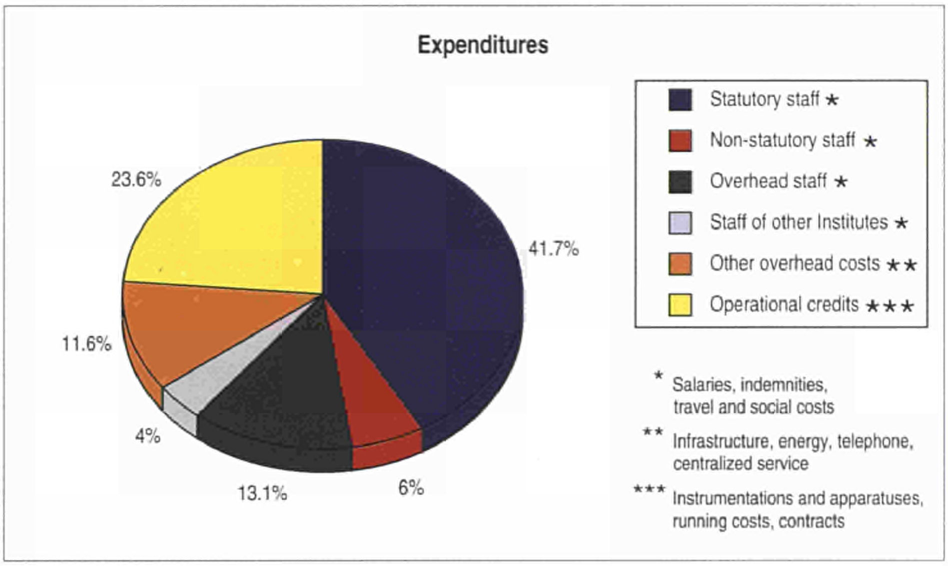
1993 has been a year of continuity and consolidation of operations, as well as of some growth with respect to the number of tasks entrusted to and to the structure of the Institute. At the very beginning of the year, the European Chemical Bureau was formally created by a Decision of the European Commission and established as an additional Unit within the structure of the Institute. The new internal organisational structure of the Institute now encompasses 10 scientific Units - in addition to the administrative one - reflecting with greater evidence the two pillars on which the bulk of the research activities rests, namely, Global Change and Environmental Chemicals.

The scientific Units are:

- Atmospheric Physics;
- Atmospheric Chemistry;
- Atmosphere-Biosphere - Interactions;
- Environmental Chemicals: Soil Water, Waste;
- Environmental Chemicals: Indoor Pollution;
- Environmental Chemicals: Life Sciences;
- European Chemicals Bureau (ECB);
- European Centre for the Validation of Alternative Testing Methods (ECVAM);
- Environmental Informatics;
- Food & Drug Analysis.



Institute's organisational chart.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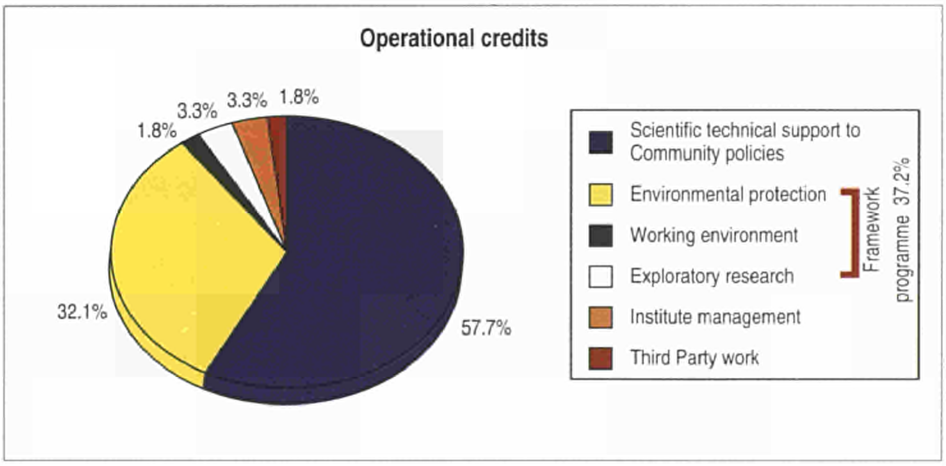
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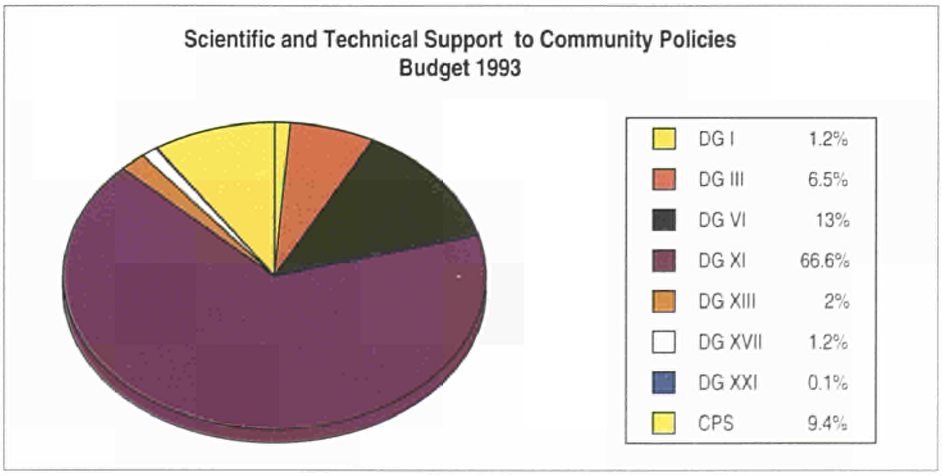

Scientific and Technical Support to Community Policies
Budget 1993

In September, following another decision of the European Commission, the European Office for Wine, Alcohol and Spirit Drinks (EOWAS) was created and established within the structure of the Food & Drug Unit, while the procedure has been started to set-up the European Reference Laboratory for Air Pollution (ERLAP), a successor of the Central Laboratory for Air Pollution (CLAP) - to be placed with the Atmospheric Chemistry Unit. The above clearly show a more marked shift of the Institute's core activities toward the "S & T Support for the Commission Policies" area, thus strengthening further the Institute's institutional role. This shift is also confirmed by the share of the operational credits, which is presented in graphical form together with other statistics aimed at helping to assess the value of the Institute's contribution to the development of the Framework Programme and to the implementation of the Commission's environmental policy.

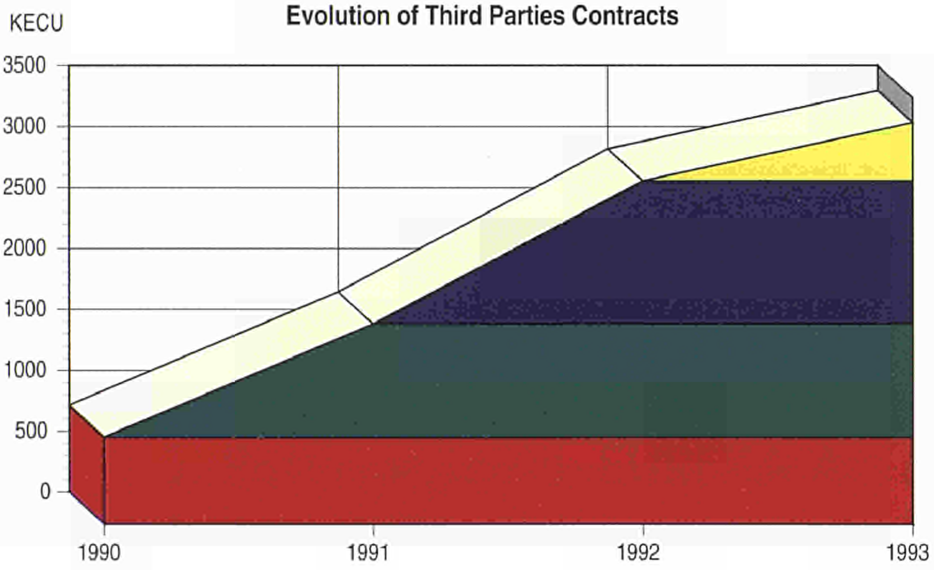
Despite the growth of both the number of the tasks and of the structure of the Institute, the level of statutory staffing could not be increased, new recruitments having just balanced departures. As a matter of fact, instead of growing up to 215 - as scheduled for the end of the year - the Institute's staff number has remained 197, i.e. at about the level of the preceeding year. This has been partially counterbalanced by a slight increase of non-statutory staff (grantholders, visiting scientists, seconded national experts) from 80 - as in 1992 - to 95, which corresponds to as much as 50% of the statutory staff.

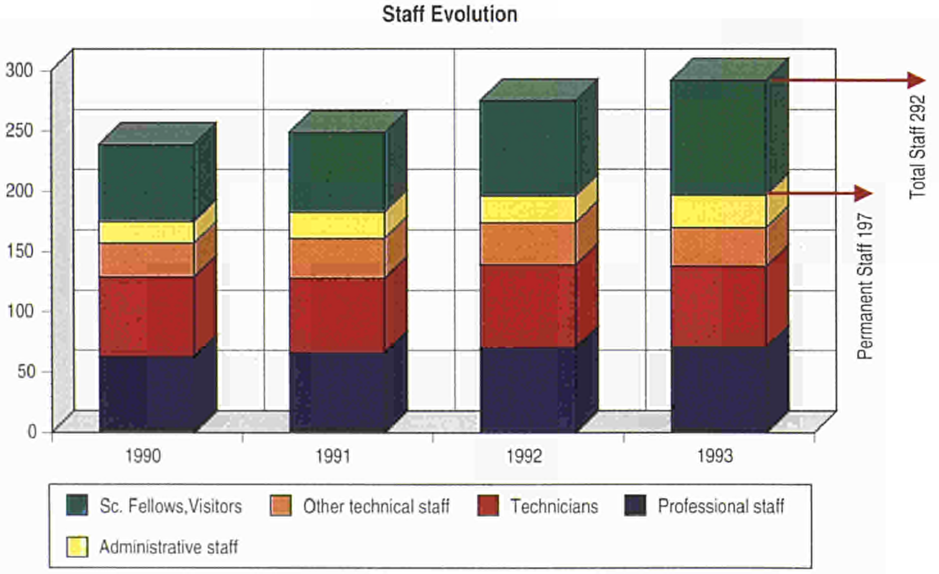
Two new large facilities have been inaugurated and made available for research work, namely:

- the Indoortron, a large volume, walk-in test chamber for indoor air pollution studies, and
- the intercalibration laboratory of the Central Laboratory for Air Pollution, wich plays a fundamental role in the drafting and the application of EC directives concerning air pollution.

Efforts to improve the present organisation of the space allocation in the Institute have continued. The construction of a new building to host ECVAM was started, the inauguration of the new premises being scheduled for the second half of next year. Further concentration of staff and facilities within core areas is clearly apparent in the map of the JRC - Ispra site.

The major achievements of 1993 are presented in the following sections, according to the rationale utilized in the past two annual reports. Section 1 presents the progress achieved in the two main research areas included in the "Environment" Specific Research Programme, i.e. Global Change and Environmental Chemicals. Section 2 is dedicated to the results within the framework of the Scientific and Technical Support for the Community's Policies. Most relevant information on the progress of the Exploratory Research is dealt with in Section 3, while Section 4 summarizes the work for Third Parties. The Institute continues to publish a biannual Environmental Research Newsletter, which provides information on Community research and legislative action in the environmental field and reaches, free-of-charge, some 4,000 subscribers world-wide.





THE ENVIRONMENT INSTITUTE

Executive Summary

Executive Summary

This report is intended to provide a rather comprehensive overview of the activities of the Environment Institute in the course of the year and of its major achievements in the development of the various projects included in the multiannual (1992-94) research programme.

The interested reader should refer to the publications in scientific journals - listed in the last part of this report - in which full descriptions of the scientific background and technicalities, as well discussion of the results achieved, are given.
As in the preceeding annual report, the activities and achievements are presented according the following arbitrary scheme:

- Specific Research Programmes
- Scientific and Technical Support for Community Policies
- Exploratory Research
- Third Party Work
- Participation to EUREKA Actions.

The last section (Appendices) contains a list of papers published in scientific journals, scientific reports, conferences, oral and poster presentations to congresses, symposia and other scientific events, as well as a glossary of acronyms and abbreviations.

1.SPECIFIC RESEARCH PROGRAMMES

This section encompasses the achievements for the projects included in the areas of the Environment Specific Research Programme to which the Institute is contributing, i.e.:

- Global Change
- Environmental Chemicals

Global Change.

Four activities represent the contribution of the Environment Institute to this theme, i.e.:

Tropospheric Chemistry;
Atmospheric Sulphur and Climate;
Atmosphere-Biosphere Interactions;
Environmental Monitoring.

As far as the first activity is concerned, work has progressed with a main focus on the degradation mechanism of dimethylsulphide (DMS) and on methodological aspects. The results of the studies on DMS are summarized in the account of the project entitled Atmospheric Sulphur and Climate. Methodological aspects have been addressed mainly by the active contribution to EUPHORE, a multilaboratory EC-funded project for the construction and operation of an outdoor smog chamber with unique characteristics, in Valencia (Spain).

Studies aimed at increasing understanding of the global impact of natural dimethyl sulphide (DMS), anthropogenic sulphur dioxide (SO_2) and soot emissions have continued within the Atmospheric Sulphur and Climate project, and the progress achieved can be summarized as follows.

Within the framework of modelling studies, a chemical reaction mechanism for the oxidation of DMS initiated by OH radicals has been developed and subjected to an uncertainty and sensitivity analysis which identified some of the key inadequacies in the present understanding of the chemistry involved. Aerosol dynamics modelling has pointed to entrainment of free tropospheric aerosol into the marine boundary layer, as a mechanism that might explain the levels and constancy of the marine aerosol. The results provided by the model are consistent with the data obtained during the '92 Hudson cruise. An efficient aerosol dynamics module has been implemented in the 3-D global transport model MOGUNTIA; but so far, the particle number concentrations calculated are generally lower than those observed. A global emission inventory has been constructed for black carbon, giving total emissions of 5.4 Tg C per year from biomass burning and 5 Tg C per year from fossil fuel use. These emissions have been incorporated into MOGUNTIA, yielding global fields of black carbon mass.

As far as laboratory investigations are concerned, the results of chamber experiments indicate that the relatively stable intermediate formed by the oxidation of DMS in air has the structure $CH_3S(O)_2OONO_2$. Initial tests have been performed with the new aerosol reactor AERREA1, showing that aerosols from the photochemical oxidation of SO_2 could be generated in a reproducible way.

As for field measurements, the analysis of the data from the '92 Hudson cruise has been completed. A clear impact of anthropogenic emissions on the number of CCN over the North Atlantic has been quantified. Measurements of DMS in oligotrophic and mesotrophic lakes showed concentrations similar to those of oligotrophic marine water, while the eutrophic Lago di Varese showed increased concentrations of DMS and other volatile sulphur compounds.

Research on atmosphere-biosphere interactions has mostly focused on biogenic emissions from Mediterranean ecosystems and their role in atmospheric chemistry and ozone formation. To this end, an European project has been developed on Biogenic Emissions in the Mediterranean Area (BEMA), with the primary goal of quantifying emission rates and vertical fluxes of reactive trace gases from various vegetation types typical for that region. Field measurements, laboratory work, and modelling activities are used to relate biogenic emissions to their resulting concentrations in air and their respective roles in tropospheric ozone formation.

A preliminary BEMA measuring campaign of two weeks was organized by the JRC at the Castelporziano (Rome) test site in June 1993, with the active participation of 12 European laboratories, in order to optimise future BEMA field measurement campaigns. Moreover, less intensive measurements have been performed at the site, in order to characterize the seasonal variability of climate, physiology, emission rates and concentrations, and to map the distribution of the major vegetation types.

Two major test ecosystems were selected for continuous measurements during the campaign: a 30-year-old plantation of domestic pine (*Pinus pinea*) and holm oak (*Quercus ilex*), with representative shrub undergrowth (*Erica, Rubus, Cytisus, Pistacia, Phyllirea, Myrtus*), and a seminatural Mediterranean greenland, the so called "pseudosteppe" area, for research on low-vegetation species (*Asphodelus, Calamintha, Pteridium, Cistus*).

The results from this preliminary campaign - to be discussed next year in the course of a special workshop - have provided, at first sight, clear indications as what to expect from future field campaigns and where effort should be focused.

Quercus ilex, Pinus pinea and several shrub species show high emissions rates of monoterpenes.

Other shrubs and herbs (*Pteridium, Myrtus, Erica*) are strong emitters of isoprene. Generally, it seems that biogenic emissions are two-three times higher than in temperate ecosystems. Up to a five-fold variability of average daytime monoterpene emission rates from oak (5 - 20 [μg $^{-1}$ (LDW)hour $^{-1}$]) and pine (1-5 [μg $^{-1}$ (LDW)hour $^{-1}$]) can be attributed to natural variability between branches, trees, days and seasons.

In contrast with emissions by most other oak species, the evergreen sclerophyllous Mediterranean oak emits large amounts of monoterpenes, despite having no monoterpenes accumulated in its leaves or bark. The typical daily and seasonal drought stress on plants growing in Mediterranean climate allowed a physiological control of monoterpene emissions to be demonstrated. These findings have been confirmed by the data from experiments performed in the Ispra greenhouse.

Despite high emission rates, the ambient air concentrations of terpenes and isoprene are surprisingly low during the daytime and very low at night. This may possibly be caused by an effective dilution of the compounds due to the permanent land/sea breeze circulation and to photochemical processes, as indicated by daily patterns of ozone, with minima close to zero at night, a sudden increase with sunrise, and maximum peaks of 50 - 100 ppb in the afternoon. Both nitrogen oxides, NO and NO_2 ,were strongly negatively correlated with O_3 levels.

Environmental Chemicals

This is a very broad research area covering a wide range of activities which can be grouped under three main headings, namely:

- Evaluation of Chemicals, encompassing the implementation of the ECDIN databank and Trace Metals Exposure and Health Effects;
- Indoor Pollution;
- Chemical Waste and Water Quality.

The implementation of the ECDIN data bank has continued, and identifications for 122,392 compounds are included in it at present. Updating of the following data files has been completed:

- Abiotic Degradation;
- Concentration in the Environmental Media;
- Bioaccumulation/Biodegradation;
- Mutagenecity;
- Experimental Toxicity;
- Aquatic Toxicity.

In addition, the specific data files on "Experimental Toxicology" and "Effects on Reproduction" have been updated. A third CD-ROM version of ECDIN has also been made available.

Research in the field of indoor pollution has been focused on the development and validation of methods for the assessment of emission and adsorption of volatile organic compounds (VOCs) from and on indoor materials. Results of an initial international comparison experiment for the validation of a guideline for VOC emission measurements have been published. As a follow-up, more-detailed guidance for the measurement of VOC emissions from thin film sources such as paints has been developed and a further intercomparison experiment has been prepared. An improved model for describing the adsorption of VOC on indoor surface materials has been developed.

The further equipping and the initial application of a walk-in type environmental test chamber (Indoortron) have been implemented. The equipment for generating test atmospheres containing a broad range of VOCs at typical indoor concentrations has been developed, and the chamber has been used for testing cleansing devices. The development and application of the analysis of semi-volatile organic compounds (SVOC) and particulate organic matter (POM) in house dust and indoor air has continued. Several adsorbents have been tested for sampling from indoor air and the supercritical fluid extraction (SFE) of SVOC and POM. An inexpensive method for preparing high purity CO_2 for SFE has been set up and tested.

The European Collaborative Action (ECA), "Indoor Air Quality and Its Impact on Man", has published a report on biological particles in indoor environments. Work done by the ECA has focused on a procedure for the evaluation of VOC emissions from indoor materials and on the question of how good indoor air quality and a rational use of energy can be reconciled. In addition, work on guidelines on VOC sampling in indoor environments, and also on the design of intervention studies aimed at improving indoor air quality in buildings, has continued.

In the field of soil-pollutant interaction studies within the framework of Chemical Waste, research based on the comparison of laboratory investigations with observations of natural processess and modelling has continued. An 1D hydrodynamic transport code was coupled to routines of uncertainty and sensitivity analyses. This coupled code is being tested on the basis of the results of laboratory experiments on the transport behaviour of Cr(III). These experiments show that Cr(III) mobility increases considerably due to its association with dissolved organic matter (humic acids). Alternative mechanisms of reactive transport are being compared, in order to identify the relative importance of uncertain variables on the probabilistic outcome.

Laboratory migration studies were performed in parallel, with Se(VI) and fractured granite columns, in order to identify the physico-chemical interactions of Se with fracture-filling material. From these experiments, it appears that loss of Se(VI) from the water flow is due to a redox reaction resulting in the formation of strongly adsorbed Se species. The surface speciation of Se on iron sulfide present in the granite was investigated by X-ray Absorption Spectroscopy using synchrotron radiation, at the SERC facility in Daresbury (UK). Laboratory diffusion experiments of Sr in clay were also modelled by using a coupled reaction-transport model.

The influence of surfactant agents present in groundwaters, which facilitate the unwanted transport of hazardous chemicals in the environment, is being investigated. The results of studies on PCBs and chlorobenzenes underline, by contrast, their strong solubilizing effects, which may be beneficial in soil remediation, aiding desorption and/or biodegradation of the poorly water-soluble organic contaminants.

In parallel with the migration studies, analytical methods have been developed and validated by inter-laboratory comparisons, for the quantitative analysis of PCBs and organochlorine pesticides in various environmental samples. Supercritical Fluid Extraction and dual column GC-ECD have been adopted and a prototype instrument has been designed and tested. Headspace solid phase microextraction, in combination with ion trap MS, was also successfully employed for the VOC analysis. An easy quantitative method for the determination of surfactants in water, using continuous flow - fast atom bombardment mass spectrometry (CF-FAB-MS), has also been developed.

As far as water quality is concerned, further progress has been achieved in the development of the MITO project. A second experimental cruise in the northern Adriatic Sea showed the possibility of detecting algae in very low numbers and quantifying the numbers of cells and the total fluorescence. Concerning the nocivity associated with algal blooms, the best conditions for revealing the presence of the okadaic acid have been studied. This hepatotoxin is a well-known algal product, being concentrated by mussels, with the liver (or the hepatopancreas) as its main target organ. The use of murine primary hepatocyte cultures for the determination of okadaic acid toxicity, by measuring vital dye (neutral red) uptake, gave excellent results and has been adopted as a standard method.

In the context of the AQUACON

MedBas Project, the Analytical Quality Control and Measurement Error Assessment Study has been developed at the request of the EU Member Countries of the Mediterranean area. A number of sub-projects have been launched, for organizing inter-laboratory analytical exercises on various matrices (rainwater, drinking water, sediment, foodstuff, waste, etc.).

2. SCIENTIFIC AND TECHNICAL SUPPORT FOR COMMUNITY POLICIES

As in past years, scientific and technical support - in the form of both theoretical and experimental research and expertise - has been provided for a number of Directorates General or Services of the Commission, and in particular:

- Directorate General III (Internal Market and Industrial Affairs), for the design and the implementation of a databank on pharmaceutical products;
- Directorate General VI (Agriculture), for the analysis of wines and dairy products, and for the setting up of a European databank of wine fingerprints by Nuclear Magnetic Resonance;
- Directorate General XI (Environment, Nuclear Safety and Civil Protéction), for several topics of wide concern in the field of environmental protection, within the framework of the Radioactive Environmental Monitoring (REM), of the European Centre for the Validation of Alternative Methods (ECVAM), and of the European Chemical Bureau (ECB);
- Directorate General XVII (Energy), for analytical work connected with the control of fissile materials;
- Directorate General XXI (Customs and Indirect Taxation), for expertise on the characterization of goods imported into the European Union;
- Consumer Policy Service, in the framework of a general analytical activity concerning, in particular, cosmetics, foodstuffs, water and other matrices.

In the following paragraphs, only major achievements in the scientific and technical support provided for Directorate General XI are summarized, as they represent the bulk of the EI effort is this area.

Short descriptions of all the activities performed and of the most significant achievements are given - where appropriate - in the section headed "Main Achievements".

Scientific Technical Support to Directorate General XI

As has already been mentioned, emphasis has been placed on several topics of wide concern to DG XI and related to:

- Chemicals;
- European Chemicals Bureau;
- Atmospheric Pollution;
- Water Quality;
- Radioactive Environmental Monitoring (REM);
- European Centre for the Validation of Alternative Methods (ECVAM).

The European Centre for the Validation of AlternativeTesting Methods (ECVAM) - has entered in its operative phase, and seven prevalidation / validation studies have been started or have continued, namely:

- an EU/UK international validation study on alternatives to the Draize eye irritancy test;
- Phase I of a COLIPA/EU international study on *in vitro* tests for photoirritancy;
- a Europe/USA international pre-validation study on *in vitro* tests for skin corrosivity;
- an EU/FRAME international study on the use of a battery of *in vitro* tests for predicting acute lethal potency and for use in the classification and labelling of chemicals;
- an EU/FRAME international pre-validation study on *in vitro* tests for neurotoxicity;
- an EU/BRIDGE pre-validation study on an assay for the inhibition of gap-junctional intercellular communication as a means of identifying tumour promoters;
- a pre-validation study on the ECITTS approach to biokinetics and neurotoxicity testing.

In addition, two workshops were held and dealt with the practical use of cultured hepatocytes and of *in vitro* methods in phototoxicity testing.

The European Chemical Bureau (ECB) was formally established within the structure of the Environment Institute on January 1st 1993, with the aim of carrying out and coordinating scientific/technical work needed for the implementation of EU legislation in the area of chemicals control.

In view of the updating of Annex I to Directive 67/548 EEC, the classification and labelling of the following substances has been tackled:

- man-made mineral fibers;
- gases;
- sensitizing substances;
- substances harmful in the environment;
- carcinogenic, mutagenic and teratogenic compounds.

Furthermore, a feasibility study has been carried out on the transfer from

DG XI to the ECB of summary notification dossiers sent by EU Member States.

Preparatory work for the installation and operation of the EUCLID database in specially-protected security premises has been completed.

In the area of atmospheric pollution, the harmonisation programme of Directive 85/205/EEC was continued via the new calibration facility of the Central Laboratory of Air Pollution. The second intercomparison exercise was organized at Ispra with the attendance of eleven laboratories from six Member States. The results of the two intercomparisons (the first was held in May 1992 at the Landesanstalt für Immissionsschutz, Essen, Germany) show that about 80% of the twenty laboratories participating in the two exercises were within a tolerance limit of ± 10% of the standard values.

Following the results of the first intercomparison exercise on VOC measurement, which showed that the performance of the measurement techniques as currently applied was poor, a second intercomparison has been organised with the participation of 20 laboratories which routinely deal with air quality measurements.

In the context of a convention between the Commission (DGXI/B/3) and the "Ministére de la Région Bruxelloise", an air pollution monitoring campaign was organised in the Brussels area, with the aim of:
- assessing the impact of emissions by traffic on urban air quality;
- demonstrating the use of new air quality monitoring techniques in urban areas;
- making the population aware of air quality problems in large cities.

The summer campaign took place from June to September 1993. It will be followed by a second campaign in the winter of 1993/1994.

The scientific work resulting from the adoption of the Directive concerning the ecological quality of surface waters has continued. This study gives an overview of common lake and reservoir problems in EU Member States. Quantitative evaluations of the procedures with regard to short-term and long-term effectiveness, cost and potential negative impact were also considered.

Work on the impact of trace compounds and elements has also been continued.

During the reference period, the non-point sources and discharges of selenium and nitrogen compounds (ammonia, nitrite and cyanide) have been studied along with the discharge of mercury, berillium and thallium due to point sources.

The official version of the European Waste Catalogue (EWC) accepted by the Steering Committee, has been published in the Official Journal of the EU. The official translations into the nine languages of the Community will be ready at the beginning of 1994.

The conversion of the REM data base application software was continued and is, except for the Oracle query interface, at its final stage. The input of 1987 - 1990 monitoring data was completed and 1991 monitoring data input was started.

The data input processor, EasyProteo, was further developed and is almost completed; shipment of the software and user manual to the data producing institutes and a training course are plannned for the first half of 1994.

Atmospheric model development continued, with special emphasis on long-range transport models and mesoscale models applicable to complex terrains.

A new CEC - CIS collaboration programme, ISP 6, was started at the end of 1993. The aim is to integrate, on a European level, radioactivity measurements immediately related to the Chernobyl accident into a common informatics platform.

The Commission's nuclear emergency system for the exchange of urgent radiological information, ECURIE, was further tested (by means of bilateral and multilateral exercises). The on-going debugging of the coding-decoding software (CDS) resulted in an official release available on a world-wide basis.

The ETEX project, in cooperation with WMO and IAEA, is proceeding satisfactorily. The project aims at testing the capability of atmospheric models to predict the evolution of a pollutant cloud in real time. The final experiment will be carried out in 1994.

3. EXPLORATORY RESEARCH

This research area encompasses four projects namely:
- Absolute Chemical Analysis by Laser Methods;
- Surface Enhanced Raman Scattering as a New Analytical and Diagnostic Tool for Atmospheric Chemistry;
- Laboratory for Separation Science;
- Development of an Atmospheric Aerosol Tracer.

The second-named project is a new one, while the remainder represent the extension or the continuation of projects started in the past.

The first project is aimed at studying the feasibility of an absolute analytical method based on laser-excited atomic and molecular fluorescence or ionization.

Following the theoretical modelling of the interaction with the laser radiation which was performed last year, it was shown that the ionization technique was even better than the fluorescence technique as a potential method of absolute analysis. With a carefully controlled set-up, consisting of a flame, an immersed electrode and a fast detection system, it was shown for the first time that sodium atoms in an air-acetylene flame could be ionized with total efficiency by means of a two-step excitation process obtained with two excimer-pumped, pulsed dye lasers tuned at allowed visible transitions of sodium. The highly excited atoms underwent rapid collisional ionization with the flame gases. This represents the most direct experimental proof that the method can be placed on an absolute basis. In fact, one could speak of "absolute coulometry".

Spontaneous Raman Spectroscopy has the capability of detecting and characterizing atmospheric aerosols, such as sulphates and nitrates. However, the weak value of its cross section limits the sensivity attainable. The recent discovery of the Surface Enhanced Raman Scattering (SERS) effect has led to significant improvements in the sensitivity (up to many orders of magnitude). The aim of the proposed research is to apply the new technique to the study of heterogeneous processes involving atmospheric sulphur species.

A basic infrastructure for the application of the SERS technique to tropospheric aerosol chemistry has been assembled. The set-up consists of a Multichannel Raman Spectrometer based on the use of Charge Coupled Devices (CCD) as array detectors. Excitation is provided by a cw Argon-ion laser, which also pumps a small tunable dye laser. The Raman spectrum is dispersed with a double-monochromator or by a simple acousto-optic tunable filter. A new concept of photon detection, based on monitoring the change in the operation frequency of a neon lamp, has also been successfully tested.

Within the framework of the project "Laboratory for Separation Sciences", research on the analysis of the oligoribonucleotides by fast atom bombardment mass spectrometry (FAB-MS) has been continued by checking the effects of various matrices on analytical sensitivity. Diethanolamine has shown to be the best choice for the complete analysis of ribonucleic acid (RNA) strands.

The instrument used was a high resolution mass spectrometer with forward geometry and a high voltage magnet, allowing for a masss range of up to 3,000 a.m.u. at 8 KV accelerating voltage.

The electrospray ion source has been investigated for ion masses up to 10,000 a.m.u.. Preliminary results obtained with a prototype applying a transformation software to reconstruct mass spectra, showed that this approach was successful for a protein with an average molecular weight of 14,305 (lysozime).

In a parallel way, the applicability of membrane techniques to waste purification has been further investigated. For this purpose, a pilot plant has been set up to allow the combination of different types of ultrafiltration membranes.

For spyral-polyamide membrane A, cut-off tests were run using 100 and 300 ppm solutions of dextrans and polyethylene glycols (PEG), the best results having been achieved with 300 ppm PEG.

Further tests are being conducted with polyvinylalcohol (PVA) and PVA copolymers.

Experimental evidence has been obtained which shows that, in the case of waste water from the textile industry, spiral wound modules offer the best compromise between operability, surface-to volume ratio, power requirements and replacement costs.

The aim of the project "Development of an Atmospheric Aerosol Tracer" is to develop a technique for tracing atmospheric aerosols.

Chemiluminescent substances can be detected very sensitively; that makes them promising candidates for use as an aerosol tracers. In fact, chemiluminescent substances can be detected at very low concentrations, by using rather simple and inexpen-sive equipment to detect the light emitted when they undergo their specific chemiluminescent reaction. A "luminometer" was built, by combining a good photomultiplier with a low dark current and a photon counting unit. This luminometer was equipped with a special holder to allow for a direct chemiluminescence measurements on a wettable filter disc of up to 47 mm diameter. The tracer can be quantified directly on the filter on wich the aerosol sample is obtained.

Measurements with luminol, however, have shown that this substance is not photostable. As a consequence, tests on an other two substances have been planned.

Another approach has been attempted: the background concentration of gold was measured and, although still relatively high, is such that, the use of gold, as an aerosol tracer appears to be feasible.

THE ENVIRONMENT INSTITUTE

1. Specific Research Programmes

ENVIRONMENT

The Institute's efforts have been focused essentially on two main topics of the Environment specific programme, namely:

- Global Change;
- Environmental Chemicals.

GLOBAL CHANGE

This research area includes four main topics, namely:

- Tropospheric chemistry;
- Atmospheric Sulphur and Climate;
- Atmosphere-Biosphere Interactions;
- Environmental Monitoring.

They encompass a multiplicity of activities aimed at contributing to understanding of the transport, diffusion and chemical processes of biogenic and anthropogenic emissions. These studies, as in the past, have involved a great deal of laboratory experiments, theoretical modelling and field measurements.

Tropospheric Chemistry: Laboratory Studies of Reaction Mechanisms and Kinetics

Trace gases emitted by natural sources are oxidised in the troposphere which is modified by increasing concentrations of anthropogenically emitted pollutants, primarily NO_x. This situation is understood to introduce changes in the oxidizing capacity and in the radiation transfer regime of the troposphere. Attempts to model the anthropogenic perturbation require understanding of the chemistry of an important biogenic species, such as isoprene, terpenes and organic sulphur compounds.

Isoprene and dimethylsulphide (DMS) have been the focus of research in the Institute in recent years (see annual reports 1990, 1991, 1992), with laboratory studies on the kinetics and mechanisms of atmospheric reactions. These studies have mainly addressed the nighttime degradation of these species by reaction with NO_3 radicals. The knowledge acquired, especially in product studies, is now being applied to the investigation of the reaction of these species with the most important daytime oxidant, the OH radical.

The results of the studies performed on the oxidative degradation of DMS are described under the section devoted to the Atmospheric Sulphur and Climate project.

Testing of a non-photochemical source of OH radicals.

In most laboratory chamber experiments, OH radicals are produced by methods requiring irradiation of the reaction mixture with UV-light, such as the photolysis of CH_3ONO or H_2O_2. Photolabile reaction products or intermediates will then also be exposed to radiation, and this may preclude their detection and influence the product distribution resulting from the reaction. Thus, a non-photochemical method for production of OH radicals would be useful for providing insight in the possible photochemical steps involved in atmospheric processes. Such a method, for obtaining OH-radicals by thermal reactions only, is based on the reaction between hydrazine and O_3. A mechanism for this reaction has been proposed, in which the initial step is:

$$H_2N\text{-}NH_2 + O_3 \rightarrow H_2N\text{-}NH + OH + O_2.$$

Subsequent steps in the reaction lead to the formation of HO_2 while the stable, end-products are N_2 and H_2O_2. The reaction of O_3 with hydrazine is relatively fast ($k = 1.36 \times 10^{-16}$ cm^{3}molec^{-1}s^{-1}), and the yield of OH radicals is sufficiently high to make the method suitable for studies of OH-reaction rate constants and products. The latter, however, can only be studied if the hydrazine/ozone system does not significantly perturb the chemical reactions following the attack by OH.

Initially, attempts were made to apply the method to studies of product formation in the oxidation of DMS by OH radicals in the air. The reactions of ozone and hydrazine with DMS are slow and they were found to be negligible compared to the reaction with OH in the hydrazine/ozone/DMS system. However, a major problem was created by the observation of the occurrence of fast reactions of hydrazine with CH_2O as well as with SO_2, both known to be major products of the DMS-OH reaction.

Another drawback of the method is the high yield of HO_2 radicals in the hydrazine-ozone reaction, which may also perturb the processes under investigation. Clearly, the outcome of the series of experiments performed indicate that the hydrazine-ozone source in most cases will not be a convenient source of OH in laboratory chamber studies on the formation of products in atmospheric chemical reactions. It will certainly not be applicable to studies of the oxidation of isoprene where carbonyl compounds appear to be the dominant products.

Reaction of NO_3 with aromatics.

The increasing concentration of aromatic hydrocarbons in heavily polluted areas is a matter of concern, because of their toxicity and because of the oxidation products generated in a NO_x- rich environment.

Studies have been continued, in collaboration with the University of Milan, on the reaction between NO_3 and methylarenes, performed in the gas and liquid phases. The polar effects measured in the experiments of previous years have been re-evaluated. The results appear to favour a reaction mechanism in the gas phase that involves the addition of NO_3 to the aromatic ring as the first reaction step. This is then followed by the elimination of HNO_3 as a rate-determining step. No conclusion, however, has been reached on the formation of nitroarenes, an aspect that still deserves attention, because of the environmental importance of these products.

Atmospheric Sulphur and Climate

Global change studies aimed at understanding and quantifying the changes induced by man in the global biogeochemical cycles of major elements are in progress. The ultimate goal is to provide models capable of describing possible future changes and their effects, particularly on the climate. The climatic effects of changes in the global sulphur cycle are caused by the formation of sulphur aerosols, which scatter sunlight back into space and act as cloud condensation nuclei (CCN).

Quantifying the link between the gaseous precursors like DMS and sulphur dioxide (SO_2) emissions and aerosols, and CCN, in particular, is a problem of combining gas-phase chemistry, heterogeneous chemistry, aerosol dynamics and cloud processing. Furthermore, efficient ways must be found of implementing the description of these processes in global transport models. It has also been recognised that, apart from sulphur aerosols, other types of aerosols will have an effect on the global radiative balance, and must therefore be studied.

The Atmospheric Chemistry and Atmospheric Physics Units have contributed to the study of the above problems through laboratory, field and modelling activities.

Modelling

DMS oxidation mechanisms: uncertainty and sensitivity analysis

The chemical reactions involved in the oxidation of DMS in the troposphere are not yet fully understood. Although it seems most likely that DMS is a major source of sulphate aerosols in the unpolluted marine troposphere, it is not clear through which intermediates this final product is formed; neither has it been clarified how other sulphur-containing products, such as MSA, dimethylsulphoxide and dimethylsulphone, are formed, and, how important they are under the various conditions (temperature and trace gas composition) that may be encountered in the marine troposphere.

The main oxidation pathway for DMS in the atmosphere is generally believed to be initiated by reaction with the OH radical. Based on the available experimental studies of the reactions involved in this oxidation process and the hypotheses about the main reaction pathways that have been presented in the literature, a chemical reaction scheme has been set up (Fig. 1). An uncertainty and sensitivity analysis of the kinetic model represented by this reaction scheme has then been used to identify the uncertainties (reaction rate constants as well as concentrations of chemical species) that contribute most to the overall uncertainty on selected output parameters of the model. This analysis thus serves to answer the question: which parameters would it be most relevant to study in order to understand the atmospheric chemistry of DMS. The reaction scheme includes only homogeneous gas-phase chemistry and the rates are calculated for a temperature of 298 °K.

The rate constants and concentrations of trace gases involved in the model have been assigned uncertainty ranges reflecting the level of our present knowledege about them. The statistical analysis has been carried out with respect to three different output functions, namely:

- The ratio between MSA and the sum of SO_2 and H_2SO_4.(In addition, this exercise generated estimates of the most likely contributions of various pathways to the formation of SO_2 (Fig. 2) and $H_2SO)_4$.
- The sum of the peroxynitrate species CH_3SOONO_2, $CH_3S(O)OONO_2$ and $CH_3S(O)2OONO_2$.
- The ratio between SO_2 and H_2SO_4.

Consideration of the pathways leading to the formation of H_2SO_4 is of particular interest, because of the observations of Bandy et al. (Geophys. Res. Lett., 19, 1125, 1992) that suggests that H_2SO_4 may be formed from DMS in the troposphere without SO_2 acting as a major intermediate. If this is true, DMS would contribute substantially more to the growth of aerosols in the marine troposphere. The analysis highlights some rate constants (k_{23}, k_{22}, k_{18}, k_{19} and k_{21}) that need to be known more accurately in order to evaluate the importance of this pathway, but the current results indicate that the direct pathway to formation of H_2SO_4 is not likely to be a major one.

The rate constants highlighted in the analysis of the MSA/(SO_2+H_2SO_4) ratio are the same as those mentioned above. In spite of the large uncertainties inherent in these parameters, the ratios calculated by the model are in good agreement with those observed experimentally.

The calculated concentrations of the peroxynitrate species are low (less than 1% of DMS). The stabilities of these species are, however, strongly temperature dependent, so an extension of the analysis to investigate the additional effects of temperature dependencies might well lead us to attribute more importance to these intermediates. Future work will look into such temperature dependencies, as well as the coupling between gas-phase and liquid-phase chemistry in the atmosphere.

Formation of CCN from DMS

The 0-D model AERO2 has been used in Monte Carlo calculations to construct correlations between SO_4 mass and CCN, which may be applicable in large-scale models. Two scenarios are considered: a 'closed marine boundary layer (MBL)', in which all processes take place in a capped column, and an 'open MBL', in which entrainment of material from the overlying free troposphere into the boundary layer

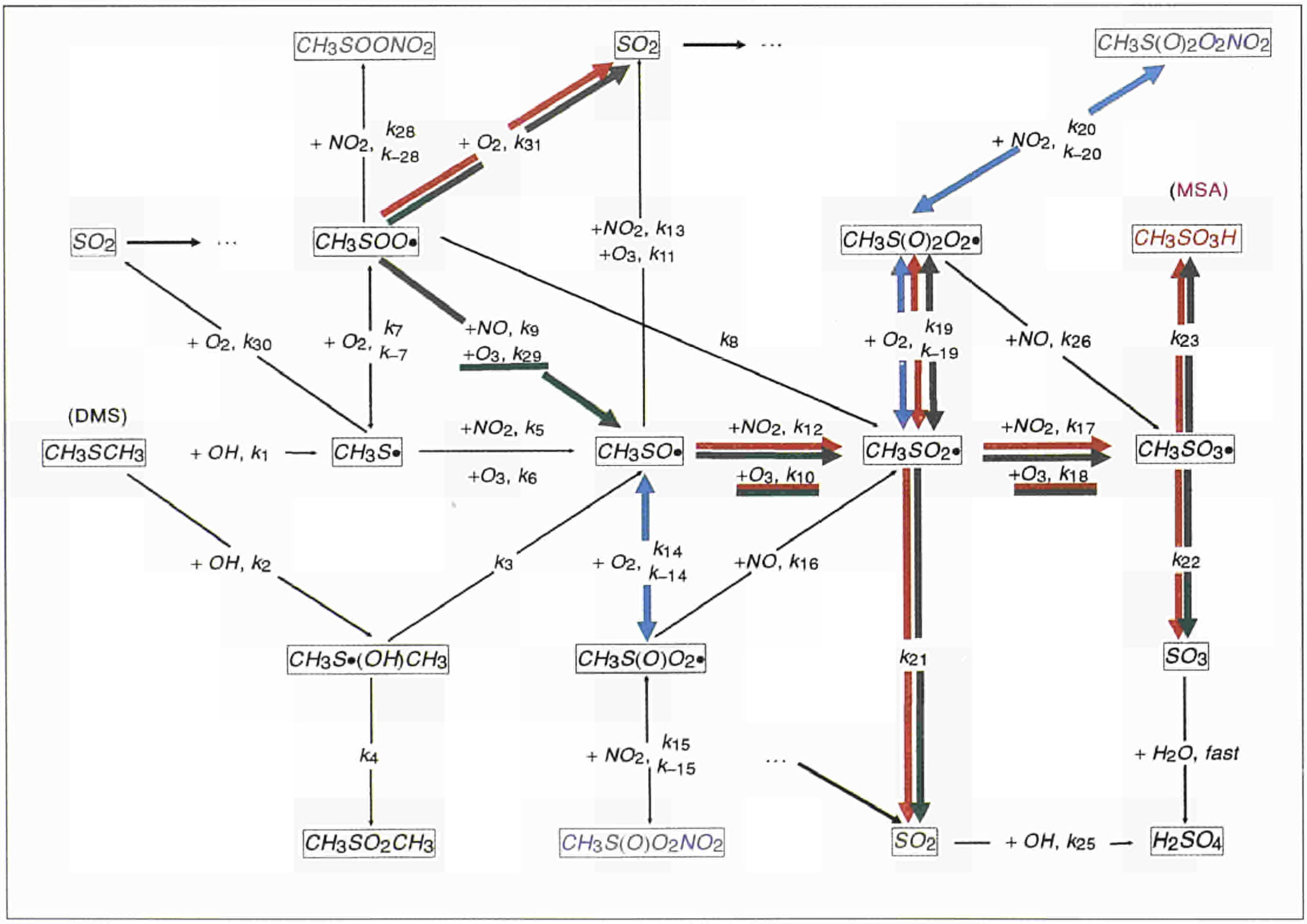


Fig. 1 Reaction scheme and sensitivity analysis. Reactions which contribute most to the output uncertainty are highlighted. Three output are considered: the ratio MSA to (SO_2+H_2SO_4) (red), peroxinitrates (blue) and the ratio SO_2 to H_2SO_4 (green)

column is considered.

The results for the two scenarios are significantly different. The closed MBL scenario runs predicted a time-scale for the formation of CCN active at 0.2% supersaturation, of at least one week, and CN and CCN(0.2%) concentrations that are generally higher and lower, respectively, than observations at Cape Grim. The open MBL scenario runs predicted a time-scale for CCN (0.2%) formation of the order of one day and CN and CCN (0.2%) concentrations that are in closer agreement with the observations from Cape Grim (see Fig.3). The resulting correlation between CCN (0.2%) and aerosol sulphate concentration is consistent with the correlation measured during the '92 Hudson cruise over the North Atlantic (see Fig. 11).

3-D Modelling of the sulphur cycle

A study of the potential gains from using faster algorithms in AERO2 in coupling the model to the sulphur version of the global transport model MOGUNTIA has led to the conclusion that, at present, AERO2 is computationally too demanding to achieve this. A version of the simpler model IMAD (Integral Model for Aerosol Dynamics), which assumes the SO_4 aerosol to be monodisperse, has therefore been developed and incorporated in MOGUNTIA.

IMAD takes the gas-phase production and emission of SO_4 as modelled by MOGUNTIA, and models the competing processes of new particle formation (nucleation) and condensation onto existing aerosol particles, together with coagulation and dry and wet deposition. In-cloud

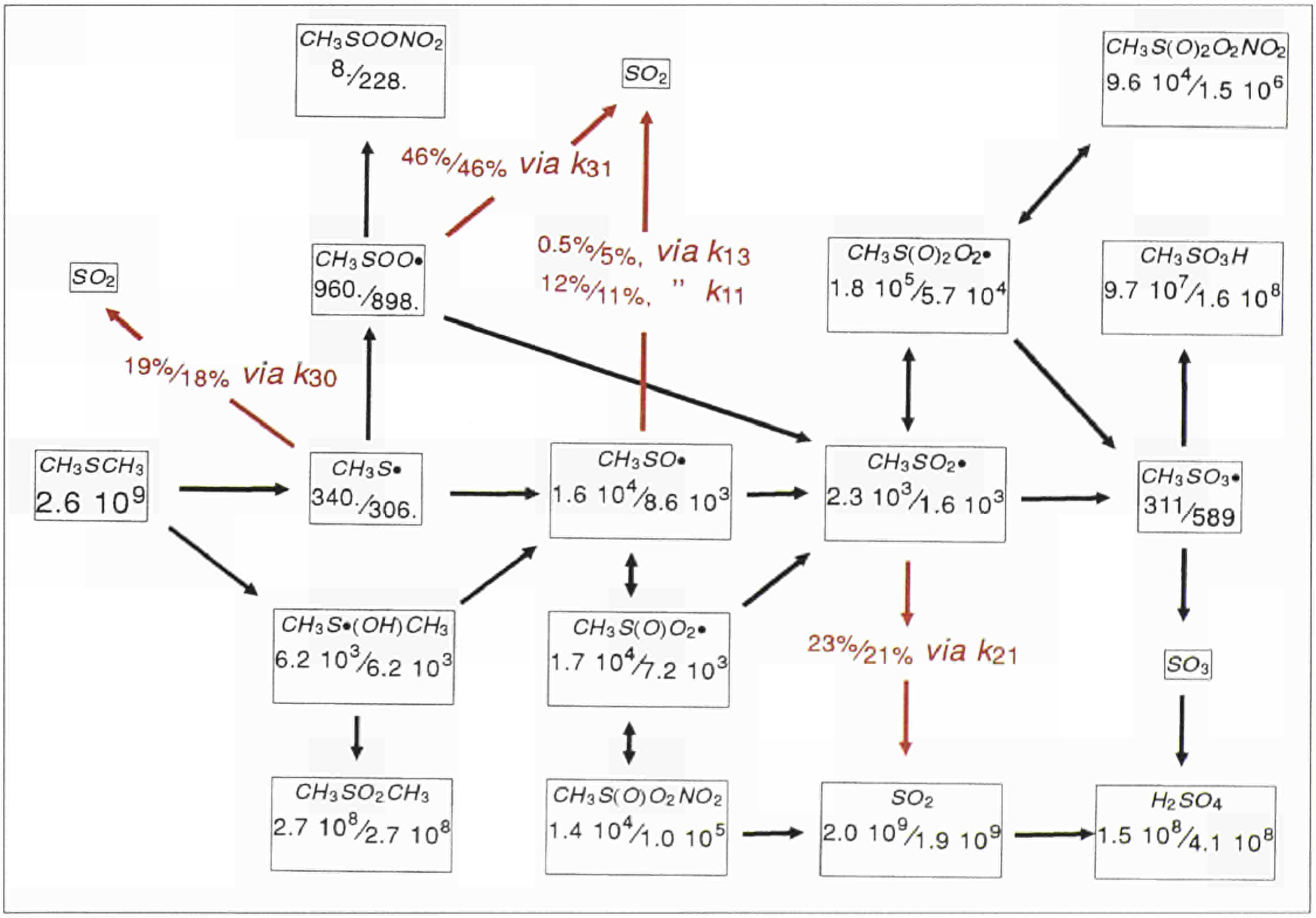


Fig.2. Uncertainty analysis. Average concentration of species in molec.cm^{-3} (boxes) in the unpolluted / polluted scenario's after 24 hours. The fraction of SO_2 formed through the various pathways is also given.

processing is not yet considered by the model. IMAD is thus a system of three simultaneous equations, describing the aerosol number concentration, the concentration of SO_4 in the aerosol phase, and the concentration remaining in the gas phase. An algorithm has been developed, which is based on a semi-analytical solution to the simultaneous equations, and gives good approximations to the solutions predicted by an efficient iterative method (4th order Runge Kutta), but with approximately 1/500th the CPU.

The IMAD/MOGUNTIA model predicts very little nucleation at the surface, and none over the oceans. Instead, the principal source region for new aerosols is the upper troposphere, which is not really surprising, given that nucleation is favoured by cold temperatures and a lack of background aerosols. The resulting January average aerosol number concentrations for the 950-850 mbar level of MOGUNTIA are illustrated in Fig. 4. A north-south gradient in aerosol number concentrations is predicted, whereas in July the highest numbers of marine aerosols (10 - 50 cm^{-3}) are predicted over the southern oceans. These values are generally too low when compared with observed values. It should, however, be noted that, as nucleation is a highly discrete and non-linear process, using the very coarse resolution conditions from MOGUNTIA as input will underestimate new particle formation. Further study will be necessary for tackling this problem.

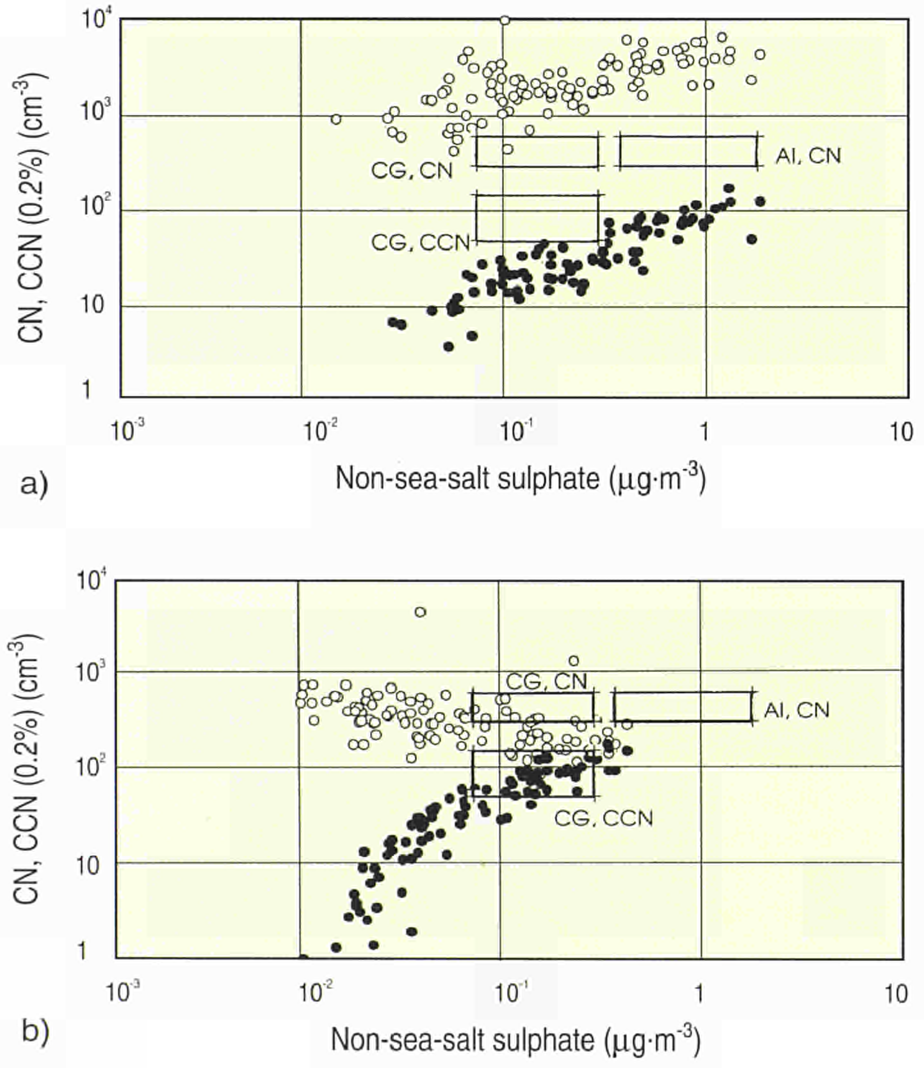


Fig.3. The number of condensation nuclei (CN) and cloud condensation nuclei active at 0.2 % supersaturation (CCN(0.2%)) as a function of the sulphate concentration in the aerosol phase, as predicted with the 0-D model AERO2. The conditions are those prevailing in the remote marine boundary layer, where the only precursor for aerosols is assumed to be DMS. The model calculations are compared with data taken at Cape Grim (Tasmania) and Amsterdam Island (Indian Ocean).

a) no entrainment of aerosols from the free tropospheric is considered;

b) entrainment of aerosols from the free tropospheric is considered.

3-D Modelling of the soot aerosol cycle

There are two principal sources of carbonaceous particulate (soot) emissions, namely: biomass combustion in deforestation and savanna fires, and fossil fuel combustion. A global emission inventory for both sources has been constructed from published data. The annual total black carbon emission is 10.4 Tg C y^{-1}, with 5.4 Tg C from biomass burning and 5 Tg C from fossil fuel use.

The above emissions inventories have been implemented in MOGUNTIA, and a simple deposition scheme developed. At present, only the mass of soot is transported by MOGUNTIA. The resulting average surface level soot mass distributions for January and July are shown in

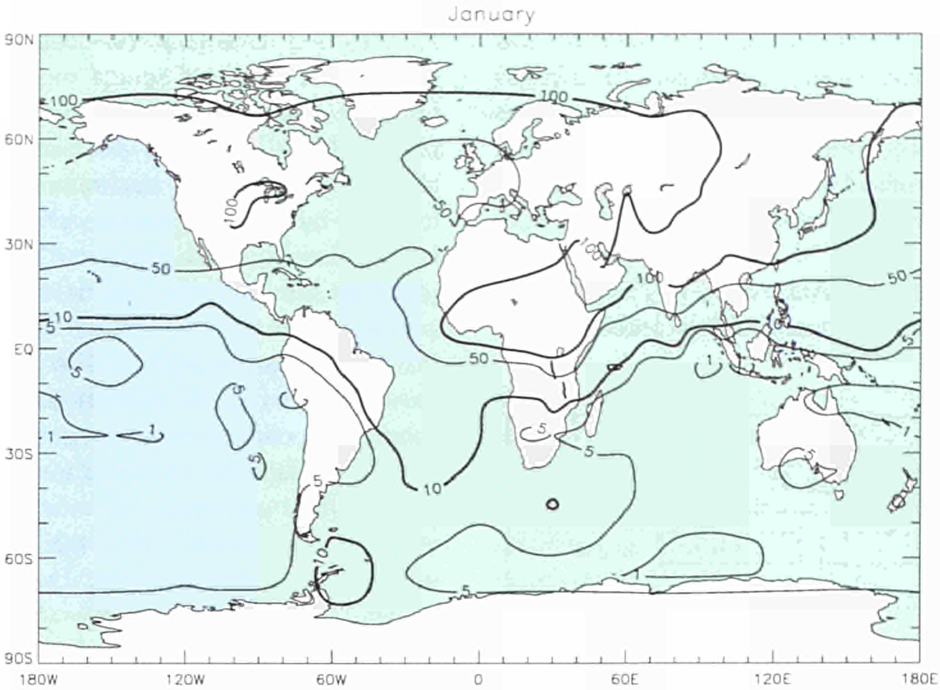


Fig.4. January average SO_4 aerosol concentrations for the 950-850 mbar level of MOGUNTIA (the level in which most marine boundary layer stratus cloud can be expected to form) Contours are at 1, 5, 10, 50 and 100 particles cm^{-3}.

Figs. 5a and 5b. Soot concentrations greater than 2,000 $ng.m^{-3}$ are predicted over Europe and Central Africa in January. The former is due to anthropogenic sources and the latter to biomass burning. Concentrations in these areas are lower in July, but a peak over South America from biomass burning is clearly visible. Between 20% and 50% of the predicted July soot burden in the Arctic of 50 - 100 $ng.m^{-3}$ is due to the inclusion of Boreal forest fires in Alaska, Canada and Siberia, which have not been considered in previous emission inventories.Comparison of these values with *in situ* data is under way.

Laboratory experiments

Structure of peroxynitrate formed in the tropospheric oxidation of DMS

Previous laboratory studies on the NO_3-initiated oxidation of DMS in air have suggested that two peroxynitrate intermediates are formed: one short lived species with IR spectral features identical to those typical of alkyl-peroxynitrates, and another, more stable species, with strong bands at 777 cm^{-1}, 1303 cm^{-1} and 1768 cm^{-1}. This last species has been shown to have a strongly temperature-dependent stability with respect to dissociation, with a life time of years at upper-troposphere temperatures. It has tentatively been assigned the formula

$CH_3S(O)OONO_2$, or possibly $CH_3S(O)_2OONO_2$.

In the presence of NO, the peroxynitrates will decay according to the following reaction scheme:

$$CH_3S(O)_xOONO_2 + M \Leftrightarrow CH_3S(O)_xOO^{\cdot} + NO_2 + M$$

$$CH_3S(O)_xOO^{\cdot} + NO \longrightarrow CH_3S(O)_xO^{\cdot} + NO_2.$$

The $CH_3S(O)_xO$ radical may then decompose to form CH_3 radicals and either SO_2 or SO_3 depending on x being either 1 or 2, or it may react with other compounds in the reaction mixture.

In the absence of NO and at low oxygen partial pressures, the equilibrium:

$$CH_3S(O)_xOO^{\cdot} + M \Leftrightarrow CH_3S(O)_x^{\cdot} + O_2 + M,$$

followed by decomposition or other reactions of the $CH_3S(O)_x$ radical, should also be considered. Thus, based on these considerations, measurements of SO_2-formation during the thermal decay of the peroxynitrate and upon addition of NO to air containing this species, were performed, to provide information about the structure of this intermediate.

The TDL-measurements of SO_2 showed that it was formed by the thermal decomposition of the peroxynitrate species, but not upon addition of NO; in fact, a small decrease in the SO_2 concentration was observed just after the addition of NO (Fig. 6), probably due to the formation of OH-radicals by the chemical reactions initiated by the addition of NO. As discussed above, this behaviour can be expected from a compound with the formula $CH_3S(O)_2OONO$, but not from $CH_3S(O)OONO$, which would be expected to form SO_2 when NO was added.

The only doubt that remains is whether some formation of SO_2 could be obscured by the simulta-neous removal of SO_2 due to its reac-tion with OH. Although this possibility seems unlikely, it must be tested in further work.

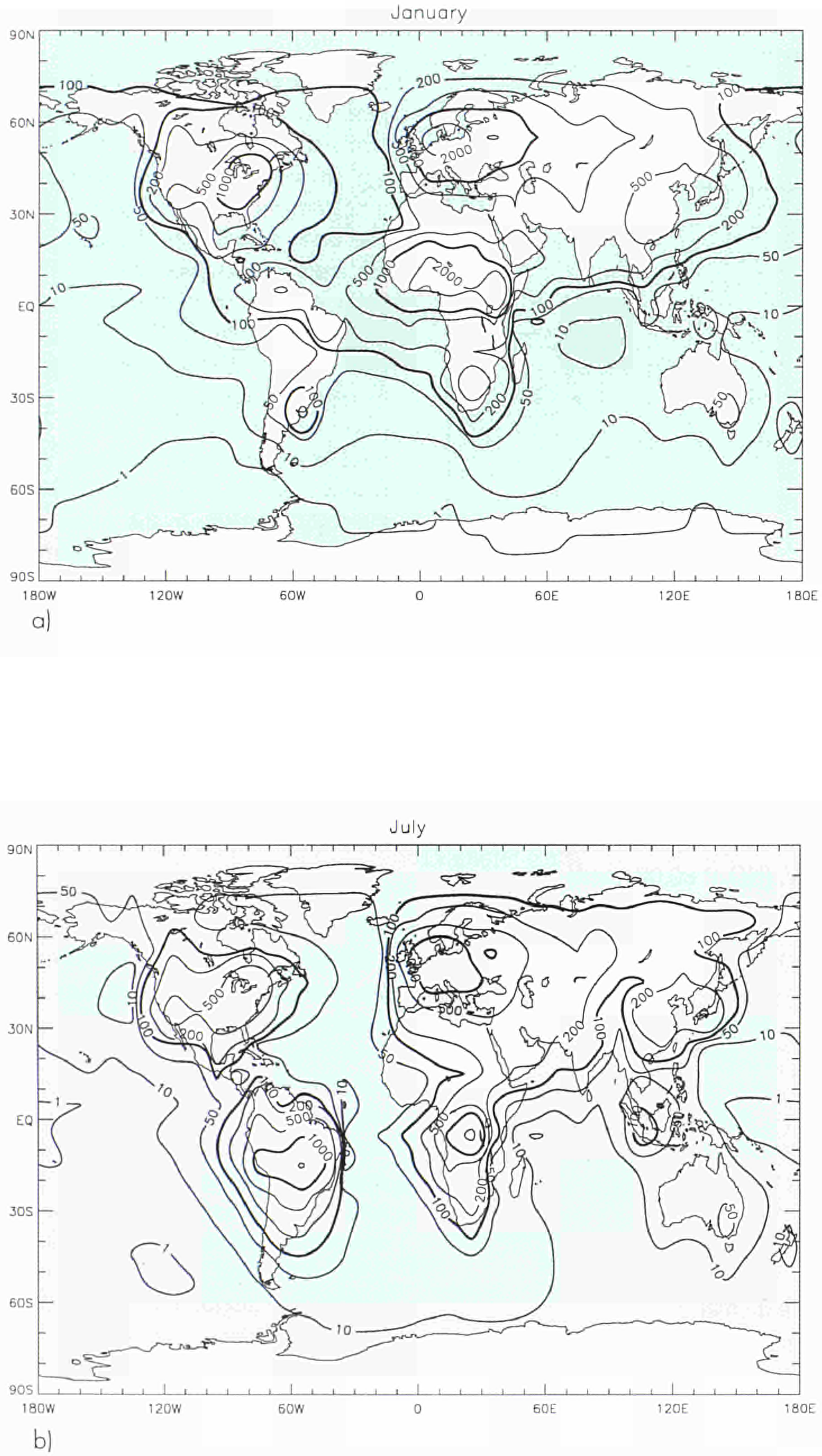


Fig.5. *January (a) and July (b) average soot concentrations at the surface (1000 950 mbar) predicted by the MOGUNTIA soot model. Contours are at 1, 10, 50, 100, 200, 500, 1000 and 2000 ng.m*$^{-3}$ *C.*

Study on the formation of H_2SO_4*-*H_2O *aerosols from the gas phase*

The aerosol dynamics models described above, need certain empirical data as input, such as nucleation rates and growth rates of H_2SO_4-H_2O particles. The aim of the present laboaratory work is to reduce the uncertainties that exist in these data.

A new laboratory device for gas/particle interaction studies, consisting of a laminar flow reactor and an OH source, was tested. The design of the set-up provides well defined experimental conditions. The laminar flow profile is a fundamental characteristic of the set-up. It allows the flow conditions, the diffusion to the walls, the chemistry and the particle dynamics to be modelled with a minimum uncertainty (compared to batch reactor systems), such that unknown parameters can be fitted into the model. Such a numerical model has been written, including all processes but for the aerosol dynamics.

Nucleation and growth properties of H_2O-H_2SO_4-particles are being studied in the photo-chemical system:

$OH^{\cdot} + SO_2 \longrightarrow HOSO_2$
$HOSO_2 + O_2 \longrightarrow HO_2^{\cdot} + SO_3$
$SO_3 + H2O \longrightarrow H_2SO_4$
$nH_2SO_4 + mH_2O \longrightarrow$aerosol particles

The OH- radicals are formed by photolytic dissociation of nitrous acid (HONO):

$HONO + h\nu(< 400\ nm) \longrightarrow NO + OH.$

Gaseous HONO is continously produced outside the reactor, with a generator described in the scientific literature. An advantage of using

HONO as a precursor for OH-radicals is that NO is formed, which regenerates OH-radicals by the reaction:

$HO_2^{\cdot} + NO \rightarrow OH^{\cdot} + NO_2$

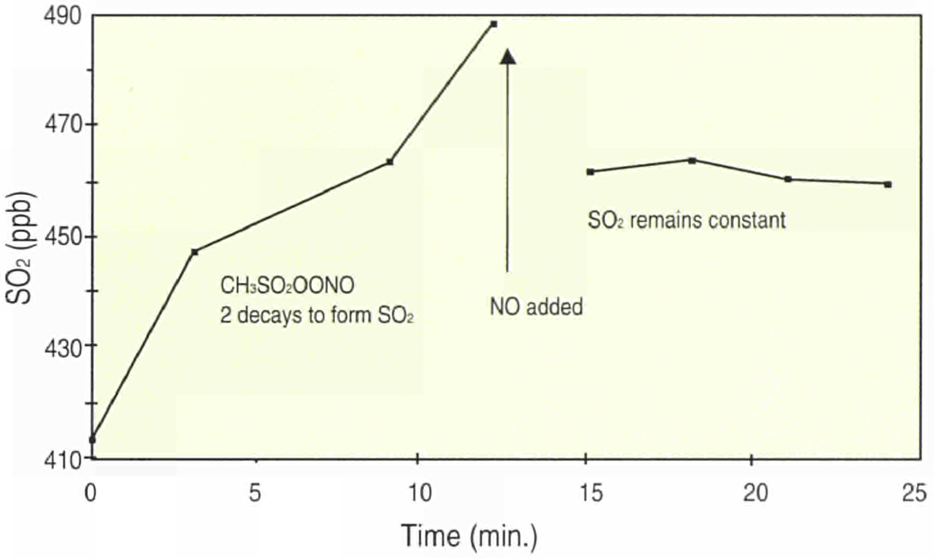


Fig.6. SO_2 formed by the atmospheric oxidation of DMS in the presence of NO_x, measured by TDL-spectroscopy in one of the experimental runs.

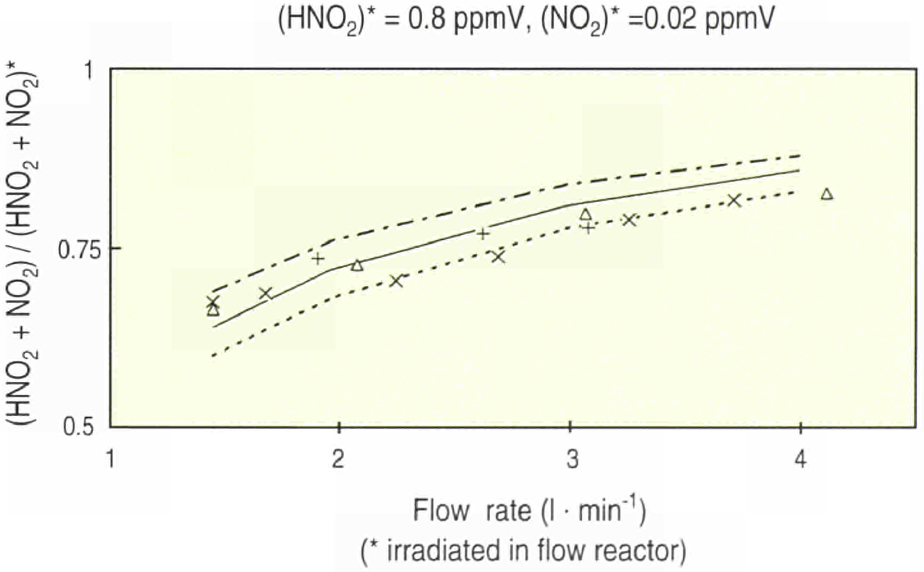


Fig. 7. Decay of (HONO + NO_2) in pure nitrogen by passing the irradiation section of 3m in the laminar flow reactor.

Δ, +, x = measured data from repeated experiments

—·— = model data for UV-lamp intensity = 16 W m^{-2}

——— = model data for UV-lamp intensity = 19 W m^{-2}

------ = model data for UV-lamp intensity = 23 W m^{-2}

In a first set of experiments, dark reactions of HONO with the reactor walls and the its photolytic dissociation were studied in a mixture of nitrogen and 1 ppmV of HONO. The dark dissociation of HONO on the reactor walls produces NO and NO_2 along the centerline of the reactor at a rate of 30 - 150 ppbV min^{-1} (3 to 15 % min^{-1}), depending on the previous use of the reactor. The photolytic decay of HONO was used as a chemical actinometer. Figure 7 shows first results of fitting the light intensity in the numerical model to the decay of HONO measured at the beginning and the end of the irradiation section of the flow reactor. Apart from the light intensity, the fitted model further shows that, for an initial HONO-concentration of 1 ppm, an OH-concentration of about 108 molecules cm^{-3} at the centerline of the reactor can be expected.

Preliminary tests have shown that, for an input SO_2-concentration of 1ppm, sufficient H_2SO_4 is formed for the particles to grow bigger than the detection limit of the TSI Differential Mobility Particle Sizer System (DMPS). Figure 8 shows the size distributions of H_2SO_4 particles formed in the laminar flow reactor and measured at the end of the irradiation section. A good stability and reproducibility of the results is obtained. Comparing measured particle size distributions as a function of residence time, relative humidity, initial SO_2-concentration and OH-concentration with the results of our coupled flow-diffusion-chemistry-aerosol model will yield information on nucleation rate and condensation (accommodation coefficient), as is needed for use of the models.

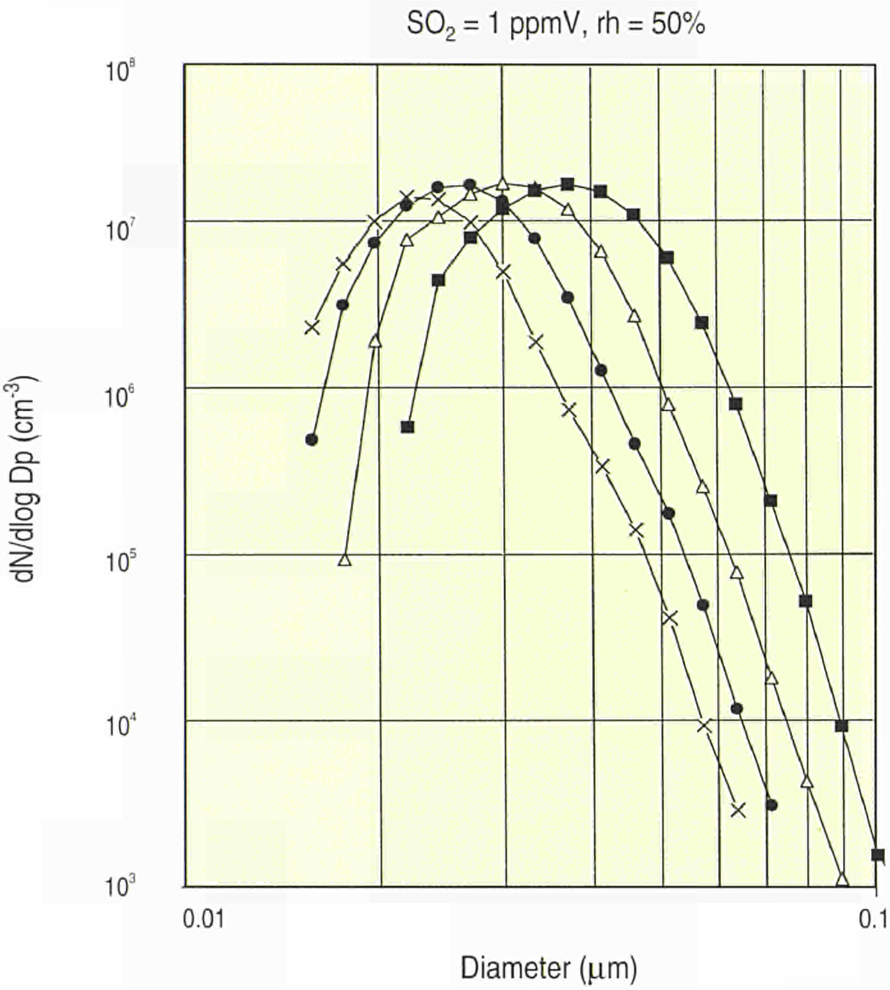


Fig. 8. Size distributions of H_2SO_4 - H_2O particles formed in the laminar flow reactor for different flow rates (residence times: x = 38 s, ● = 50 s, D = 72 s, ■ = 110s).

Sampling device	Time resolution
High volume sampler (30 $m^3 \cdot hr^{-1}$) for ionic composition of total aerosol load (Rieme)	12 - 36 hr.
On-line measurements of black carbon light absorption coefficient with aethalometer (Magee Scientific)	10 - 60 min.
Differential Mobility Particle Sizer (DMPS) system for aerosol size distributions in the size range 0.02 - 1 µm (TSI model 3071 & 3020)	15 min.

Table 1. *Instrumentation on board the CSS Hudson for characterisation of aerosol properties*

Field measurements

Aerosol measurements in the North Atlantic: the Hudson '92 cruise

During the Hudson '92 cruise (September - October 1992), an extensive dataset on physico-chemical properties of the North-Atlantic aerosol was collected (Table 1). The measurements were made in a region which has not only biogenic sources for sulphate (from DMS), but which is also impacted by pollution plumes from Europe as well as from north-east America, adding an anthropogenic sulphate component to the aerosol mass. The data analysis was aimed at evaluating the anthropogenic signal in properties of the aerosol that are climatologically relevant, and in particular, the concentration of particles that can be activated to form cloud droplets.
The typical marine aerosol bimodal size-distribution in the 0.01 - 1µm diameter size range, with a minimum round 0.1µm, was observed throughout the whole cruise, when the ship was 500 - 1,000 km away from either continent (Fig. 9). The shape of the distribution was explained (Hoppel et al. Geophys. Res. Lett., 1986, 13, 125) as being the consequence of 'cloud processing' of those particles that are larger than the critical size for cloud droplet nucleation (typically around 0.1 µm).
The large cloud water droplets accumulate sulphate rapidly via the aqueous-phase oxidation of SO_2, and upon evaporation of the cloud, the residual aerosol particles have shifted to significantly larger sizes than the non-activated, interstitial aerosol, resulting in a gap between the two size-distributions.

It can be argued that the second mode consists of "cloud processed nuclei" (CPN) and that they consist of the CCN that are activated at the supersaturations prevailing over the ocean. Hence, the analysis which has been done consisted of fitting the sum of two lognormal distributions to all available bimodal distributions, yielding concentration, mean geometric diameter and geometric standard deviation for both modes. The CPN concentration was then further correlated to black carbon as an *in situ* measured tracer for anthropogenic origin of the air mass. A regression analysis on a log-log scale shows a major anthropogenic contribution in the concentration of CPN, although it is noteworthy that the slope of the black carbon - CPN regression is lower than one, i.e. the relative effect of pollution on the CPN concentration decreases with increasing pollution (Fig. 10).

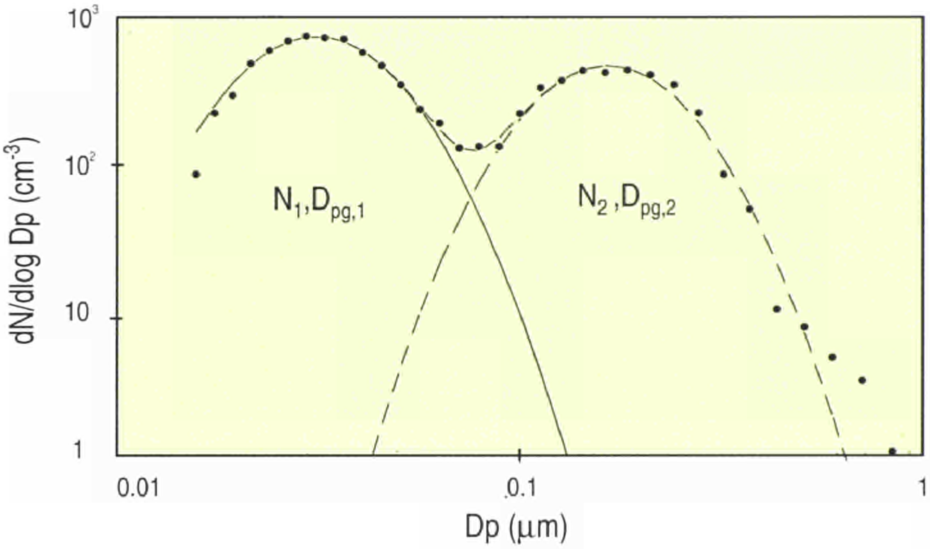


Fig. 9. Example of the typical bimodal size distribution of the marine aerosol, measured during the Hudson-92 cruise. The two modes can be fitted with the sum of two log-normal distributions, yielding concentration N_i *and geometric* mean diameter $D_{pg,i}$ of each mode separately.

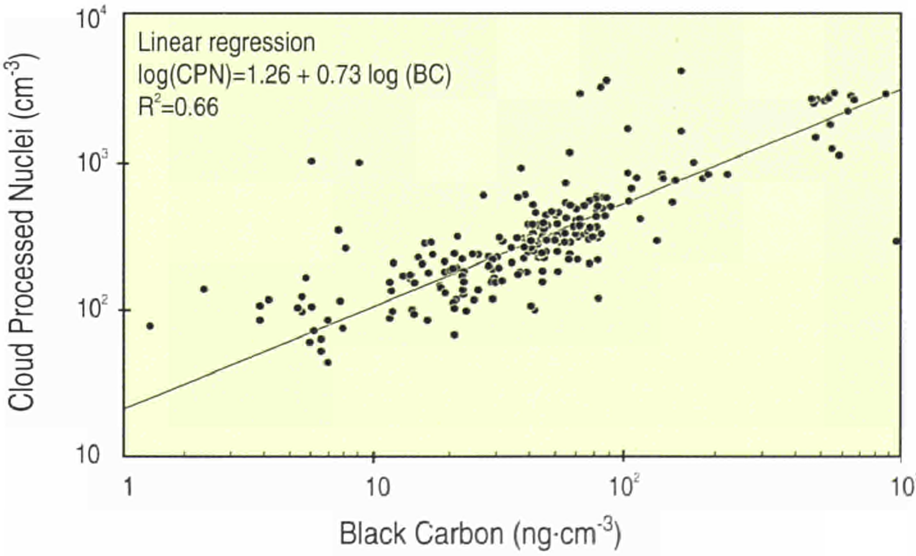


Fig. 10. Scatter plot of the cloud processed nuclei (CPN) concentration versus atmospheric black carbon over the North Atlantic. The R^2 *value of the linear regression indicates that 66% of variation in CPN is explained by the variation in black carbon, hence by anthropogenic pollution.*

The CPN concentration was also correlated to the non-seasalt (nss) sulphate concentration on the filter samples. Also in this case, a strongly positive correlation between nss-sulphate and CPN has been found. This correlation could be an important tool in assessing the climatic effects of sulphate, since most models predict only sulphate mass, without any information about the number of CCN the mass equates to. This result was compared with literature correlations between nss-sulphate and concentrations of CCN (measured with a CCN counter) and cloud droplets under various conditions of location and pollution (Fig. 11). It appears that the result from this approach are consistent with the overall trend. This provides *a posteriori* support for the proposed mechanism, suggesting that CPN, CCN and cloud droplets refer to similar subsets of the aerosol population. An explanation for the large variability in CPN at a given sulphate mass must be found in the fact that sulphate is not the only chemical compound in the aerosol. And even if sulphate were the only compound, small variations in the size distribution could still give large variation in CCN(Sc) at a given mass. Finally, at low sulphate concentrations, the measured

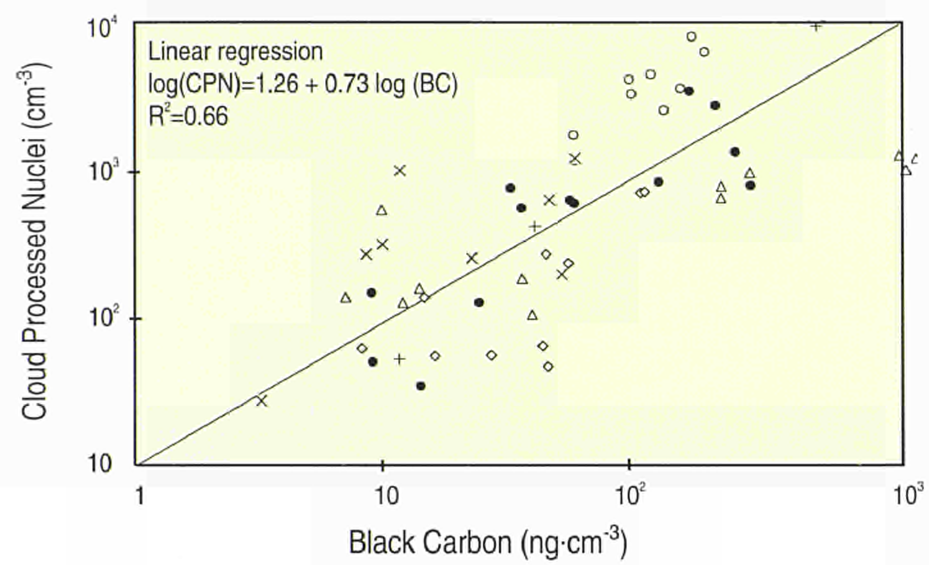


Fig. 11. Measured cloud droplet and CCN concentrations versus the sulphate content in the respective particles, compared with the CPN versus sulphate obtained in this study. The full line is the linear regression through last data.

• *This study, CPN*

\+ *Pueschel et al., J.Climate & Appl. Meteor., 1986, 25, 1908, cloud droplets*

x *Leaitch et al., (1992), J. Geophys. Res. 97, 2463, cloud droplets*

◇ *Berresheim et al., (1993), J. Geophys. Res. 98, 12701, CCN (0.3%)*

○ *Novakov and Penner (1993), Nature 365, 823, CCN (0.5%)*

Δ *Hegg et al., (1993), J. Geophys. Res. 98, 14887, CCN (1%)*

correlation in Fig. 3 broadly confirms the model calculations that explain sulphate on the basis of DMS emissions alone.

DMS in freshwater lakes: a long-term field study.

Up to now, DMS has mainly been studied in marine environments, because the larger surface areas of these ecosystems makes them obviously the most important source of atmospheric DMS. Other sources of DMS in the atmosphere, such as land vegetation or freshwater ecosystems, have only recently received attention. DMS flux estimates for these habitats are scarce as yet. Additionally, such minor contributors to the natural sulphur flux in the atmosphere may present a good site for the investigation of some phenomena which are difficult to access in marine ecosystems.

The area around Ispra is rich in freshwater lakes, and many of them are easily accessible throughout the year, making possible long-term studies of, for example, seasonally variable processes. In July 1993, a field study of Lake Maggiore, Lake Monate and Lake Varese was initiated to identify and quantify DMS in freshwater samples. The objectives of this study are to obtain water-to-atmosphere flux estimates for DMS during a full seasonal cycle and to identify sources of this compound in the lake waters. Lake Maggiore and Lake Monate are oligo-mesotrophic lakes, while Lake Varese is a highly eutrophic lake, with massive H_2S production during summer months. Comparison of these lakes offers the possibility of investigating the influence of trophic status and variable oxygenation of lake waters on DMS concentrations and thus DMS water-to-atmosphere fluxes. Sampling of the lake water was performed in cooperation with the Marine Environment Unit of IRSA and the Istituto Italiano di Idrobiologia at Pallanza.

DMS production in the marine habitat is the result of phyto-, zoo- and bacterio-plankton activity. The relative importance of each type of organism is difficult to assess, because all activities take place in open water. Because of the depth of the oceans, sediment processes are of minor importance to surface DMS levels in the marine environment. In contrast, in comparatively shallow freshwater lakes, sediment processes are closely linked to open water processes. Here, it is both meaningful and possible to investigate both the bacterially dominated bottom sediment and the open water. Comparison of the two compartments will indicate the relative importance of the bacterial (sediment) and food web (open water) contributions to DMS production.

DMS was found to be present in all samples. Samples from the stratified Lake Varese, however, also contained a variety of other volatile sulphur compounds (VSCs). Work to identify

Environment	range of concentration	source
Seawater		
. oligotrophic open Atlantic	0.24 - 2.0 nM (mean = 1.05 nM)	(1)
. Northwest African Upwelling	0.69 - 5.1 3nM (mean = 1.97 nM)	(1)
. North Pacific	mean summer = 2.2nM mean winter = 1.3 nM	(2)
hypersaline lakes	0.4 - 33 nM	(4)
Freshwater:		
. Canadian freshwater lakes	0.31 - 11 nM	(4)
. North Italian freshwater lakes	0.1 - 4.8 nM	(5)

Table 2 . Dimethylsulfide concentrations in some aquatic ecosystems:
The data were extracted from:
(1) IRSA/El Hudson 1992 cruise, unpublished data,
(2) Bates, T.S., et al., J. Geophys.Res., 1987, 92, 2930,
(3) Simo, R. et al.; Dimethylsulfide, Oceans, Atmosphere and Climate, Restelli, G. and Angeletti, G. (Eds.), Dordrecht, 1993, 173,
(4) Richards, S.R., et al. Limnol. Oceanogr. 1991, 36, 468 and
(5) present measuring campaign

and quantify these components is in progress. The DMS concentrations in the lake waters were in the range of oligotrophic marine waters,and therefore at the lower end of the concentration range in marine environments.(Table 2).Increased DMS concentrations were detected in Lake Varese, and depth profiles indicated that sediments are a source of DMS and other VSCs in this lake (Fig. 12).

Environmental Monitoring

Stratospheric ozone.

The Brewer ozone spectrophotometer, on loan from the Italian Ministry of the Environment as part of an agreement with the University "La Sapienza" of Rome, has been operated continuously throughout the year. The instrument was used in the 1991-1992 European Arctic Stratospheric Ozone Experiment (EASOE), and it is now involved in the 1993-1994 SESAME campaign. The 1992-93 preparatory exercise that completed its main measurement phase at the end of March 1993, has confirmed the anomalously low ozone column values previously measured in the 1991-1992 period.

Figure 13 shows the monthly averages of the total ozone column, measured at Ispra for the periods from January 1991 to December 1992 (dotted line) and from January 1992 to December 1993 (heavy dotted line), and at Arosa (CH), where the monthly means have been averaged over thirty years (1957-1988, full line).
From the figure, it appears that the 1993 ozone values in the winter months, and particularly in February and March, are lower than those measured in 1992, and that they remain lower for a quite long period, reaching the 1992 level only in August.

Figure 14 shows the ratio between the total ozone measured from January to August 1993 and that measured in the corresponding months of 1992. The data represent five-day averages to reduce the synoptic noise. Twenty days of July are missing, because of the failure of the Brewer instrument.

The 1993/1992 ozone ratio appears to decrease to a minimum of about 0.75 during many days of January and February and to remain lower than one, except for some sporadic episodes, up to the end of July.

The mean values of ozone measured at Ispra from the 1st of January up to the end of June are, respectively, 343.3 Dobson Units (D.U.) for 1992

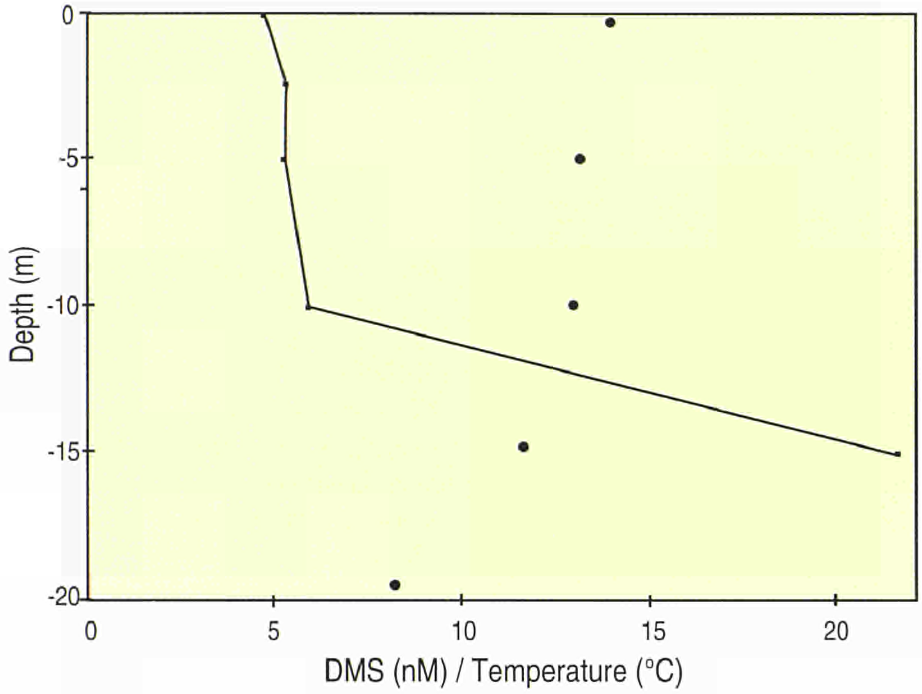


Fig.12. Depth profile for dimethylsulphide in Lake Varese (N. Italy). Closed squares represent DMS concentrations, points represent temperature. The presented profile was taken in November 1993. Maximum depth is approximately 25 m.

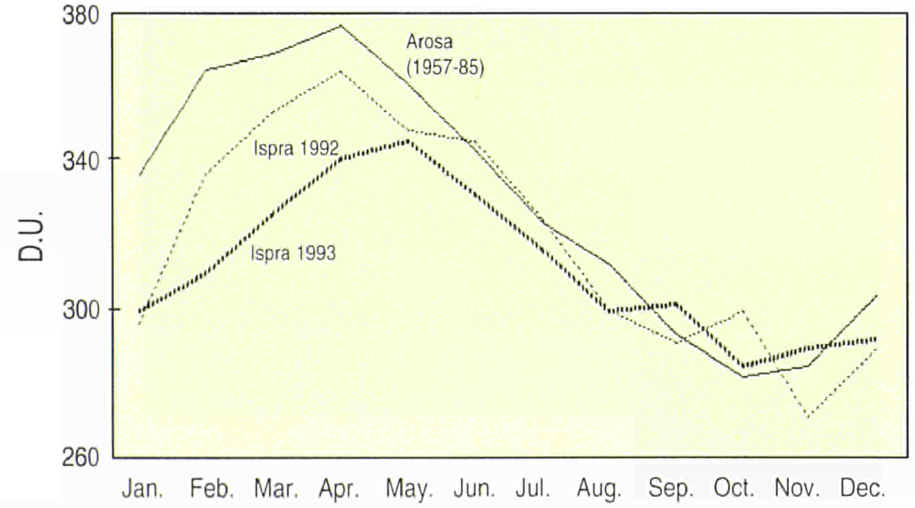


Fig.13. Monthly averages of total ozone column values measured at Ispra site during 1992 and 1993 . The data from Arosa (CH) are the averages over the periode1957-1988.

and 328.1 D.U. for 1993, giving a 1993/1992 ratio of 0.96. This means an average decrease of the ozone cover, in the first six months of 1993, of about 4% with respect to the situation in 1992. The mean ozone data for August 1992 and 1993 are identical (300.7 D.U. and 300.1 D.U., respectively), indicating full recovery of the normal ozone levels.

In order to have at least a qualitative confirmation of the anomalous trend of ozone in 1993, an analysis of the UV-B irradiation measurements taken every day by the Brewer instrument has been made. An enhancement of the UV-B in 1993 would confirm the decrease of ozone; unfortunately, a simple relation between ozone and, UV-B cannot be established due to the strong dependence of the UV-B field on clouds and atmospheric aerosols.

In order to reduce this influence, the UV-B data have been ratioed to the total irradiation values measured daily with a pyranometer by the meteorological service of Ispra. The pyranometer detects solar radiation in the range 305-2800 nm, so that its sensitivity to ozone is negligible, while its response, as for the Brewer instrument, is affected by the presence of clouds and aerosols. Due to the different wavelength ranges encompassed by the two instruments, the influence of the atmospheric parameters on the radiation detected is not the same, and this normalisation procedure can be considered only as a rough approximation to the undistorted UV-B radiation.

Using the normalised data, the ratio between the 1993 and 1992 UV-B values averaged over the first six months of each year, is 1.08. This

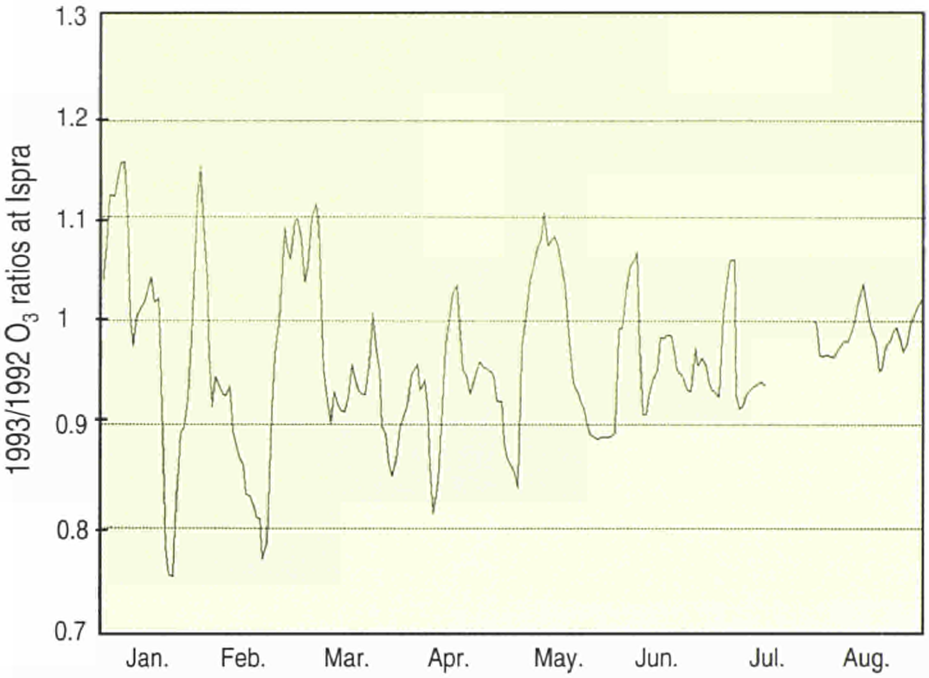


Fig. 14. 1993 / 1992 ratio of five days averages of total ozone column measurements at Ispra. A predominant ozone deficit in the first half of 1993 is clearly apparent.

value, even if only indicative, shows an excess of UV-B for the first half of 1993 compared to the same period of 1992, supporting the concept of a deficit of ozone occurring in the corresponding months of 1993.

Tropospheric ozone in the pre-alpine and alpine regions.

As a follow-up of previous studies on the mechanisms responsible for influencing the tropospheric ozone distribution in the pre-Alpine region, ozone measurements available in the pre-Alpine and Alpine regions from 1987 to 1991 have been collected in a database. A first analysis shows that the southern slopes of the Alps may suffer from high ozone levels. The large contribution of ozone episodes in these regions in the warm season is shown by the monthly average values, which at intermediate altitude (400 up to 1800 m) are comparable or even 10-20 ppbv higher than in the medium troposphere. These data, and some airborne measurements made in 1991 by a Swiss group, confirm the presence on the warm days of an "ozone front" up to 1800 m high, which is formed above the Po plain by thermal convective motions and which moves towards the Alpine slopes during the warmest hours of the day.

A working group on "Tropospheric ozone and photo-oxidants in the Alpine region" has been set-up as a JRC initiative. Participants from Switzerland, Austria, Italy and Germany are collaborating to define a common project. The main objective is to set up a data base of ozone episodes in the Alpine region, that will serve as a reference for the evaluation of possible strategies of precursor reduction and for the definition of air quality standards in the Alpine countries.

Reconstruction of surface ozone historical data.

Great concern about the increasing trend of tropospheric ozone at mid-latitudes of the northern hemisphere has focused attention on historical ozone obervations made by the Schönbein technique one century ago. An *ad hoc* procedure to convert the original readings into present-day concentrations (in ppbv) was set up and validated. The same procedure was applied to observations made at tropical latitudes; the results show that historical levels were lower than those observed at mid-latitudes of both the northern and southern hemipheres.

Historical time-series of ozone levels, provided by various institutes, have been analyzed by the procedure perfectioned in previous studies. Particularly interesting are the data from Vienna, probably the longest record in the world (1853-1920). The converted data show no significative trend for the ozone levels observed in those years, in contrast to the recent data from Arkona, a remote station on the Baltic sea, for which a positive trend of about 1% per year has been observed. Fig. 15 shows the evolution from 1853 to 1983 of the mean ozone level, as deduced from the two data series.

Application of spectroscopic techniques

The general-purpose multi-spectral

detection system described in the 1992 Annual Report has been calibrated in terms of the wavelength and intensity dependence of the diode array. The system was implemented with two other lasers, an ArF excimer laser operating at 193 nm and a Nd-YAG laser operated at 532 and 355 nm, to create a Laser Photofragmentation Spectroscopy apparatus. This anlytical tool will be applied to the detection and characterization of atmospheric sulphur species such sulphur dioxide, dimethylsulphide, methanesulphonic acid and sulphuric acid in the gas phase and in liquid aerosol, in the context of chemical studies related to the Atmospheric Sulphur and Climate project. The principle of the technique is the following: the sample is photofragmented by the excimer laser or the YAG laser, and the fragments created are then interrogated by the tunable dye laser, whose firing can be delayed in time with respect to the former lasers. Then the fragment fluorescence is measured. In some cases, the fragment can also be photoionized. The advantage of the photofragmentation technique is that it permits the detection of atmospheric species that do not directly fluoresce under laser irradiation and normal tropospheric conditions. From a theoretical evaluation of the overall efficiency of the various processes (fragmentation, excitation and detection), it can be anticipated that sensitivities of the order of parts per trillion can be achieved, assuming that interferences from ubiquitous atmospheric gases (e.g. NO_x) and other sulphur species (e.g. CS_2) can be reduced to a minimum.

The detection of atomic chlorine resulting from the fragmentation of volatile organic compounds will also be attempted, since some chlorine lines can be excited at a more accessible wavelength region of the dye laser employed.

Laser photofragmentation spectroscopy will also be applied to the analysis and characterization of aerosols. In this case, the experimental set-up (Fig.16) will involve the handling of the aerosol flow through the measurement cell and an aerosol sampling inlet.

Aerosol tracer.

This study was undertaken within the more general framework of the research area "Atmospheric Sulphur and Climate: Field Experiments" with the purpose of testing the release of gold in the atmosphere as a potential aerosol tracer.

The detection of gold in atmospheric particulate matter, collected on filters, has been carried out by exciting the atomic fluorescence of the vapour resulting from the atomization of acidic solutions of the filters in an electrically heated graphite furnace. Two laser beams were used to excite the atoms to a high level, from which radiation in the low ultraviolet was detected. The absolute analytical sensitivity of the technique lies in the femtogram range. A background concentration of about 11 pg of gold per cubic meter, with a standard deviation of about 7 pg m^{-3}, was assessed.

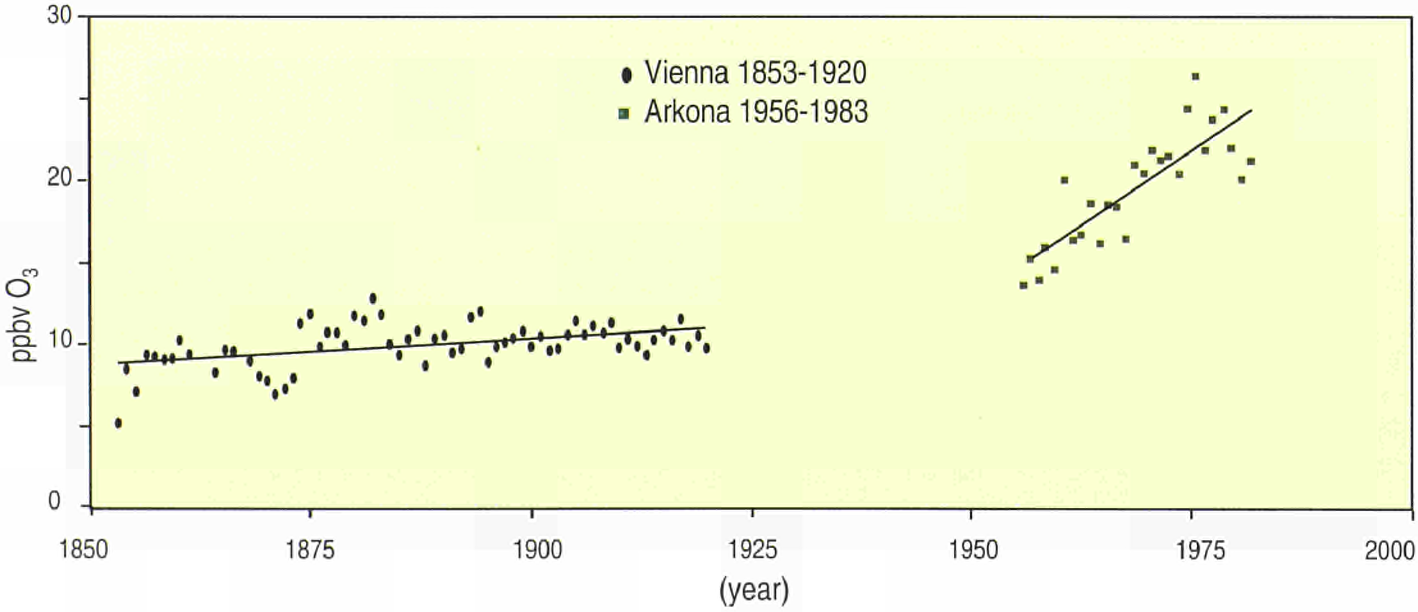


Fig.15. Ozone trend at mid-latitudes as obtained from data series from Vienna (1853-1920) and from Arkona (1956 - 1983) measuring stations.

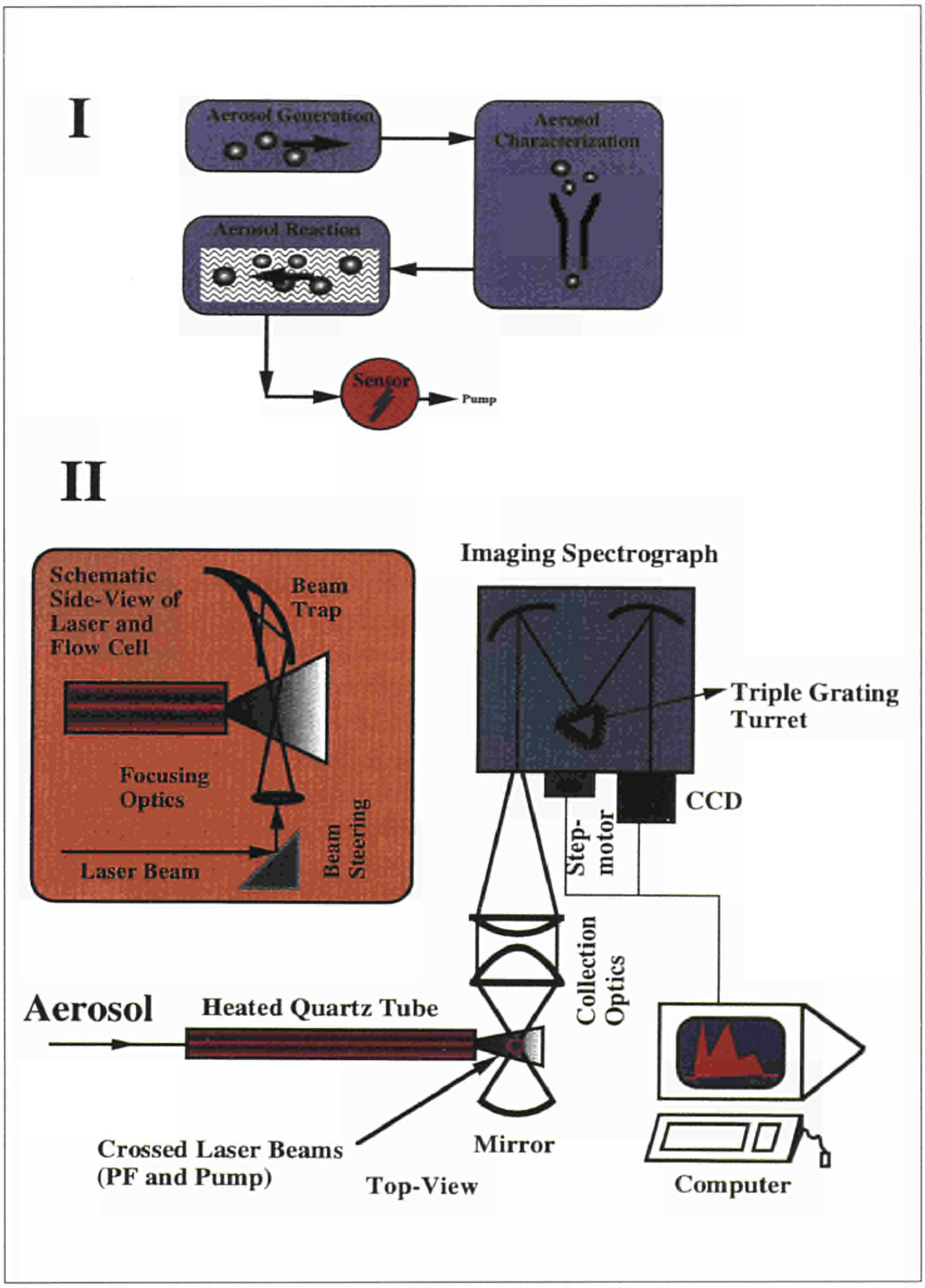


Fig.16. Schematic Diagram illustrating the instrumental set-up used for the technique of Laser Photofragmentation Spectroscopy of Aerosols.

I : Generation and characterization of aerosols. The polydispersed stream of aerosols, after being characterized (particle number density and size distribution) is arranged into a monodispersed stream, which can further react with selected gaseous species before being fragmented by the laser beam.

II. Spectroscopic Detection of Fragments. The aerosol stream, desolvated in a heating tube, is probed at the exit of the tube by a crossed pair of focused laser beams, which fragment the species and interrogate the fragments formed. Some fraction of the fluorescence emitted is collected, spectrally filtered by a monochromator, and detected by a multichannel (Charge Coupled Device, CCD) detector. The data are processed and analyzed by dedicated computer software.

Atmosphere-Biosphere Interactions: the BEMA project

The activities in the field of atmosphere-biosphere interactions have continued to be mainly addressed to the study of vegetation emissions in the Mediterranean basin and their role in atmospheric chemistry and ozone formation in that area. BEMA, a project on Biogenic Emissions in the Mediterranean Area, has been developed in collaboration with 12 European laboratories. The main project activities include:

- field experiments at selected Mediterranean sites, to evaluate the types and variation of the vegetation emissions under different physiological and meteorological conditions, and to study their fate in tropospheric chemistry;
- laboratory experiments in plant exposure chambers, and in teflon bag reaction chambers to evaluate, in selected plant species, the type and variation of the vegetation emissions under controlled conditions, and their atmospheric transformations.

Field Measurements

Before BEMA went into its operational phase, a preliminary measuring campaign was performed in June 1993 as a test study to assist in further development of the overall BEMA concept, a first check on it feasibility, and the tuning of scientific approaches and experimental techniques. The main objectives of this two week-experiment were:

- to test individual laboratory methods for concentration and emission measurements under field conditions;
- to compare in-field sampling and

analysis methods;

- to screen the chemical composition of emissions and concentrations;
- to develop preliminary ideas on local patterns of biological, chemical and meteorological conditions;
- to check the in-field applicability of micrometeorological methods for vertical flux measurements;
- to try first estimates of VOC fluxes from specific ecosystems and the comparison of cuvette and micrometeorologial techniques;
- to determine scientific and infrastructural needs and deficiencies to be improved in the major experiments to come;
- to establish interdisciplinary cooperation among the laboratories participating in the BEMA activities.

The BEMA concept relies heavily on experimental field campaigns to be conducted at sites in Italy, France and Spain within the next four years. Up to now, only the Italian site, "Castelporziano", has been identified, where installing the required infrastructure could be managed in relatively short time and which additionally provides numerous scientific data from earlier measurements; and which was therefore chosen for the preliminary study.

The Castelporziano nature reserve covers ca. 4,800 ha between Rome and the sea-shore at Ostia; public access is limited by fencing. The site, ranging from sea level to 85 m a.s.l. is rather flat and is covered by 48.4 % broadleaved trees, 13.2 % sclerophyllic trees, 14.4 % pine plantation, and 9.6 % cork oak plantations. As a result of its geographic location, Castelporziano shows aspects typical of rural Mediterranean conditions (almost no local anthropogenic emissions; land /sea-breeze influences), but also provides some unique features: large aerial sources of man-made emissions, being 10-15 km northeast (City of Rome) and northwest (Fiumicino airport), and line sources from motor traffic during the morning and evening rush-hours east and west. Therefore, the land-breeze during the night is advecting polluted air, while cleaner air masses pass the area between ca. 10.00. - 17.00 hr. with the daytime sea-breeze. Mean air temperatures (period 1981-91) range from ca. 8.3°C in January to 23.0 °C in August, maximum temperatures of more than 30°C have frequently been recorded in July and August. The annual precipitation is 740 mm, with an extended dry period in May (30 mm), June (27 mm), July (4 mm) and August (23 mm), and maximum rainfall in October (130 mm).

Two major experimental plots were selected for continuous measurement: a 30-year-old pine/oak plantation with representative shrub undergrowth (*Erica, Rubus, Cytisus, Pistacia, Phyllirea, Myrtus*), and a semi-natural Mediterranean greenland, the so-called "pseudosteppe" area, for research on low-vegetation species (*Asphodelus, Calamintha, Pteridium, Cistus*). Concentrations of selected compounds and meteorological parameters were monitored in the vicinity of the provisional field laboratory at the school near the castle before, during and after the core campaign.

JRC-EI experimental activities during the campaign focussed on:

- concentration measurements of biogenic and anthropogenic hydrocarbons and their reaction products, together with concentrations of "common" trace gases, e.g. O_3, NO_x;
- simultaneous evaluation of emission rates from oak- and pine-trees and of their respective soils at the forest site by using dynamic cuvettes suited to measure the mass balance of trace gas exchange (VOCs, H_2O, CO_2, O_3, NO_x) in partly controlled environments;
- characterization of the physiological status of the plants, e.g. by measuring photosynthesis, transpiration, xylem water potential;
- micrometeorological support to determine emission/deposition fluxes (VOCs, NO_2, O_3), by using tower based measurements at the pseudo-steppe site (e.g. surface energy balance, friction velocity);
- release of artificial tracers from below and above the canopy, in order to simulate the distribution of biogenically emitted compounds.

In addition, two more small ad hoc measuring campaigns were carried out in August and October 1993, to characterize the seasonal variability of emission rates and of physiological activity. Permanently working sensors have been installed in the pine/oak forest to follow the seasonal course of whole tree transpiration, soil water, soil temperature, leaf and air temperature, radiation and rainfall. Continuous readings of these parameters are needed to validate a model that simulates biogenic emissions as controlled by physiological/environmental factors under Mediterranean conditions.

General measurements:

The Castelporziano meteorological and chemical conditions during the campaign can be characterized as follows: during daytime, almost undisturbed insolation led to surprisingly high radiation values, which seemed to be used almost exclusively for sensible heating due to the lack of available liquid water. Therefore, especially in the second half of the campaign, air temperatures were considerably higher than their 10-year averages. Wind speed and direction, however, behaved as expected, and developed, under the influence of the land/sea-breeze regime, strong diurnal cycles, with winds from S-SW during day and N-NE at night. Also, ozone, showed well-expressed daily patterns with minima close to zero at night, followed by a sudden increase with sunrise, and maximum peaks in the afternoon of 50-100 ppb. Both nitrogen oxides, NO and NO$_2$ were strongly negatively correlated with to O$_3$ levels.

The general physiological status of the trees and shrubs in the forest can be defined as transitory to normal Mediterranean summer drought conditions. In the open greenland "pseudosteppe", the dominnant plant species were already decayed, the site showed a brownshaped aspect. In the forest, soil water was still available at 30-50 cm, but was already limited in the uppermost horizons. The measurements of xylem water potential and of transpiration of the trees reflected this situation: the predawn water potential (values appearing after nocturnal water resaturation) of the trees indicated a slight drought stress in the case of oak (ca -5 bar) and a more severe drought stress of pine (ca. -10 bar); the rates of photosynthesis and of transpiration were higher in oak than in pine, oaks reacted actively and clearly with stomatal closure during midday.

Cuvette measurements:

Fig.17 shows the midday depression of transpirational water loss in oak trees in cuvette Q1 for the period June 9-10, when the group of Prof. Torres (Toulouse) performed on-line measurements of monoterpene emissions in this cuvette. The transpiration rate of the oak branch in Q1 followed the sun exposure pattern, with values being slightly higher on June 10, with full sunshine than, on June 9, with some clouds during midday; a clear midday depresssion appeared on both days, indicating stomatal closure due to the extremely high Air-to-Leaf Water Vapor Pressure Deficit (ALVPD) typical of Mediterranean summer drought conditions. The emission rates of monoterpenes followed this pattern, with slightly higher values on June 10 and a pronounced midday depression on both days.

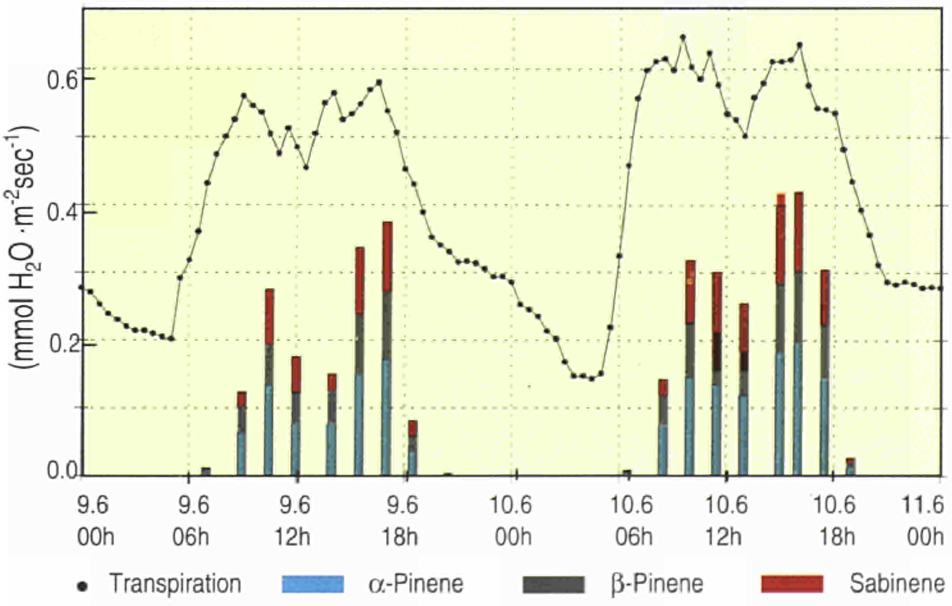


Fig. 17. Diurnal rates of monoterpene emissions and of transpirational water loss for Quercus ilex (BEMA campaign, June 9 -10, 1993)

Quantitatively, the most important monoterpenes emitted from *Quercus ilex* are α-pinene, β-pinene and sabinene; the average daytime emission rate of α-pinene as the main compound varied between 5 and 20 [µg g^{-1} (LDW) hour^{-1}] with different days, branches and trees, being clearly higher than any other values reported in the literature for conifers and other plants. The main compounds emitted from *Pinus pinea* were limonene, ocimene, linalool, and 1,8-cineol, with emission rates in the range of 1-5[µg g^{-1} (LDW) hour^{-1}]. Interestingly, ocimene as a main compound emitted in June, could no longer be observed in October. For both tree species, the emission rates of the major monoterpenes were orders of magnitude higher than the emission rates of isoprene.

This day-night pattern of biogenic emissions was demonstrated by the effect of an experimental darkening of the cuvettes. Cuvettes P1 and Q2 were fully darkened by wrapping with tinfoil for 24 hours on June 12, and in alternation the cuvettes P2 and Q1 on June 13. The emissions rates simultaneously measured in all four cuvettes during both days are plotted in Fig.18, together with the transpiration data. The emission amplitude of the oak branches is significantly higher than that of the pine branches. Oak emission in the darkened cuvettes was about 100-300 times lower than in the light, while the pine emissions decreased in reponse to the treatment by 2-8 times only.

Concentration measurements:

Concentration measurements in the pseudosteppe were carried out to estimate the ambient air concentration of biogenic hydrocarbons, e.g. terpenes, and volatile low molecular carbonyl compounds, e.g. formal-dehyde, acetaldehyde and acetone. The dominant monoterpene hydrocar-bons were found to be α- and β-pinene. Ambient air concentrations measured at ground level ranged from 80 to 370 ng m^{-3} and from 200 to 380 ng m^{-3} for β-pinene and α-pinene, respectively. No significant differences in the ambient air concentrations of these compounds between morning and afternoon air samples were observed. Ambient air concentrations, for, for example, formaldehyde, as the main volatile carbonyl found, ranged from 4 to 24 μg m^{-3}. Highest concentrations were found in the morning hours, with a clear decrease in the late afternoon. The dominant compounds found in the emission gas of selected shrub species (*Cistus*, *Pteridium*) present in the pseudosteppe were aldehydes (C_2 to C_{10}). In addition, monoterpene hydrocarbons, i.e. limonene, sabine-ne, ocimene, myrcene, α-pinene and alcohols, e.g. ethylhexanol, were found only at trace levels.

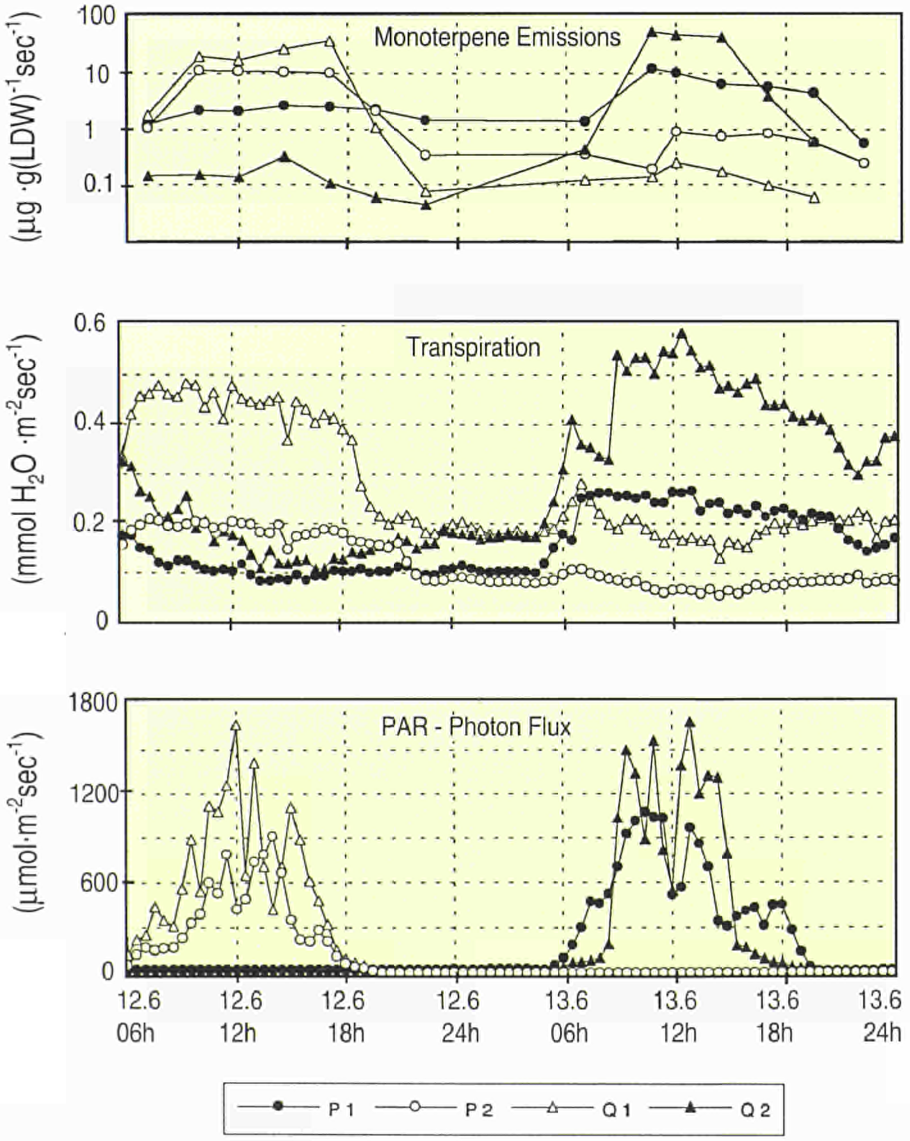


Fig.18. The effects of artificial cuvette darkening (Q2, P1 on June 12; Q1, P2 on June 13) on monoterpene emission and transpiration by pine and oak (BEMA campaign, June 12-13, 1993).

In the pine/oak forest, measurements were mainly focused on the determination of the ambient air concentrations of terpenes and aldehydes. The most abundant monoterpenes found in this area were α- and β-pinene, sabinene and limonene. Concentrations ranged from 1.1 to 1.4 μg m^{-3} for α-pinene and from 0.5 to 1.0 μg m^{-3} for β-pinene. Sabinene and limonene were detected in lower concentrations (~0.5 μg m^{-3}). Compared to the ambient air concentrations found in the pseudosteppe, the concentrations of monoterpenes measured in the pine/oak forest were clearly higher. Ambient air concentrations of formaldehyde were found to be lower than those in the pseudosteppe, ranging from 2.5 to 12 μg m^{-3}. However, in contrast to the daily variation in the pseudosteppe with higher values in the morning hours, in the pine/oak forest the ambient air formaldehyde concentration increased in the afternoon.

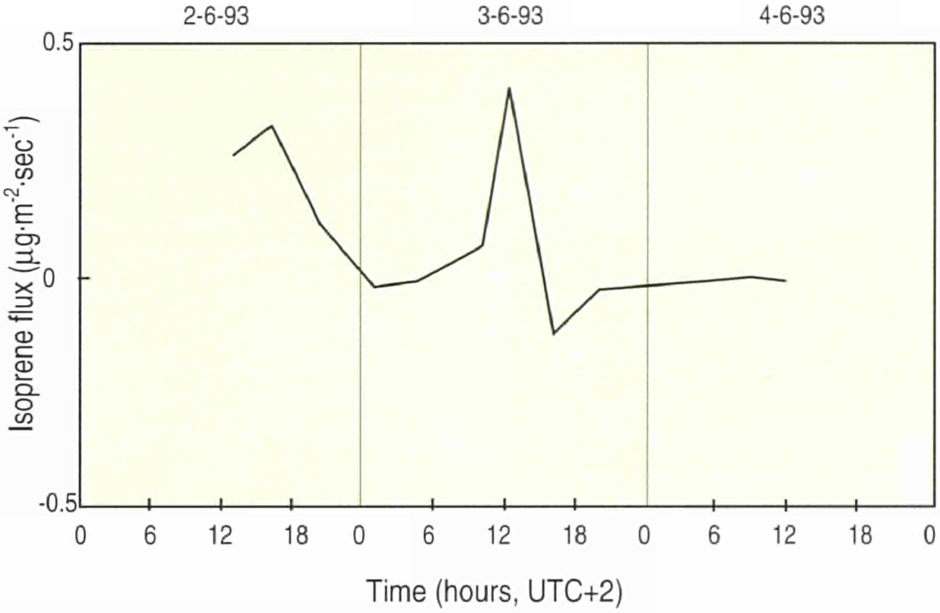


Fig.19. Preliminary determination of vertical fluxes of isoprene by the gradient method (BEMA campaign, June 2-6, 1993).

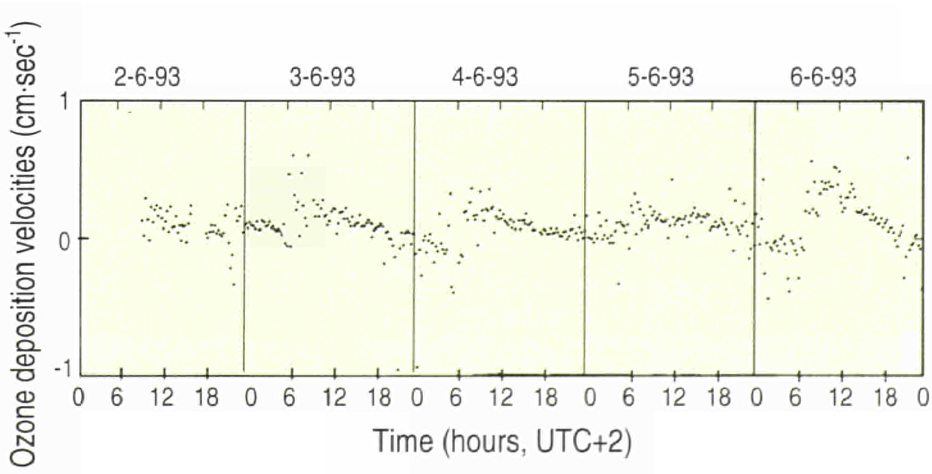


Fig.20. Ozone deposition velocities at the pseudosteppe site (BEMA campaign, June 2-6, 1993).

Micrometeorological measurements:

The application of the vertical gradient method is based on the use of the Fickian-like law which governs atmospheric turbulence-driven diffusion:

$$F = -K_z \frac{\partial C}{\partial z}$$

where F is the flux, C is the concentration, z is the measurement height (above ground level), and K_z is the turbulent vertical diffusion coefficient. The latter can be derived from micrometeorological observations using the classical surface-layer theory formula

$$K_z = \frac{ku^* z}{\Phi(z/L)}$$

where k is the von Karman's constant (= 0.4), u* is the friction velocity, z is the measurement height, **Φ** is the surface layer stability function, and L is the Monin-Obukhov length. The values of u* and L are directly derived from micrometeorological measurements and the analytical form of F is taken from the literature.

The micrometeorological measurements were carried out in the pseudosteppe area by two sonic anemometers placed at heights of 2 and 8 m above ground. The coefficient K_z was determined by this method during the campaign. Using concentration measurements carried out along a 14 m high mast erected near the micometeorological tower, fluxes can be determined using the first equation. A preliminary example regarding isoprene is presented in Fig. 19. It clearly shows that a maximum upward flux occurs around noon.

Figure 20 shows an example of

ozone deposition velocities measured during the Castelporziano campaign. The deposition velocity is equal to the flux divided by the concentration. It shows a maximum at noon of around 0.3 cm s^{-1} and no deposition during night-time. This observation is in agreement with most recent literature data.

The most relevant micrometeorological data within the frame of the BEMA project are the turbulent heat fluxes. The sensible and latent heat fluxes were observed during the campaign. The data show the expected classical behaviour, roughly following the curve of the solar elevation angle. The Bowen ratios (sensible heat flux divided by the latent heat flux) were quite high, ranging between 2 and 3, which is the consequence of the very dry state of the site at which the observing station was located.

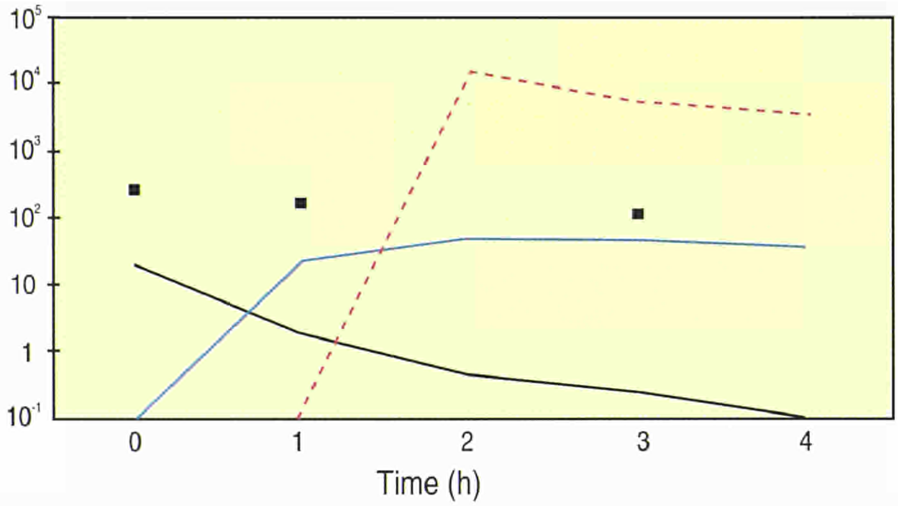


Fig.21. Time variation for ozone formation in the β-pinene/NOx-air photochemical system (β-pinene initial conc. 246 ppbv; NO initial conc. 19 ppbv; T=23.6 °C; RH 58%; UV-intensity ca 25 W/m≤).

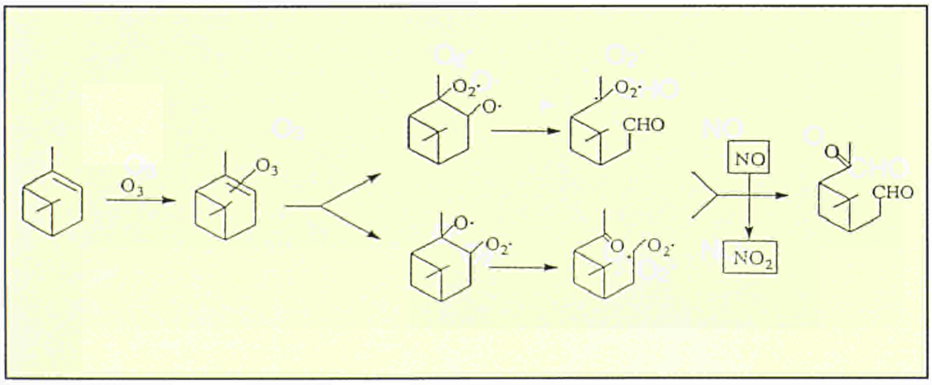


Fig. 22. Ozonolysis of α-pinene: formation of reactive intermediates; conversion of NO to NO_2

Laboratory Experiments

Teflon bags

Previous work was focused on the investigation of the ability of selected anthropogenic and biogenic compounds (α- and β-pinene, isoprene, toluene) to form ozone in the NO_x-air photochemical system. Compared to isoprene/NO_x and toluene/NO_x-air mixtures, α- and β-pinene are less reactive (40 %) in terms of ozone production rates (ppb min^{-1}), with the reactivity being in the order isoprene >toluene >>α- and β-pinene. In 1993, laboratory studies were conducted to address relevant questions on the atmospheric fate of natural hydrocarbons, and in particular, of monoterpenes. The experiments were mainly focused on the formation and isolation of oxidation products for mechanistic considerations and on the role of the Criegee intermediates for the conversion of NO to NO_2 under simulated atmospheric conditions.

From the experiments performed in these studies, there is an indication that the reaction products formed during the sunlight irradiation of terpene/NO_x-air mixtures do not have any impact on the ozone build-up. Sunlight irradiation of, for exemple, β-pinene/NO_x-air mixtures initially leads to ozone formation, which subsequently is partly destroyed through fast reaction with the remaining β-pinene. The reaction products formed did not appear to have the ability to produce additional ozone (Fig. 21).

In addition, a series of experiments were performed in the dark using Teflon bags as chemical reactors (see annual report for 1992) to study the

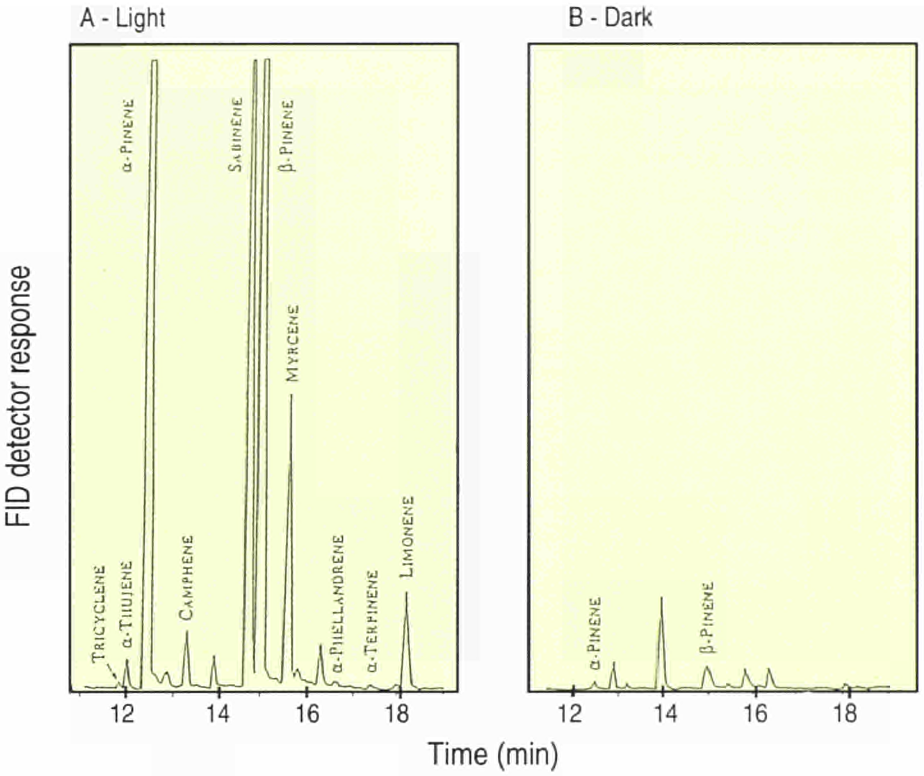


Fig.23. GC-FID chromatograms showing monoterpene emission from Quercus ilex in light (A) and dark (B) at the same temperature of 15 °C

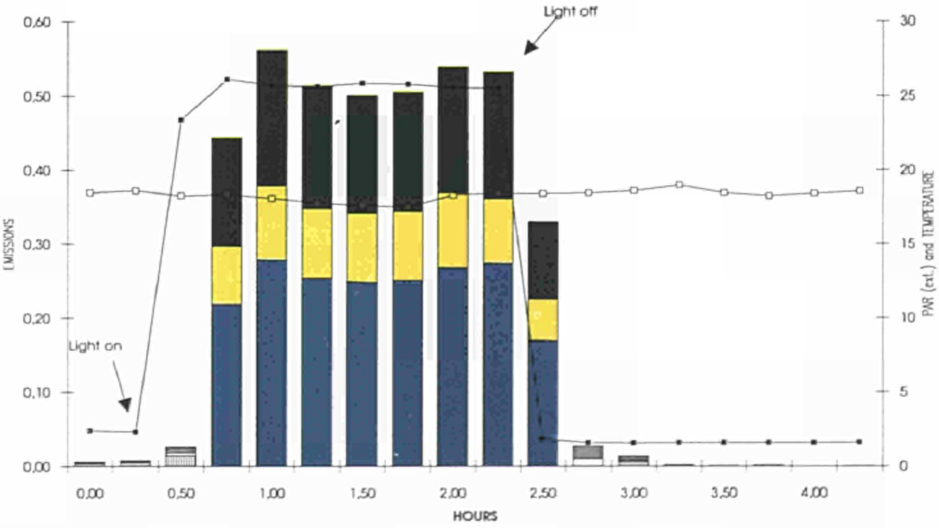


Fig. 24. Effects of a 2 hour light treatment on monoterpene emissions from a dark adapted Quercus ilex sapling at constant temperature.

oxidising capacity of the Criegee intermediates formed during the atmospheric oxidation of monoterpenes and isoprene. Criegee intermediates have been considered responsible, as indicated for α-pinene, for example, in Fig. 22, for the conversion of NO to NO_2. Up to now, however, no experimental evidence exists on the "hypothetical" oxidation of NO to NO_2 via the above mentioned mechanism.

In a typical experiment, α-pinene (100 ppbv) and ozone (60 ppbv) were left to react for four hours in Teflon bags in the dark. After two hours all the ozone had been consumed, so that no detectable ozone was present in the bag. It was observed that the added NO (25 ppbv) was slowly oxidised to NO_2. Control experiments made in parallel did not show any NO_2 formation. The results obtained provide clear evidence for the oxidising potential of the terpene/ozone reaction products. However, the conversion rate of NO to NO_2 (0.03 ppbv min^{-1}) estimated under the experimental conditions used in these studies was rather low and therefore did not significantly influence the total ozone budget in the terpene/NO_x photochemical system.

Plant Exposure Chambers.

A second laboratory activity contributing to BEMA has been performed in plant exposure cham-bers in the greenhouse, comprising:

(i) screening the types and amounts of compounds emitted from Mediterranean tree and shrub species; and
(ii) searching for the environmental and physiological key factors controlling these emissions.

Six Teflon-covered CSTR-chambers (Continuous Stirred Tank Reactors, 1,200 l) are used to study simultaneously the mass balance of trace gas exchange at long-term exposed tree samplings. Short-term experiments are performed with a similar CSTR system of six size-adjustable cuvettes (25-400 l) of the same type as used in the field campaigns.

Several forest trees (*Picea abies, Pinus halepensis, Pinus pinaster, Pinus pinea, Quercus suber, Quercus ilex*) have been examined for the type and amount of emissions and for the parameters controlling them. Monoterpene emissions from conifers are loglinearely correlated to leaf temperature, whereas physiological activity, light exposure, realistic pollutant exposure to O_3/SO_2 and drought stress, play a minor role; however, temperature control can be superimposed by factors such as wetting of needles or mechanical stress due to strong winds or due to the mounting of the branch in the cuvette.

Most interesting are the results obtained with the holm oak (*Quercus ilex*). Up to now, all oak species investigated have been described as strong isoprene and non-monoterpene emitters, but holm oak is the opposite. As confirmed later during the BEMA field campaigns (Fig. 18), this evergreen oak species emits large amounts of monoterpenes, in contrast to another evergreen oak species, *Quercus suber* (cork oak), where terpene emissions were low or not detectable. In addition, monoterpene emissions from the holm oak are triggered by light and physiological activity instead of temperature, as has been shown in experiments under various light and temperature conditions. Representative emission spectra of holm oak exposed in the light vs. the dark at a constant temperature of 15 °C are shown in Fig. 23. In another experiment, performed in a temperature controlled cuvette, a holm oak sapling adapted to the dark was exposed to the light for a two-hour period. The emission rates shown in Fig. 24, together with temperature and light exposure, clearly indicate a strong and fast reaction of monoterpene emissions to light.

Because the holm oak (in contrast to conifers) has no monoterpenes accumulated in its leaf or bark, the emitted compounds should be derived from an immediate, unknown metabolic pathway.

The experimental data give some indications that plant-intrinsic physiological factors govern the emission process, while outside environmental factors have only indirect effects. It is not easy to understand the relative contribution, of physiology and environment to the emission process, because the factors are not at all independent. However, this feature needs further investigation in order to develop an understanding of the process and the algorithms needed for the calculation of emission inventories.

The European IGAC Project Office (EIPO)

During 1993, EIPO, created to provide a better coordination between the CEC Environment programme, tropospheric chemistry research projects and the worldwide IGAC project, entered in its active phase.

EIPO is a bureau which is located at Ispra. It is managed jointly by the JRC and DG XII/D, and controlled by a Scientific Steering Group (SSG), which decides on its general directions. EIPO began operation in early 1993. During that year, it provided financial support to seven IGAC workshops (see below), responded to a number of information requests, and helped European scientists active in atmospheric chemistry to establish links with each other.

Funding was provided for the following workshops:

1. NARE (North Atlantic Regional Experiment), Norwich, UK, January 27-29;
2. TRAGEX (Trace Gas Exchange: Mid-Latitude Ecosystems and Atmosphere), Munich, FRG, April 23-24;
3. BIBEX (Biomass Burning, Experiment), Victoria Fall, Zimbabwe, June 2-5;
4. GLOCHEM (Global Atmospheric Chemistry Survey), Mainz, FRG, June 28-30;
5. ACE-2 (Aerosol Characterisation Experiment-2), Ispra, June 12-14; Seattle, USA, September 14-16;
6. MILOX (Mid-Latitude Ecosystems as Sources and Sinks for Atmospheric Oxidants), Atlanta, USA, September 15-17;
7. MAGE (Marine Aerosol and Gas Exchange), Bordeaux, France, October 25-29.

Moreover, EIPO supported the participation of European scientists in the 1st IGAC Conference, held at Eilat (Israel) in April.

Steps have are now in progress toward setting up joint CEC/IGAC research projects.

ENVIRONMENTAL CHEMICALS

This is the EI's second large research area covering various activities, which can be grouped under main headings, as follows:

- Evaluation of Chemicals;
- Indoor Air Pollution;
- Soil, Water, Waste.

Although, at first sight, these three topics would appear not to be connected to each other, it must be stressed that a common denominator is represented by the chemical compounds which are produced and utilized in such amounts as to generate unwanted consequences for the environment and for human health.

Various matters are dealt with, such as the cataloguing of chemicals data, the impact on indoor air quality, the interaction with soil, analyticals problems in connection with the various ecosystems of concern, and water pollution.

ECDIN - Databank

As was already mentioned in preceding Annual reports, ECDIN is a factual data bank, aimed at bringing together a wide variety of data on chemicals which are being produced industrially in such amounts as to be of environmental significance.

The following major categories of information are covered:

- Identification (3 files)
- Physico-chemical Properties
- Production and Use (4 files)
- Legislation and Rules (2 files)
- Occupational Health and Safety (5 files)
- Toxicity (5 files)
- Concentrations and Fate in the Environment (9 files)
- Detection Methods (2 files)
- Hazards During Transport and Storage

ECDIN contains information on 122,392 compounds, including all substances contained in the "European Inventory of Existing Chemical Substances" (EINECS).

In the course of 1993, within the framework of the agreement between JRC and Umweltbundesamt (specific data collection for more than 300 chemicals substances of interest for the German Ministry of Environment), the following data files were updated:

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- Abiotic degradation
- Concentration in the environment
- Bioaccumulation/Biodegradation
- Mutagenicity
- Experimental toxicity
- Aquatic toxicity

In order to compile, in the most suitable way, the toxicological sector of ECDIN, two main updatings have been performed on the specific data files "Experimental Toxicology" and "Effects on Reproduction"

Experimental Toxicology

This file contains selected information and information to be evaluated on experiments concerning the toxic effects produced by exposure of animals to chemicals. The data file records 36,000 experiments concerning 18,005 substances.

The effects divided in acute, subchronic and chronic exposure experiments are recorded together with descriptions of the animal species, route of administration and time of exposure.

For each experiment, the following information are reported:

- Type of the study (acute, chronic, etc.);
- Exposed organisms and number of exposed animals;
- Effects (histological, biochemical, etc.);
- References.

When, for each chemical, more than 10 experiments are recorded, a toxicological summary is provided and inserted in the file. The texts of the summaries list essential information in a clear but short matrix. Summaries have been produced for about 350 chemical substances. The layout of presentation is shown below.

Effects on reproduction (including Teratogenicity)

This is a new file, included in the toxicological sector of ECDIN in order to improve the description of the low doses/long-term effects of chemicals both on humans and animals.

The data file gives information, which refers to the effects of chemical substances on the developing fetus, when pregnant women are exposed to toxic agents. In a wider sense, it also provides information on the effects of chemicals on reproductive capacity.

The layout for presentation of the data is shown below.

A data collection both for human and animal studies, was carried out for experiments regarding 63 chemical substances. In the future, collection will proceed, with the international evaluated literature being used as the main references.

As far as ECDIN diffusion is concerned, at present, the data bank is distributed in two principal ways, namely, on-line and CD-ROM.

The on-line diffusion of ECDIN is currently organised through commercial information institutions or companies. In Europe, the German Institute DIMDI (Deutches Institut für Medizinische Documentation und Information), on behalf of the Commission, is the host for the distribution of ECDIN on-line. In the United States, the host for ECDIN is TDS (Technical Data Services, Inc.), based in New York.

Currently, the ECDIN Database is transferred from the ADABAS database system to ORACLE/SQL Forms, for reasons of flexibility and providing better interface possibilities.

In order to benefit from the advantages of the CD-ROM technology, the whole data base of ECDIN has been made available on a CD-ROM, a new version having been published in 1993.

Indoor Pollution

The Institute's contribution in this field consists of (i) research aimed at the assessment of organic indoor pollution, its sources and sinks, and (ii) the management and scientific coordination of the European Collaborative Action (ECA), "Indoor Air Quality and Its Impact on Man".

Indoor pollution by organic compounds is of considerable concern. Many organic indoor pollutants are known or are suspected of causing carcinogenic, neurotoxic, allergenic, immunotoxic, irritating or sensory effects. In particular, volatile organic compounds (VOCs) are often implicated, and sometimes have been shown to play a role in situations leading to complaints about inadequate indoor air quality in office buildings or other indoor environments. Building and furnishing materials, and household and hobby products, are important indoor sources of these compounds. By adsorption processes, indoor materials may also act as sinks of organic indoor pollutants and, by subsequent desorption, they may become secondary source of them.The Institute's research activities are focused on the development and validation of methods for the analysis of organic indoor pollutants and for the characterization of their sources and sinks.

Work performed in 1993 was aimed at:

- improving a small chamber method for the determination of VOC emissions from indoor materials and products,
- studying the adsorption of VOCs on indoor materials,
- the completion of, and initial experiments with, the new Indoortron laboratory, and
- further analysis of semi-volatile

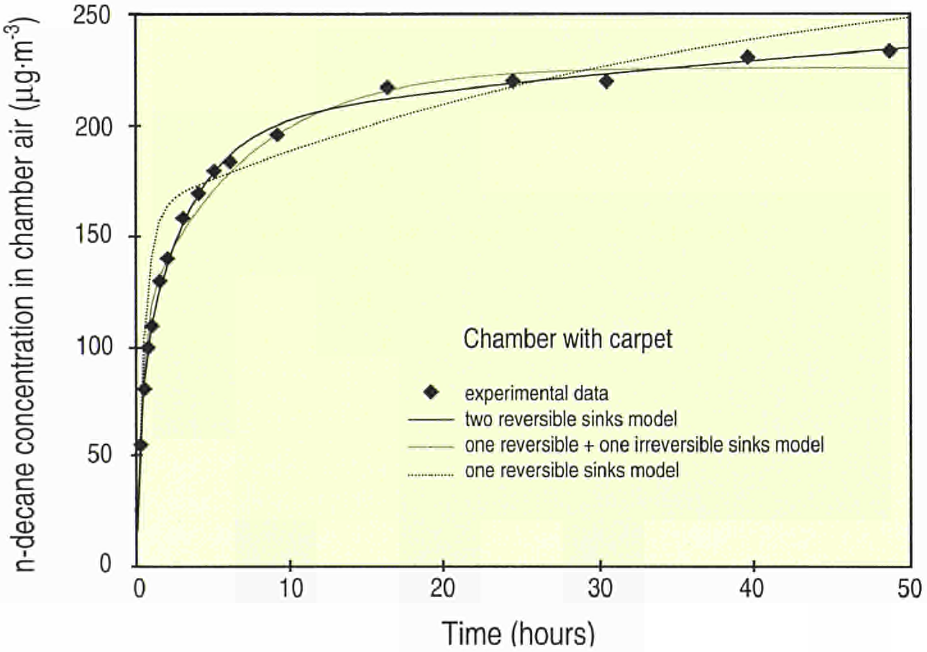


Fig.25. Modelling of the dynamic adsorption of n-decane on a carpet. From time zero, a constant flow of n-decane is introduced into an environmental chamber (0.45 m³ volume) containing 0.5 m² of a Nylon carpet with SBR backing. The new model with two reversible sinks fits the experimental concentration vs. time data substantially better than the one-sink model. Compared to the model with one reversible and one irreversible sink, the new model still fits the experimental data better, but also shows more clear that at the end of the experiment (after 48 hours), the chamber concentration is still increasing, i.e. no steady state has yet been reached

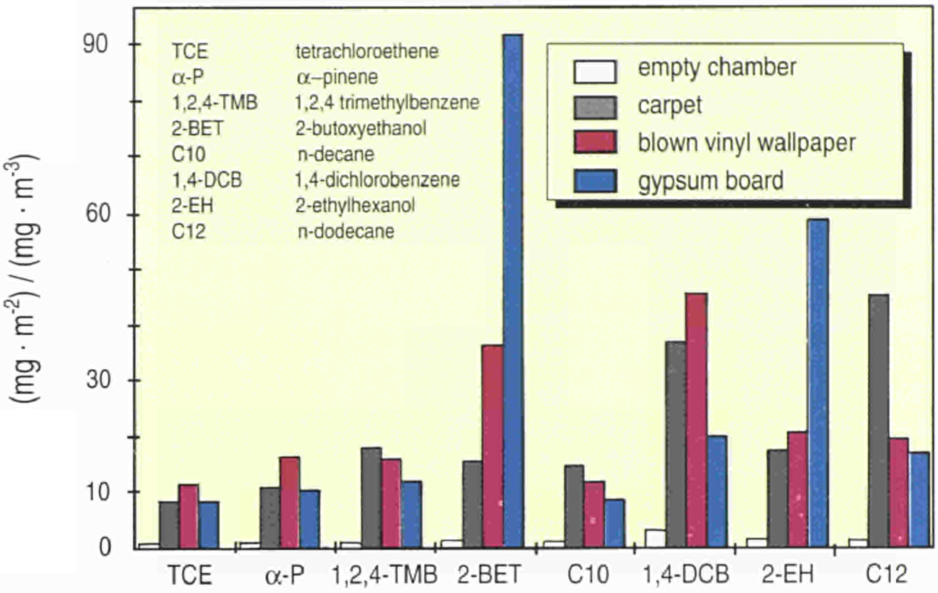


Fig.26. Distribution of eight test compounds between three adsorbing materials, the chamber walls and the gas phase. The figure shows the distribution coefficients, defined as the ratio of the sum of the masses adsorbed in two reversible sinks (as estimated by the new model) per m^2 of sorbing material and the chamber concentration at the end of the experiment. The coefficients range from about 1 $m^3.m^{-2}$ for the empty chamber to about 90 $m^3.m^{-2}$ for the adsorption of 2-butoxyethanol on gypsum board with cartoon finish.

organic compounds (SVOC) and particulate organic matter (POM) in house dust and indoor air using combined supercritical fluid extraction gas chromatography (SFEGC).

VOC emission measurements

Measurements in small test chambers of VOC emissions from a thin film source material (a water based floor wax) have shown unacceptably large differences between the results obtained in a previous international intercomparison experiment. Of the potential factors contributing to these differences, film thickness and homogeneity and air velocity at the sample surface had not been controlled in this experiment. Because of the availability of a simple technique (Kastenrakel) for the application of homogeneous paint films, a water-based paint has been selected for a further intercomparision experiment. Extensive tests have been performed at the EI with the selected paint, in order to develop guidance for the new experiment and, in particular, for preparing the paint films and controlling the surface air velocity. Paint samples have been distributed to 25 laboratories in Europe, North America and Australia, which applied to participate in the intercomparison experiment. At the end of the experiment, all paint samples will be analyzed at the JRC for film thickness and homogeneity.

VOC sorption measurements

Adsorption of VOC on indoor materials modifies their indoor concentrations and hence, human exposures. Adsorption will lower peak concentrations (e.g. during painting or other VOC-emitting activities), but the subsequent desorption will prolong the presence of VOCs. In order to characterize the adsorption properties of indoor surface materials, dynamic and static chamber studies were started in 1992. Eight typical indoor pollutants, covering a wide volatility range and representing lipophilic and hydrophilic compounds and three indoor materials (Fig.26), were selected for a quantitative adsorption study. The tentative descriptions of the dynamic adsorption data derived from two models involving one reversible sink or a reversible plus an irriversible sink, were both unsatisfactory but yielded indications that a description with two reversible sinks with different adsorption/ desorption constants or dynamics would probably be adequate. This model was developed in 1993 and initial data from its application have been obtained. They are displayed in Figures 25 and 26. Figure 25 gives an example (adsorption of n-decane on a carpet) of the improved fitting of the experimental data obtained with the new model. Figure 26 shows the distribution of eight test compounds betweeen the three adsorbing materials and the vapour phase after 48 hours of dynamic adsorption. The distribution coefficients demonstrate that adsorption depends strongly on both the adsorbed compounds and the adsorbing material. The boiling point of the adsorbed compounds, which increases from TCE to C12, is obviously only one among many other factors determining adsorption behaviour. The important role of the adsorbing material becomes most evident when looking at the distribution coefficients for gypsum board, which are smallest for all

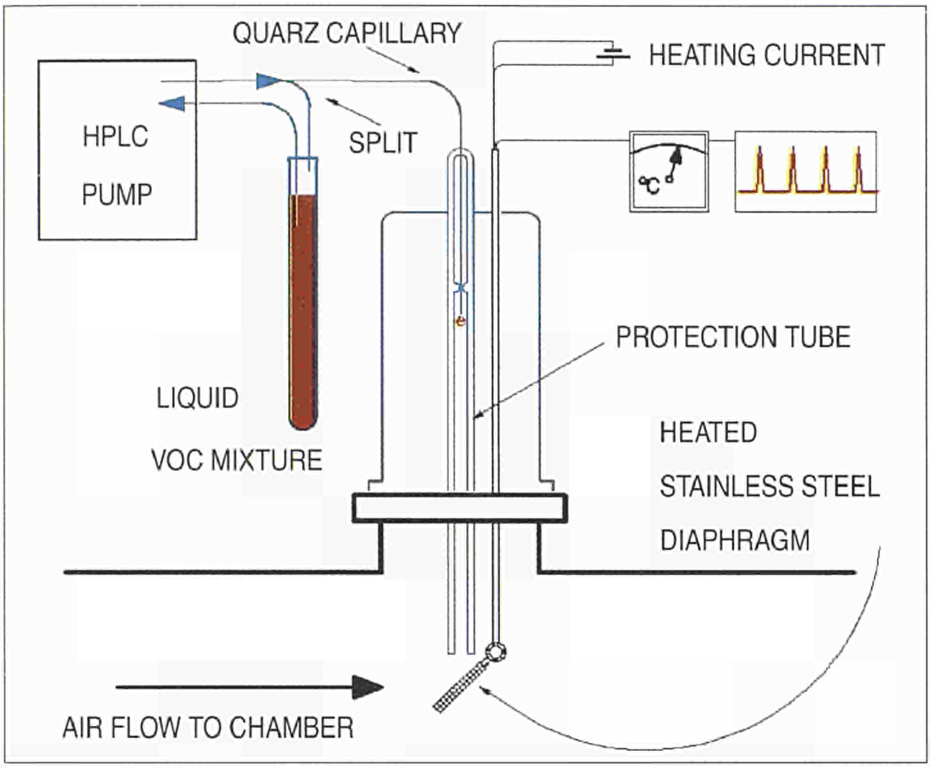


Fig.27. Scheme of the device for VOC injection into the air supply flow of the Indoortron test chamber. An HPLC pump delivers constant, small amounts of a liquid mixture of VOCs via a flow splitter through a quarz capillary (100 µm i.d.) to a stainless steel diaphragm placed in the air supply stream. Droplets of the liquid VOC mixture fall at regular intervals (about 4 min) onto the diaphragm and cause short negative temperature peaks. Recording these peaks, the constancy of the VOC flow can be monitored.

compounds except for the two alcohols (2-BET and 2-EH), for which the highest distribution coefficients (i.e. the strongest adsorptions) are observed.

Further equipment and the initial use of the new Indoortron laboratory

The production of test atmospheres containing known amounts of VOCs at typical indoor concentrations (10-100 $\mu g\ m^{-3}$), including polar and higher boiling compounds (e.g. ethylhexanol, n-undecane), is important for the validation of sampling and analytical methods. Because of adsorption phenomena, small scale devices for the production of such test atmospheres are usually only reliable for hydrocarbons with relatively low boiling points. The Indoortron test chamber, with its high volume and low surface-to-volume ratio, offers the possibility of producing these atmospheres by direct injection of liquid mixtures containing a broad range of test compounds into the clean, dry air supply. A device has been developed (Fig. 27), which allows the controlled injection of less than 1 $\mu l\ min^{-1}$ of liquid VOC mixtures. Therefore, at the highest air supply flow of 60 $m^3\ h^{-1}$, total VOC concentrations of less than 1 $mg\ m^{-3}$ can be obtained with concentrations of less than 10 $\mu g\ m^{-3}$ for individual compounds.

During the testing of the VOC injection device, the flow measurement and control of the Indoortron supply air turned out to work incorrectly. A streamliner had to be introduced in front of the supply air flow meter and the flow meter had to be recalibrated. An automic device for measuring the decay of SF6 trace gas concentrations in the test chamber has been built, in order to allow for independent air flow control.

The chamber has been used for testing two air cleansing devices for use indoor, which were supposed to reduce respirable particulate matter (RPM), and also organic vapours, such as formaldehyde, in indoor air and particularly in smoking areas. Figure 28 shows an example of the performance of one of the devices. None of them were effectively able to reduce formaldehyde.

Determination of SVOC and POM in house dust and indoor air

The on-line combination of supercritical fluid extraction (SFE) with gas chromatography (GC) and mass spectrometry (MS) had been used in 1992 for first analyses of semivolatile organic compounds (SVOCs) and particulate organic matter (POM) in house dust and indoor air samples. In 1993, three adsorbents (Tenax, Carbotrap C and polyurethane foam (PUF)) were compared with respect to their suitability for air sampling. Tenax and Carbotrap C were superior with respect to their breakthrough volumes, but did not allow extraction of the higher boiling compounds of interest (bp>n-C_{32} for Tenax, bp>n-C_{16} for Carbotrap C). PUF plugs, which can be accommodated in the on-line extraction cell,

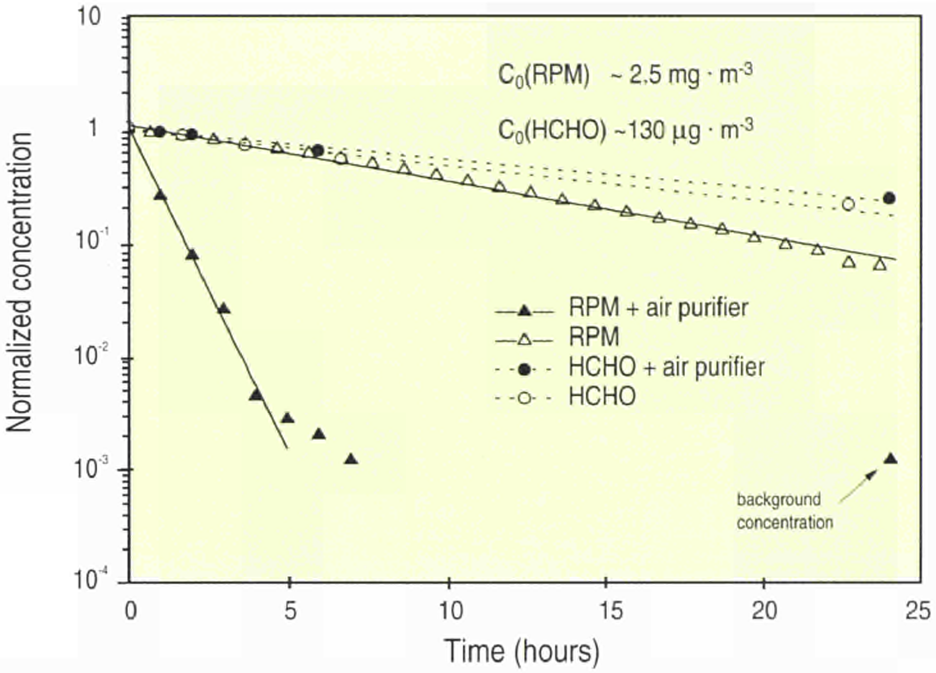


Fig.28. Decay - with and without an air cleaning device - of the concentration of respirable particulate matter (RPM, <3.5 µm) and of formaldehyde (HCHO) after automatic smoking of three cigarettes in the Indoortron test chamber. Whereas there is no significant differences for the decay of formaldehyde with and without the air cleaning device, the RPM decay corresponds to an air change rate of 1.3 h^{-1} with the air cleaning device and to only 0.1 h^{-1} without it. If the increase of the air change rate of 1.2 h^{-1} corresponding to 36 m^3 h^{-1} (chamber volume=30 m^3) is compared to the air flow through the air cleanser of 240 m^3 h^{-1}, a filter efficiency of 15 % results for RPM.

CO_2 type	Amount of organic impurities per gram of CO_2 [µg · g^{-1}] without charcoal filter	 with charcoal filter
SFE grade (brand 1)	67	16.2
SFE grade (brand 2)	75	8.6
Analytical grade	170	8.9
Technical grade	204	17.7

Table 3. Organic impurities in different CO_2 types, with and without a charcoal filter.

can be extracted readily, but have a breakthrough volume of less than 3m^3 for the compounds at the lower end of the boiling point range of interest (bp < n-C_{20}; 70% breakthrough of n-C_{18}).

In view of the considerable cost of high purity CO_2 needed for SFE, an attempt was made to use activated charcoal for purifying inexpensive technical grade CO_2. A stainless steel column of 4 cm internal dia and 50 cm length, filled with charcoal (type DeguSorb F 12/470 of Chemviron Carbon), was inserted in the liquid CO_2 flow between the CO_2 cylinders and the SFE pump. The purity (total content of organic compounds) of four CO_2 brands of different quality was measured with and without the charcoal filter. Table 3 shows the results. The least expensive technical grade CO_2 with the charcoal filter contained 3.8 times less organic impurities than the cleanest SFE grade CO_2 without the charcoal filter.

Management of the European Collaborative Action (ECA), "Indoor Air Quality and its Impact on Man".

In 1993, the European Collaborative Action, "Indoor Air Quality and Its Impact on Man", published two further reports: Report nr. 12 collates and evaluates available knowledge on health effecs, occurrence, sampling and analytical methods, and observed values of biological particles in indoor environments. Report nr. 13 summarizes the results of a first set of interlaboratory comparisons of VOC emission measurements in small test chambers, prepared and organized by the EI and aimed at validating a guideline which was published earlier by the ECA.

Following preparatory work performed in 1992, the Steering Committee decided to charge three new working groups with the following tasks:

- Proposal of a procedure(s) to evaluate building materials with regard to their emissions. Initially, work will be limited to flooring materials. Three subgroups and a co-ordinating group are preparing proposals for the chemical and sensory characterization of organic emissions, for their toxicological evaluation, for exposure assessment based on emission data, and models for predicting the prevalence of discomfort and for risk characterization.
- Identification of ways of integrating good indoor air quality (IAQ) and a safe and efficient use of energy. The group is preparing a document identifying:
- human requirements and critical building factors related to energy use in buildings;
- cases where requirements of IAQ and energy efficiency are in accordance and where they are potentially conflicting;
- trends for the future in construction, remodelling, energy use, occupant and society demands on environmental quality, and their consequences for IAQ;
- research needs and guidance required by the building community.

The group is also charged with critically reviewing international and European national documents relating to IAQ, energy use, or both.
- Identify and define an indicator of indoor pollution by VOC.
"Total volatile organic compounds" (TVOC) is a quantity which is often used to characterize indoor pollution by VOCs or VOC emissions from indoor materials and products. Yet no satisfying definition of this quantity exists. The new working group is charged - in collaboration with WHO Euro - with developing and defining a "descriptor" of VOCs (e.g. a combination of VOCs belonging to different compound classes), which could be used as an indicator of exposure and which might be interpreted in terms of effects on health and/or comfort.

In addition to these new activities, work for guidelines on VOC sampling in indoor environments and on the design of intervention studies aimed at improving indoor air quality in buildings, has continued.

An important event which took place in 1993 was *Indoor Air '93*, the sixth International Conference on Indoor Air Quality and Climate, held in July '93 at Helsinki. The Commission and the ECA served as co-sponsors and many Steering Committee members participated in the preparation and running of the Conference. JRC staff contributed four papers and chaired two sessions.

Chemical Waste

Soil - Pollutant Interaction Studies

The surface and subsurface transport of toxic organic compounds and metals has become pertinent with regard to risk assessment of accidental spills or gradual leakage from landfill repositories. Modelling environmental mobilities of synthetic chemical residues represents a field of current geochemical research effort. For reliable predictions of the behaviour of such contaminants in soils and groundwater systems, it is important to understand how the quantity and modes of inputs and outputs are linked to water motion and the dispersal process. Research in the Institute is based on the comparison of laboratory investigations with observations of natural processes and with modelling. This was also the subject of a workshop held in Alsace (F) and co-organized with the CNRS-Strasbourg (F), the ETH/EAWAG-Zurich (CH) and the University of Heidelberg (D).

The intrinsic variability of hydrodynamic and geochemical conditions in aquatic environments causes uncertainties which affect both models and parameters. Therefore, methods of probabilistic analysis are required to model reactive transport. A 1-D hydrodynamic transport code was coupled to routines of uncertainty and sensitivity analysis. A review of the available literature was conducted aimed at identifying the existing computer programmes in the area of chemical transport modelling. Intercomparison and verification tests were performed on the codes qualified during this first stage of the selection procedure. The work done in this period was mainly concerned with the implementation of the selected code in the UNIX environment, the appropriate modifications to accomodate kinetic reactions, the construction of a module to perform mass balance computations, and, finally, a new strategy of time-stepping, in order to improve the stability criteria of the numerical scheme and to reduce the memory requirements of the programme. The coupled code will be tested on the basis of the results of laboratory experiments on the transport behaviour of Cr(III), as is described below.

The reduction of hexavalent chromium

to the trivalent state is considered a safe strategy for the disposal of Cr-containing wastes. This is based on the much lower solubilities of Cr(III) compounds with respect to Cr(VI) compounds. Surface-mediated redox transformations and complexing with dissolved organic matter (DOM) may, however, lead to an enhancement of environmental mobility. Previous studies using laser fluorescence spectroscopy have shown that Cr(III) ions bind strongly to humic acids (HA), an important component of DOM. Laboratory migration experiments were carried out, both in the presence and in the absence of HA. The results of these transport experiments showed that Cr(III) mobility increases considerably due to association with HA. Comparison of HA transport under aerobic and anaerobic conditions indicated that partial biodegradation of the organic molecules occurred, involving bacteria attached to the sand particles. The inclusion of a MnO_2-coated sand layer, as an oxidizing agent, further contributed to the DOM removal from the water-flow and acted as a sink rather than as an oxidizing point for Cr(III), probably because of a kinetically limited redox reaction of Cr(III) to Cr(VI) at the pH of the groundwater. Modelling of the transport of Cr influenced by multiprocess nonequilibrium is under way to estimate values for adsorption rate constants. Alternative mechanisms of reactive transport are being compared, in order to identify the relative importance of uncertain variables on the probabilistic outcome.

In this context, the Institute is contributing to an international project combining modelling and field studies for the understanding and prediction of the movement of metallic contaminants in fractured granite. The test site under investigation is a granitic formation in central Spain. The laboratory work is carried out in collaboration with the CIEMAT, Madrid. The contributions to the field activities, are described in the section on "Third Parties Work".

In the course of the year, laboratory migration studies of Se(VI) through granite columns were performed, in order to identify physico-chemical interactions with fracture filling materials and to design the migration experiments to be carried out in the field.

The breakthrough curves for Se transport through a drill-core column of granite were obtained at two different flow-rates, under anoxic conditions (Fig.29). In both cases, a pulse of 10^{-5} M Se(VI) was applied to the column. A first column experiment was conducted at 16 ml.d^{-1}. The flow-rate was then adjusted to 2 ml.d^{-1} and a second migration experiment was run with the same column. The breakthrough curves for tritiated water (HTO) and chloride (not shown) were obtained, to establish the hydrodynamic properties of the column. The position of these breakthrough curves changed with the flow rate. This was associated with a change of permeability (i.e. effective porosity) of the core observed between the two runs, probably due to the movement of particles into the fracture network when the applied pressure head was changed. For both experiments, the position of the Se peaks always matched that of the conservative tracers, irrespective of the pore water velocities. This indicates that adsorption of Se(VI) was negligible, in agreement with the observations from the literature. However, the total recovery of Se mass that entered the

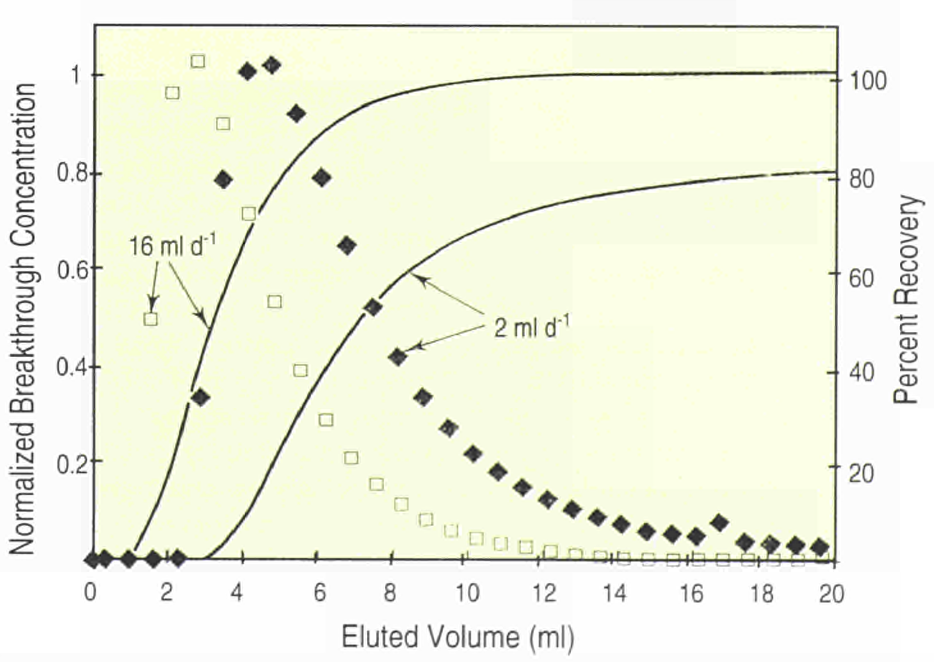


Fig. 29. Effect of the groundwater flow-rate on the Se(VI) breakthrough from a drill-core granite column. The experiments were made under anoxic conditions. The solid lines represent the percentage recovery of Se.

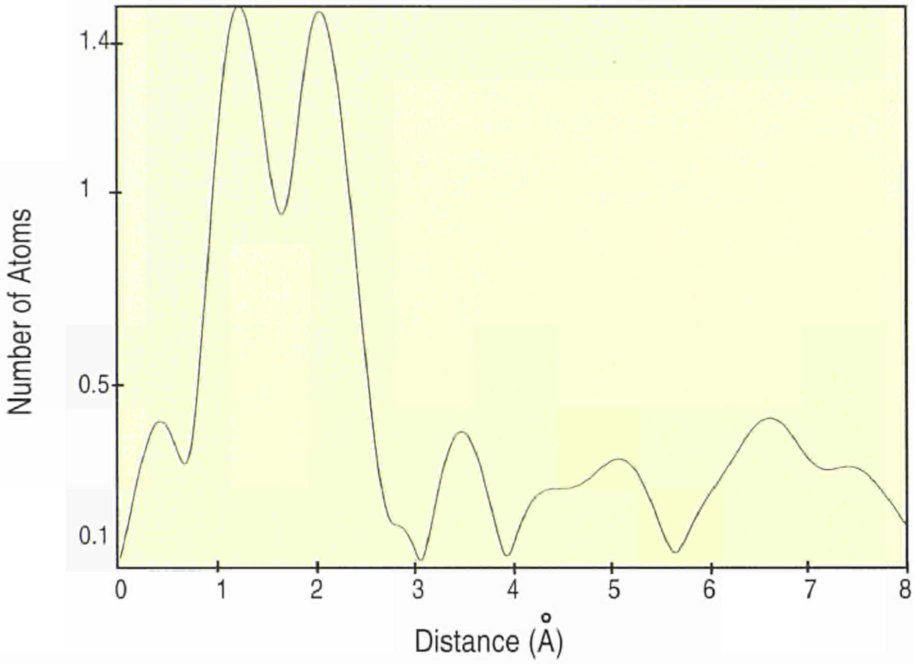


Fig. 30. Fourier Transformed EXAFS data of Sr adsorbed on a mixture of illite and kaolinite.

column (solid lines in Figure 29) showed that a loss occurred during the low-velocity experiment. Considering that residence time increases as flow rate decreases, this is an indication of a rate-limited retention of Se. It appears that the loss of Se(VI) from the water flow is due to a redox reaction forming Se species strongly adsorbed by the granite.

In the present experiments, no microorganisms were found in the anoxic groundwater, either at the column inlet or at the outlet. Therefore, a microbially-catalyzed redox pathway does not seem to be in operation. An alternative explanation applies to a possible role for electron exchanging minerals as reducing agents. Mineralogical investigations of the granite used in the present work found clays and calcite as main fissure filling minerals. Calcite has been found to contain up to about 4% of Mn, probably forming a solid solution by exchanging Mn for Ca in the calcite structure. Small crystals of iron sulfides have also been identified. Static adsorption measurements of Se(VI), however, showed a negligible affinity of Se for all mineral components, with the exception of the iron sulfides.

Since the remobilization of the adsorbed Se, and then its transport behaviour, are controlled by its chemical form, the surface speciation of Se on the sulfide was investigated by X-ray Absorption Spectroscopy (XAS) using synchrotron radiation. Close examination of the spectrum of the adsorbed species indicates that it may consist of contributions from Se in a variety of oxidation states from (0) to (VI), with (II) and (IV) being the most common. Kinetics experiments showed that the Se adsorption on the iron sulphides and the subsequent redox transformation are under kinetic control.

A cross-hole transport experiment can be devised as a pulse injection of selenate and bromide ions labelled, respectively, with stable isotopes of Se and Br. The Se removal from the groundwater flow as a function of the imposed hydraulic gradient can then be predicted with respect to the conservative ion, on the basis of a transport model coupling hydrodynamic data typical of the site and mechanistic data derived from laboratory studies. However, this requires, the identification of a relationship between apparent rate constants, to be determined on a laboratory scale, and the actual amount of Se reducing inclusions encountered in the water conducting fractures connecting the boreholes at the test site.

In the absence of groundwater intrusion, diffusion forms a principal mechanism of chemical dispersion. Laboratory diffusion experiments of Sr in clay were modelled with a coupled reaction-transport model. These showed that net Sr flux is controlled through variable Sr speciation among solution and particle surfaces, dependent on prevailing conditions, e.g. pH, alkalinity. This involves the interplay of variable mass fraction of species having variable adsorption selectivities and with variable preferences for alternative diffusion pathways. Diffusion coefficients obtained using three independent approaches in the laboratory showed both internal and external reproducibility. Based on the laboratory results, a mechanistic diffusion model was developed, involving two chemical species: Sr^{2+} and $SrCO_3(aq)$. Sr^{2+} was predominant, with an increasing importance of $SrCO_3(aq)$ above pH 8. The presence of minor $SrCO_3(aq)$ significantly increased the total adsorption affinity of Sr for the clay.

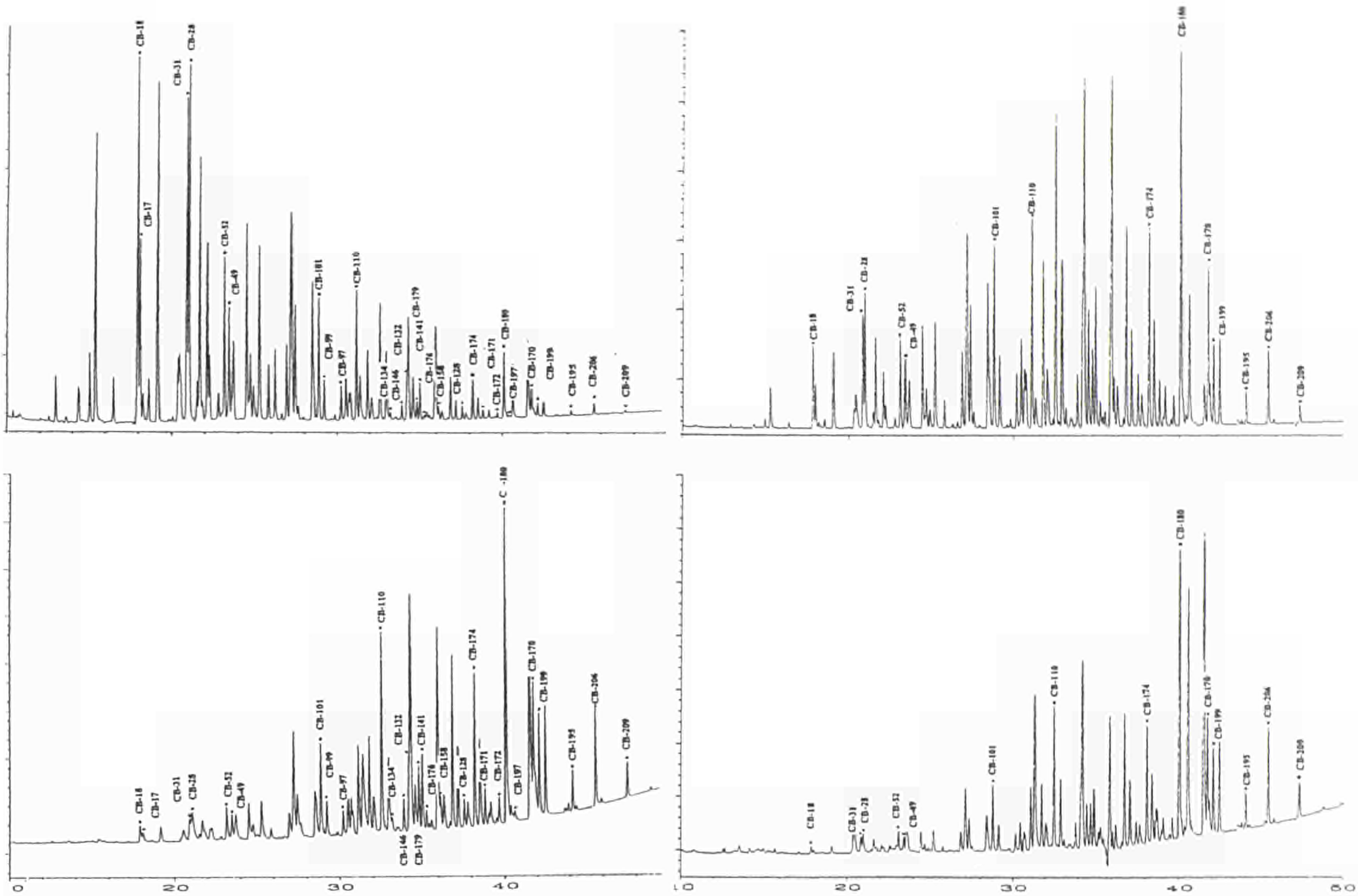


Fig. 31. Chromatograms by SIL-8/HT-5 of extracted PCBs from the solution phase (upper) and the soil (low) after partitioning in pure water (left) and 10^{-2} mol l^{-1} SDS (right) respectively.

Model verification required the inclusion of both molecular (porewater) and surface diffusion pathways, with the latter representing the predominant contribution. Although Sr^{2+} has a relatively lower affinity for the clay, it appears to be relatively more mobile on the surface with respect to the porewater and with respect to $SrCO_3(aq)$. At lower pH, with greater mass fraction of Sr^{2+}, transport was enhanced. EXAFS (Extended x-ray Absorption Fine Structure) measurements using synchrotron radiation were carried out at the SERC facility in Daresbury, UK, in order to verify whether the predicted two-species adsorption model for Sr, postulated on the basis of macroscopic and empirical sorption measurements, is correct. Figure 30 shows the Fourier-transformed EXAFS data of Sr adsorbed on the clay. Interpretation of these data in terms of local atomic structure is under way.

The influence of surfactant agents present in groundwaters is being investigated.

Apart from concern over the environmental fate of surfactants *per se*, interest in them stems principally from two opposite appreciations:

- the utilisation of the strong solubilizing effects above their critical micellar concentration (CMC) in soil remediation, aiding desorption and / or biodegradation of the poorly water-soluble organic contaminants; and
- the potential of surfactants at concentrations below their CMC to facilitate unwanted transport of other hazardous chemicals in the environment.

The results recent studies on polychlorinated biphenyls (PCBs) and chlorobenzenes underline the action of surfactants, at concentrations below their CMC, in mobilising otherwise strongly adsorbed hydrophobic compounds in soil-water systems. In aqueous solution, surfactants like dodecylsulphate (DS) can be assumed to exist in principally two states. Below the CMC, surfactants exist in the monomeric state. At the CMC, the concentration of surfactant monomers remains constant, while excess surfactant leads to the formation of pseudophase micelles.

The chromatograms of PCBs in the soil and the solution phase after partitioning in pure water and 10^{-2} mol l^{-1} Sodium dodecyl sulphate (SDS) are shown in Figure 31 (SIL-8/HT-5). It is evident from the figure that the presence of surfactants has little effect on the PCB profile in the soil, even at this high dose (10^{-2} mol l^{-1}). In the solution phase, on the other hand, a significant change of the PCB profile can be observed. Lower chlorinated and higher chlorinated biphenyls (CB) congeners are the most abundant in the solute with pure water and in the presence of surfactant, respectively. This observation strongly supports the suggestion that the phase distribution is largely controlled by a solute activity coefficient in the water phase, but not in the organic phase, of soils or sediments.

The apparent soil-water distribution coefficient (Kd*) is depicted for selected CB congeners as a function of the surfactant concentration in Figure 32. One congener is shown for each chlorination class of di- to deca-CB. With the addition of SDS at the lowest concentration (10^{-4} mol l^{-1}), the apparent distribution coefficient was slightly reduced for all studied congeners.
The reduction increased with the degree of chlorination of the PCBs (diCBs 23%, triCBs 30%, tetraCBs 50%, pentaCBs 65%, hexaCBs 79%, heptaCBs 84%, octaCBs 85%, nonaCBs 84%, decaCB 86%). When SDS was added at a higher concentration (10^{-3} mol l^{-1}) the apparent distribution coefficient decreased further at 2.5 x 10^{-3} mol l^{-1}, which remains signifi-cantly below the CMC (8.2 10^{-3} mol l^{-1}). Nevertheless, the reduction was related to the degree of chlorination of the PCBs (diCBs 73%, triCBs 71%, tetraCBs 85%, pentaCBs 93%, hexaCBs 98%, heptaCBs 99%, octaCBs 99%, nonaCBs 99%, decaCB 99%). With the addition of DS at 10^{-2} mol l^{-1}, which is above the CMC, the apparent distribution coefficient dropped sharply by 2-3 orders of magnitude. For a soil which does not interact with the surfactant, a four-phase distribution model satisfactorily describe the soil/ water/surfactant, monomer/ surfac-tant micelle interactions, similar to a three-phase distribution model developed for the water solubility enhancements of hydrophobic compounds by surfactants. The calculated monomer DS-water partition coefficients normalised to organic carbon ($K_{mn}oc$) for 28 CB congeners are comparable with K_{DOC} values for natural aquatic humic substances, where K_{DOC} is the partition constant of the CBs between Dissolved Organic Carbon (DOC) and water. The observed non-linear relation between K_{mc} and K_{mn} probably results from steric hindrance of the entrance of large CB molecules into the microscopic micelles or from micelle-dissolved organic carbon interactions.

Contacts were established with leading institutions in Europe, to explore the possibility of starting a project on the measurement of greenhouse gas emissions from soils. The focus of this activity would be on the establishment of sampling networks for monitoring the effects of seasonal and land use changes on gas fluxes. A close connection will be established with international programmes on global change, such as IGBP/IGAC.

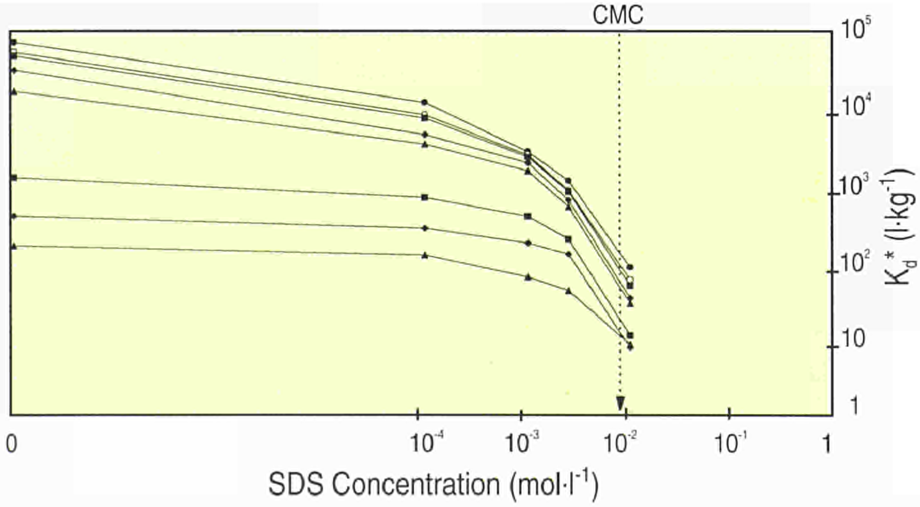


Fig. 32. The effect of SDS in the solute phase on the apparent soil-water distribution coefficient (Kd) for selected PCBs (from the bottom to the top PCB congeners No. 8, 31, 52, 110, 153, 180, 199, 206, 209).*

Analytical Development

A systematic study of supercritical fluid extraction (SFE) in trace organic analysis has been continued. Methods have been developed and validated in interlaboratory comparisons for the quantitative, interference-free, analysis of polychlorinated biphenyls (PCBs) and organochlorine pesticides in various environmental samples. Off-line SFE and high resolution dual-column gas chromatography - electron capture detection have been adopted. The reduction of sulphur in supercritical CO_2 before solid-phase trapping of the supercritical fluid extract, combined with subsequent liquid chromatography, has permitted a direct analysis of sediment extracts without any additional clean-up. A prototype SFE instrument, designed for multiple simultaneous extractions in co-operation with Fisons Ltd., has been successfully tested. The feasibility of using this instrument for the extraction and sample preparation of polyaromatic hydrocarbons, polychlorinated dioxins and polychlorinated furans in the analysis of soils, sediments and fly ashes, is being investigated.

A novel sampling technique has been investigated for the analysis of volatile organic compounds (VOCs) in drinking water. This approach in head-space gas-chromatography (HS-GC) analysis is based on a simple device for solid-phase micro extraction (SPME) in the head space. It has the potential of eliminating a series of problems previously encountered in classical HS-GC analysis, such as introduction of moisture and oxygen to the GC, adsorption of analytes to the walls of the headspace sampler, low sampling efficiency for less volatile compounds, and non-selectivity in the sampling. Headspace solid-phase micro-extraction (HS-SPME) is a solvent-free sample preparation technique, in which a fused silica fiber coated with polymeric organic liquid is introduced into the headspace above the sample. The volatile organic analytes are extracted and concentrated in the coating, and then transferred to the analytical instrument for desorption and analysis. The SPME device for this investigation (Supelco, Italy) uses a fine fused silica fibre coated with a short (10 mm) thin (100 mμ) layer of polydimethyl-siloxane. The fibre is housed in a stainless-steel needle, which allows for penetration of the membrane covering the sample vial. Once inside the sample vial, the fibre can be pushed out of the housing and exposed to the headspace above the water sample at 80°C (Fig. 33). Experiments showed that by this time, equilibrium is established between the headspace and the polydimethyl-siloxane. At this point, the fibre can be pulled into the housing and the SPME device removed from the sample vial and inserted into the injection port of a GC or a GC-MS system.

The combination of HS-SPME with ion-trap mass spectrometry (ITMS) was successfully employed for the analysis in water of a total of 59 VOCs ranging from methyl chloride to trichlorobenzenes. The ITMS has the advantage over quadrupole spectrometry of producing full-scan mass spectrograms at low detection limits. The main physico-chemical parameters important for HS-SPME analysis were found to be moderate

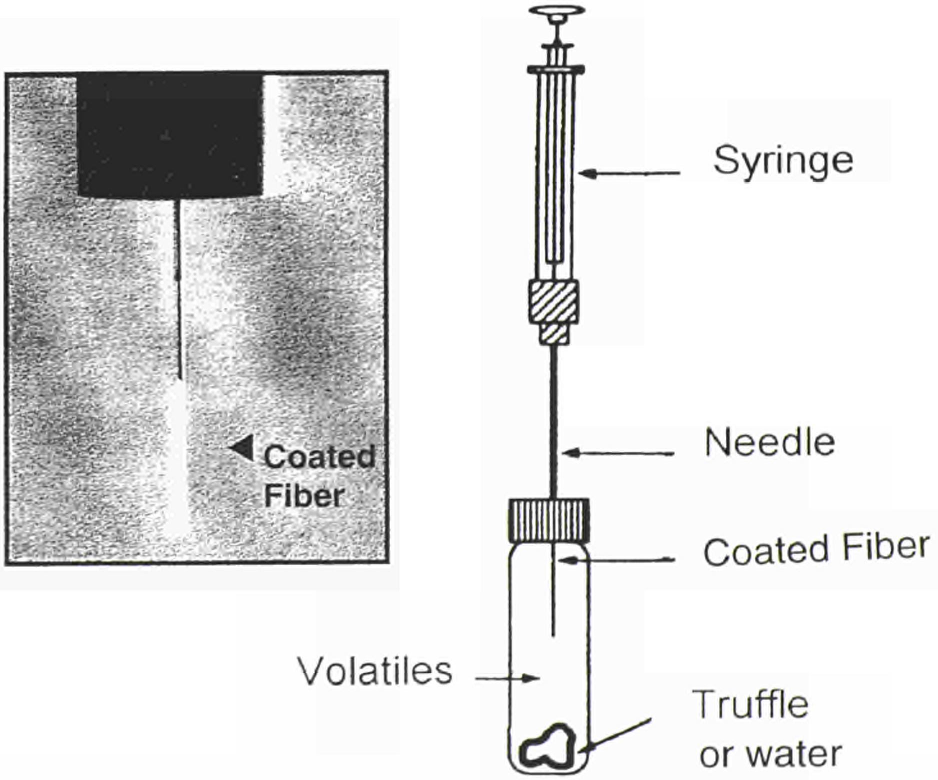


Fig. 33. Schematic of the sutup for headspace solid-phase micro-extraction with enlargements of the coated fiber in the device used for this study.

volatility (not too low and not too high) and high lipophilicity of the analyte.

Sulphur-VOCs emission from soils and their role in the global sulphur cycle are relevant to JRC programmes. Most sulphur-containing C1 to C6 organic compounds fall in the volatility and lipophilicity range of the 59 VOCs investigated , so HS-SPME with ITMS should be an ideal combination for the analysis of sulphur-VOCs. Due to the well-known presence of these compounds in truffles, the method was tested on these fungi. Due to the selectivity obtained with HS-SPME, very clean chromatograms were obtained and a series of sulfur-VOCs identified and quantified. Figure 34 showns the mass spectra of sulphur-VOCs extracted from white truffle aroma (upper spectra) compared to library mass spectra (lower spectra).

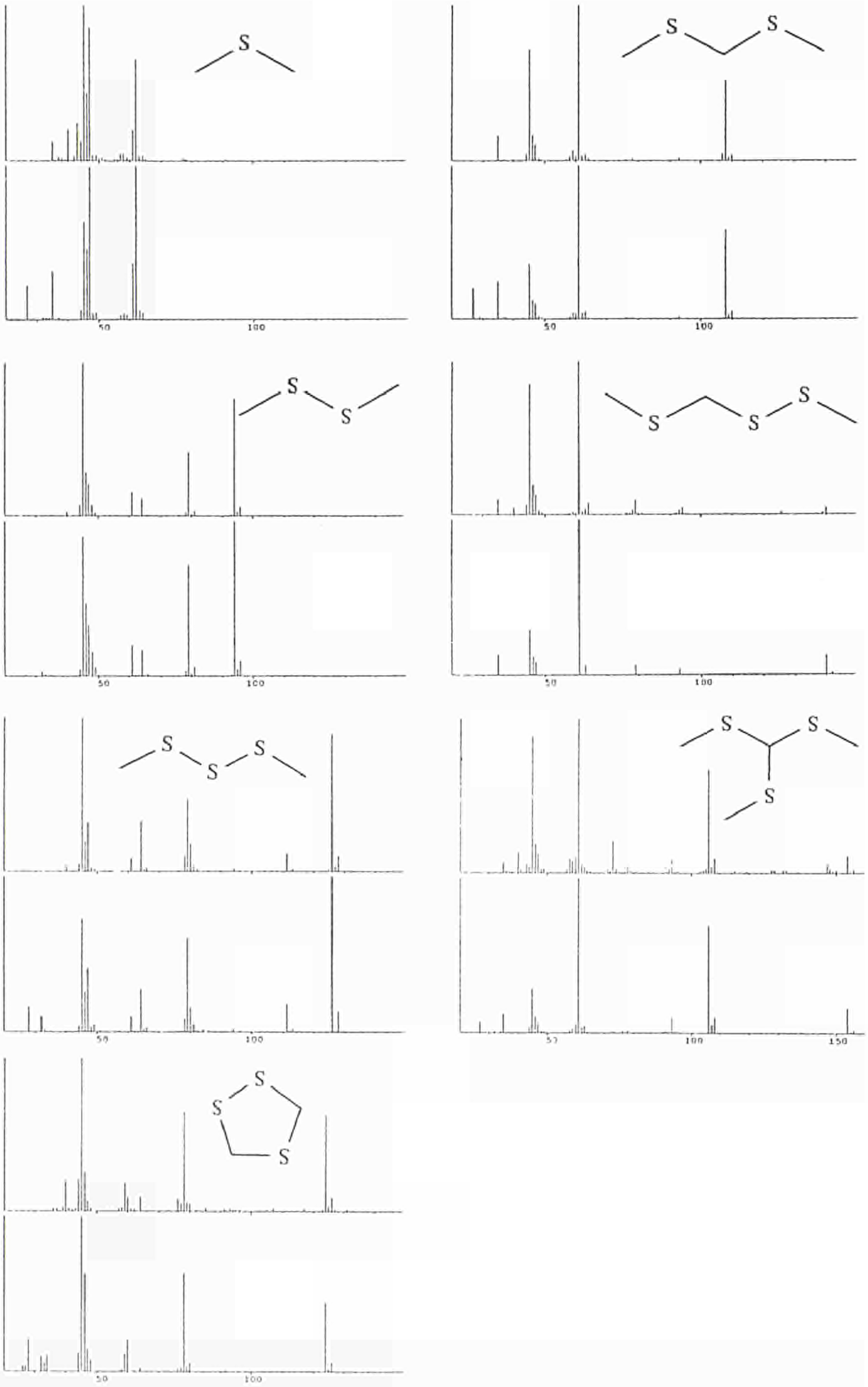


Fig. 34. Mass spectra of sulfur-VOCs extracted from white truffle aroma (upper spectra) compared to library mass spectra (lower spectra).

Mass spectrometric techniques have been also applied to surfactant analysis (see soil-pollutant interaction studies). These compounds are normally divided into anionics, non-ionics and cationics. The anionics account for 80% of the total industrial surfactant output, while the cationics comprise only about 6%. Traditionally, anionics have been measured using the methylene blue method, a non-specific complexo-metric method incapable of differentiating individual homologues. It is also prone to interference from naturally present anionic material. Chromatographic techniques have also been used during the last 15 years, including gas chromatography after derivatization and liquid chromatography using fluorimetric or UV detection. Compared to the above techniques, mass spectrometry is more versatile and generally more rapid, since it can be used to analyse surfactants without prior chromatographic separation.

Alkylbenzenesulphonates have been qualitatively analysed using fast atom bombardment (FAB) tandem mass spectrometry and field desorption mass spectrometry. The use of continuous flow FAB (CF-FAB) coupled with tandem mass spectrometry permits the quantitative analysis of alkylbenzensulphonate surfactants.

CF-FAB has been shown to be more sensitive than static FAB and to permit easy quantitation by flow injection analysis. In addition, CF-FAB reduces the surface activity effects which occur in static FAB.

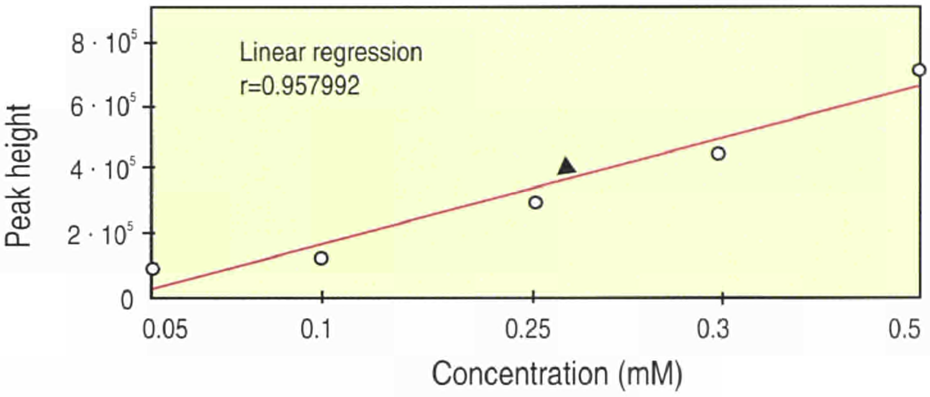


Fig. 35. Calibration curve for sodium dodecyl sulphate.

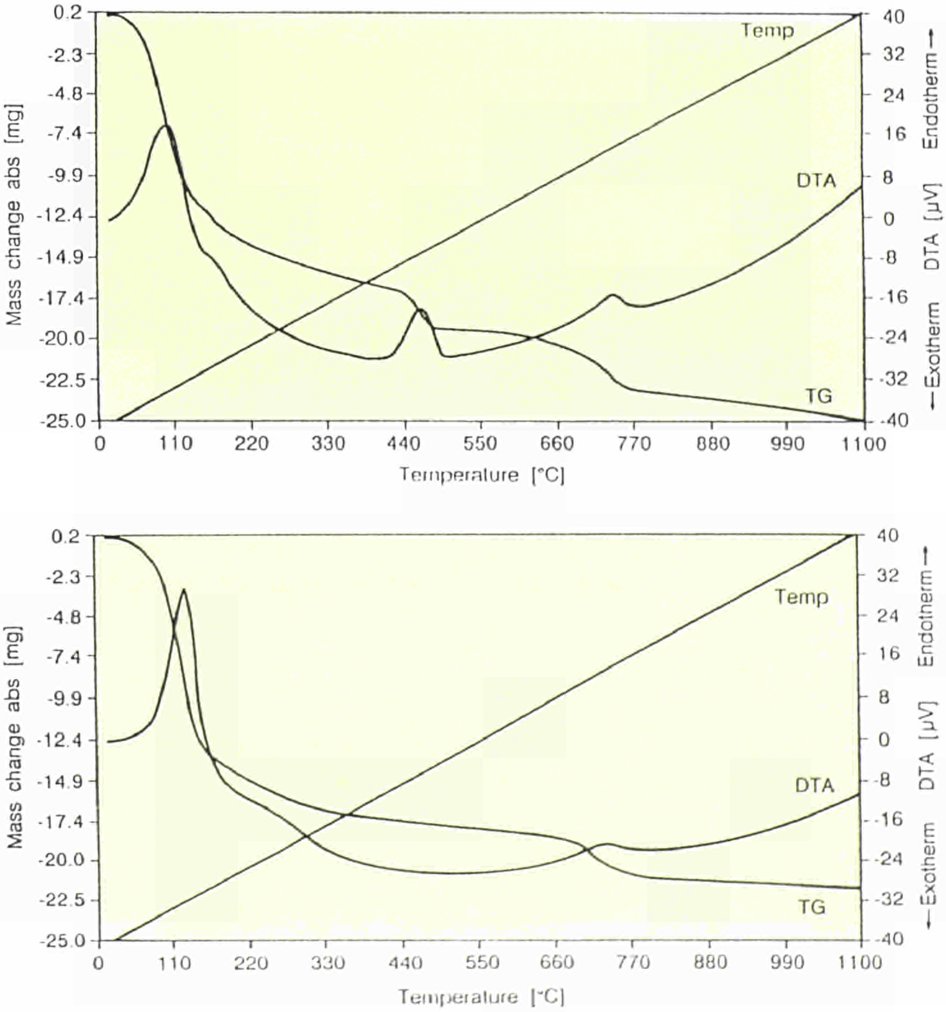


Fig. 36. Thermal decomposition of. a) OPC, b) OPC + aluminum sulphate.

Because of the selectivity of this technique, sample preparation is simple, usually requiring only concentration by solid-phase extraction of the analyte from liquid samples, or methanol extraction using sonication from solid samples.

An easy quantitative method for the determination of surfactants in water using CF-FAB-MS has been developed for each of the three major surfactant classes: sodium dodecyl sulphate (SDS) for the anionics, polyethylene glycol tert-octyl-pentyl ether (Triton-X) for the non ionics, and hexadecyl-trimethyl-ammonium-bromide (HTAB) for the cationics.

Good quantitative responses could be achieved for the anionic and the non-ionc model compounds, while for the cationic surfactants, the response proved to be higly non-linear. A typical calibration curve for SDS is given in Figure 35.

Waste Management

To evaluate possible materials for the disposal of tritiated water (HTO), ordinary Portland cement (OPC) has been proposed as a matrix for solidification/stabilization. Because of difficulties in ensuring that materials retain HTO, combination of a sequence of physical barriers must achieve a high degree of immobilization, in order not to exceed a maximum release rate of 10^{-3} % per day of tritium as HTO.

Water in cement materials can be divided into two categories:

- liquid water in large pores and

capillaries; and
- water of crystallization.

Water, therefore, behaves differently when escaping. Evaporation of water and water from cement, modified cement, molecular sieves and artificial clay, was measured by a thermobalance (Linseis Germany) coupled with differential thermal analysis (DTA).

The weight loss curves of water release from samples were obtained by heating:

- continuosly to 1100°C in air at a rate of 10 °C min^{-1}, to determine total amount of water in the sample;
- to 50 °C in static air; or
- to 50 °C in inert gas (N_2), at a rate of 0.5 l min^{-1}.

The best result for water release rate, i.e. 1.1×10^{-3} min^{-1} at 50 °C (or 1.1×10^{-4} min^{-1} at 30°C), one order of magnitude less than the value reported by previous authors, was obtained with the modified cement in which aluminum sulphate forms the compound:

$6CaO.Al_2O_3.3SO_3.31H_2O$
(ettringite)
as confirmed by XRD analysis.

The profile of decomposition in the range 20 - 1100 °C for OPC (Figure 36a) is modified by the effect of the ettringite formation (Fig. 36b).
In the second profile, the decomposition of $Ca(OH)_2$ in the range 400 - 500°C disappears.

In the experiments carried out at 50 °C, only 1 % of water is desorbed, as compared to 22.2 % contained in the material.

To evaluate the possible use of a material in retaining HTO, two important factors must be considered:

- the amount of tritiated water released; this should be as low as possible, compared with the amount initially present in the materia; compounds in which water is chemically bounded should be used;
- the structure of the material should accomodate water in it, as in pores, in order to slow down the release of water and to approach the requirement of a release rate of 10^{3} % per day as previously indicated.

This activity will not be continued in 1994, due to the retirement of the scientist responsible.

WATER QUALITY

Mito Project

Flow cytometry

Within the framework of the MITO Project, in 1993 was carried out the second experimental joint campaign, sponsored by the Institute, for monitoring phytoplankton biomass in marine waters via Flow Cytometry (FCM). This campaign took place in the northern Adriatic Sea, with the collaboration of the University of Münster (Germany), the University of Milano (Italy) and the Istituto di Biologia del Mare (Fano, Italy).

The campaign dealt with the application of FCM to the enumeration of phytoplankton in natural seawater samples via chlorophyll autofluorescence and electrical impedance sizing. To this end, a stationary Partec PAS III FCM and a prototype of a portable Flow Cytometer (CA III, Partec) were installed in the Fano Institute. The main purpose of the campaign was to get more experience in handling natural seawater samples with respect to FCM analysis and therefore to achieve further information for the improvement of the technique and the design of the portable instrument.

Between 7-9 September 1993, water samples from four stations and various offshore distances were taken in the Fano area. Because of very low cell density within the samples, a concentration procedure by nylon-net filtering was carried out (raw samples of 25 l or 50 l were passed through a filter set of 20, 40, 60 and 82 µm and the filtrates were resuspended in approximately 150 ml of 0.22 µm filtered seawater).

Raw and concentrated seawater samples were analysed via FCM. The chlorophyll content of the raw samples was determined spectrophotometrically (Strickland and Parsons, 1968) and species composition, as well as fluorescent characteristics, were examined by light and fluorescence microscopy.

The flow cytometric measurements showed that, at all the sampling stations, the phytoplankton density was rather low. The number of total counts in a particle size range of 21 to 82 µm varied between 15,000 and 35,000 per liter of seawater. By far the largest number of counts occurred in the filtered size fraction of 21-40 µm. Between 50% and 74% of the total counts were present within this fraction. The 41-60 µm fraction provided 19 to 40%, and the size class 61-82 µm provided 6 to 19%, of the total amount measured in all three size classes (Table 4 and Fig. 37).

The histograms for the 21-40 µm fraction of all the water samples showed at least one distinct peak (Fig.38 A-D). Microscopic analysis suggest that, in all the samples, this peak represented autofluorescent signals of a species of the dinoflagellate genus *Prorocentrum* (Fig.39). *Prorocentrum* was the only organism occuring in a reasonable amounts in all the seawater samples. Only very few other algae were visible by light and fluorescence microscopy.

The mean channel position of this peak shifts according to the different stations and sampling days between ch 320 and ch 430, corresponding to relative fluorescence values (RF) from 2.5 to 7.4 (based on the fluorescence of the standard beads used). Apart from the mean channel, the shape of the peak also changed (Fig.38).

The number of counts within the peak (corresponding to the number of *Prorocentrum* sp.) of the 21-40 µm fraction varied between 1,000 and 3,900 l^{-1} and made up 68% to 91% of the total counts recorded for this range of fluorescent signals.

As shown in Figure 37, a slight accumulation of counts also appeared in the 41-60 µm fraction between channel 350 and 450 (9-27% of the total counts of this range), whereas in the 61-82 µm fraction, nearly no signals of such fluorescence intensity were recorded(1-8%).

The events indicated via FCM deliver information on the number of particles with a defined fluorescence intensity (under given conditions) present in a sample. This parameter is suitable for providing an idea of the amounts of algae with common fluorescent features. It gives no indication of parameters such as pigment content or particle size. In the histograms shown in Figures 37

SIZE FRACTION	Station1		Station2		Station3		Station4	
	total	peak	total	peak	total	peak	total	peak
08.09.1993								
21 - 40 µm	1141	1582	18659	3889	14479	2594	15115	1106
41 - 60 µm	1482	70	5066	423	6282	198	3925	117
61 - 82 µm	2960	154	1467	59	2160	61	2081	25
total 21-82 µm	15483	1806	25192	4371	22921	2853	21121	1248
09.09.1993								
21 - 40 µm	8607	1000	14410	1463	12114	2193	16537	1294
41 - 60 µm	3748	94	6238	585	6123	545	13618	378
61 - 82 µm	2413	83	4270	101	2081	68	3112	51
total 21-82 µm	14768	1177	24918	2149	20318	2806	33267	1723

Table 4. *Total counts/liter seawater and counts in distinct peak area of stations sample from 1-4 on 8 and 9 September 1993*

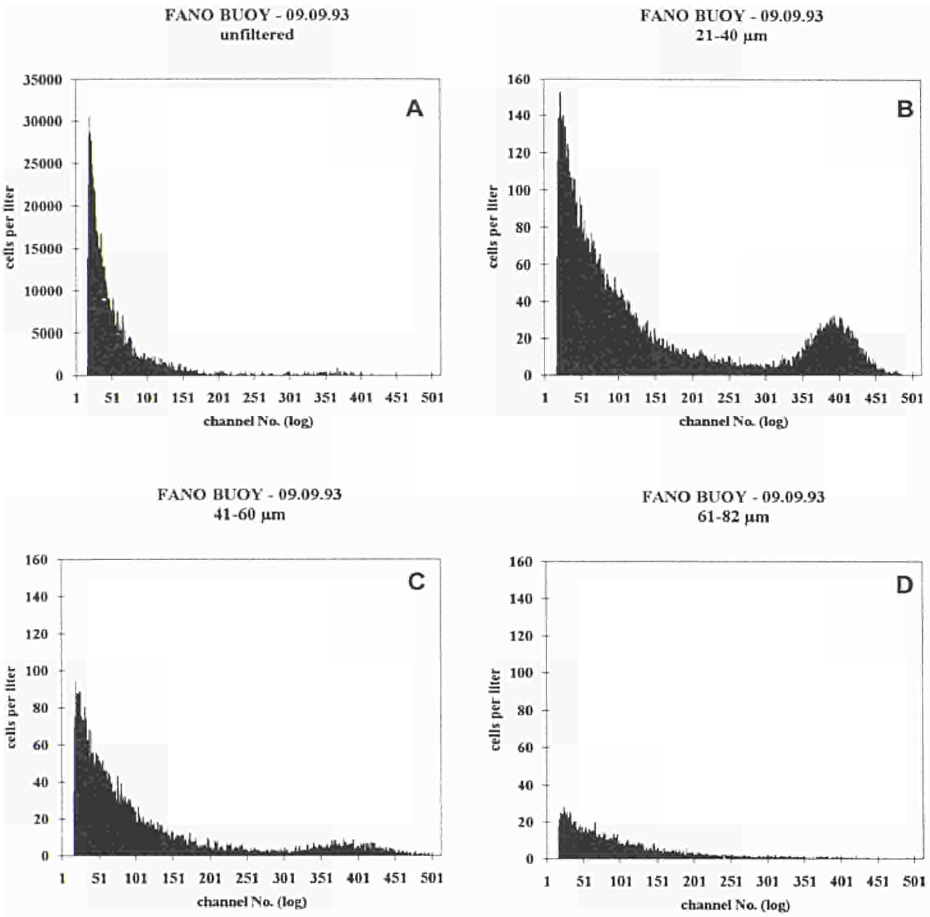


Fig. 37. Histograms of the unfiltered sample and three size fractions Station 3, Fano Buoy, 09.9.1993

and 38 A-D, a particle with an RF value of 0.1 (=ch 20) is depicted as one count, as well as a particle with a RF of 16 (= ch 500, axis in log-scale). The impact of low fluorescent particles on the total amount of fluorescence (due to the content of photosynthetic pigments), which must be seen as a measure of the biological activity of a sample, is indeed much smaller than Figure 38 A-D conveys. In this Figure, E-H, the amount of fluorescence per liter seawater, is depicted, corresponding to the samples of Figure 38 A-D. By comparison, it is obvious that the main portion of the measured fluorescence is based on *Prorocentrum*. The high level of signals in low fluorescent channels (Figures 37 and 38) contribute only a very small portion to the total fluorescence.

In this way, the total relative fluorescence delivers a reproducible and directly comparable measure for bulk algal analysis and is also suitable for judging their biological activity and changes in a defined algal population in natural water samples.

Furthermore, the mean fluorescence per cell of a given population, which is easily calculated by division of them total flurescence by the number of counts, contains information about the physiological status of the population examined.

Table 5 shows these values for four sampling spots on 8 and 9 September. It becomes obvious that the phytoplankton situation at the different stations developed in different directions. The total relative fluorescence (of the entire sample) decreased at all stations, less at stations 1 and 4 and dramatically at stations 2 and 3. This can be interpreted as a general decrease of phytoplankton.

The total fluorescence of the *Prorocentrum* peak was more or less stable at station 1, whereas the fluorescence per cell increased. By contrast, the total peak fluorescence was decreased heavily at station 2 and 4, with a constant fluorescence per cell at station 2 and a decrease at station 4. Both values increased at station 3. These data are significant in showing that there were different developments of the *Prorocentrum* population at the different sampling locations.

In the context of this campaign,it was possible to show that also under conditions of low cell densities in natural seawater samples, FCM provides a useful tool for the rapid analysis of phytoplankton. The results show that it is indeed possible to detect algae at very low numbers (some thousands per liter) in seawater samples with FCM and to quantify the number of cells and the amount of total fluorescence. Furthermore, with reference to quantity and physiological quality, the development of a specific population within the water could be followed and comparisons between different sampling stations conducted.

Via the relative-fluorescence value (RF), a direct comparison of measure-

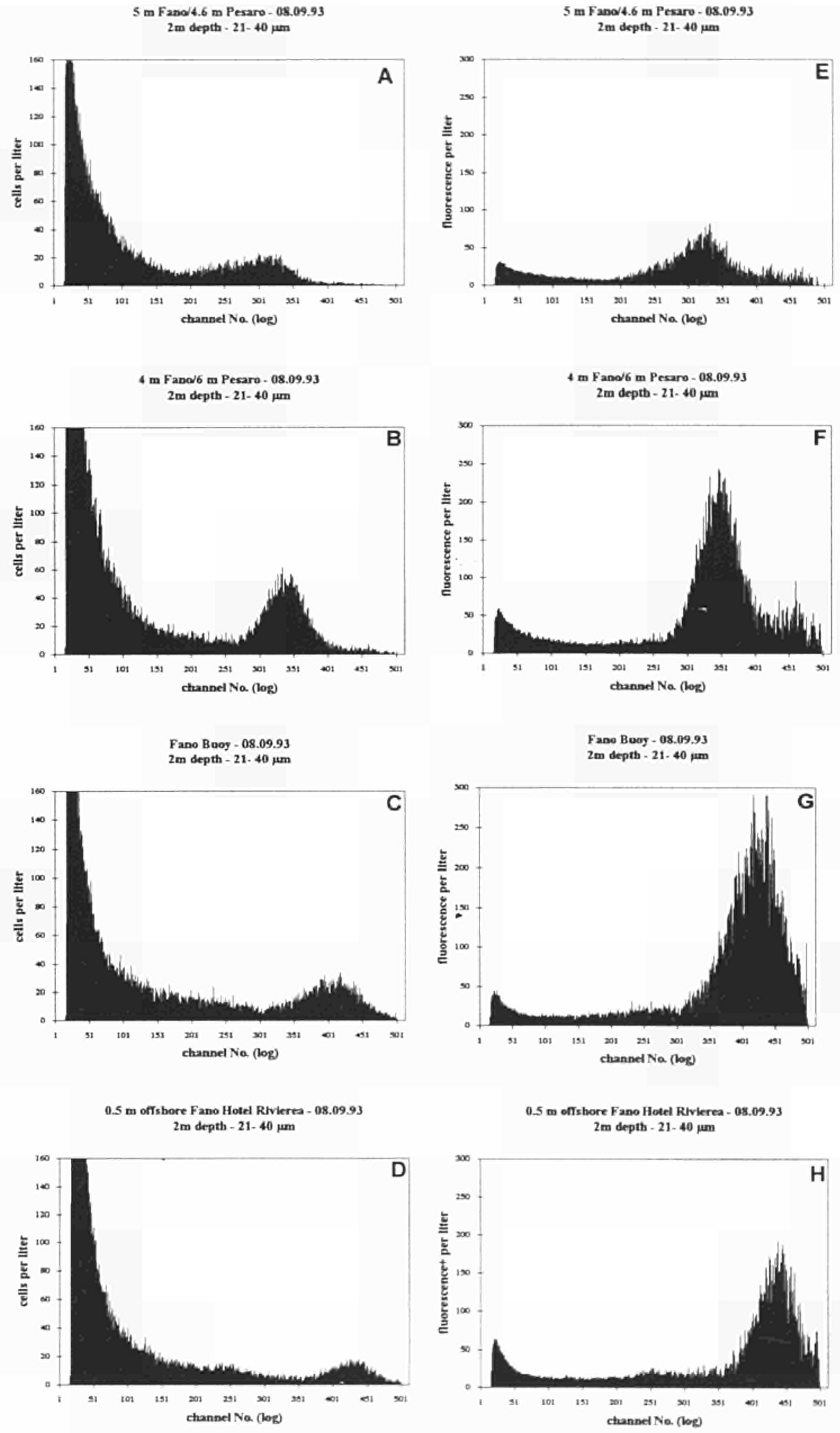


Fig.38. Frequency histograms (A-D) and fluorescence histograms (E-H) of the size fractions 21-40 mm

ments can be carried out and differences in the phytoplankton structure of water can be monitored and compared over a period of time. Which biological characteristics of the water sample correlate with the RF-value has still to be examined in detail.

To obtain a second measure of algal biomass, in addition to the fluorescence,it is essential to apply cell sizing via FCM. This combination of fluorescence measurements and cell-sizing allows the calculation of the biovolume of water samples and distinct populations within them, and also make it possible to obtain information about the physiological status of the algae present.

Algal toxicity

The toxicity associated with uncontrolled growth of various species of algae constitutes a very important problem with respect to ecological and economical aspects. As is well known, algal blooms are sometimes related to the production of various toxic chemical compounds.

These toxins can be grouped in various classes (DSP, NSP, ASP, etc.) in relation to their action towards different tissues or organs. Since the growth of more than one species of alga can occur in water basins simultaneously, it is clear that the toxicological characterization of lakes and brackish or marine shore areas is often very complex.

Taking into consideration the knowledge acquired up to now in this specific field, the measurements routinely carried out for the description of the hazard associated with algal blooms are either highly specific for single toxins or have a low sensitivity.

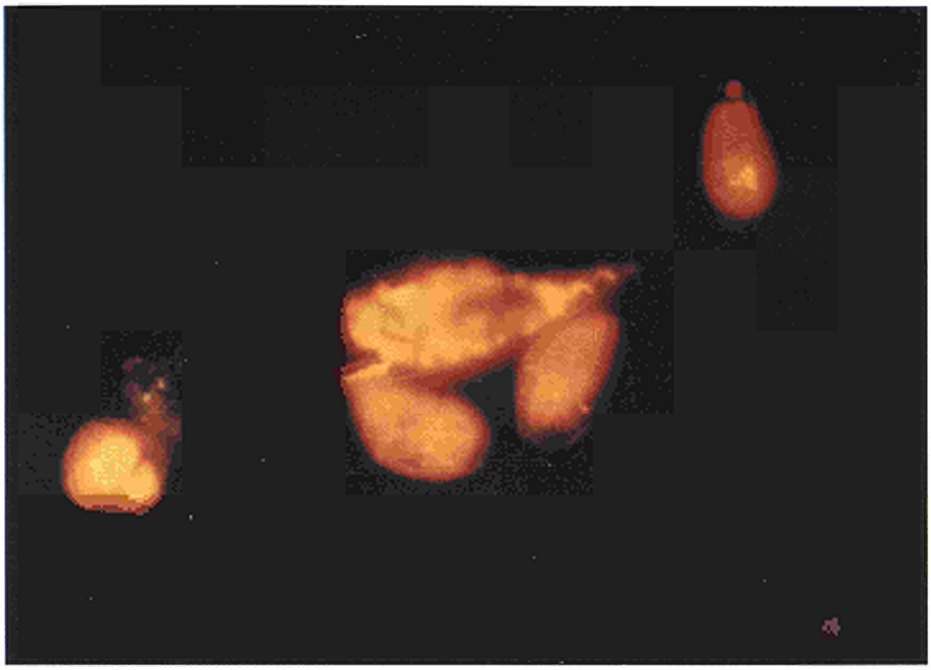


Fig. 39. Fluorescence microscopic photograph of Prorocentrum sp. (centre underneath and right), Ceraffum sp. (centre above) and an unknown Dinoflagellate (left).

Station	total relative fluorescence (rU l^{-1}) 08.09	total relative fluorescence (rU l^{-1}) 09.09	peak relative fluorescence (rU l^{-1}) 08.09	peak relative fluorescence (rU l^{-1}) 09.09	fluorescence per cell (rU) 08.09	fluorescence per cell (rU) 09.09
1	12960	11705	5737	5008	3.63	5.01
2	29822	16412	17326	7869	4.45	5.38
3	33597	21781	7682	14467	2.60	6.60
4	22864	21107	12046	8659	10.89	6.69

Table 5. Total and peak fluorescence and fluorescence per cell of Prorocentrum.

In the former case, the description of the overall toxicity of the sample requires more than one specific measurement. In the latter case, the low sensitivity of the available methods only allows evidence of the presence of toxic algal species in the water basins to be provided when the ecological conditions are dramatically compromised.

The experimental activity in this last period focused on the possibility of providing evidence with high sensivity and with a simple analytical procedure of the presence in water samples of toxins belonging to the DSP class, the hepatotoxins and the ittiotoxins. The research activity started with studies on the best conditions for showing the presence of okadaic acid (OA), a very well-known algal product detectable in the DSP-producing algae. This compound is concentrated by mussels that finally carry it (as food) to human beings, causing abdominal pains, diarrhoea and vomiting.

As is mentioned above, toxins that have the liver (or hepatopancreas) as a target organ are of concern here. It is therefore feasible that isolated mammalian hepatocytes can be used for this kind of toxicological determination. In particular, the application of some biochemical procedures should be considered as anaytical tools for these toxicological analyses.

The first step of the research activity carried out in the context of MITO project took place with the determination of the relationship between the presence of increasing quantities of purified OA in L-15 medium and the induction of mortality in hepatocytes cultured *in vitro*. The parameter considered was Lactate Dehydrogenase (LDH) release into the culture medium by murine hepatocytes after 24 hours of exposure. As is well known, the release of this cytoplasmic enzyme could be considered as an index of death of the cells in culture. Under the actual experimental conditions, it has been possible to detect concentrations of OA as low as 10^{-8} M.

The possibility of using murine primary hepatocytes for the determination of OA toxicity by measuring of Neutral Red uptake (NRU) by viable cells under simple, defined experimental conditions has also been investigated. Detection of a reduction quantities of NRU by treated cells can be taken as an index of the effect induced by the toxin.

The two approaches mentioned (LDH release and NRU) gave similar results when the same concentration of 10^{-8} M OA was used. Nevertheless, NRU measurement has been found to detect dead, as well as damaged cells. The final percentage of cells that can be considered to have beens affected by the toxic agent was therefore greater (1.5 - 2) times than that estimated by LDH analysis.

When the incubation of hepatocytes was prolonged for 72 hours, 3×10^{-9} M concentrations of OA could be also monitored. It must be pointed out that the most sensitive and most specific method for measuring OA reported in the literature (that takes advantage of the specific inhibition of Protein Phosphatase 1 and 2A, PP1 and 2A) can detect quantities about only 10-30 times lower.

This excellent sensitivity, together with practical considerations, suggested that the NRU method be used in future studies.

The standardized NRU methodology has been applied to detect the toxicity associated with *Prymnesium parvum* blooms, one of few toxic algal species that can be grown in the laboratory.
This research labora-tory activity has been carried out in order to calibrate the methodology for algal cultures, thus contributing to the main goal of the programme which remains the detection of algal toxicity in real environmental situations.

It is known that this brackish alga synthesizes and releases at least seven types of toxic proteolipids into the surrounding water during its growth and, to a greater extent, when the algae die after having reached the final stationary phase of this growth or when they are subjected to stress growth conditons.

The proteolipids released into the water have haemolytic, ittiotoxic and cytotoxic activities.

This algal specie has been grown under the best and controlled conditions with respect to the ratio of nitrogen and phosphorus (N/P=4) concentrations. In order to confirm the reliability of the method, the algae have also been grown under stress conditions characterized by a lowered or enhanced N/P ratios (0.8 and 20, respectively).

The preliminary results show that the reduced N/P ratio induced the maximal production of toxins by *Prymnesium parvum* both released into the medium and retained in the cells. Increasing the concentration of phosphorus induced, on the contrary, the lowest production of toxins.

Moreover, it seems that the chemical nature of the released toxins in the culture medium during the exponential phase of the algal growth is different from that retained within the cells.

This experimental activity is being continued, in order to better characterize the toxic parameters during the laboratory study phase. The knowledge acquired will then be applied to the planning of further studies in the MITO project.

Modelling

Numerical modelling of biological activity in the Adriatic sea has continued.

The first approach, using a fine grid topographic model for the North-Adriatic, and a separate coarse grid model for the whole Adriatic (aimed at providing boundary conditions for the former), was found to be not very effective. Therefore, a new preprocessor for the hydrodynamic model ISPRAMIX has been developed for producing interactively arbitrary, new, non-uniform topographic models in a very short time. This preprocessor permits the optimization of the discretisation grid for every specific application, and, for modelling the Adriatic, eliminates the need to work with two different models. Further work has been performed with an overall model of the Adriatic, with a fine grid (3,2 km x 3,2 km) in the north, which gradually changes into a coarse grid (16 km x 16 km) near the strait of Otranto. This model has about 70,000 wet grid points and requires computer simulation times of about 1/2% of the real time on a DEC 4,000-160 (Alpha) workstation (i.e. about 5 days for a 1-year simulation, including the biological part).

The next step was the implementation of a biological model developed at Ispra in collaboration with the University of Hamburg. This model requires the solution of three additional transport equations for the three model components: phytoplankton, herbivorous zooplankton, and phosphate nutrients. Assuming inflow of the nutrients via the Po river, the results shown in Figs. 40 and 41 are obtained for typical meteorological conditions. The nutrients originating

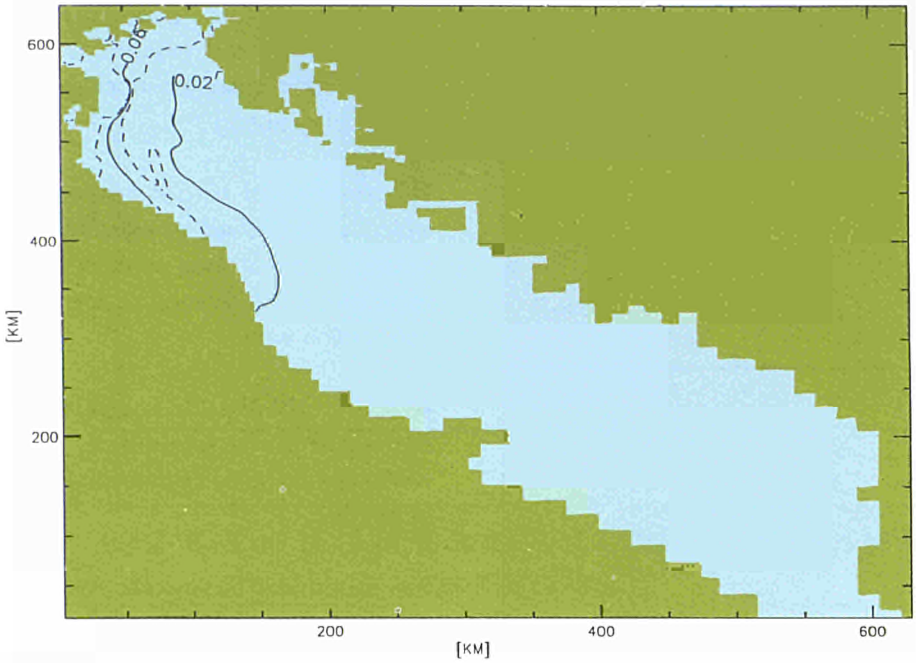


Fig. 40. Computed distribution of phosphate concentration (mMol m^{-3}) originating from the Po river.

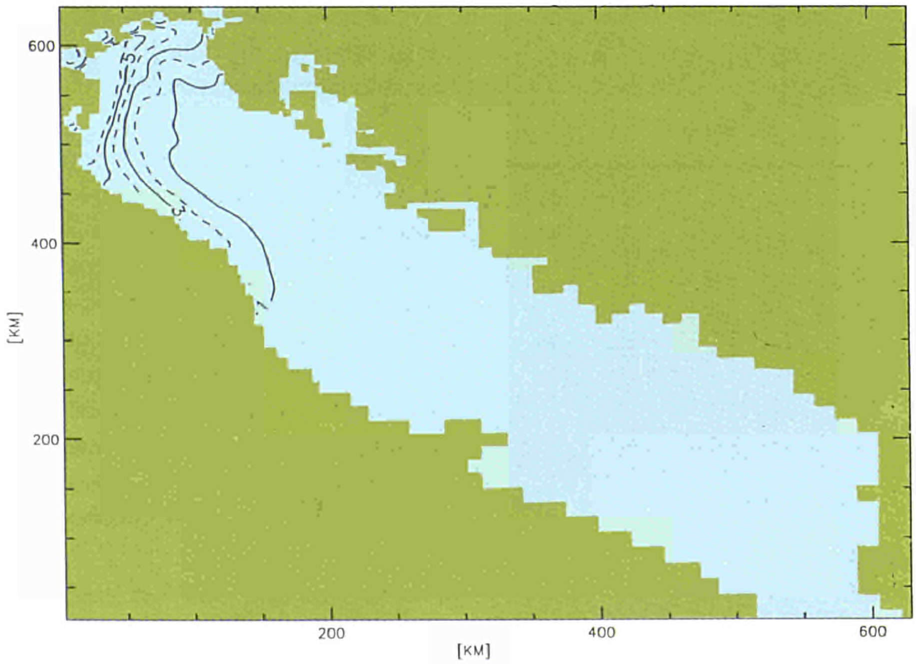


Fig. 41. Computed distribution of phytoplancton concentration (gC m^{-3}) referring to the same time as the results shown in Fig. 40.

from the Po river move preferentially along the coast of Emilia-Romagna, causing a corresponding growth of phytoplankton.

This preliminary study has produced plausible results, which demonstrate the feasibility of this kind of modelling. The next step, to be started in 1994, is the collection and preparation of suitable observational data, which are needed for initialising the model computations, for formulating the boundary conditions and for validating the different sub-models.

AQUACON-MedBas-Project

The "Analytical Quality Control and Measurement Error Assessment Studies" (Project AQUACON-MedBas) project has been developed at the request of the EC-Member Countries of the Mediterranean area (Italy, Spain, France, Portugal and Greece).

Its objective is to identify, quantify and reduce systematic and random measurement errors associated with the most critical problem areas of environmental analysis, which include many types of water (seawater, freshwater, rain water, drinking water and waste water), and sediment and sewage sludge analysis, but also biota and foodstuff analysis.

The project offers, free of charge, participation in complex collaborative laboratory studies, including field campaigns aimed at the assessment of sampling errors. The major target group of participants consists of the public laboratories, which, with pressure from national and supranational directives, wish to test their performance quality.

The EI provides the coordination of

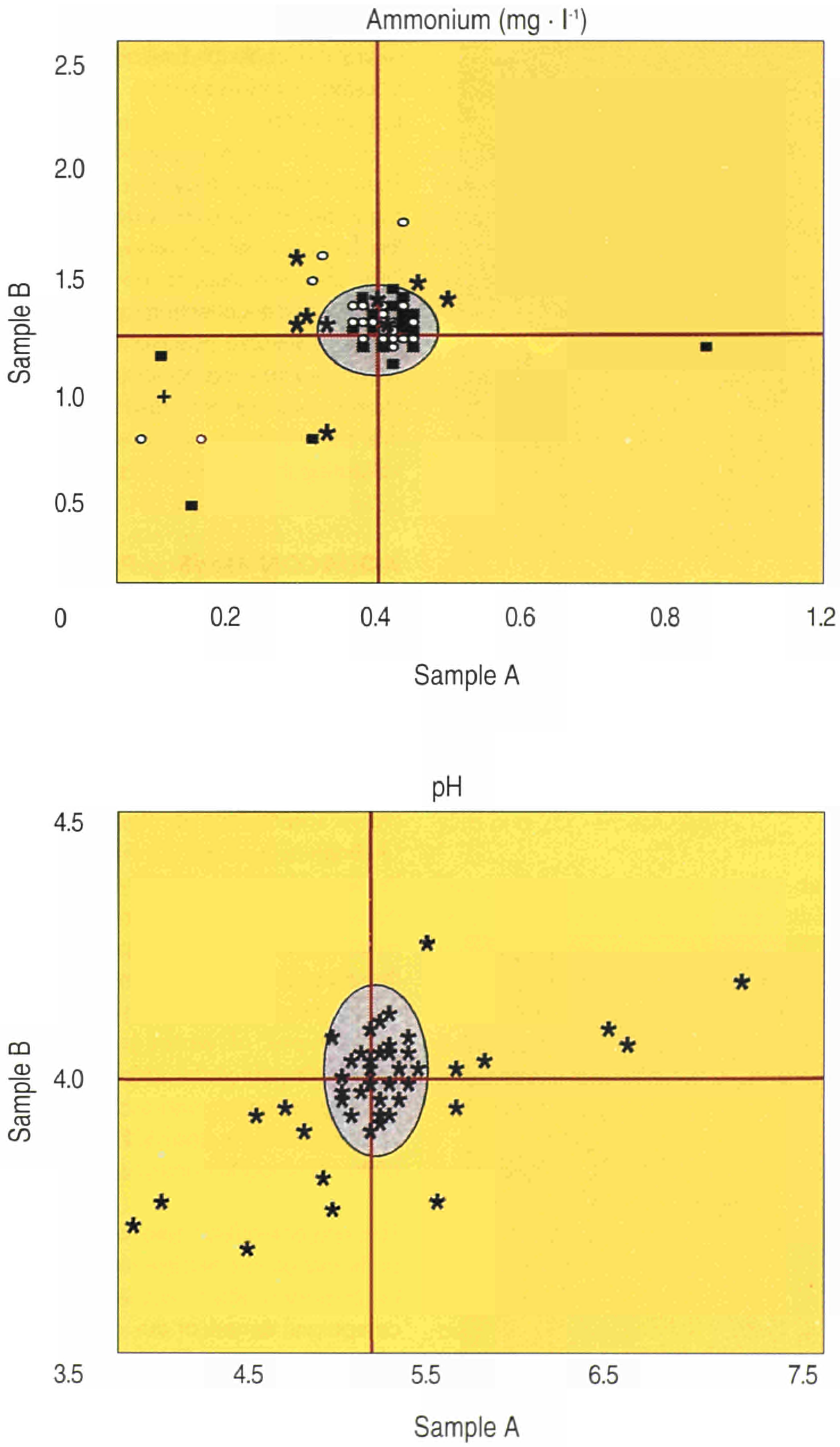


Fig. 42 (a and b). Second interlaboratory exercise AQUACON-MedBas - Subproject " Rainwater Analysis" : Ammonium and pH.
■ IC = Ion chromatography; ○ NES = Nessler; ★ PHE = Indophenol blue colorimetry; ✚ PYR = Bis-pyrazolon colorimetry.

the project and prepares the interlaboratory test materials, including, in most cases the homogeneity and stability testing.

The analytical target values are typically established by external high-quality laboratories with a good reputation for reference material certification work.

AQUACON-MedBas has been organized in 10 subprojects, all of which are currently at different stages of progress.

The subproject "Rainwater Analysis" organized its second interlaboratory exercise (80 participating laboratories). The results show that major systematic errors still persist, as indicated by the examples of ammonium and pH measurements (Fig. 42). The third interlaboratory exercise has been prepared and the samples were mailed in November 1993.

The Subproject "Mercury in the Foodchain" organized a second exploratory interlaboratory comparison, offering, this time, a low-level material (trout muscle tissue).

The results of a trained laboratory group (Fig. 43) show small data dispersions compared to the 1992 exercise, but are, in any case, in need of error removal. Subsequently, a package of test materials consisting of a sealed mercury standard solution, two solutions of mineralized powdered fish and mussel tissue, and fish and mussel tissue, has been prepared for the 1994 collaborative study.

The trout test material was also analyzed for a number of critical trace metals by the same laboratory group (Table 6), and the results

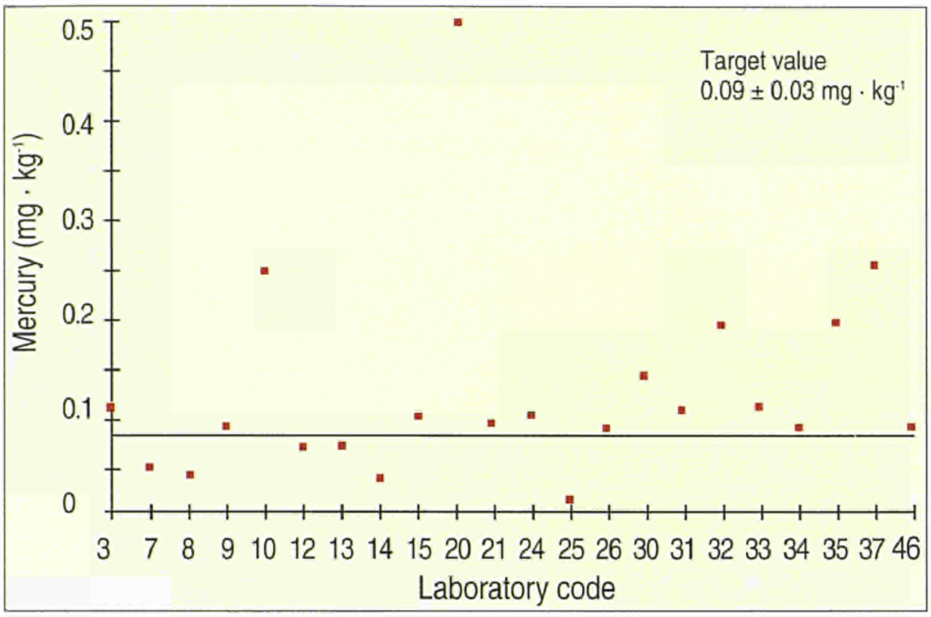


Fig.43. Second exploratory interlaboratory study AQUACON-MedBas Subproject "Mercury in the food chain": Mercury determination in trout muscle.

	Valid N	Mean	Median	Min.	Max.
Hg	22	0.13	0.11	0.01	0.50
Pb	24	0.53	0.29	0.05	2.63
Cd	22	0.08	0.02	0.01	1.07
Cu	20	3.3	2.65	1.60	10.9
Zn	19	25.1	23.0	7.50	60.2
As	9	0.81	0.95	0.20	1.50

Table 6. 2nd Exploratory Interlaboratory Study for the Determination of Some Trace Metals in Fish.

indicate, for lead and cadmium, in particular, that further developments are needed.

The test materials for the first interlaboratory exercise in the subproject "Drinking Water Analysis" have been prepared and their stability tested. The test parameters are Hg, Cd, Pb, Cu, Zn, Cr, Ni,SO_4^{2-}, NO_3^-, Cl^- and NH_4^+.

In the framework of the Subproject "Sediment Analysis", the test material package for the first interlaboratory run (metals) has been prepared, which consists of two pure metal solutions, two digested (dissolved) sediment solutions, all sealed in glass ampoules, and two dry sediments at different metal concentrations.

An exploratory interlaboratory exercise, with a trained laboratory group, has been organised in the framework of the subproject "Foodstuff Analysis". The study materials were flours, milkpowder and egg powder. The data obtained on lead, copper, cadmium and mercury showed that larger errors are hidden by the dissolution step. Consequently, the first run of the collaborative study will include solubilized materials as well, to allow for the separate evaluation of errors associated with the dissolution step.

Two sewage sludge test materials have been prepared for the subproject 'Waste Analysis", and their homogeneity has been tested. At present, their analytical characterization is in progress.

WORKING ENVIRONMENT

The aim of this work is to provide DG V/E (Health and Safety Directorate) with scientific and technical information on a number of issues relating to chemical agents in the work environment. In 1993, cooperation included the following points:

- International Chemical Safety Cards (ICSC)

A part of the information contained in

the ICSC has been included in the ECDIN data bank, for large facilities in the searching and retrieval of data. Information concerning more than 300 chemicals has been transferred to the data file on Occupational Health and Safety (OHS). Particular attention has been paid to the selection of the following types of data:

- Chemical Hazards
- Spillage / Disposal / Storage
- Packaging and Labelling

- *Monographs on Chemicals*

With reference to the series on "Biological Indicators for the Assessment of Human Exposure to Industrial Chemicals", it is planned to extend the information in the monographs to make them into full Criteria Documents (CD).

A CD will be produced of the type preferred by the Scientific Experts Group on the establishment of the EU Occupational Exposure Limits, for each chemical considered.

A CD on "Inorganic Mercury" is to be issued to DG V in 1994, at the earliest .

- *Occupational Exposure Limits (OEL)*

In the contexte of the Commission's activities on the establishment of limit values (Council Directives 80/1107/EEC, 88/6421EEC and 90/394/EEC), the JRC is investigating means of establishing out relevant contacts for data collection on these matters.

This exercise is performed by consultants of choice and improved links (UNEP - IRPTC data bank) .

An OEL data bank for the use of the OEL Scientific Expert Group will be made available to DG V in 1994.

THE ENVIRONMENT INSTITUTE

2. Scientific-Technical Support for Community Policies

As in 1992, the main part of the Institute's effort for the scientific and technical support for Community Policies was on behalf of Directorate General XI (Environment, Nuclear Safety and Civil Protection) and was concerned with the areas of Environment (encompassing Atmospheric Pollution, Chemical Waste and Water Quality), of Radioactive Environmental Monitoring (REM), the European Centre for the Validation of Alternative Methods (ECVAM) and the European Chemicals Bureau (ECB). As a result, most of this section is dedicated to descriptions of the major achievements in the above areas.

Although the support provided to other Directorates General must not be considered of lesser significance - in particular that provided to DG III, DG VI and to the Consumer Policy Service - the achievements related to these pertinent activities are presented together in the second part of this section.

SCIENTIFIC and TECHNICAL SUPPORT to GENERAL DIRECTORATE XI

Atmospheric Pollution

The Central Laboratory of Air Pollution (CLAP)

SO_2 Directive: measurement of suspended particulate matter (SPM)

In the context of Directive 80/779/EEC and in view of the standardization of SPM measurements in EC air quality networks, the Commission (DGXI/B/3) has entrusted the European Committee for Standardization (Technical Committee 264, Working Group 2) with developing a reference procedure for testing the equivalence of PM10 sampling heads with the reference measurement method of the Commission (WRAC or Wide Range Aerosol Classifier). PM10 is the fraction of SPM with a size lower than 10μm, corresponding to the fine particles that reach the thorax when inhaled.

This reference procedure has been drafted by the CEN and will be tested under field conditions in four measuring campaigns held at different locations and characterised by different aerosol size distributions and wind forces (heavy industrial area and low winds; industrial area; and strong winds; urban area; background area). Ispra has been selected as background site. During these campaigns, the PM10 fraction measured with the WRAC will be compared with those obtained with candidate PM10 sampling heads. Six different PM10 sampling heads will be submitted to the test procedure. This campaign is scheduled to take place in April 1994.

NO_2 Directive: Quality Assurance Programme

The CLAP has been equipped with a calibration facility designed especially for the organisation of intercomparison and intercalibration exercises. The calibration unit is a computerized dynamic diluter, which allows for the generation of complex gas mixtures (up to 8 components + ozone and water vapour) that can be supplied to up to 12 participants.

In the context of the harmonisation programme of Directive 85 / 205 / EEC on air pollution by NO_2, two intercomparison exercises were organised with the aim of controlling the NO_2 calibration procedures implemented in the EC air quality monitoring networks. A first exercise took place in May 1992 at the Landesanstalt für Immissionsschutz (Essen - Germany). The second exercise was organised in April 1993 at the new calibration facility of the CLAP. The exercises were addressed to laboratories responsible for Quality Assurance/Control in the national air quality monitoring networks.(Fig. 44). A total of 20 laboratories from the 12 European Member States took part in the exercise. Gas mixtures of NO and NO_2 with concentrations ranging from 5 to 500 μg m^{-3}, were generated and supplied to the participants for measurement (Fig.45). Different calibration techniques were implemented by the participating laboratories: namely, a permeation method (reference calibration method of the EC directive), static volumetric dilution, dynamic volumetric dilution, the Griess-Saltzman wet chemical method, gas-phase titration, and pressurised standard gas cylinders. The effects of factors which interfere, such as the water vapour content of the gas sample, on the response of the analysers were also investigated by supplying standard mixtures with water vapour contents increasing from 0 to 100%.

When compared with the standard values, the measurements obtained by the different laboratories and with different calibration procedures showed good agreement. About 80% of the measurements were within a tolerance limit of ±10% of the standard values. For NO_2 concentrations above 350 μg m^{-3}, the Griess-Saltzman method generally showed a lower response (5 to 8%) when compared to the other methods. It was also noticed that all the chemiluminescence analysers involved in

Fig.44. The calibration bench of the CLAP at the Institute hosted, in April 1993, the second intercomparison of NO_2 *calibration procedures. The exercise was attended by 11 laboratories, in the context of the DGXI Quality Assurance Programme of Directive 85/203/EEC on* NO_2*.*

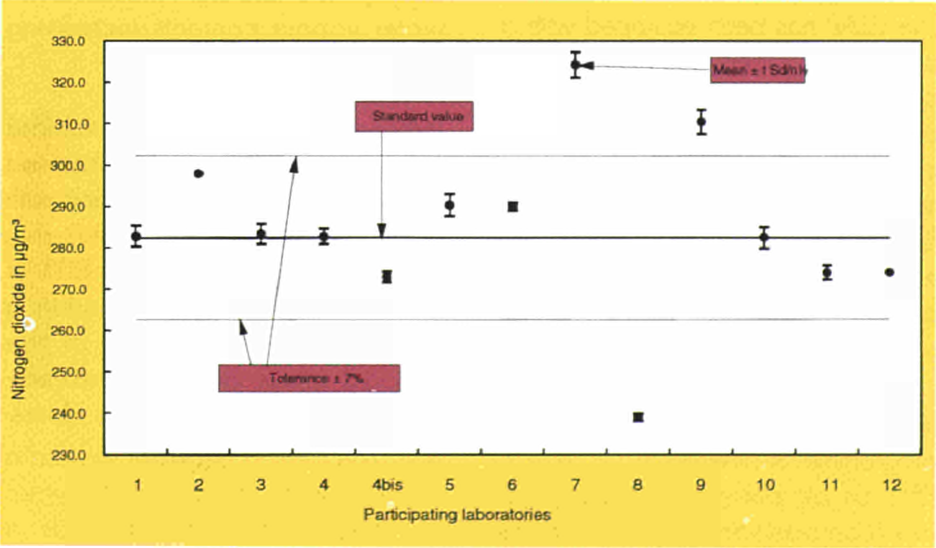


Fig.45. Intercomparison of NO_2 *calibration standard.*

the exercise showed a negative interference with the water vapour content of the gas sample. For an increase in relative humidity from 0 to 100%, a typical decrease in sensitivity of 10% was measured.

O_3 Directive: VOC measurement techniques

With the acceptance of Directive 93/72/EEC on air pollution by ozone, the Commission has made an important step toward the control of photochemical air pollution. This Directive will require the monitoring of ozone concentration levels, but also recommends the measuring of ozone precursors such as NO_2 and VOCs at selected stations of the air quality monitoring networks. In view of the harmonisation of VOC measurements, the CLAP had organised in 91/92 a first intercomparison of methods for VOC measurement. This intercomparison has shown that the current performances of gas chromatographic techniques are still poor and must be improved, if they are to meet the requirements of a reference method for the determination of VOCs.

A second intercomparison was organised in December 93 - January 94. About 20 laboratories routinely dealing with air quality measurements participated in the exercise. Participation was also extended to laboratories from the EFTA countries. The exercise was performed with the support of the National Physical Laboratory in the UK, which provided the hydrocarbon mixtures.

The intercomparison consisted of the measurement of both a gravimetric standard mixture and an authentic urban air sample. The gravimetric mixture contained 26 individual hydrocarbons (C2 to C9), with concentrations ranging from 5 to 80 ppb by volume. The hydrocarbons in the gravimetric mixture largely comprised the compounds relevant to the formation of photo-oxidants proposed by the working group on "VOC Measurement Techniques" of the CEC. The gas mixtures were contained in passivated aluminium cylinders of 7 litre capacity at a pressure of 7 bar, and were distributed by road and air couriers to the participating laboratories. The results will be available for evaluation early in 1994.

Application and development of VOC diffusive samplers

The monitoring of VOCs by the air quality networks generally requires expensive and sophisticated measurement techniques. Diffusive samplers offer a cheap and easily implemented alternative to these techniques. The diffusive sampling method for VOCs is comparable to the NO_2 method already implemented by the CLAP for network design studies. The VOC diffusive sampler consists of a stainless-steel tube, one end containing a chromatographic absorbent for fixing the pollutants. The pollutants are collected by molecular diffusion along the tube to the absorbent. After exposure of the samplers over a period of two weeks, the tubes are returned to the laboratory for analysis. The hydrocarbons are thermally desorbed and measured by gas chromatography.

The diffusive samplers have been tested and validated under laboratory conditions. In a first phase, the study was limited to the compounds benzene, toluene and xylenes (BTX). An exposure chamber providing for the simulation of ambient conditions has been constructed. It has been possible to determine the uptake rates of the samplers and to test the effects of ambient parameters such as wind velocity and the changing concentrations of pollutants. The first results of the laboratory validation study are promising and a first field validation study campaign is planned for early 1994 (see the Brussels campaign, below).

Case studies: the Milano and Brussels air pollution campaigns

In February 1993, a national campaign was organized at Milan by the Institute of Air Pollution, CNR, Rome. The study was focused on meteo-rological and chemical characterization of the serious smog episodes which frequently occur at this time of the year in Milan. The JRC long-path differential optical absorption monitor (DOAS-OPSIS) was installed in the centre of the city at about a 30 m elevation on the tower of the Brera Arts Academy. This exercise has permitted a comparison of the data recorded with the DOAS system with data provided by other conventional and non-conventional monitors in a heavily-polluted environment.

In the context of a convention between the Commission (DGXI/B/3) and the Ministère de la Région Bruxelloise, an air pollution monitoring campaign was organised in the Brussels area with the aim of:

- assessing the impact of emissions by traffic on urban air quality;
- demonstrating the use of new air-quality monitoring techniques in urban areas;
- sensibilizing the population of air quality problems in large cities.

A first summer campaign took place from June to September 1993, which was followed by a winter campaign from December 1993 to February 1994. The participation of the CLAP involved various aspects:

- The exposure of the population to NO_2 was determined by measuring the distribution of the pollutant over the metropolis. 200 passive samplers were installed in the Brussels area and exposed over successive two-week periods. The NO_2 passive sampler consists of a plastic tube, one end containing a specific absorbent for fixing the pollutant gas. The pollutant is collected by molecular diffusion to the absorbent, where it is retained for subsequent measurement in the laboratory. In the case of NO_2, the gas is collected on stainless-steel mesh discs coated with triethanolamine and is determined spectrophotometrically by a variation of the Griess-Saltzman method. The summer campaign permitted the localisation of critical areas where the population is exposed to the highest risks and where air quality should be monitored with the highest priority. During the winter campaign, the NO_2 survey was extended to include BTX measurements by the diffusive sampling method, with 80 samplers distributed over the metropolis.

- To demonstrate the use of DOAS systems under real field conditions and to estimate the pollution dispersion and possible chemical conversion inside a "canyon" street, two mobile units equipped with point monitors and two DOAS systems were deployed in an area of high traffic and characteristic structure (rue de la Loi); the mobile units were located one in front of the Berlaymont building (Fig. 46) and the other along the street. Monitors for SO_2,

Fig.46. The mobile laboratory in Brussels during the air quality measuring campaign.

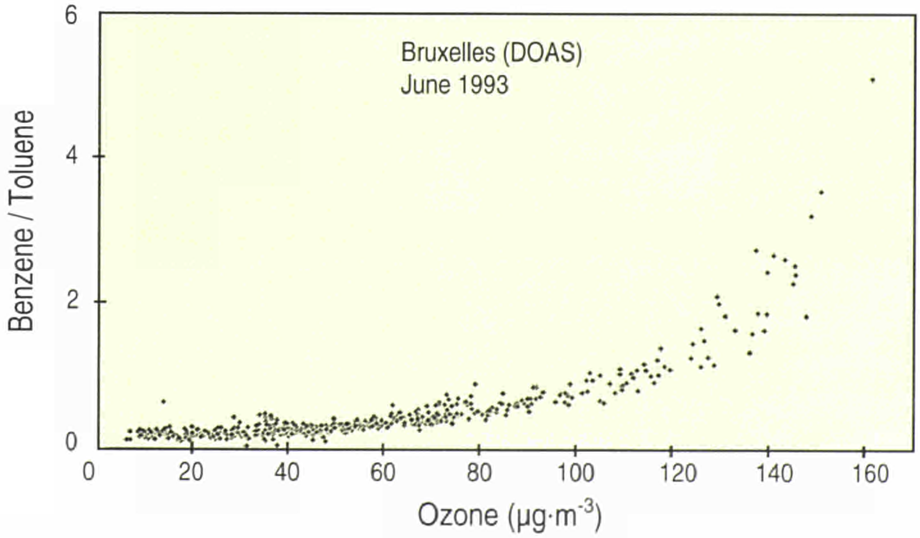


Fig.47. Ambient air concentrations of benzene, toluene and other pollutants were measured during the air quality campaign in Brussels by DOAS systems. The ratio benzene / toluene, measured 30 m above ground, is modified by the local photochemistry. The different rate constants of the reactions of the OH radicals with the two aromatic hydrocarbons is much faster (the reaction with the toluene) is responsible for the modification. The photochemical activity is expressed in the diagram by the O_3 concentration (also measured by the DOAS instrument), which is taken as an approximation of the OH radical concentration.

NO, NO_2, ozone, particulates, CO, benzene, toluene, m-xylene, and samplers for organic acids, were distributed inside the two vans. One DOAS instrument (SANOA, Atmos, France) measured some metres above the street along a pathlength of 300m; the other (OPSIS, Sweden) measured at about 30 m elevation above the ground along a path of 846 m. The DOAS systems measured SO_2, NO_2, ozone, particulates, CH_2O, HONO, NO_3, benzene, toluene and p-xylene. (Fig.47) The campaign will be repeated in the cold season (February 1994).

EMEP Monitoring Programme

EMEP is the co-operative programme for the monitoring and evaluation of the long-range transmission of air pollutants in Europe. Its main objective is to provide Member Countries with information on the depositions, concentrations and fluxes of atmospheric pollutants across national boundaries.

About 100 stations located in 35 European countries participated in the 1993 EMEP activity.

Following article 9 of Council Resolution N. 81/462/EEC and at the request of DG XI, JRC Ispra has been operating an EMEP monitoring station at Ispra since November 1985. The following parameters are measured, here:

- in air: SO_2, NO_2, NO, O_3, CO and PAN, continuously; non-methane hydrocarbons, methane and NH_3, occasionally.;

- in atmospheric particulates: SO_4, NO_3, NH_4^+, Cl, H^+ and TPS on a regular daily basis; heavy metals, in

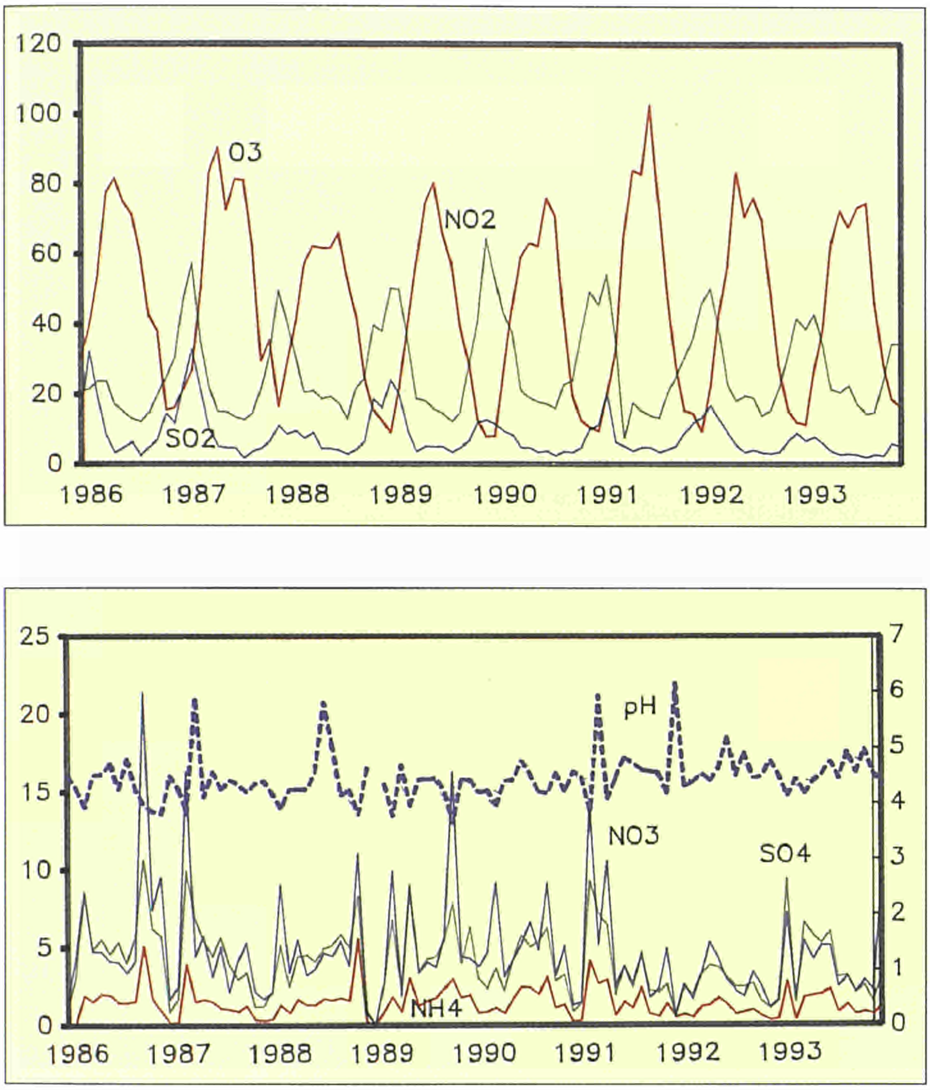


Fig.48. Monthly average concentration of O_3, SO_2, and NO_2 in air ($\mu g\ m^{-3}$) above) and of NH_4^+. NO_3, and SO_4 in rain (mg l^{-1}, below) measured at the EMEP station. The pH values of the rain samples are also shown.

8-day sampling periods;

- in atmospheric precipitations: SO_4^{--}, NO_3, Cl^-, NH_4^+, Na^+, K^+, Ca^{++}, Mg^{++}, pH and electrical conductivity, in one-day sampling periods. Heavy metals in a monthly sampling period.;

- seven meteorological parameters.

Detailed results of all the data collected are reported in annual reports and transmitted monthly to the Norwegian Institute for Air Research (NILU), acting as EMEP Chemical Coordinating Centre, to DG XI and to the Municipality of Varese.

Figure 48 represents the monthly average concentrations measured at this station during the last eight years, of O_3, NO_2, SO_2, in air and of pH, NO_3, SO_4^{--} and NH_4^+ in rain.

Ten selected EMEP monitoring stations (including the JRC) have carried out a study for the determination of HNO_3/NO_3 and NH_3/NH_4^+ in air using the annular denuder technique; this study was based on 20 days of continuous measurements every three months. Using the same analytical method, sporadic measurements of day and night air samplings have been performed.

Starting from 1986, the measurement of some heavy metals in rain has been performed. The median concentrations of these elements, expressed as µg l^{-1} during the period 1986-1992,are reported in Table 7.

The C2-C5 VOC (Volatile Organic Compounds) measurement in air at different EMEP sampling sites located in the Mediterranean Basin was started in May 1993. Up to now, the weekly samples collected at three EMEP stations (Spain, France and Italy) have been analysed. In Table 8, the mean concentration values of the main components measured at the JRC Ispra station between July and December 1994 are reported.

The PAN (Peroxyl Acetyl Nitrate) intercalibration exercise, in which 12 European laboratories were involved, has accomplished its task with the standards distributed in the last intercomparison exercise, launched in July 1993; the final report of the whole activity will be presented by the coordinator (NILU) during the next year. Continuous monitoring of PAN has been performed at the JRC Ispra station since 1992.

In Figure 49, the values for all the measurements performed in 1992

	World rural*	Ispra	Ratio Ispra,world rural
Zn	36	38.72	1.08
Pb	12	14.47	1.21
Cd	0.5	0.29	0.58
Cu	5.4	3.67	0.68
Ni	2.4	2.57	1.07
Co	0.75	0.63	0.84

* Source: Galloway,J.N.and al: Atm. Env., 1982,16,l667

Table 7. Median metal concentration in wet deposition; comparison between Ispra and the world rural.

COMPOUNDS	Mean	Max.	Min.
ethane	6.23	13.09	2.63
ethene	4.45	16.39	0.33
propane	1.81	6.02	0.06
propene	1.35	4.50	0.12
ii-butane	1.01	2.72	0.07
acetylene	3.14	11.30	0.08
n-butane	4.75	25.79	0.66
Sum butenes	4.99	22.53	0.24
cyclopentane	0.12	0.62	0.00
i-pentane	1.04	4.52	0.03
propyne	0.03	0.07	0.00
n-pentane	0.51	2.95	0.00
Sum pentenes	0.97	7.40	0.00
1, 3-butadiene	0.24	2.85	0.00

Table 8. VOC July / December 1993; two samples by week at 14.00 h. (ppbv)

and 1993 are shown and classified by cumulative frequency. The differences between the 1992 and 1993 values are probably due to the various times of measurement and meteorological conditions (solar irradiation, cloudiness, etc.).

Prevention and Reduction of Environmental Pollution from Asbestos

In view of implementation of the Directive EC 87/217, the Institute contributed to the development of an ISO standard involving the use of the fibre count method for the determination of fibres in asbestos plant emissions. Participation in the second fibre counting trial for asbestos and non-asbestos fibres, organised by the Asbestos International Association, has taken place. This method has now been accepted by the Member States.

Water Quality

Within the context of the collaboration with the DG XI, the scientific work has continued in the light of the adoption of the Directive concerning the ecological quality of surface waters.

A report on restoration and management techniques for lakes and reservoirs was completed. It examines the various source categories that describe major stresses on lake water quality relative to human use and ecological integrity, i.e. point sources (industrial, municipal, combined sewer overflow) and diffuse sources (agriculture, urban runoff, construction, land disposal, resource extraction, long range atmospheric transport, natural).

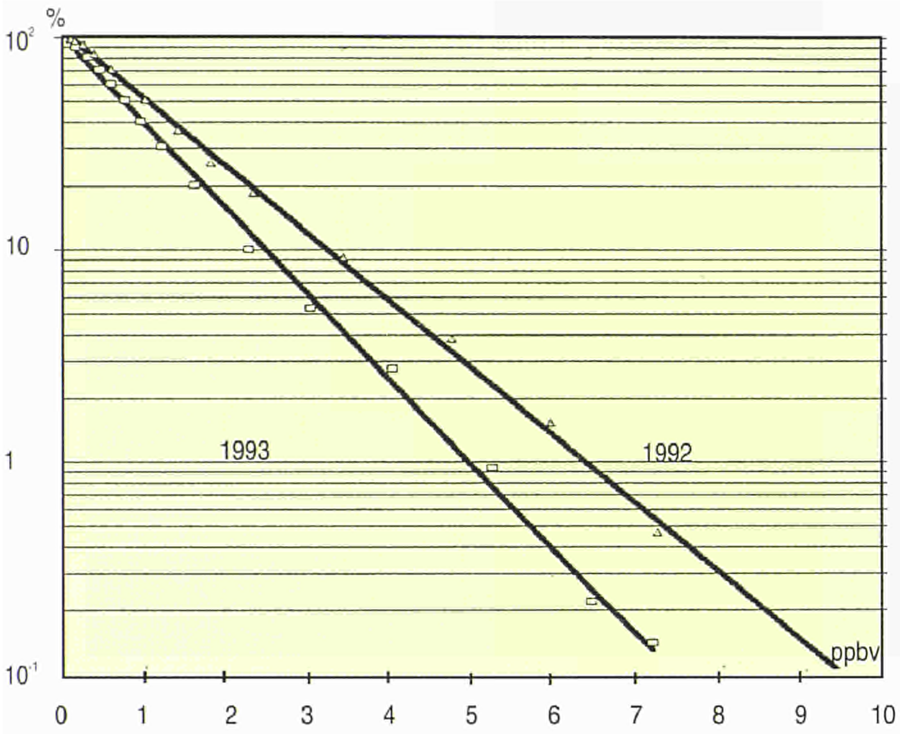


Fig.49. PAN comulated frequency; hourly measurements from May 1992 to September 1993 at JRC Ispra.

The study gives an overview of common lake and reservoir problems in EUMember States.

Six types of lake or reservoir problems are frequently encountered namely:
- nuisance algae;
- excessive shallowness;
- excessive rooted plants (weeds or macrophyted) and their attached algal mats;
- drinking water taste, odor, colour, and organics;
- poor fishing;
- acidic conditions.

For each of these major problem areas, several in-lake and management techniques have been found to be effective, long-lasting, and generally without significant negative impact when used properly.

Best management practices to control four primary interactive processes, i.e. erosion control, runoff control, nutrient control, and pesticides or toxic control, were discussed. Their effectiveness, capital costs, longevity, credibility and adaptability in a variety of geographic areas and situations have been reported.

Once problem identification has occurred, a management choice can be made among a variety of physical, chemical and biological control techniques. Particular care must be taken, however, in considering potentially deleterious side-effects associated with these management methods. A natural ecosystem is made up of innumerable, complex interactions (biotic and abiotic) that are incompletely understood. Alteration of a system to control an undesirable characteristic can produce unwanted responses in other features. Management objectives should include the maintenance of a relatively natural ecosystem with ecologic diversity (as opposed to a community swimming pool), while upgrading usability.

A possible classification of in-lake rehabilitation and management tehniques was summarized.

Qualitative evaluations of the procedures with regard to short- and long-term effectiveness, costs and potential negative impact, were also considered.

Some recent case-studies in the Member States and in countries outside the EU were used to illustrate the control of nuisance algae and phosphorus release from sediments (eutrophic waterbodies) and to mitigate acidic conditions.

Finally, the study reported some general guidelines for lake/reservoir management, organized according to a two-fold scheme, i.e. a) the lake hydrology and morphology, and b) the possible environmental effects that can be associated with the different water uses (Tables 9 and 10). It is interesting to notice that some water uses which need restrictive quality standards (e.g. drinking water and bathing) are compatible with several restoration techniques. Other uses as faunistic and floristic are incompatible with almost all internal measures for nutrient control.

The work on the impact of trace compounds and elements (Directive 76/464/EEC) has continued.

During the reference period the non-point sources and discharges of selenium and the nitrogen species, ammonia, nitrite and cyanide, have been studied along with the

uses	BIO	SED-TR	SED-S	SED-DR	CIR	HY-AE	ILC	CPN	HY-W	BO$_2$	DIL	WASH
Area												
< 10 ha	O	O	O	O	O	O	O	O	O	O	O	O
10 ÷100 ha	-	O	O	O	O	O	O	O	O	O	-	O
100 ÷ 3000ha	x	O	-	-	-	-	-	-	-	x	-	?
>3000 ha	x	-	x	x	x	x	x	x	x	x	x	?
Depth/Maximum Stratification												
> 3 m/Not stratified	O	O	x	x	O	x	x	x	O	O	x	O
3 ÷ 6 m/polymittic	O	O	-	x	O	x	x	O	O	O	x	O
6 ÷10 m / $V < 0.5\ V_E$	O	O	O	-	O	-	-	O	O	-	-	O
10 ÷ 40m / $0.5V_E < V_I < V_E$	O	O	-	O	O	O	O	-	-	-	O	O
> 40 m / $V_I > V_E$	O	-	x	O	O	O	O	x	x	x	-	O
Renewal Time												
< 4 months	O	O	O	-	O	O	O	O	O	O	O	O
4 months-3 years	x	O	-	O	O	O	O	O	O	O	O	O
> 3 years	x	-	x	-	O	O	O	O	-	O	O	O

NOTES

WAS = Washout
DIL = Dilution
B-02 = Bottom oxygenation
CPN = Chemical precipitation of nutrients in the water column
ILC = Internal loading control by chemical precipitation
HY-AE = Hypolimnetic aeration
CIR = Aeration by artificial circulation in the water column
SED-DR = Dredging of the upper layers of the sediments
HY-W = Hypolimnetic withdrawal
SED-S = Sediment sealing
SED-TR = Sediment treatment
BIO = Bio manipulation

Indication of applicability

x = Prohibitive
- = Limitations
O = Suitable
? = There are not well-documented experiences to confirm its effectiveness, difficult to evaluate
= = Heavy limitations

Table 9. Relationship between the main hydromorphometric characteristics and the suitability of some in-lake restoration techniques.

discharge of mercury, beryllium and thallium due to point sources.

In general, very little information appeared to be available on these non-point sources in the Member States, so no country-by-country evaluation was possible.
Figures for the total emission of selenium from all sources in Europe totalled 188.4·103 kg y^{-1} (Table 11), a break-up among non-point sources (Table 12), however, offers an incomplete picture. The major non-point source seems to be dry and wet atmospheric deposition, but data from only five Member Countries are available, the UK being at the top with 91 t y^{-1} (onto agricultural land only).

Data concerning the non-point sources of the toxicologically more important nitrogen species, ammonium, nitrite and cyanide, in the aquatic environment are surprisingly scarce when considering the general

uses	BIO	SED-TR	SED-S	SED-DR	CIR	HY-AE	ILC	CPN	HY-W	BO_2	DIL	WASH
Drinking water	–		–					–				
Industry			–					–				
Irrigation									–			
Bathing					–	?			–			n.c.
Sport fishing	–											
Navigation												
Aquatic sports												
Aesthetical									=			n.c.
Commercial fishing					–	–			=			
Cultural (*)					=				=	–	=	
Weighboushood from urban zones			–	–					=			
Faunistic and floristic conservation	=	–	x	–	x	x	–	=	x	x	x	x

(*) It is intended the hystorical-cultural perception that public has of the lake value.

Table 10. Environmental impact of some in-lake restoration techniques with regard to the water uses.

COUNTRY	EMISSIONS
B	11.4
Dk	3.8
F	18.0
D	46.6
former DDR	24.1
Gr	3.1
Ir	1.0
I	24
L	0.2
Nl	7.9
P	1.4
E	10.9
UK	36.0
Total	**188.4**

Table 11. Emission of selenium for all sources in Europe in 1979 (in tonnes y^{-1}*)*

SOURCE	SELENIUM	CYANIDE
Domestic sewage	1.4	
Sewage sludge (dumping into the sea)		
Agriculture		
- Pesticides		0.3 - 0.4*
- Fertilizer and manure		
Mining deposits,landfill and dumps		
Deposition to the aquatic environment		
Surface run-off due to deposition	8 - 10	
Surface run-off due to sewage		26 - 31
Sludge on agricultural land		
Surface run-off due to the use of P-fertilizer	0.3	
Surface run-off from landfill	3.9	
Release from sediments	0.4	

* Only the Netherlands

Table 12. Discharges of selenium and cyanide into the aquatic environment in the EU due to non-point sources. (in tonnes y^{-1}*)*

importance of the nitrogen cycle in the environment.

Most information refers to the surface-runoff of ammonia and 605651 t N-NH_3 are transported annually to surface waters in the EU (Table 13), and the total non-point discharges are estimated to be 1,261,000 t y^{-1}, domestic sewage, atmospheric deposition and inorganic fertilizer spread being the most important single sources (Table 14).

Few non-point sources for nitrite can be evaluated, due to the general lack of analytical data in the literature.

Country	Surface run-off of ammonia Sewage sludge	Atmospheric deposition	Animal manure fertilizer	Inorganic	Total
B	7	2726	1347	9000	13080
Dk	39	2655	1331	18850	22875
F	130	20764	9022	130200	160116
D	573	7118	9406	77000	94097
Gr	n.d.	2340	1985	20200	24525
Ir	3	2993	2621	17450	23067
I	n.d.	10633	5055	49350	65038
L	7	149	78	850	1084
Nl	54	4683	2440	21800	28977
P	n.d.	1543	998	7850	10391
E	4	8509	5243	56050	69806
UK	27	11541	7927	73100	92595
Total	**844**	**75654**	**47453**	**481700**	**605651**

Table 13. Surface runoff of ammonia from various sources to surface waters in EU Member States. (ton N - NH3)

SOURCE	AMMONIA
Domestic sewage	
direct	205
indirect	164
Sewage sludge	
disposal at sea*	5
Atmospheric deposition	
direct, inland waters	48
direct, continental waters	233
Surface run-off	
sewage sludge	1
indirect atmospheric deposition	76
animal manure	47
inorganic fertilizers	482
Leaching	n.d.
Total	1261

* B, Ir, Nl and the UK only

n.d. = data not available

Table 14. Discharge of ammonia and ammonium in the aquatic environments of the EU (N ,kton y^{-1})

Country	Direct discharge Ammonia + Ammonium	Nitrite
B	13332	909
Dk	178	12
F	52515	3222
D	11854	727
Gr	17489	1073
Ir	5101	313
I	44773	2747
L	132	8
Nl	2316	142
P	17814	1093
E	39308	2412
UK	17816	1093
EC	**204798**	**13751**

Table 15. Direct annual discharge of ammonia and ammonium from domestic waste water into surface water of the EU-Member States. (ton y^{-1})

Country	Direct discharge Ammonia + Ammonium	Nitrite
B	1776	101
Dk	3898	221
F	22835	1293
D	42822	2425
Gr	780	44
Ir	683	135
I	26957	1526
L	259	15
Nl	10692	605
P	884	50
E	14564	825
UK	37543	2126
EC	**163693**	**9366**

Table 16. Annual discharge into surface waters of ammonia and ammonium and of nitrite from sewage plants treating domestic wastes, per EU Member States. (ton y^{-1})

Branch of industry	B	Dk	F	D	Gr	Ir	I	L	Nl	P	E	UK	EC
Mineral oil refining		2	12	12			6		3	1	3	10	49
Gen. elec.power	2	?	?	?	?	?	?	?	1	?	?	10	13
Man. of metals	4			100					36			16	156
Non-ferrous metal ind.									4				4
Man.ind.chem.	21	2							25				48
excl.fert/chlor-alk.													
and tit.dioxide.ind.				430					71			918	1419
Man. of paint													
(tit.dioxide.ind.)			1	70					21		1	230	323
Fertilizer ind.	12-108		38-340				31-278		339			3	423-1068
Chlor-alkali ind.	94		45	90					46	322		2679	3276
Pharmaceutical ind.		1											1
Soap ind.	1												1
Other chem.products								2					2
Elect.-tech.ind .	?	?	?	?	?	?	?	?	5	?	?	?	5
Shipbuilding	2												2
Food and drink ind.	3												3
Slaught/prep. meat	1	6	25	13		3	11		7	1	10	15	92
Grain milling	1	1	4	2			4		1	1	3	3	20
Sugar man./ref.	?	?	?	?	?	?	?	?	1	?	?	?	1
Distilleries												28	28
Textile ind.	12	1											13
Man. of paper				30									30
Cleaning/disinfection	2	?	?	?	?	?	?	?	14	?	?	?	16

Table 17. Total discharge of mercury into the aquatic environment in the EU Member States (kg y^{-1}) (rounded).

Major sources seem to be discharge from domestic waste water and sewage plant effluents (Tables 15 and 16).

Analytical data on cyanide are still scarce, so few non-point sources could be quantified. (Table 12)

The discharges of mercury, thallium and beryllium to the aquatic environment due to point sources, showed that insufficient data are available for emission coefficients to be developed.

The total discharges of mercury in the EU are estimated to be 5,925-6,570 kg y^{-1} (Table 17), the most important single sources being fertilizer industry and chlor-alkali production plants.

Studies on the discharges of undesired substances into the aquatic environment, which covered the point sources of the 14 most important metals and some nitrogen species, will be completed in 1994, applying a reduction model which is currently being developed.

Chemical Waste

Information of the European Waste Catalogue (EWC)

The work programme for DG XI, as described in the Annual Report for 1992, was accomplished to a large extent. The programme structures and algorithms of the local system (MS-DOS, PC) and the central system (UNIX, work station) have been set up and tested. National waste catalogues (B, D, DK, F, I, NL, UK,

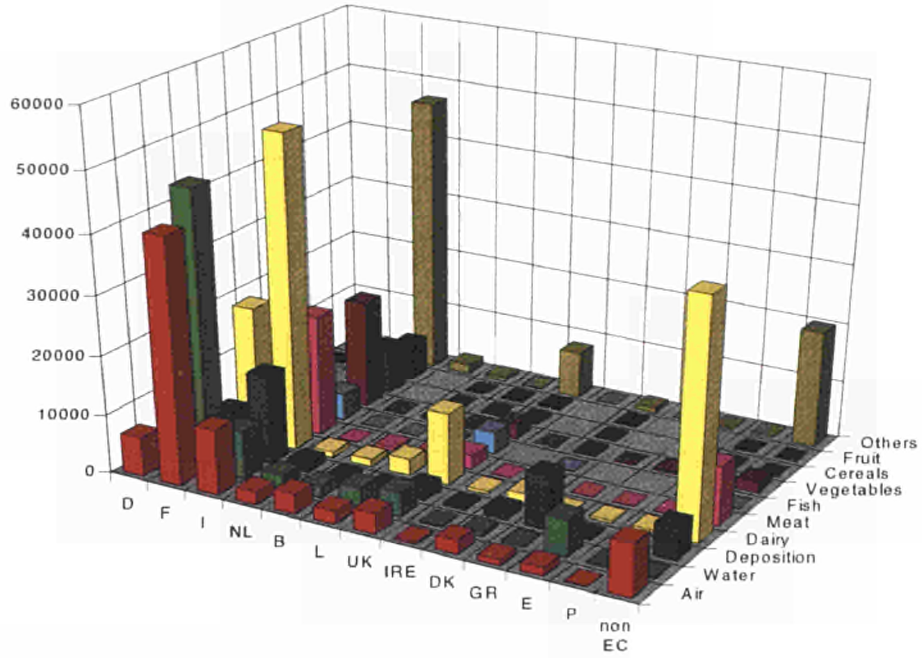


Fig 50. Overview of the REM data bank contents.

CH), and international catalogues and lists (OECD, NACE, Basel Convention), have already been loaded into the systems. Two preliminary versions of the European waste catalogue, elaborated by a group of independent experts (D, I), have also been introduced.

The official version of the European Waste Catalogue (EWC) accepted by the "steering committee" during the session held in October 1993 will be published in the Official Journal of the European Communities. The official translations into the nine languages of the Community will be ready at the beginning of 1994. Then the official version of the EWC will be introduced into the two informatic systems.

During the work of the Committee it became evident that it has not been possible, within the time limits fixed by Directive 91/689/EEC, to define hazardous wastes in terms of an inclusive binding list, as required by Article 1 of the Directive. Therefore, the date for drawing up a Community list of hazardous waste has been postponed (see Proposal 93/C 271/06). For this reason, up to now, it has not been possible to introduce the hazard attribution of the wastes into the informatic systems.

Radioactive Environmental Monitoring (REM)

REM data bank

The Radioactivity Environmental Monitoring (REM) data bank was set-up by the JRC-Ispra in 1988, to bring together and store in a harmonised way environmental radioactivity data produced in the aftermath of the Chernobyl accident. In this way, the data bank has two main objectives:

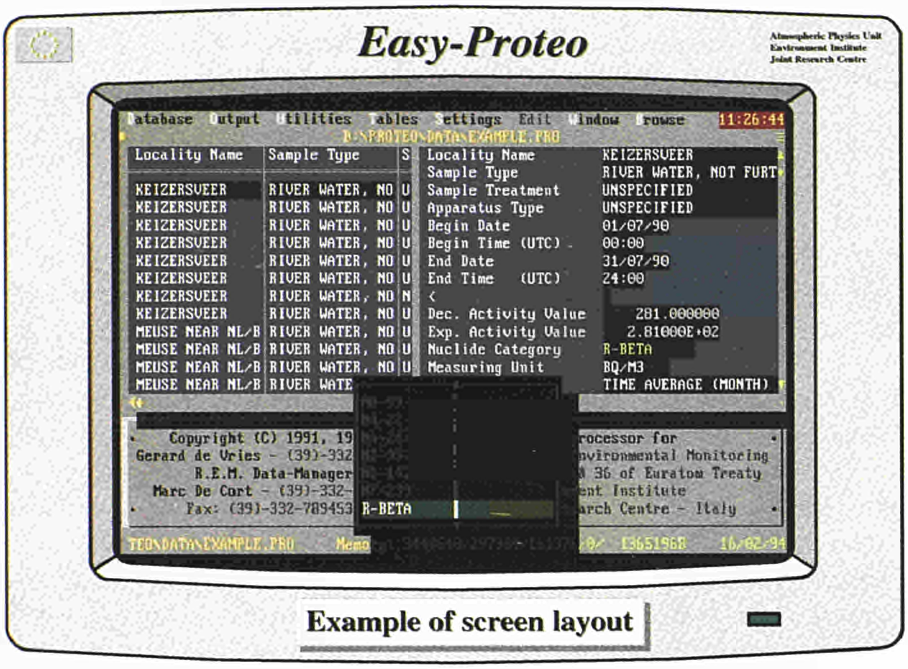
- to keep a historical record of the Chernobyl accident, for further scientific study;
- to store the radioactivity monitoring data of the EU Member States in view of preparation of the Monitoring Report.

By means of this report, the Member States will be informed of the radioactivity levels in the environment of the European Union, as stated in art. 35 - 36 of the Euratom Treaty.

The information held by the bank covers radioactivity measurements from the 12 EU Member States, as well as from other European countries for both environmental samples and foodstuffs from 1984 onwards. Best represented are air, deposition, water, milk, meat and vegetables (Fig. 50). The current total number of data records stored in REM is over 500,000.

Up to now, most of the data are sent to the JRC in the form of reports. After being digitised by means of data input processing tools, such as Proteo or EasyProteo (see below), the data are exported into the standard REM data exchange format (card image format) and up-loaded in the REM data bank.

Data in the bank are available to external users via network connections to REM (X.25, internet or modem). Whilst querying the bank, the user can off-load the selected dataset on his PC. Later on, having closed the connection to REM, he can continue using the data with the



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                         D:\PROTEO\DATA\EXAMPLE.PRO
 Locality Name  Sample Type     S  Locality Name          KEIZERSVEER
                                   Sample Type            RIVER WATER, NOT FURT
 KEIZERSVEER    RIVER WATER, NO U  Sample Treatment       UNSPECIFIED
 KEIZERSVEER    RIVER WATER, NO U  Apparatus Type         UNSPECIFIED
 KEIZERSVEER    RIVER WATER, NO U  Begin Date             01/07/90
 KEIZERSVEER    RIVER WATER, NO U  Begin Time (UTC)       00:00
 KEIZERSVEER    RIVER WATER, NO U  End Date               31/07/90
 KEIZERSVEER    RIVER WATER, NO U  End Time   (UTC)       24:00
 KEIZERSVEER    RIVER WATER, NO N  <
 KEIZERSVEER    RIVER WATER, NO U  Dec. Activity Value       281.000000
 MEUSE NEAR NL/B RIVER WATER, NO U Exp. Activity Value      2.81000E+02
 MEUSE NEAR NL/B RIVER WATER, NO U Nuclide Category       R-BETA
 MEUSE NEAR NL/B RIVER WATER, NO U Measuring Unit         BQ/M3
 MEUSE NEAR NL/B RIVER WATE                               TIME AVERAGE (MONTH)

     Copyright (C) 1991, 19                  rocessor for
 Gerard de Vries - (39)-332                  nvironmental Monitoring
         R.E.M. Data-Manager                 36 of Euratom Treaty
   Marc De Cort - (39)-332-                  ent Institute
       Fax: (39)-332-789453 R-BETA           arch Centre - Italy
 TEO\DATA\EXAMPLE.PRO    Memo                /0/  13651968    16/02/94
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Fig 51. *Example of screen layout of the data input processor EasyProteo*

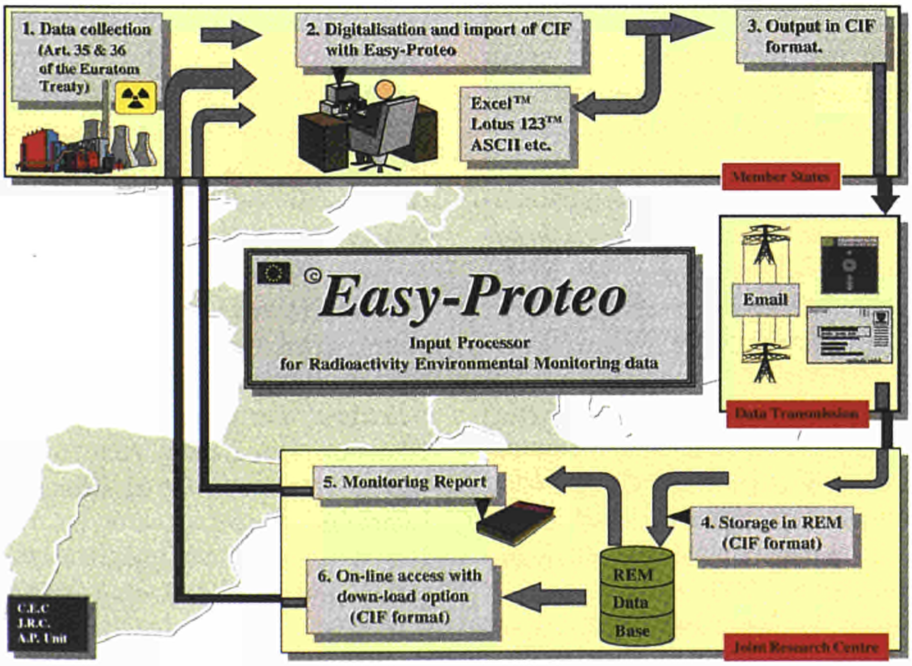


Fig 52. *Schematic overview of the data flow of environmental radioactivity measurements between the EU Member States and the CEC*

REMGRAF package (1991) or with EasyProteo.

At present, two versions of the data bank exist on the UNIX server URANO: a backup version running under ADABAS 5/NATURAL 2 and, in accordance with the general CEC strategy, a version under Oracle/SQL. The ADABAS version will cease to exist when all the application software is rewritten for Oracle, has is foreseen for 1994.

Over the year 1993, further conversion from the ADABAS to the Oracle data base was performed: completion of the data loading routine, the data management program (REMUTIL) and the data query program for external users (REMNEW).

At the beginning of 1993, the input of 1987 - 1990 monitoring data was completed and data checking was continued for the rest of the year. The input of 1991 monitoring data was started.

Due to the necessity of digitising and checking the monitoring data, an important delay in data management and monitoring report preparation was experienced.

To have an input processor better adapted for digitising monitoring data, the development of EasyProteo was started in December 1991. The data producer has a number of facilities that not only speed up data input (e.g. data block and data base copy commands), but prevent the inserting of typing errors (by means of using selection tables) and perform a first data check at the level of input (Fig. 51).

Beside the possibility of exporting the

data into the REM data exchange format, EasyProteo also permits the exporting of the digitised data into different commercial formats (e.g. Excel, Lotus123, ASCII,...). In this way Member States can also benefit from their digitising efforts (Fig. 52).
The software development and debugging were continued during the past year and are now at the final stage.
A large number of improvements were added (e.g. dialog boxes with context-sensitive help, moving of data blocks between data bases, merging of data bases, import of REM card image format, table printing). A completely new and improved user manual was written.

Atmospheric Models for pollution episodes

The activity carried out was aimed at assessing the concentration fields derived from emission episodes over a wide range of distances and conditions. To do this, long-range distance and mesoscale dispersion models, together with mesoscale flow models, were developed.

In the category of the long-range distance dispersion, the software procedure for concentration data assimilation was improved by the use of multiple level trajectories. Furthermore, support was given to the Swiss Meteorological Service, which uses Ispra model LORAN in the ETEX experiment. In LORAN, a new real-time procedure aimed at matching the model results with observations was developed and tested using the Chernobyl data-sets.

For the mesoscale, a new lagrangian skewed quasi homogeneous dispersion model for use in pollution episodes over complex terrain, was developed and compared with observations. For the same range of distances, development and application of flow models continued to simulate the formation of sea breezes and valley breezes in complex terrains. A non-hydrostatic version of the model TVM was started, which is capable of enlarging the field of applicability of such models.

Harmonisation of radioactive monitoring techniques

The proposals made by the Institute with respect to harmonising the measurements and reporting of environmental radioactivity in the EU Member States resulted in the creation of two working groups:

- the first working group deals with data transfer between the Member States and the CEC and with the establishment of a dense monitoring network;
- the second working group is dealing with the establishment of a sparse network of sensitive monitoring stations and with the organisation of intercomparison exercises for measuring techniques of environmental radioactivity.

The intercomparison exercises are performed in collaboration with the International Reference Centre of the World Health Organisation (WHO) at Le Vesinet (F).

The second intercomparison exercise, executed in 1992, concerned the determination of ^{40}K, ^{134}Cs and ^{137}Cs in milk samples. The results of the 16 participating EU laboratories were analysed in 1993. All measurements, except one, were within 15%.

In November 1993, the third exercise, on the measurement of natural uranium, ^{226}Ra and an artificial radionuclide in mineral water, was started.

CEC - CIS collaboration programme

In the framework of the 'Joint Study Project 1' (JSP1), as a part of the development program CHECIR, DG XII/F/6, the JRC-Ispra is participating in the setting-up of a communication system for the exchange of Chernobyl contamination measurements with the Studie Centrum voor Kernenergie (SCK, Mol, Belgium) and the Kurchatov Institute of Atomic Energy (KIAE, Moscow, Russia). KIAE is the co-ordinating institute for the Chernobyl measurements stored in the data banks of several Russian institutes. During the year 1993, a number of tests for the exchange of large amounts of data by means of e-mail, X.25 and on diskette, were performed between the JRC and KIAE. In December, a data base server was installed at KIAE, permitting on-line query by internet connection.

In the same collaboration programme, the JRC - Ispra is the CEC co-ordinator for Joint Study Project 6: "Compilation of a European Atlas of Radioactive Contamination and External Exposure resulting from the Chernobyl Accident". The scope of the project is to integrate, as much as possible, data related to the Chernobyl accident from former Soviet Union into a common information system.
The data will be entered into a geographical information system (GIS), in order to facilitate the production of maps and to make the data available on a common informatics platform for further

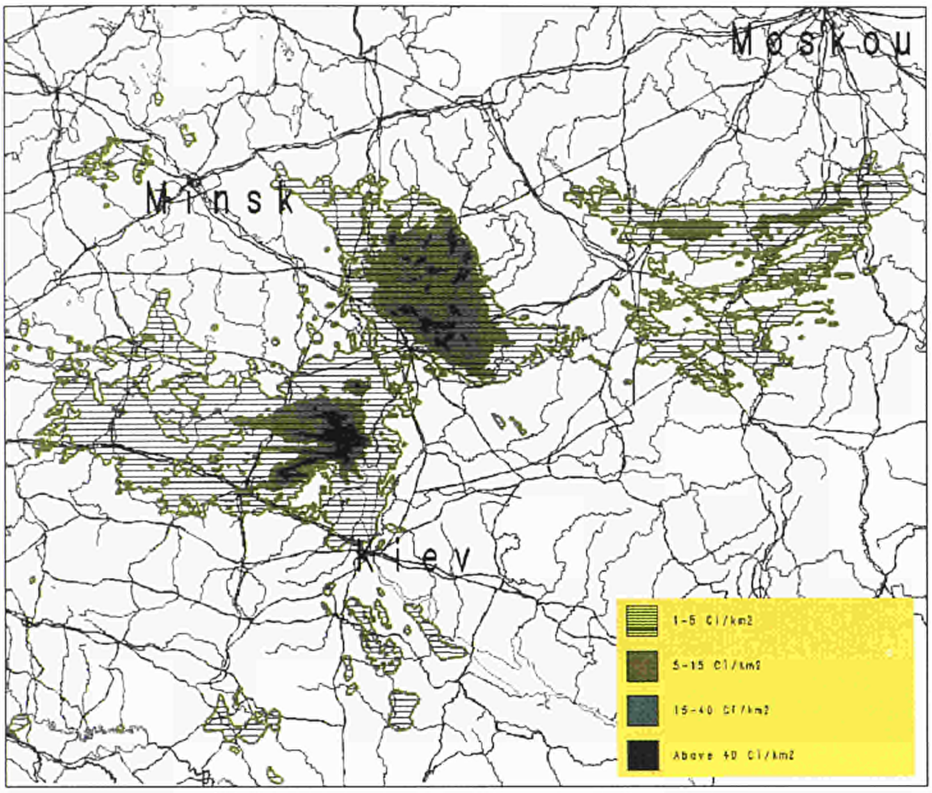


Fig 53. Digitized map of Cs^{137} contamination in Russia, Ukraine and Belarus (original map: The International Chernobyl Project, IAEA)

scientific study.
Although, in the first stage, priority is given to caesium deposition measurements, all secondary information relevant to the accident (e.g. population density, land cover, agriculture roads, rivers, landmarks, ...) is planned to go eventually into the GIS. Although only started in November 1993, the digitalisation of existing deposition maps of the Chernobyl area was started in order to gain practical experience (Fig. 53).

The GIS (ARC/INFO) is to be installed on an IBM Risc 6000 model 580 (20 Gb) at the beginning of 1994.

ECURIE

After the nuclear accident at the Chernobyl nuclear plant, a system for meeting the requirements for early warning and exchange of information was set up by the International Atomic Energy Agency (under the Early Notification Convention - 27 October 1986 - and the Early Assistance Convention - 26 February 1987).
A similar system was established by the CEC (following the Council decision of 14 December 1987, and resulted in the European Community Urgent Radiological Information Exchange (ECURIE) system, developed in close collaboration with the EU Member States.

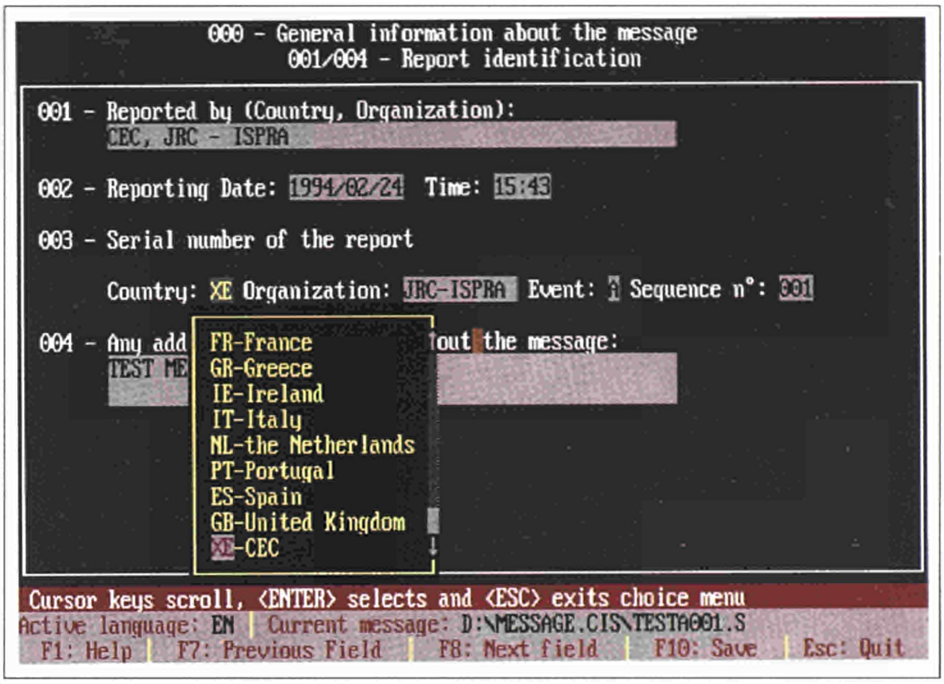
The ECURIE system consists of a telex communication network between the CEC and the Member State contact points for the transmission of radiological emergency messages. Since Member States belonging both to the IAEA and the EU have to comply with similar obligations, it was decided that the IAEA and the CEC should cooperate as closely as possible. This resulted in an identical code - the Convention Information Structure (C.I.Structure) - into which messages containing radiological information are encoded and sent. The data are transmitted between the CEC and its Member States in encoded form, to ensure a maximum reduction of transmission and translation problems.

In 1991, work on the Coding Decoding Software was started with the aim of providing Member States with software, in order to reduce to the maximum extent the introduction of errors. Therefore, the software was designed and developed to be as user-friendly as possible, making use of selection tables for input where possible and data checking at input level.

In 1993, the Coding-Decoding Software (CDS) was developed together with the IAEA (decoding part) and by the JRC-Ispra (encoding part) (Fig. 54).

The CDS was further improved and tested for the interface to automatically mail by telex (Telexbox3). Together with the IAEA, the software and the user manual was revised. This resulted in release 3.4.1 (30 September 1993), with worldwide availablility.

With the aim of further integrating the decoding and encoding parts, translation into the different official EU languages and the incorporation of multi-message-management, preparation of a new version of CDS has started.



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000 - General information about the message
001/004 - Report identification

001 - Reported by (Country, Organization):
      CEC, JRC - ISPRA

002 - Reporting Date: 1994/02/24  Time: 15:43

003 - Serial number of the report

      Country: XE Organization: JRC-ISPRA  Event: A Sequence n°: 001

004 - Any add                    out the message:
      TEST ME

Cursor keys scroll, <ENTER> selects and <ESC> exits choice menu
Active language: EN | Current message: D:\MESSAGE.CIS\TESTA001.S
```

Fig 54. Example of screen layout of the Coding-Decoding Software (CDS)

In order to remain operational, different levels of exercises between the CEC and the Member State contact points have been performed over the past year, to test various aspects of the emergency system:

- level 1 exercise: testing of communication, once every 3 months
- level 2 exercise: testing of communication and contact of radiological duty officer, once every 3 months
- level 3 exercise: simulation of a nuclear accident with exchange of radiological measurements between the contact points, once a year.

ETEX tracer experiment

The preparation of the experiment is proceeding without major difficulties, although a variety of practical problems had to be solved almost daily. Two dry-runs were carried out in April and December 1993. Both of them have indicated no major faults in communication. The results of the various modelling teams show greater differences than expected. The decision to postpone the date of the experiment to the fall of 1994 has been taken to allow for a more relaxed preparation and tuning of all the components of the project.
Moreover, the delay has enriched the experiment by adding auxiliary measurements which were not envisaged initially, such as airborne sampling and direct airborne measurements.
At present:

- the samplers for the central European countries (assembled by the Seibersdorf laboratory) have already been shipped to the contact points in the respective countries. A training session on their use will be made in Budapest during next March.
- the samplers for Germany (modified TECORA samplers) have been assembled, and they are in the final testing stage. They will be transferred to the contact point during March 1994.
- the samplers for the other destinations (new JRC design) are at the final assembly stage and they will be available for shipping at the end of March 1994.
- the sampling columns are being prepared. Several problems have been encountered in their manufacture and clean-up. The procedure is now routine, and the preparation of the 10,000 columns required should be completed on schedule without major problems.
- the choice of the release site is under way. Missions to the candidate sites will be made in February 1994. Three types of balloons will be launched by Swiss, French and Danish teams to follow the trajectory of the cloud in the short, medium and long range.
- the new release equipment (two units capable of releasing 10 g s^{-1} of PFC each) will be available at the end of March 1994.
- new equipment for PFC analysis has been acquired and will be installed in February 1994. The designed performance of the analytical laboratory (with two sets of equipment running) is 800 analyses/day.

The European Centre for the Validation of Alternative Methods (ECVAM)

As was mentioned in the preceeding Annual Report, ECVAM was set up with the following duties:

- to coordinate the validation of alternative test methods at the Community level;
- to act as a focal point for the exchange of information on the development of alternative test methods;

- to set up, maintain and manage a data base on alternative procedures;
- to promote dialogue among legislators, industries, biomedical scientists, consumer organisations and animal welfare groups, with a view to the development, validation and international recognition of alternative test methods.

In view of the above, ECVAM was located at Ispra, in order:

- to use the technical infrastructure of the JRC;
- to benefit from the multidisciplinary scientific support of the JRC;
- to help expand the JRC's role in pre-normative research.

Current Validation Studies

In 1993, ECVAM entered its fully operative stage and was involved in seven pre-validation/validation studies , namely:

- An EU/UK international validation study on alternatives to the Draize eye irritancy test, which involves nine tests, 60 test materials, and 37 laboratories in nine countries (7 in the EU, the USA and Japan). The primary aim of this study is to find non-animal methods or batteries of methods for identifying chemicals likely to cause severe irritation in the eye. In addition, it is hoped that progress will be made toward finding alternative methods for predicting lesser degrees of irritancy, at least for certain types of chemicals.

- An EU international study on the inhibition of gap junction intercellular communication as a means of identifying tumour promoters. It is now widely accepted that carcinogenesis is a multi-stage process, involving initiation, promotion and progression before tumour formation. Each of these stages is likely to be affected by genetic, life-style and environmental factors. One theory of tumour promotion is that certain chemicals interfere with intercellular communication, thus facilitating the progression from transofrmation to tumour development. This study involves a method for identifying tumour promoters, based on their ability to inhibit the transfer of a dye injected into one cell into neighbouring cells via channels involved in intercellular communitcation. Five laboratories, in France, Italy and Sweden, are testing 16 coded chemicals. (see Figg. 55 and 56)

- Phase I of a COLIPA/EU international study on *in vitro* tests for photoirritancy, which involves two main tests (a blood cell photohaemolysis method and a fibroblast-like cell neutral red uptake method), plus a number of subsidiary methods (e.g. complement activation, histidine photooxidation), six or seven laboratories, and 20 test materials. This pre-validation study was successful in that the 12 positive chemicals and the 8 negative chemicals were correctly identified. As a result, a formal validation study with 30 test materials is to be conducted in 1994.

- A Europe/USA international pre-validation study on in vitro tests for skin corrosivity, which involved three tests (the skin resistance method, Skin^2 and CORROSITEX™), seven laboratories in the UK, France, Germany and the USA, and 50 test materials. The results were sufficiently encouraging for a formal validation study to be planned for 1994-95.

- An EU/FRAME international study on the use of a battery of *in vitro* tests for predicting acute lethal potency and for use in the classifying and labelling of chemicals, which principally involves the University of Kiel, Germany, and the University of Nottingham, UK. More than 100 basal cytotoxicity tests have been developed, for most of which no specific purpose has been defined. The aim of this study is to see whether a carefully-selected small battery of such tests could be used to classify and label chemicals and as a prelude to more-sophisticated target organ toxicity studies.

- An EU/FRAME international pre-validation study on *in vitro* tests for neurotoxicity, which involves cell and organotypic culture methods, laboratories in the UK and Sweden, and 40 test materials. A tier-testing strategy has been developed at the University of Hertfordshire, UK, which involves a step-wise progression from more-simple to more-complex (and therefore more-expensive) testing methods. This study will assist with the future planning of similar studies on other types of toxicity.

- A pre-validation study on the ECITTS approach to biokinetics and neurotoxicity testing. ECITTS is the ERGATT/CFN Integrated Toxicity Testing Scheme. One of the problems is using *in vitro* toxicity tests is that they lack the organ/system features which affect the uptake, distribution, metabolism and ex of chemicals *in vivo*. This study involves a combination of computer and *in vitro* systems and collaboration with RITOX, Utrecht, The Netherlands, and the University of Stockholm, Sweden.

In addition, the organisation of a series of ECVAM Workshops has been launched. The aim of these workshops is to invite such groups of

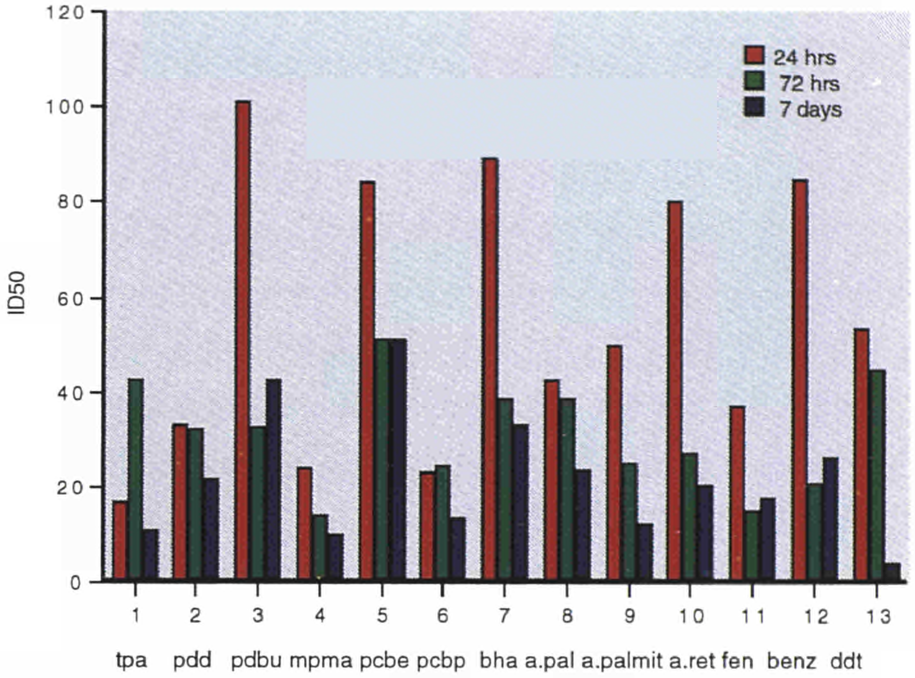


Fig 55. Comparison among times of exposure -3T3-L1

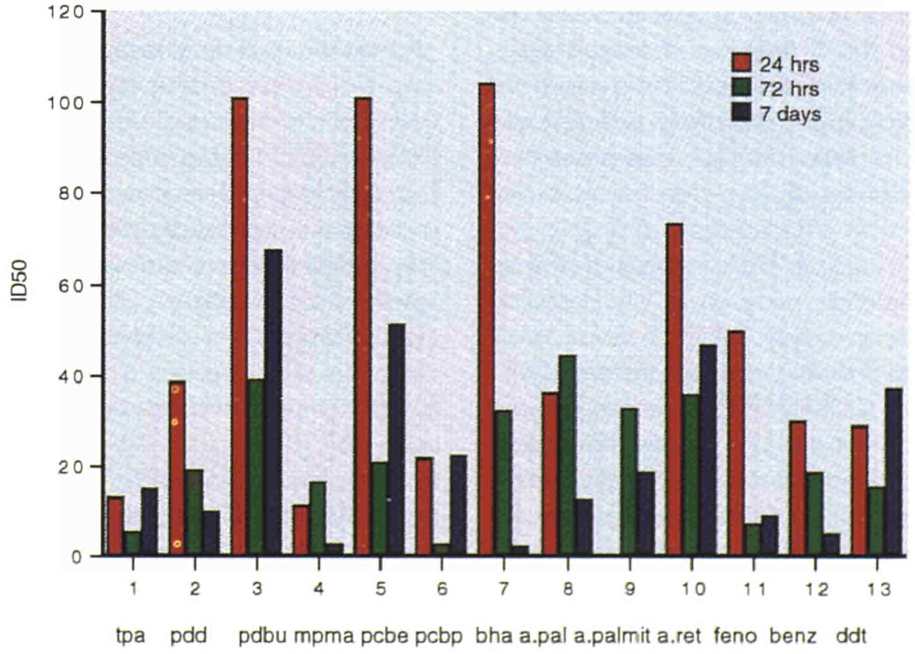


Fig 56. Comparison among times of exposure - A31-1-1

experts to provide state-of-the-art reviews on selected areas of practical *in vitro* toxicology, pharmacology and biologicals and biomaterials testing, with particular emphasis on what further steps should be taken, in order to facilitate the emergence of relevant and reliable non-animal procedures for introduction into regulatory testing. A report on each workshop will be published in *ATLA* (*Alternatives to Laboratory Animals*).

The first two workshops were held at Ispra and dealt with the use of cultured hepatocytes (liver parenchymal cells) and the use of *in vitro* methods in phototoxicity testing.

Also worth mentioning is the technical support provided within the framework of Directive 86/609 EEC on the approximation of laws, regulations and administrative provisions of the Member States regarding the protection of animals used for experimental and other scientific purposes. This support has concerned a number of issues confronting DGXI and the Competent
Authorities in the Member States, including the humane killing of animals, the use of non-human primates as laboratory animals, and ways in which statistics of animal use in the Member States shoud be collected, analysed and published.

The European Chemicals Bureau (ECB)

Following a Commission Communication to the Council and the European Parliament, the European Chemicals Bureau (ECB) was established within the Environment Institute with effect from 1 January 1993.

The principal task of the Bureau is to carry out and co-ordinate the scientific/technical work which is needed for the implementation of EC legislation (directives, regulations) in the area of chemicals control.

Thus, the Bureau will assume an increasingly important role in the assessment, management and control of risks which may be posed by new and existing chemical substances which circulate in the EU.

This work signifies a substantial extension of previous scientific support activities for DG XI, which has, among other tasks, responsibility for EU legislation on chemical substances.

The main tasks of the Bureau include the following five major work areas:

- Classification and labelling of dangerous substances (Directive 67/548/EEC and subsequent amendments/modifications).
- Notification of new substances (6th and 7th Amendments of the Directive)
- Testing methods (Annex V of the Directive)
- Existing Chemicals (Council Regulation N 793/93)
- Export/Import Control (Council Regulation N 2445/92)

Additional and complementary tasks can be expected at later stages.

Increasingly, meetings with national experts concerned with the implementation and management of EC legislation on chemical substances in the member states are organised and co-ordinated by the Bureau at Ispra.

Classification and Labelling

Dangerous substances which are subject to classification and labelling requirements, are listed in Annex I of Directive 67/548/EEC. This Annex has to be continuously adapted to technical progress in the light of new scientific information, as more substances are added to the list and as the Commission progressively evaluates the thousands of potentially hazardous chemical substance which are on the market in the EC.

For instance, the Bureau is active in the classification and labelling of the following subjects and substance groups:

- man made mineral fibres;
- gases;
- sensitizing substances;
- substances dangerous for the environment;
- carcinogenic, mutagenic and teratogenic compounds.

EU Notification system for new chemicals and new chemicals database.

The 6th Amendment of the Dangerous Substances Directive has introduced a legal requirement for the notification of new chemicals which are put on the European Market. In this context, the Bureau has to ensure the exchange of summary notification dossiers sent by the EU Member States. This will include the receipt of dossiers on diskette and on paper.

Equally, the Bureau is also to be responsible for the exchange of summary notification dossiers with the EFTA countries within the context of the agreement on the extended European Economic Space.

A feasibility study for the transfer of these activities from DG XI to the Bureau was completed and the actual transfer is planned for 1994.

All incoming dossiers which are received on diskette, and any follow-up information and updates, have to be down-loaded into the New Chemicals Database (NCD). The Bureau is responsible for the maintenance, updating and management of the NCD.

Following a modification of the polymer definition, the Bureau is processing submissions from industries with the aim of preparing the 'List of No-longer Polymers' for the publication in the Official Journal of the EU. In addition, the Bureau is hosting expert meetings on "polymers", "control measures" and "informatic aspects" of the notification system.

Testing methods

The Bureau also has to co-ordinate the development, updating and adaptation to technical progress of the experimental testing methods which have to be applied to determine the properties of hazardous or dangerous chemicals.

This work is performed in co-ordination with the OECD, in order to lay down testing methods which can be used worldwide and are also accepted outside the EU. This includes the following activities:

- organisation and evaluation of ring tests (example: Daphnia Reproduction Test);

- co-ordination and approval of test methods at meetings with the EU national co-ordinators;

- adaptation to technical progress;

- liaison with the OECD (test guide-

lines, programme);
- cooperation with the European Centre for the Validation of Alternative Methods (ECVAM).

Existing Chemicals Regulation

EUCLID Database.

The EUCLID (European Chemicals Information Database) data bank is the primary tool for the risk assessment and management of existing chemicals in the European Union. The data are supplied in standard format in all nine EU languages on diskettes (Harmonised Electronic Dataset - HEDSET) (Fig.57).

Data are to be collected in three phases:

- for HPV chemicals ($> 1{,}000\ t\ y^{-1}$) in Annex 1 of the Regulation, within 1 year of the taking effect of the regulation;
- for remaining HPV chemicals within 2 years;

- for chemicals in EINECS in the production range between 10 and 1000 t/v, within 5 years.

A help-desk for HEDSET is operational to assist industry in the installation and use of the HEDSET software. The help-desk is equipped with an answering machine and a telefax machine.

Most of the enquiries dealt with configuration problems of the different PC systems in the companies. ECB staff give advice to re-configure the PCs used for HEDSET in the companies. Some questions on the classification of substances were raised.
Questions of a political nature concerning the Regulation were forwarded to DG XI.
In 1993, the help-desk received 123 requests for assistance from 51 different companies. Calls for assistance came from companies in UK (25), D(24), I (24), F (12), B (10), NL (8), L (4), IRL (3), SP (1). Calls from non-EU countries came from the USA (8), Sweden (2), Israel (1) and Australia (1).

At the end of 1993, 23 EUCLID software installations were operational outside the ECB, i.e. in Industry (21), Competent Authorities (1) and 1 installation currently under evaluation by the US EPA (Washington).

The database contains the following chapters:

- general information
- physico-chemical data
- environmental fate and pathways
- ecotoxicity
- toxicity

As part of the data are of a proprietary and confidential nature, EUCLID has to be installed and operated in specially protected (controlled access, security surveyance and alarm system) security rooms.

Priority Setting and Risk Assessment

Based on the data collected and stored in the EUCLID databank, the Bureau participates in the elaboration of harmonised procedures for priority setting and for the risk assessment of existing chemicals. In this context, the Bureau is responsible for producing a ranking of the high production volume chemicals (initially, the Annex I substances). This ranking forms the basis of the periodic priority lists. The ranking consists of several steps, namely:

Fig 57. HEDSET and EUCLID. Data collected with the HEDSETprogram will be loaded into the EUCLID database.

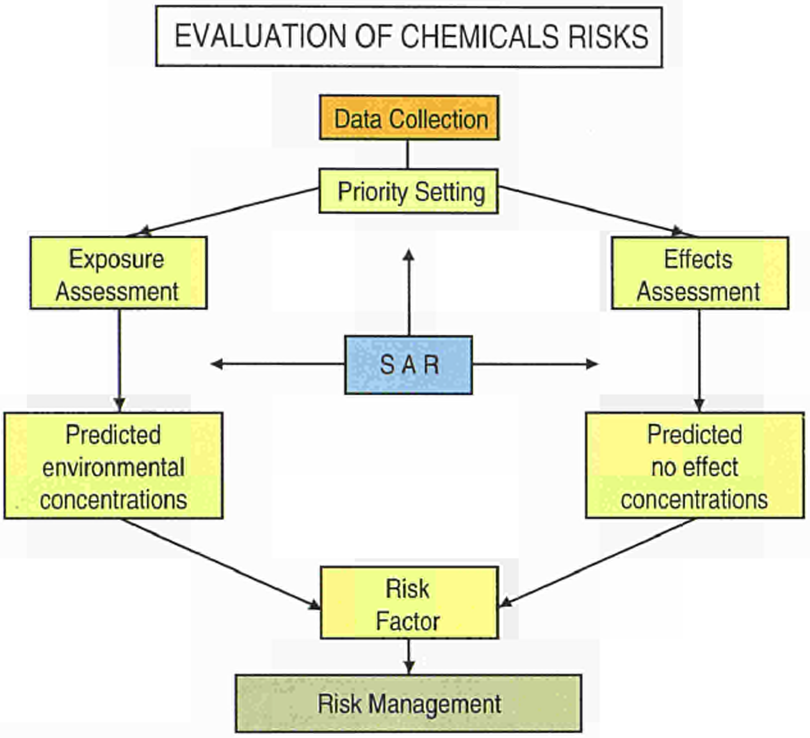


Fig 58. Flow scheme for chemicals risk assessment.

- data extraction from EUCLID;
- data selection as input to the ranking method;
- the ranking;
- filling of data gaps, where possible using validated QSAR;
- an analysis of the ranking and data to provide insight and to avoid errors.

This procedure is being developed by the Bureau in collaboration with and with advice from Member States, industry and several international organisations.

Substances on the priority list are subject to a thorough risk assessment. This risk assessment will be carried out by the Member States following the principles laid down in the risk assessment regulation and using the guidance given in three technical guidance documents on risk assessment. The Bureau is responsible for the completion of one of these guidance documents, namely, the document giving guidance on the use of QSAR within the risk assessment process.

The various steps undertaken in the risk assessment process are illustrated in Fig. 58.

Evaluation of Chemicals Risks

Export/Import of dangerous chemicals

Starting from 1994, the Bureau will also be in charge of information exchange with the Member States, third countries and UNEP/FAO, and of the monitoring of the export or import of chemicals which are subject to restrictions in their use and applications because of their potential hazard (prior information consent).

Quantitative Structure-Activity Relationships (QSAR)

With the increasing demand for reliable chemicals data, the application of validated QSAR methods is acquiring a new significance. For instance, the risk assessment of the multitude of chemicals, which may present a threat to the environment and human health, requires such a wealth of chemical, physicochemical and toxicological data, that experimental capacities are and will for some time remain largely insufficient to satisfy every need. The critical application of QSAR may fill many of the existing data gaps.

Thus, in the last decade, QSAR and SAR models have been developed and applied for the estimation of a broad range of chemical properties and biological activities. The first step involves the selection of a relevant training set with well documented data. Consequently, appropriate structural parameters, molecular descriptors or properties have to be chosen for the best available QSAR correlation. Based on a statistical analysis of the resulting data sets, the required modelling or regression correlation can be derived.

Based on these concepts, a computer program was developed and installed for the clustering of a large number of structures. The algorithm is able to group sets of chemicals of the size of the EINECS inventory (more than 100,000 chemicals) into groups according to structural similarity.

This program will be applied to the development of QSAR models in two international collaboration projects in this field:

- a project sponsored by DG XII with the aim of validating QSAR models for the prediction of the fate and effects of chemicals in the environment, with participation of six laboratories from the EU and Sweden;

- an extension of the EPA/EU collaborative QSAR project on new chemicals to existing chemicals, focusing on high production volume chemicals (Annex 1 of the Existing Chemicals Regulation). This project is co-ordinated by ECB.

Based on the unique source of data on chemical substances provided by the chemical databanks managed by the Bureau (EUCLID and New Chemicals Database), the Bureau is in a central position to exploit and validate QSAR models for environmental chemicals in close collaboration with expert laboratories in the Member States.

Also, preparatory work for the International Workshop on QSAR in Environmental Sciences 1994 is progressing according to the planned time-scale.

Once the Bureau is fully operative, the actual range of work areas could be gradually extended to include scientific and technical support in relation to other pieces of legislation on chemicals, e.g. on:

- biocides;
- plant protection products;
- preparations;
- consumer products.

This expansion may eventually lead to the participation of other DGs in the work of the Bureau.

In this future, the Bureau will have to collaborate on a technical-scientific level with the EFTA (European Free Trade Association) countries for the notification of new chemicals and risk assessment of existing substances, with OECD for test guidelines and existing chemicals evaluation, with UNEP/FAO (United Nation Environment Programme/Food & Agricultural Organisation) for the export/import control of certain dangerous or restricted substances; with EPA (Environment Protection Agency) for QSAR and existing chemicals evaluation. Also, the Bureau can provide technical assistance in the field of chemicals control to the responsible authorities for countries in the process of entering the Community or accepting EC legislation on chemical substances.

OTHER MISCELLANEOUS CONTRIBUTIONS

DG III (Internal Market and Industrial Affairs)

The scientific and technical support provided to DG III has concerned two major items, namely, the European Pharmaceutical Data Bank (ECPHIN) and the chemical products and food.

ECPHIN

The ECPHIN project was launched with the original objective of achieving a system capable of addressing the following problems:

- Increase transparency in the pharmaceutical market, in order to achieve cost containment in the health sector and to reduce the distortions in the intra-EEC trade of medicinal products.

- Eliminate disparities in the presentation of technical information on medicines among the Member States.

- Provide the documentation necessary for the management of existing EEC procedures for the authorisation of new medicines.

- Provide an information repository for pharmacovigilance documents which could play the role of source and dissemination method for side-effects, restrictions on indications or withdrawals of medicinal products throughout the Community.

- Provide the processing tools necessary for elaborating a Community repertory of drugs available in the EEC.

At the very beginning of the project, i.e. during the pre-analysis phase, it was supposed that DG IX informatic services would have provided the necessary mainframe and telecommunication systems to support the ECPHIN data bank. This assumption was rapidly abandoned and JRC became, in addition to the system developer, also the host services and telecommunication provider.
The database design developed for the feasibility study was strongly affected by the specific software tool selected for implementation, i.e. Adabas-Natural on a mainframe system. From an *a posteriori* analysis, the systematic inattention during the feasibility, phase I and phase II of the ECPHIN project for the needs to establish a credible data life-cycle is certainly the major conceptual drawback of this project. The implementation which emerged at the end of phase II restrict the representation of a medicinal product within 31 information items organised in a

hierarchical data model. The implementation in Adabas-Natural at this stage results basic both for what the data set available and the retrieval system provided to users are concerned.

In the meantime the context of the regulatory and control activity in the Community regarding medicinal products has changed significantly during the past five years.

The creation of the European Agency for the Evaluation of Medicinal Products (EMEA), with the related problem of data and information exchange among the national authorities, the Commission and the EMEA itself, certainly represents a major development with implication for all the information and communication projects in this field. The need for data / information exchange and communication is at present a predominant requirement, which is endorsed by the Commission programmes on telecommunication with particular reference to the IDA programme (Interchange of Data between Administrations) activity in relation to medicinal products. Despite the poor technical and conceptual conditions in mid -1993, significant work was done on the codification process for route of administration, pharmaceutical form and packaging.

The main development with respect to the ECPHIN system is the introduction of the concept of distributed systems.

This concept results in a more natural co-operation model among the participant organisations. The ECPHIN had achieved by the end of 1993, significant progress of results which can be summarized as follows:

- Development of a new and more comprehensive data model based on the relational theory, offering the advantage of gradual extention of the information components and files maintenance.

- Extension of the information domain to SPC, in order to handle technico-scientific information in two stages, a first stage with SPC loosely associated with the rest of the relational model, and a second stage with a more comprehensive integration.

- Updating of the system with a new data set related to the end of 1993 or the beginning of 1994. The updating exercise was intended not only to take in more-recent data, but also to study the technical characteristics of the data supplied by the Member States, in order to develop a consistent set of program-mes for the efficient processing of these data.

- Value addition to the available data by implementing codification and by setting up a consistent nomenclature system based on CAS numbers. In addition, a more accurate implementation of the ATC (Anatonical Therapeutical Code) codes has been introduced.

- Study of the problems related to the establishment of a viable data life-cycle for ECPHIN, which could be supported by the participant authorities. This will be based on the generation of common benefits deriving from the principle that the accumulation of information is not a linear problem.

- Study, development and experimentation related to intercommunication, access and dissemination systems capable of delivering ECPHIN information and user co-operation all over the Community, in a style consistent with the currently available technologies. The traditional host-terminal communication protocols will still be involved, but they no longer represent the necessary communication standard. ECPHIN will support a full client-server structure converging over time on a proper OSI set of communication protocols .

- Design and implementation of powerful user interfaces for both retrieval and data processing, taking advantage of the available client-server structure.

Chemical products and food

The following activities are worth of mention:
- Participation as the EC laboratory in the activity of the CEN/TC 38/W612 "Creosote", charged with developing official standards for methods of sampling and analysis of creosote and creosoted timber. Four standards for sampling creosote timber, the extraction of creosote from the sample, the analysis, determination of the benzo[α]pyrene content of creosote, and determination of the water-soluble phenol content of creosote. The EI plays an active part in the interlaboratory tests (analysis and statistical evaluation), in order to determine the repeatability and reproducibility of the methods for measuring benzo[α]pyrene and water soluble phenol content.

- The collection of food analytical methods, also including detection limits, repeatability and reproducibility, has been started, in order to comply with the request of the Member States concerning the need for comparison or harmonisation of the various analytical methods for food.

- The sample preparation procedure of the EEC method concerning the analysis of biphenyls in citrus fruits peels was evaluated. A very simple method for sample preparation, without concentration of the biphenyl extract in vacuum (evaporation leads to loss of the biphenyl), was developed.

A comprehensive survey of the literature concerning analytical methods for proof of authenticity or adulteration of vanilla extracts was prepared. Extracts from vanilla capsules from different origins and commercial vanilla extracts were analysed by various chromatographic methods, also using chiral column phases. A new method (SFE) for extracting vanillin from sugars was developed. Scientific and technical support has been provided for various DG III needs (control of food dyestuff, analytical procedures, etc.).

DG VI (Agriculture)

The agreement between DG VI and the EI concerns two main activities relating to dairy products and wine. In the field of dairy products, the following major achievement are worth mentioning:

Detection of cow's milk in ewe's and goat's milk cheeses

Participation in seven collaborative trials regarding the validation of the EC reference method for the detection of cow's milk in cheeses prepared from mixtures of goat's and ewe's milk: 50 samples were investigated. This study will be extended to cheeses prepared from mixtures of goat's, ewe's and buffalo's milk. This method, based on the detection of gamma 2 and gamma 3 caseins, is suitable for differentiating the caseins of cow's milk and milks of other origins (goat's and ewe's milk). The results obtained in three collaborative trials concerning the detection of whey proteins in samples of cheeses made from mixtures of ewe's and goat's milk with added UHT cow's milk or heat denatured bovine whey protein, are not yet satisfactory.

Heat treatment of milk

Research was conducted on chemical indicators for evaluating the heat treatment of milk by means of the whey proteins α-lactoalbumine and β-lactoglobuline. Participation continued in collaborative trials regarding pasteurised and high pasteurised milks. Reverse-phase HPLC is suitable for differentiating these two types of heat treatment applied to milk. The limit values of β-lactoglobuline, proposed by DG VI, associated with the negativity or positivity of the enzyme peroxidase, will permit the classification of these two types of milk and their distinction from sterilised milks.

Determination of furosine in milk and dairy products

Furosine is analysed by ion-pair reversed-phase HPLC in acid-hydrolysed dairy products. The level of furosine in heat-treated foods is related both to processing and storage conditions, and may represent a suitable indicator of the quality of dairy products. Moreover, on the basis of the furosine value, it seems possible to detect very low levels of milk powder both in raw and pasteurised milk. This method, proposed by Prof. Resmini, will be studied by the Chemists Group of DG VI for "Milk and Dairy Products".

Repartition of cholesterol in industrial dairy products chain

The distribution of cholesterol in milk and dairy products has been investigated; a constant increase of cholesterol in milk fat as a result of skimming and heat treatment of milk, has been observed.

During the cheese-making process, the cholesterol level increases in the whey, reaching double the concentration in ricotta cheese; the butter obtained from separated cream contains a lower amount of cholesterol than the butter obtained from whey.

Non-milk fat in butter

A comparative study of the data obtained by two GC methods for the determination of the fatty acid composition and the triglyceride content of pure and adulterated butter samples has been performed.

The establishment of a data bank for butter purity control is under way.

Wine

As far as wine is concerned, scientific support has continued in applying the NMR technique to the control of the origin of ethanol present in the following samples:

- wines, spirits and alcohols produced by distillation of surplus wine, denatured ethanol added to gasoline, etc., sent by DG VI inspectors or by official national organisations;
- wines for the European data bank, sent by the Member States not yet fully equipped for this kind of control;
- validation by the JRC laboratory of 10% of all the wines sent by the Member States for the European

data bank;

- participation in the interlaboratory campaign launched by the *ad hoc* ISO Working Group to establish the origin of the sugars present in some citrus fruit juices (after fermentation).

The NMR measurements, and all the other information required by EC regulations N. 2347 and 2348/91, for European wines produced in the 1991 vintage, have been received from the official laboratories of the wine-producing Member States. The storage of all these data, including the JRC pertinent validation results, in the future European wine data bank, will be achieved at the beginning of next year. The first software version of this data bank (in six different languages) will be distributed to the official Community laboratories.

A second NMR spectrometer was installed in October 1993, to deal with the increasing number of samples to be analysed. A new mass spectrometer, specially equipped to perform the analysis of natural isotopes in foods or beverages, will be installed at the beginning of the next year.

The evaluation of an interlaboratory study to evaluate the performance of a method for the NMR analysis of samples of wine and ethanol has been carried out; 17 European laboratories participated in this study.

In agreement with DG VI, "The European office of wine, spirits and alcoholic drinks" has been officially established at the JRC Ispra (EC Approval COM (93) 360, 16 September 1993).

All these activities involved the active participation of the National Experts at EC meetings organised by DG VI.

DGXII (Scientific Affairs, Research and Development)

Sixth European Symposium "Physico-Chemical Behaviour of Atmospheric Pollutants", Varese 18-22 October 1993.

The Sixth European Symposium on "Physico-Chemical Behaviour of Atmospheric Pollutants" was held in Varese, at the Congress Centre Villa Ponti, from October 18th to 22nd, 1993.

As in the past - the first one was held in 1979 in Ispra, - the symposium was jointly organised by the EI and DG XII (Unit D - Environmental Technologies).

The main objective of the symposium was to review the current status of the research which is part of the Concerted Action in "Atmospheric Chemistry". This task now appears rather well accomplished, since over 180 contributions (6 from the Institute) were presented in oral and poster sessions, to an audience of more than 240 scientists from 19 countries.

As for past symposia, the meeting was an opportunity for initiating and strengthening collaboration among laboratories: an objective certainly as important to the CEC as that of reviewing the status of the research.

The proceedings will be published as *Air Pollution Research Reports*, in the first half of 1994.

DGXVII (Energy)

ECSAM

In the context of the ECSAM support to DG XVII, accurate and precise potentiometric determinations of uranium have been performed in about 60 $UO_2$1UF_4 powder and pellet samples. Furthermore, technical support has been provided for the maintenance of the transportable mass spectrometers.

CPS (Consumer Policy Service)

Due to the transfer to the IRMM (Geel) of the greater part of the activity concerning the agreement between the JRC and CPS, the Institute's activity has been focused on selected topics, as follows:

Microbiological control of cosmetics

Some categories of cosmetics, such as shampoos and toothpastes, have been investigated.

The samples were collected from shops and markets in several countries of the European Union (Germany, France, Spain, Portugal, Great Britain, Ireland, Belgium, Netherlands, Luxembourg, Denmark), and analysed for:

- Total aerobic microbial counts;
- Search for and isolation of microbial species potentially pathogenic in man;
- Search for and isolation of bacterial species which are reliable indicators of faecal contamination.

An overall evaluation of the results obtained, revealed a persistence of mycetic strains in products retained for a long time before use. Therefore, the preservatives contained in the cosmetic products examined, can be supposed to have chiefly an anti-bacterial property. Moreover, the possible microbial contamination of the cosmetic formulations confirmed the nature of the problem.

Determination of α-quartz and fibrous asbestos in cosmetic talc

Within the framework of the analytical methodologies for cosmetic talc, 15 body talc samples were collected from various European countries (England, Germany, Italy, France, Switzerland, The Netherlands). A structural and elemental characterisation was carried out using different techniques (phase-contrast optical microscopy, X-ray spectroscopy, X-ray diffraction and elemental analysis). Methods have been developed for the quantitative determination of the hazardous compounds tremolite and α-quartz.

Furthermore, the detection limit using the X-ray diffraction method for the asbestos mineral tremolite was established. Although there were remarkable differences in structural and elemental composition between the talc samples, no detectable amount of the hazardous fibrous asbestos mineral, tremolite, were detected. Concerning α-quartz, the detected concentrations are relatively low, so the consumer is not exposed to any risk of silicosis.

Identification of chemical compounds

In the autumn of 1993, the CPS asked the ECB to examine the identification of a set of chemical compounds identified by chemicals names, CA Registry Numbers and/or EINECS numbers. The compounds are candidates for a list of ingredients in cosmetics. An automatic check identified some errors in the numbers supplied and in the pairing of these numbers, and a manual control also highlighted errors in the pairing of names and numbers. The complete list contains more than 6,000 compounds, and it was not intended to make a throughout chech of the complete file, but only to give an indication to the CPS of the types of problems present in the compilation.

Product analysed	Total samples analysed	Positive	%
Maize	97	30	30.9
Chopped maize	95	33	34.7
Straw	109	34	31.2
Cotton seed	77	19	24.7
Total	**378**	**116**	**30.7**

Table 18. Research of mycotoxins (aflatoxins, zearalenone, ochratoxins) in animal feeds.

Microbiological control of food

A study was carried out of products intended for animal consumption, to confirm the results obtained previously concerning contamination by aflatoxins. Other agricultural products and meat represent the largest proportion of human food intake.

In the present research, in addition to the detection of the most important aflatoxins (B1, B2, G1, G2), other categories of mycotoxins (ochratoxins and zearalenone) were taken into consideration. Table 18 shows an overall picture of the research performed. The various kinds of products analysed are reported (maize, chopped maize, straw, cotton seed) and, for each of them, the number and the percentage of product batches positive in terms of aflatoxins, ochratoxins or zearalenone are emphasised. Some of the above-mentioned toxins were identified in a survey of 116 product batches.

Table 19 specifies the number and the percentage of the analysed product batches in which the various kinds of micotoxins were identified. It must be emphasised that several batches were simultaneously positive for aflatoxins, zearalenone or ochratoxins. Micotoxin concentrations higher than the limit values laid down by laws were found only in 22 samples, representing 5.8% of the total examined (378 - Table 18) This finding has, however, only a relative significance, when the particular type of chronic intoxication to which the micotoxins give rise, with the wide range of possible accumulations in human and animal tissues, is considered.

Fumosins represent another group of dangerous mycotoxins, as was only

Category of toxins	Number of samples	% of positive samples
Aflatoxins (B1, B2, G1 ,G2)	108	28.6
Zearalenone	45	11.9
Ochratoxins	18	4.8

Table 19. Product batches positives for each category of the mycotoxins.

recently recognised; their characteristics have been investigated.

A study of the characteristics of drug-resistance of strains of *Listeria monocytogenes* was also carried out. The bacterial strains have been isolated from different kinds of foods (milk, soft cheese, meat, vegetables).

The identification of the strains and the detection of their drug-resistance were performed using the automicrobic system Vitek. The results of our investigation showed that strains of *Listeria monocytogenes* were able to grow while in contact with several antibiotics. This evidence of drug-resistance increases concern about the serious consequences of Listeriosis for man.

THE ENVIRONMENT INSTITUTE

3. Exploratory Research

Four projects have been developed within the context of Exploratory Research, namely:

- Absolute Chemicals Analysis by Laser Methods;
- Surface Enhanced Raman Scattering (SERS) as a New Analytical and Diagnostic Tool for Atmospheric Chemistry;
- Advanced Separation Techniques;
- Development of an Atmospheric Aerosol Tracer.

Apart from the second project which is aimed at studying the feasibility of utilizing the recently-discovered Surface Enhanced Raman Scattering process for the characterisation and quantitative measurement of atmospheric aerosols the other projects are the continuation or the result of former projects whose aims were described in previous Annual Reports.

To summarize, through the first project, the feasibility of an absolute method of analysis of molecular and atomic species by means of innovative laser-based technologies, were theoretically and experimentally addressed.
Advanced Separation Tecniques were used to explore the possibility of analytical refinements to improve the quality and the specificity of environmental analysis through highly sophisticated separation techniques. The problem of tracing atmospheric aerosols for pollutant diffusion and transport studies was tackled in the fourth project, the use of chemiluminescent substances being the approach investigated.

Absolute Chemical Analysis by Laser Methods

In the previous Annual Report, the major emphasis was placed on the attractive possibility of time-resolving the fluorescence signal during the laser excitation pulse. In this way, it was possible to understand and tame the interaction between the atomic system and the radiation and to prove that, under saturated conditions, the fluorescence signal was stable, even in the presence of strong fluctuations of laser intensity. Such conditions are essential, if one wants to apply the technique to the concept of absolute analysis.

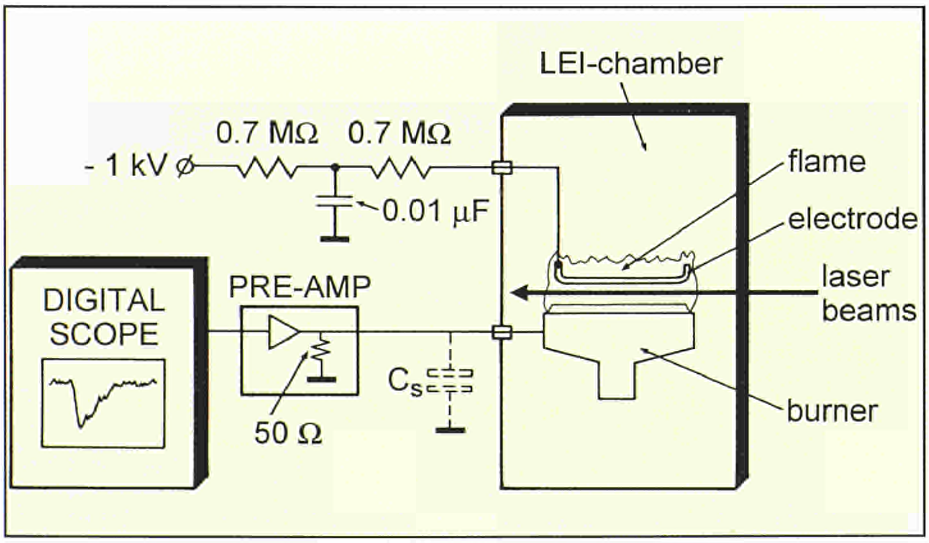


Fig.59. Simplified schematic diagram for the absolute detection of Laser Induced Ionization (LEI) pulses of sodium atoms in the air-acetylene flame. To preserve the temporal characteristics of the current waveform, the signal is fed into a wide band pre-amplifier (300 MHz) directly connected to a fast digital oscilloscope. The stray capacitance, Cs, of the overall circuit limits the maximum voltage developed.

As an attractive alternative approach to fluorescence, it was also argued that the ionization technique would be even better than the fluorescence method as a potential absolute method of chemical analysis. In fact, provided that 100% ionization efficiency could be reached during the interaction, i.e. during a very short excitation pulse, the measurement of charges can be calibrated much more easily then by the measurement of photons. When this were achieved, one could speak of "absolute coulometry". The real challenge here would be to demonstrate the unity ionization efficiency on a time-scale of several nanoseconds (which is typical of the employed excimer-pumped dye laser pulse). By careful control of the limiting noise in the experiment, consisting of a flame, an immersed electrode and a fast detection system, it was possible to show for the first time that sodium atoms could be ionized completely, in about 15 ns, by means of a two- step excitation provided by two dye lasers tuned at allowed transitions in the visible range.

The experimental set-up is shown in Fig. 59. Particular care had to be taken, in order to minimize the radiofrequency pick-up from the firing of the excimer laser, which is severe, due to the necessity of using a wide

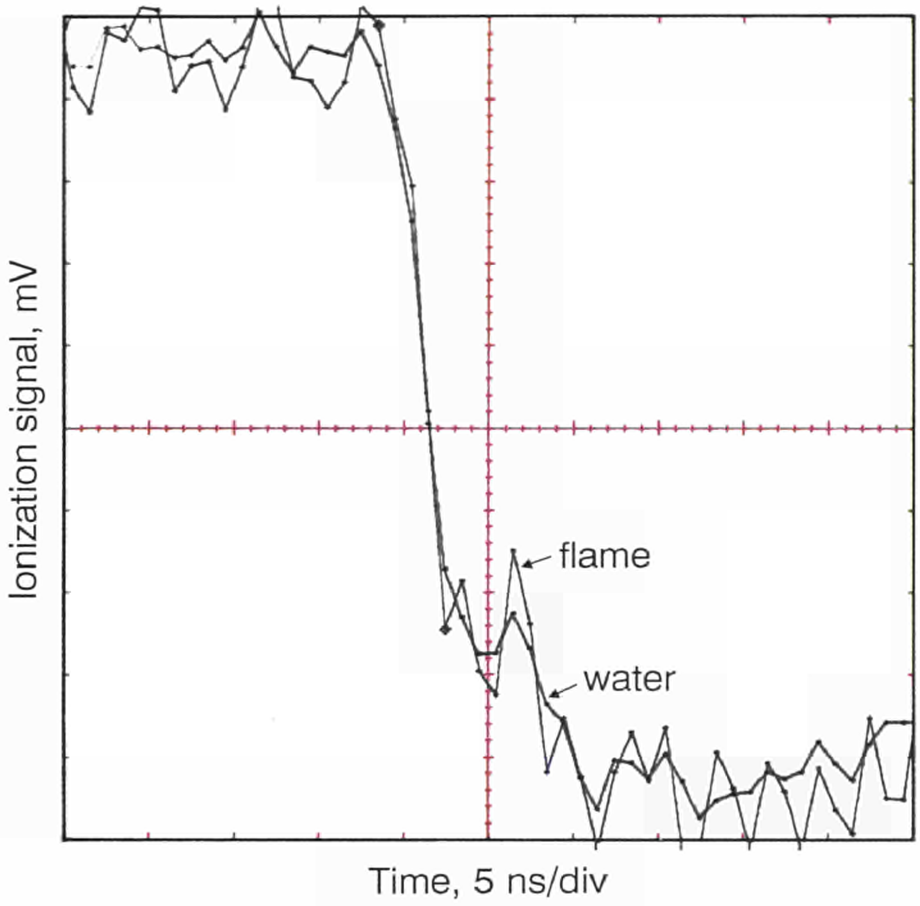


Fig.60. Ionization waveforms (the signals are negative) showing the time resolution of the overall detection system and the extremely high sensitivity of the technique. The number density of sodium atoms in the cases shown (unseeded flame or just pure water aspirated) is less than 108 atoms per cubic centimeter.

electrical bandwith of the detection electronics. In Fig. 60, both the high sensitivity of the technique as well as the demonstration of a unity ion yield are illustrated. The only sodium present here is either due to contamination or that present in the pure water. The signal reaches its maximum value well within the 15 ns duration of the excitation pulse, indicating an ionization rate greater than 0.3 GHz. In order to emphasize the capability of our system to distinguish between different ionization rates, Fig. 61 shows three rise times in which the ionization efficiency is purposely varied by decreasing the laser intensity, either by inserting neutral density filters in front of the beam or by defocussing it into the flame.

These results represent the most direct experimental proof that the ionization method actually works. From the experience obtained with both the fluorescence and ionization techniques, it can be safely concluded that the most difficult step in the successful application of the concept of absolute chemical analysis by laser spectroscopy lies in the accurate knowledge of the efficiency of formation of free atoms in the vapour phase rather than in understanding the interaction between the atoms and the exciting radiation.

As a corollary to this research, the experience gained by the use of several commercial dye lasers has led to the design of a novel, simple and efficient dye laser, which can be pumped by an excimer or by a Nd-YAG laser. The major advantage of this new design is that it minimizes the amount of ASE (Amplified Spontaneous Emission), which is detrimental to the correct functioning of the laser, and nevertheless is present in the output of all pulsed, high-gain dye lasers. The ASE is due to the amplification of the photons spontaneously emitted in the oscillator cavity, since the oscillator and the amplifier share the same propagation direction of the laser output. In our configuration (Fig. 62), the oscillator axis is spatially separated from that of the amplifier: in this case, only the radiation which has already been spectrally filtered by the diffraction grating can be amplified. The laser, which was tested with a XeCl excimer pump, is characterized by a conversion efficiency greater than 10% and a spectral bandwith of about 3 cm^{-1}: it is therefore suitable for the excitation and ionization of several atomic and molecular species.

Surface Enhanced Raman Scattering as a New Analytical and Diagnostic Tool for Atmospheric Chemistry

Spontaneous Raman Spectroscopy has been widely used in the past as a means of detecting and characterizing atmospheric aerosols, such as sulphates and nitrates, due to the inherent capability of the technique to

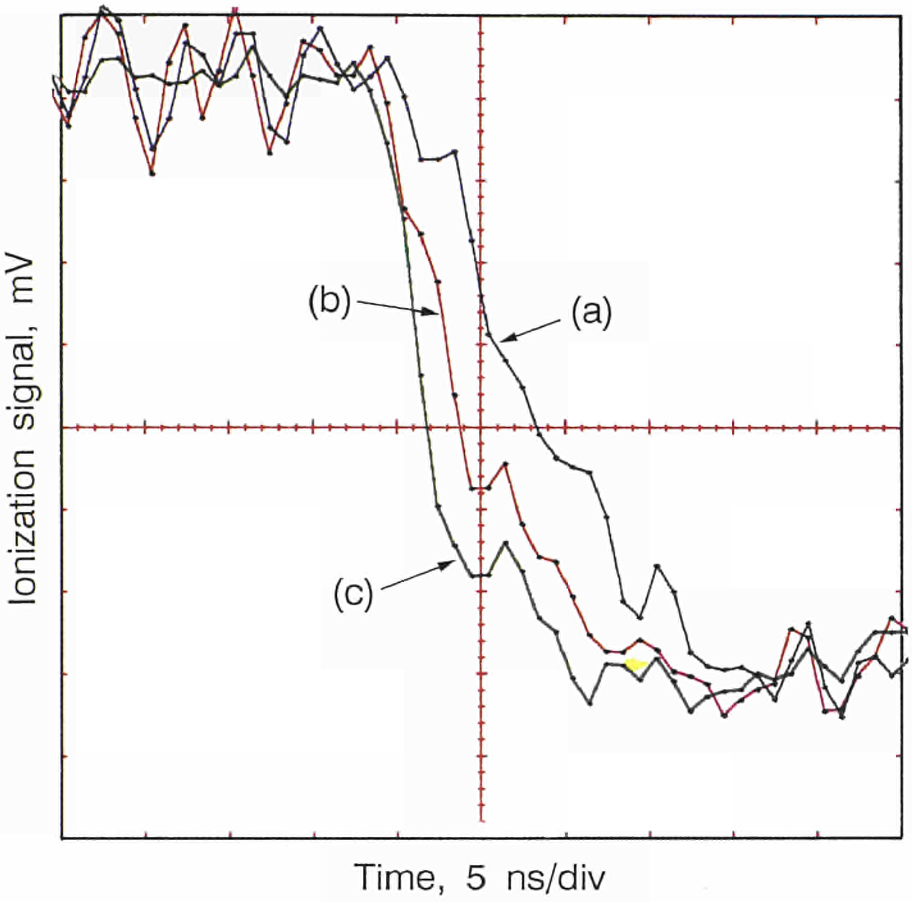
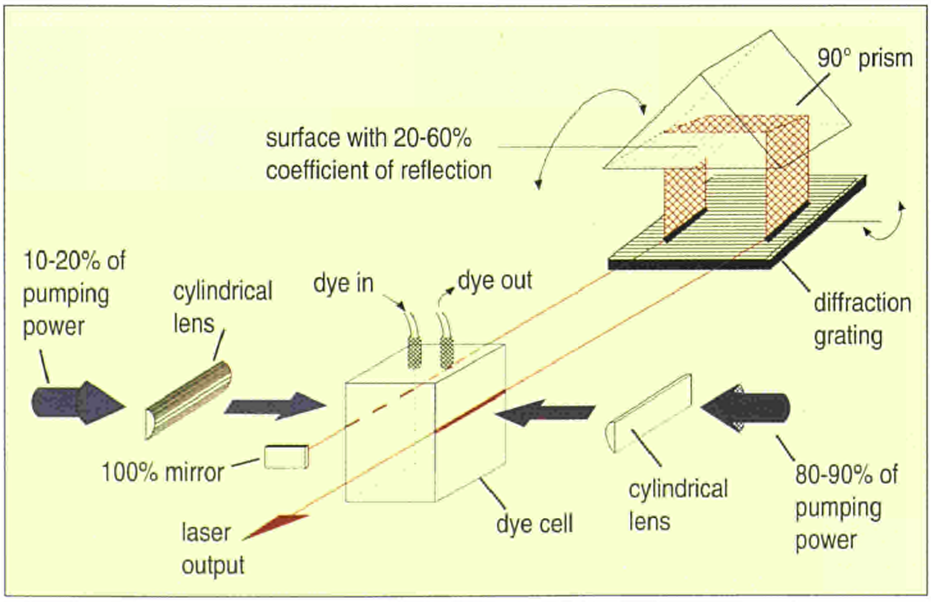


Fig.61. Experimentally observed rise times (negative) for three limiting ionization rates: (a) Na= 0.5 ppm, laser unfocussed, second step intensity decreased by 2,000 times; (b) pure water, laser focussed, second step at medium intensity; (c) water, laser focussed, second step at full intensity. A clear difference in the rise times is observed and resolved.



quantify, as well as chemically identify, the scattering molecules. The major disadvantage of this method lies in its low scattering cross section, which limits the sensitivity attainable. The recent discovery of the Surface Enhanced Raman Scattering (SERS) effect, which occurs when the molecules are adsorbed on colloidal Ag, Au or Cu surfaces, has led to a significant increase in sensitivity (e.g. enabling the detection of submonolayers of adsorbates) due to an enhancement of up to six orders of magnitude of the scattering cross section.

The assembling of the basic infrastructure for the application of SERS to tropospheric aerosol chemistry has been undertaken. Fig. 63 illustrates our experimental set-up. As shown, the main focus of our research will be on species involved in the atmospheric sulphur cycle, H_2SO_4, and DMS. Since the understanding of the surface effect will eventually determine the analytical and diagnostic potential of the technique, a major effort is now devoted to the preparation of the silver substrate, which has to satisfy the requisites of ease of use and reproducibility of preparation, long term stability and adaptation to aerosol sampling equipment. Chemical reduction of metal salts is one of the most popular preparation method. In addition, a

Fig.62. Essential schematics of the novel dye laser design described in the text. The pumping power, as usual, is split between the oscillator and the amplifier. The two geometrically separated paths for the oscillator and amplifier beams are clearly seen.

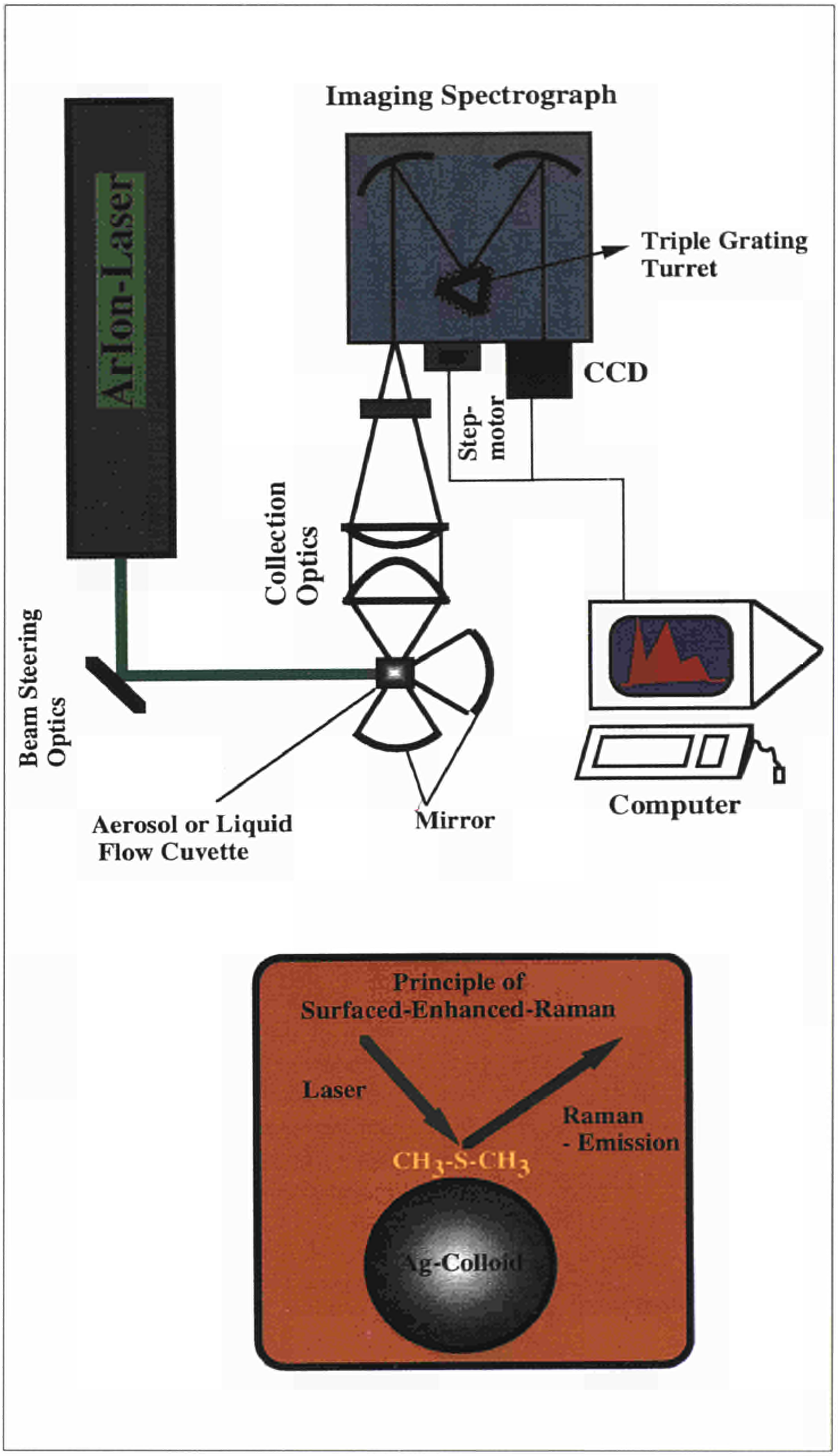


Fig.63. Schematic diagram of our Multichannel Raman Spectrometer based on the use of CCD (Charge Coupled Devices) as array detectors. The experimental facility is used for the application of the Surface Enhanced Raman Scattering technique (SERS) to the characterization and detection of aerosols.

recently described procedure based on the direct ablation of the metal by a laser will be investigated. In this way, the DMS aerosol and the Ag colloid produced in the ablation process could be mixed on line, while probing the resulting stream with the Ar-ion laser.

Advanced Separation Techniques

The matrix influence on the analysis of small oligoribonucleotides by fast atom bombardment mass spectrometry (FAB-MS) has been studied. The choice of the matrix has a decisive influence on the absolute sensitivity in FAB-MS. The surface activity of the analyte in the matrix is a system parameter and has to be optimised to give the best sensitivity for a given class of compounds. Although glycerol is the standard matrix for FAB-MS, a variety of other compounds have been employed. Glycerol, thioglycerol and triethanolamine are used as matrices for the analysis of RNA by FAB-MS, but there is no comparative work about matrix selection for these specific analytes in the literature. The complete analysis of RNA strands by mass spectrometry requires the determination of both the molecular weight and the sequence. Both can be determined by using FAB-MS. Of all matrices tested, diethanolamine proves to be the best choice for the analysis of these components in negative ion FAB-MS and allows for analyte concentrations in the low nanomole range. The ribonucleotide heptamer reported in Fig. 64 shows the present limit of the method. Not all sequence ions appear, and the signal/noise ratio for the upper mass range is hardly acceptable. Two different series of sequence ions are

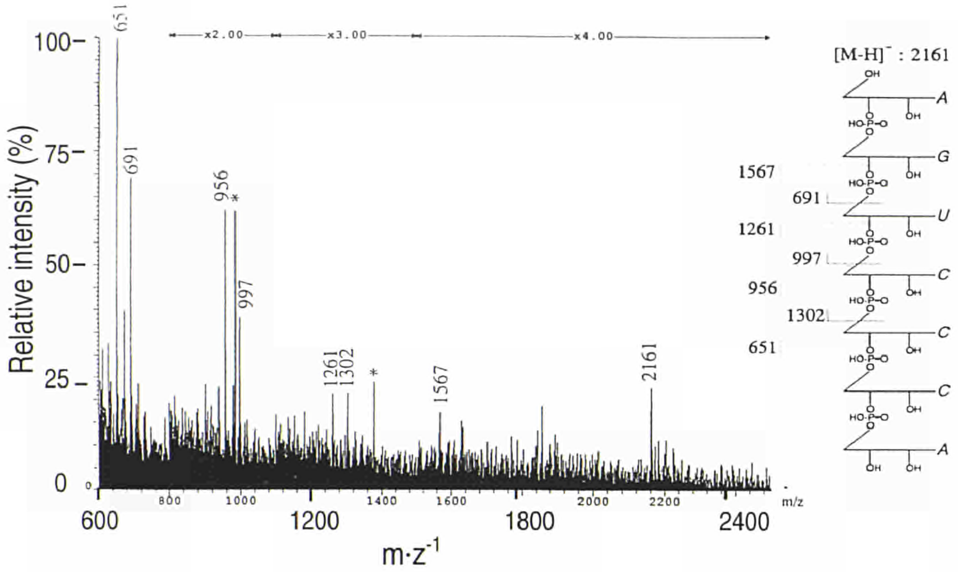


Fig.64. *RNA heptamer $6.8x10^{9}$ mol µl^{-1} Δ 0.5 OD (260 nm).*

predominantly present in FAB-MS analyses: 3'-sequence ions with a phosphate group at the 3'-terminus, indicating a sequence in the 5'->3' direction w$_n$, and 5'-sequence ions with a phosphate group at the 5'-terminus, indicating a sequence in the 3' -> 5' direction, called d$_n$. The less-intense fragments, resulting from P-O bond breakage, are called b$_n$ in the 5' –>3' direction -and y$_n$ in 3'–> 5'-direction. The numerical subscript gives the position in the sequence. The nominal masses of the measured fragments are shown. Sequence ions are w$_2$ 651 m/z, w$_3$ 956 m/z, w$_4$ 1261 m/z, w$_5$ 1567 m/z, d$_2$ 691 m/z, d$_3$ 997 m/z and d$_4$ 1,302 m/z. Since the bond involving the 3'-o atom, connected to a secondary carbon of the sugar moiety, is more

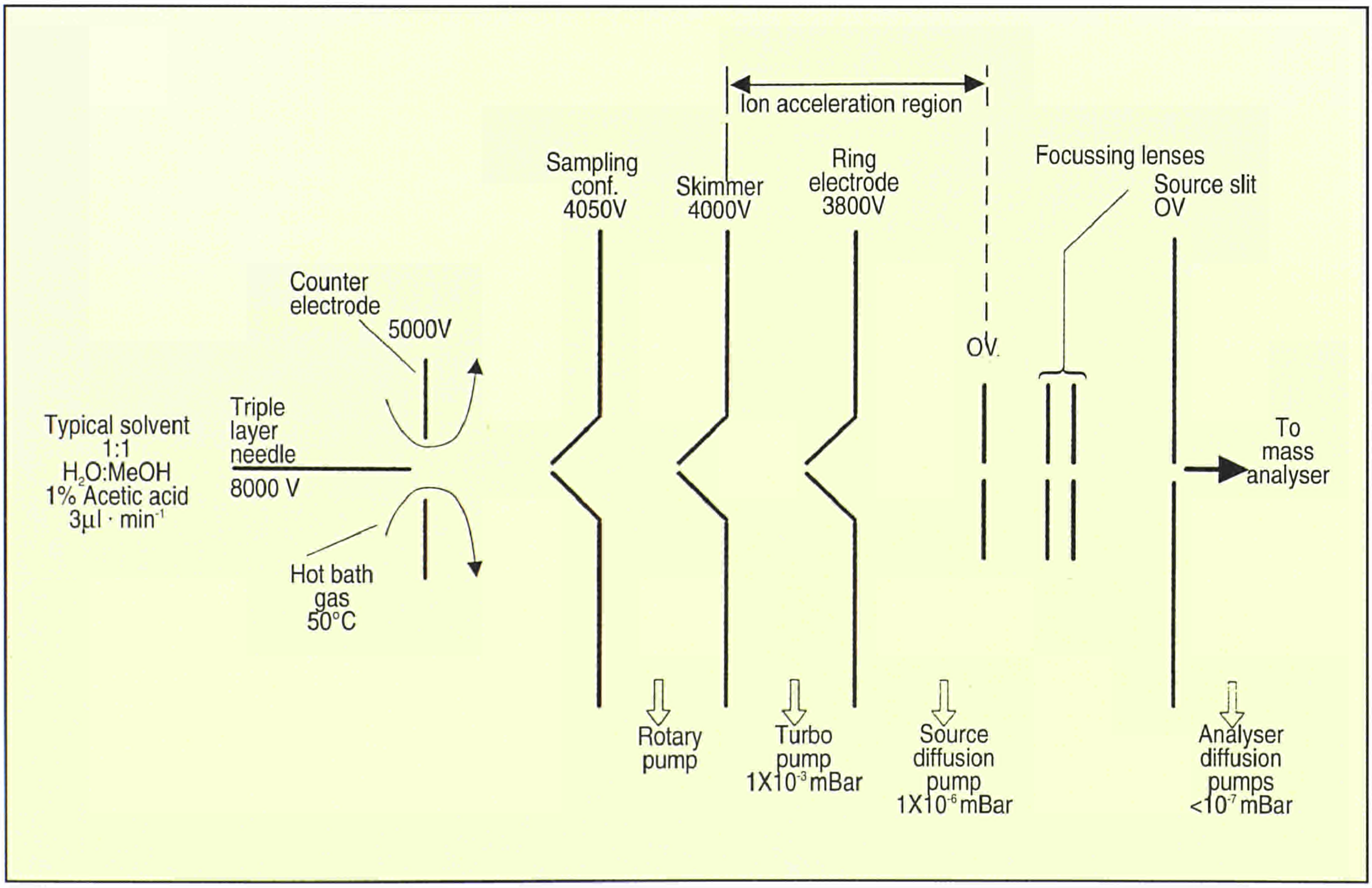


Fig.65. *Electrospray ionisation source schematic.*

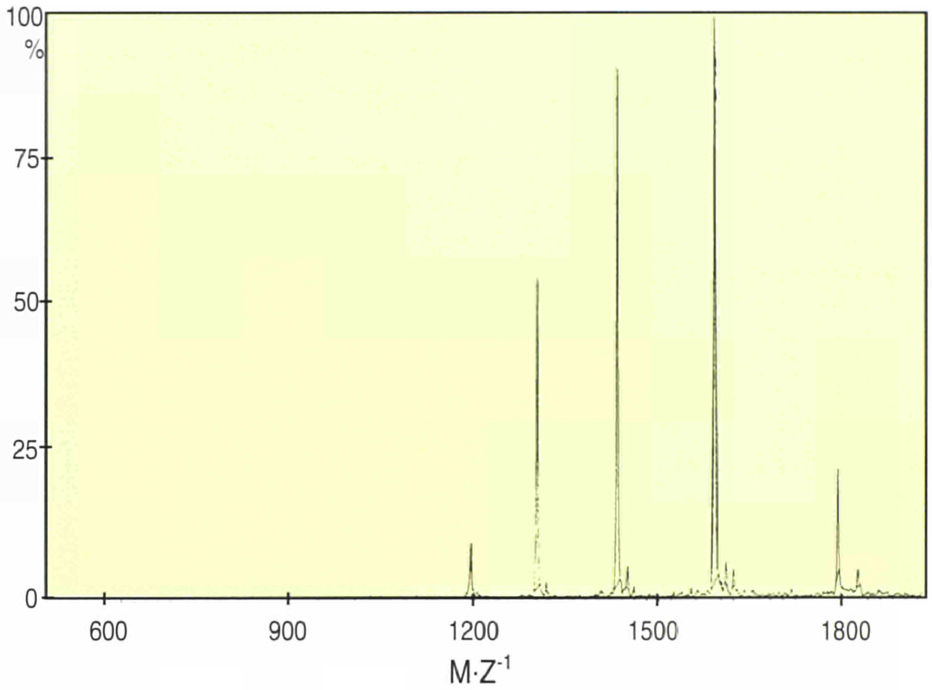


Fig.66. Electrospray ionisation mass spectrum of Lysozyme (RMM = 14305)

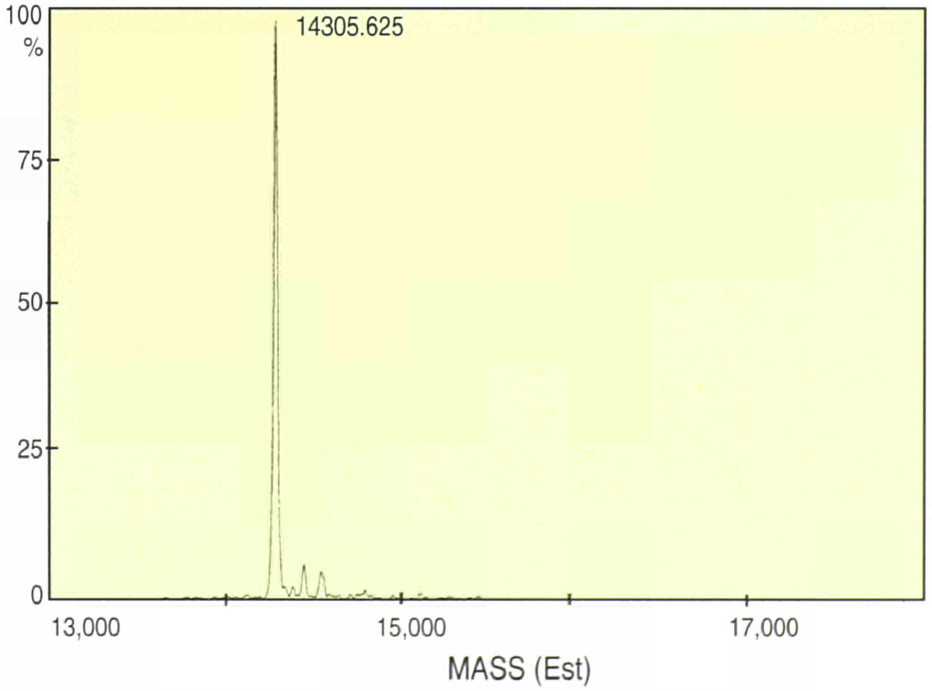


Fig.67. Transformed mass spectrum of Lysozyme (RMM = 14305)

labile then the one involving the 5'-atom, connected to the primary carbon of the sugar, the 5'-sequence ions are expected to be more intense than the corresponding 3'-sequence ions. Exact mass calibration is achieved by using a gold-plated tip on the FAB probe and measuring the signals of the sputtered gold clusters. These ions are readily formed by bombardment of the probe tip with fast Xenon atoms. The asterisks in Fig. 64 mark the gold clusters used as calibration ions.

The instrument used for these experiments is a high resolution mass spectrometer with forward geometry and high field magnet allowing for a mass range up to 3,000 a.m.u. at 8kV accelerating voltage. Of course large nucleic acids require a much higher mass range. One of the possibilities taken into consideration for the analysis of ions of nominal masses up to 100,000 a.m.u., is the use of an electrospray ion source. Fig. 65 shows a schematic representation of the prototype electrospray ion source that has been installed on a double focusing magnetic sector mass spectrometer. Electrospray MS can be applied to the determination of the relative molecular mass of large molecules, because of the tendency for multiple charged ions to be formed. Mass spectrometers analyse mass-to-charge (m/z) ratio and, for example, a molecule of RMM 30,000 having 20 charges gives a peak near m/z 1500. In Figure 66, the first spectrum resulting from the prototype electrospray is reported, showing multiple charged ions of lysozyme, a protein of average molecular weight (14,305). Initially, electrospray data were presented as in Fig.66 as a series of multiple charged ions and a textual output of the actual average molecular mass.

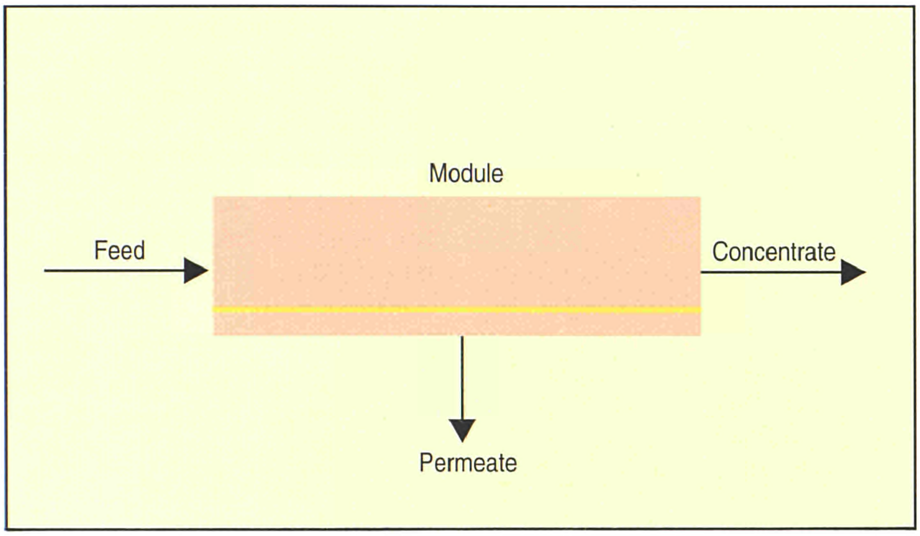


Fig.68. Schematic representation of a membrane process where the feed stream has been separated into a concentrate and a permeate streams.

However, transformation software now exists that presents the data as a reconstructed mass spectrum, as if the sample had yielded a singly-charged molecular ion. Such a transformed spectrum is given in Fig.67.

Future improvements of the electrospray source ion optics will allow for lower detection limits down to the picomole range for molecule as large as entire t-RNA's.

The Application of Crossflow Membrane Techniques in the Treatment of Wastewaters

With the future need to safeguard the quality of freshwater supplies and

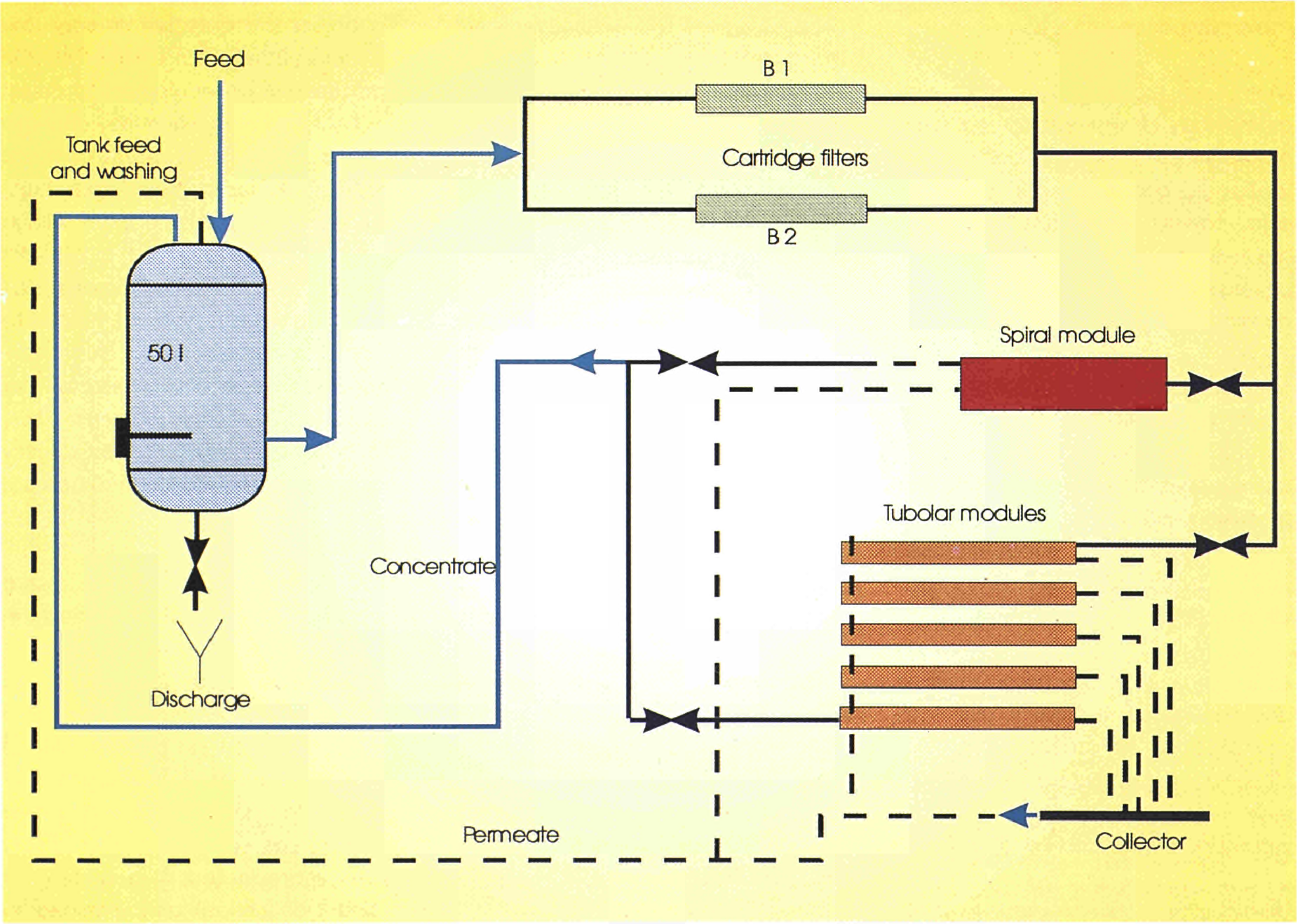


Fig.69. Ultrafiltration Plant Flow Diagram.

reduce fresh water usage by the introduction of reclamation schemes, the control of wastewater discharges will become of great importance. Many water pollutants resist degradation by the self-purification processes of the water environment as well as the controlled environment of the conventional biological treatment systems, and eventually find their way into drinking water supplies.

In the membrane process application in wastewater treatment, the wastefeed is separated into a stream that goes through the membrane, the permeate (mainly water), and a fraction of feed that does not go through the membrane, the concentrate, containing most of the undesirable components (Fig.68).

Membrane processes are rather new as methods of separation, and were not considered as technically important for separation until 25 years ago. Today, membrane processes are used for a wide range of applications and the number of such applications is still growing.

The use of membrane processes for waste purification is gaining considerable attention. Among the available membrane operations, the most promising in pollution abatement are electrodialysis (ED), reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF).

At the EI, a pilot plant was planned and constructed in order to allow the combination of different types of ultrafiltration membranes. It combines eight tubular modules and one-spiral wound membrane module (Fig. 69).

Ultrafiltration is a low pressure membrane filtration process used for separating macromolecules and suspended solids from water. A semi-permeable microporous membrane performs the separation. Water and low molecular weight solutes pass through the membrane and are removed as permeate.

These membranes are generally defined by their cut-off threshold, i.e. the smallest molecular weight component retained at a given coefficient of retention, usually 0.90, and the permeability, i.e. the flux of a component through the membrane per unit of pressure.

The permeability of the membrane is one of the most important primary considerations. High permeabilities lead to the potential for higher product fluxes. The water permeabilities determined for each of the membranes under study were the following: 0.141 m^3 m^2.h.bar (tubular); 0.091 m^3 m^2.h.bar (spiral-polysulfone); 0.023 m^3 m^2.h.bar (spiral-polyamide); 0.011$m^3 m^2$.h.bar (spiral-polyamide A).
For spiral-polyamide-membrane A, cut-off tests were run using 100 ppm and 300 ppm solutions of dextrans and polyethylene glycols (PEG) of different molecular weights. The best results were obtained with 300 ppm PEG solutions (Fig.70).

At present, test are run with solutions of polyvinylalcohol (PVA) and polyvinylalcohol copolymers, Elvanol T-66 and Elvanol T-25, kindly supplied by DuPont. PVA is a high molecular weight polymer, often encountered in industry, which contributes significantly to the organic pollution load of industrial effluents such as those of finishing textile mills (BOD 200-3000 mg l^1).

One of the major goals of this work is to set up a membrane module sequence yielding permeate streams that can be recovered as process water running in parallel with pollution abatament and PVA recovery.
The two types of modules suitable for textile industry waste water application are tubular and spiral-wound. For these effluents, the spiral-wound modules seem to offer the best compromise between operability, surface-to-volume ratio, power requirements and replacement costs.

Development of an Atmospheric Aerosol Tracer

In the search for an appropriate aerosol tracer, chemiluminescent substances have been investigated. These can be detected at very low concentrations, using rather simple and inexpensive equipment to detect the light they emit when they undergo their specific chemiluminescent reaction. A "luminometer" was built, using a good photomultiplier with a low dark current and a photon counting unit. This luminometer was equipped with a special holder to allow for measuring the chemiluminescence directly on a wettable filter disc of up to 47mm diameter. Thus, the tracer can be quantified directly on the filter on which the aerosol sample is obtained.

Three substances, which have approximately equal chemi-luminescence efficiencies were chosen: luminol, lophine and lucigenine. So far, several experiments have been performed to test the photostability of luminol (5-amino-2,3-dihydro-1,4-phtalazinedione). For this purpose, glass plates, or paper filter discs, were impregnated with a defined amount of luminol and exposed to sunlight or to a xenon lamp, which was equipped with a pyrex filter to

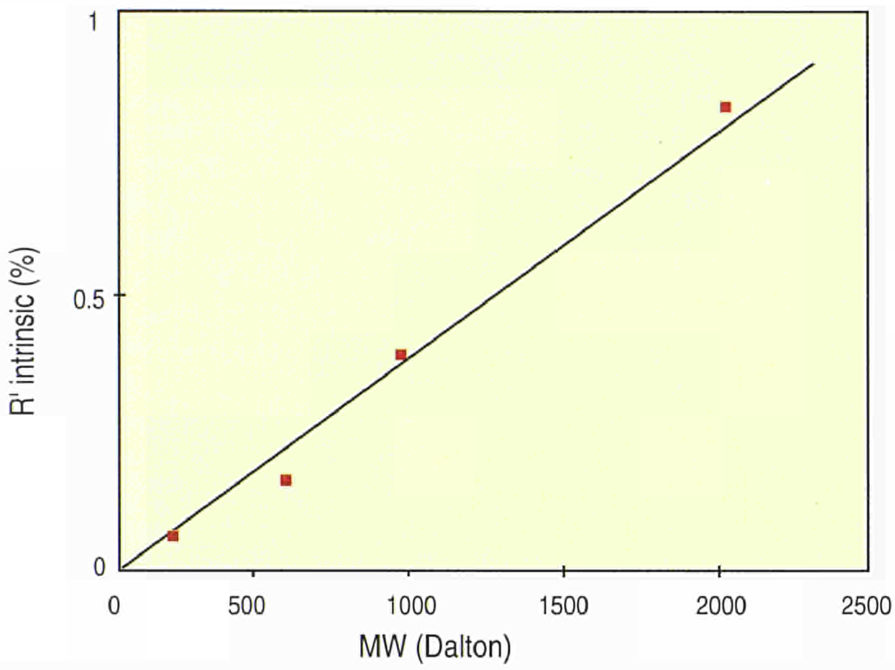


Fig.70. *Determination of the cut-off by plotting the intrinsic retention coefficient (R') against the molecular weight. Membrane = Spiral-Polyamide A; Solution = PEG 300 ppm with molecular weight 200, 600, 1000 and 2000*

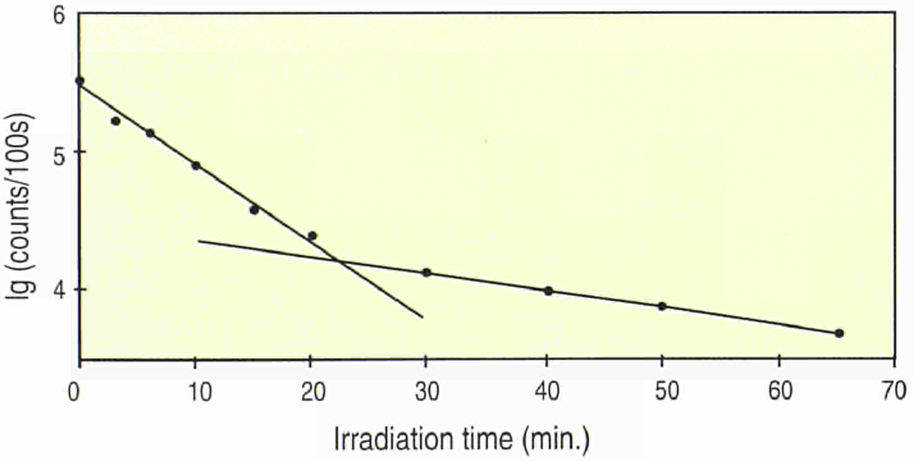


Fig.71. Decadic logarithm of the photon counts of the chemiluminescence of 10 pmol of luminol as a function of irradiation time. The diagram suggests that two first-order reactions take place and that the luminol decomposes very rapidly. The first-order reaction constants are 0.05527 $min.^{-1}$ and 0.01092 $min.^{-1}$, corresponding to half-lives of 12.5 min. and 63.5 min. respectively. Clearly, the lifetime of luminol irradiated by solar light is too short to be suitable for even short-range tracer experiments.

produce a spectrum similar to that of sunlight at ground level.

At first, the UV absorption spectra of irradiated samples were, after redissolving in methanol, compared to those of standards. Amounts of 100 µg were irradiated for up to 43 h, and no change was to be seen in the spectrum. With only 2 µg of luminol being irradiated, the spectrum had changed slightly after 7 h of sunlight irradiation and more pronouncedly after a 73 h exposition to the xenon lamp. The UV absorption spectrum is not very characteristic for a specific substance, i.e. a small change in the molecule might not show in the spectrum. Anyway, these results did not point toward a rapid decomposition of luminol, i.e. at least for a regional experiment, it still seemed stable enough.

For a comparison of the chemiluminescence intensities of irradiated and non-irradiated samples, 10 pmol, equivalent to 1.77 ng of luminol, adsorbed on a paper filter, was exposed to light. In contradiction to the previous results, these measurements demonstrated a loss of chemiluminescence intensity with increasing irradiation time Fig.71). The absolute counts obtained from 10 pmol of luminol differ from day to day, because the reagents used to trigger the chemiluminescence have to be prepared freshly every day. The 3σ detection limit achieved for luminol is about 1.2 pg.

One suggestion to explain these results is that the observed photochemical changes are only minor modifications of the molecule, which are not visible in the UV spectrum, but greatly reduce the chemiluminescence efficiency. Also the amounts used for chemiluminescence measurements are by a factor of 1,000 lower than those used for the comparison of the UV spectra, which may result in different kinetics of the photoreactions, as these occur mainly on the surface of the material, where the light intensity is highest. The importance of this becomes evident when the results of the spectra comparison of 100µg and 2µg are considered.

Inhibition of the chemiluminescence by a product formed under irradiation is not very likely, as fresh luminol added to an irradiated sample shows no significant difference in luminescence intensity. Anyway, it is clear that luminol is not fit for use as an outdoor aerosol tracer. The other two chemiluminescent substances, lophine and lucigenine, are still to be tested.
Parellel to the work described above, the idea of using gold as an aerosol tracer arose. Being a rare element (~4 ppb mean crust concentration), gold can be expected to have a low background in the atmospheric aerosol as well. Gold can be detected very sensitively by means of laser fluorescence. A detection limit in the lower femtogram range is achieved. The amount of gold on 11 filter samples of atmospheric aerosol has been measured and a mean of 11.2 pg m^{-3} with a standard deviation of ± 6.9 pg m^{-3} was observed.

Clearly, this is still a relatively high and, most importantly, variable background, but it might be possible to separate the "tracer gold" from the natural gold background. The background gold is likely to be present as an oxide, whereas the tracer could be, for example, a halide. This halide can be atomized at a lower temperature than the oxide and thus can be separated from the background. Tests with gold are planned for 1994.

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Executive Summary
1. Specific Research Programmes
2. Scientific-Technical Support for Community Policies
3. Exploratory Research
4. Third Party Work
5. Participation in EUREKA Actions
6. Appendices

4. Third Party Work

In the course of the year, the amount of work performed on behalf of third parties has decreased, due to the fact that negotiations for new contracts of high relevance in terms of both the staff and budget involved and scientific/technical content have been started. As a consequence commitments for contracts of lesser significance in the interim would have hindered further progress in the ongoing negotiations and the possibility of performing the more important work in the future.

Fig. 72. *The JRC mobile laboratory located near an air quality monitoring station of the Regione Lombardia at Bergamo.*

Fig. 73 - *Comparison of hourly NO_2 concentrations at the JRC and the station shown in Fig. 72.*

As in the past, most of the Third Party work has concerned issues in the area of air and water pollution and analytical services.

In the following sections, only the achievements related to the most significant contracts will be summarized.

Atmospheric Pollution

The three-year contract with the Regione Lombardia includes consultant support to regional authorities on air quality problems and the validation of some air quality monitoring stations in the regional sub-networks. In July 1993, the validation of 45 monitoring stations of the regional network was completed.(Figs.72- 73)

Within the framework of the research contract with CNR/ENEL on "Chemical and Physical Aspects of the Atmospheric Pollution", ground-level ozone data recorded at 17 stations distributed at different altitude in the pre-Alpine and Alpine regions in Italy, Switzerland (Ticino) and Austria (Tyrol), have been collected and organized in a database. The ozone patterns at different sites and altitude have been analysed.

Studies on the role of NO_3 radicals in tropospheric chemistry have been conducted with the main accent on the oxidation of DMS. The results are described in the sections dedicated to the laboratory studies of tropospheric chemistry

ENRESA

Within the context of the contract with Empresa National de Residuos Radioactives S.A., cross-hole migration tests were performed between two boreholes connected by a fracture in the granite aquifer of the El Berrocal site. The suitability of a natural isotopic tracer (^{79}Br) as a hydrological marker of groundwater movement, was evaluated on the basis of laboratory and field tests. This new technique for tracing groundwater movement was compared with a fluorescent dye method. The natural isotopic ratio of ^{79}Br/^{81}Br is altered by the injection of a concentrated pulse of ^{79}Br$^-$, and the breakthrough of bromide ions is followed by measuring the variation of the isotopic ratio in the recovery borehole by ICP-MS. A two-step approach was chosen: 1) a first preliminary test demonstrating the feasibility of using the enriched isotopic tracer technique for *in situ* tests; and 2) a second test directed at characterizing the permeable system and at obtaining the hydrodynamic parameters of the fracture. The natural isotopes of bromine are ^{79}Br and ^{81}Br, with a relative composition of 50.57% and 49.43%, respectively. The spike solution was prepared from a ^{79}Br-enriched KBr salt (94.1%). The concentration of bromide ions in the groundwaters at the experimental site was in the order of 10 to 90 ppb.

Small-scale laboratory infiltration experiments, with granite cored columns and repacked columns of crushed granite, showed that the change of the natural isotopic ratio ^{79}Br/^{81}Br with time can be used to monitor the tracer breakthrough. Comparison was also made with other non-sorbing tracers, such as tritiated water, chloride and iodide. Small differences in travel time of halides were ascribed to anion exclusion and ion size effects. The *in situ* migration test data demonstrated the feasibility of the technique for monitoring groundwater movement without altering the geochemistry of the site.

Field tests with non-conservative tracers are also planned. Selenium has been chosen as a possible non-conservative tracer for the following reasons: it is a natural constituent of the groundwater at the test site (thus no foreign substances have to be added); the isotopic water tracing technique can be used by injecting the non-radioactive ^{74}Se isotope and monitoring the change of the natural isotopic ratio ^{74}Se/^{78}Se (this will permit a distinction between Se present in the groundwater and Se moving as a tracer); and hexavalent Se interacts weakly with minerals, thus allowing a field migration test to be performed on a reasonable time- scale.

Water Quality

The availability of the EI scientific experience in setting up safeguarding plans and prevention pollution schemes for the rational management of surface waterbodies was requested by the Italian Ministry of the Environment.

A study, financed by the Italian Ministry of the Environment was performed, in order to fill gaps which exist in knowledge of the limnological conditions of Lake Como. The enquiry, examined six pelagic stations: Como, Argegno, Colico, Menaggio, Lierna and Lecco. Seven on-the-spot investigations were carried out, in which 900 samples were collected and a total of over 9,000 analytical determinations were made.

The research concerned the main ecosystem components:

- chemical characteristics of river waters;
- physical, chemical and biological characteristics of the lake waters;
- structure of the phytoplankton and zooplankton populations;
- lake sediments, with reference to the content of eutrophicating substances, internal P loadings, heavy metals, organochlorinated compounds and radionuclides.

The elements which are useful in evaluating the quantity of the loads of eutrophicating substances generated in the catchment basin, were also collected and analysed, to provide the information needed to reconstruct the trophic evolution of Lake Como waters. The picture which emerges from this research shows how the lake's actual trophic state is situated at the limit of eutrophy (Fig.74).

Mathematical models suggested scenarios for improving water quality as a function of possible and hypothetical reductions in the phosphorus loads.The recovery times were evaluated from the effective flow rates, i.e. the lake water stratification periods. Table 20 summarises the predictions on the evolution of concentrations in Lake Como waters. The first column indicates the average total phosphorus loads for the various objectives; the second column reports the system response times (to 95%) and the third column indicates the respective equilibrium phosphorus concentrations.

Lake Como will reach an equilibrium phosphorus concentration of 25 mg m^{-3} in 12 years, assuming an external load of 379 tP y^{-1}, starting from a concentration of 39 mg m^{-3}. A further reduction of the external load by 35% (to 250 tP y^{-1}), corresponding to a transient of 26 mg m^{-3}, would result in an equilibrium concentration of 16

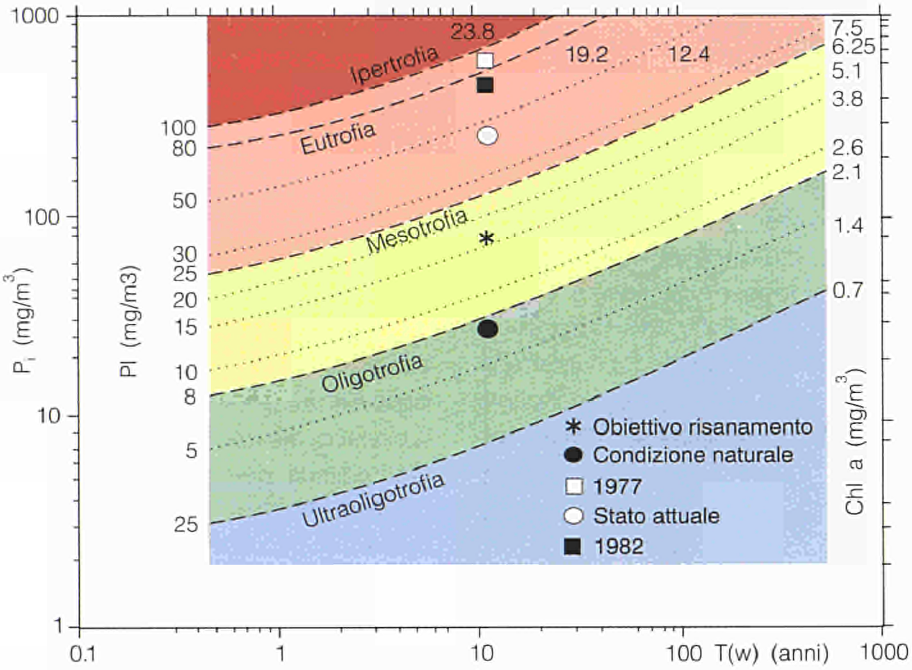

Fig. 74. Summarising diagram which correlates the concentration of incoming total P (P_i) with the total P and chlorophyll concentrations (P_l and chl a) as a function of the effective water renewal time (tw).

mg m^{-3}, reachable in about 18 years. This concentration should be assumed as a reasonable final clean-up goal for Lake Como because it would be very difficult to go below the load indicated above (250 tPy^{-1}), considering the large surface of the drainage area and the very disperse distribution of the large numbers of people living in the more mountainous part of the area. Table 20 also indicates the objectives which could be reached for the three basins, i.e. concentrations of 22 mg m^{-3} for the western basin, 16 mg m^{-3} for the eastern basin, and 14 mg m^{-3} for the northern basin.

From the analysis of the data, it emerges that the western basin will respond to the clean-up action more slowly than the other basins, and thus this part of the lake will be more sensitive to pollutant loads.

	PHOSPHORUS LOADS FOR VARIOUS OBJECTIVES (tP · Y^{-1})			RESPONSE TIME (Years)			CONCENTRATION OF P IN THE LAKE AT EQUILIBRIUM (mg· m^{-3})		
	A	B	C	$t_{1/2}$	t_p	T (min-max)	A'	B'	C'
Whole lake	379	250	190	7.7	1.52	12 - 18	25	16	14
Western basin	166		95	8.0	1.93	15 - 26	34	(22)	19
Eastern basin	40		35	6.0	1.56	10 - 12	17	(16)	15
Northern basin	225		113	7.7	1.10	9 - 11	25	(14)	12

A : actual load, initial concentration of 39 mg m^{-3} (whole lake), 50 mg m^{-3} (western basin), 33 mg m^{-3} (eastern basin), 31 mg m^{-3} (northern basin).
B : load reduced by 35% with respect to 1992, initial concentration in the lake of 26mg m^{-3}.
C : load halved with respect to 1992, concentration in the lake ot 20 mg m^{-3}.
A' : equilibrium concentrations with respect to the loads listed in A.
B' : transient concentrations with a total P load of 250 t y^{-1}.
C' : equilibrium concentrations wlth the loads halved with respect to 1992.

Table 20. Scenarios of phosphorus load reduction in lake Como.

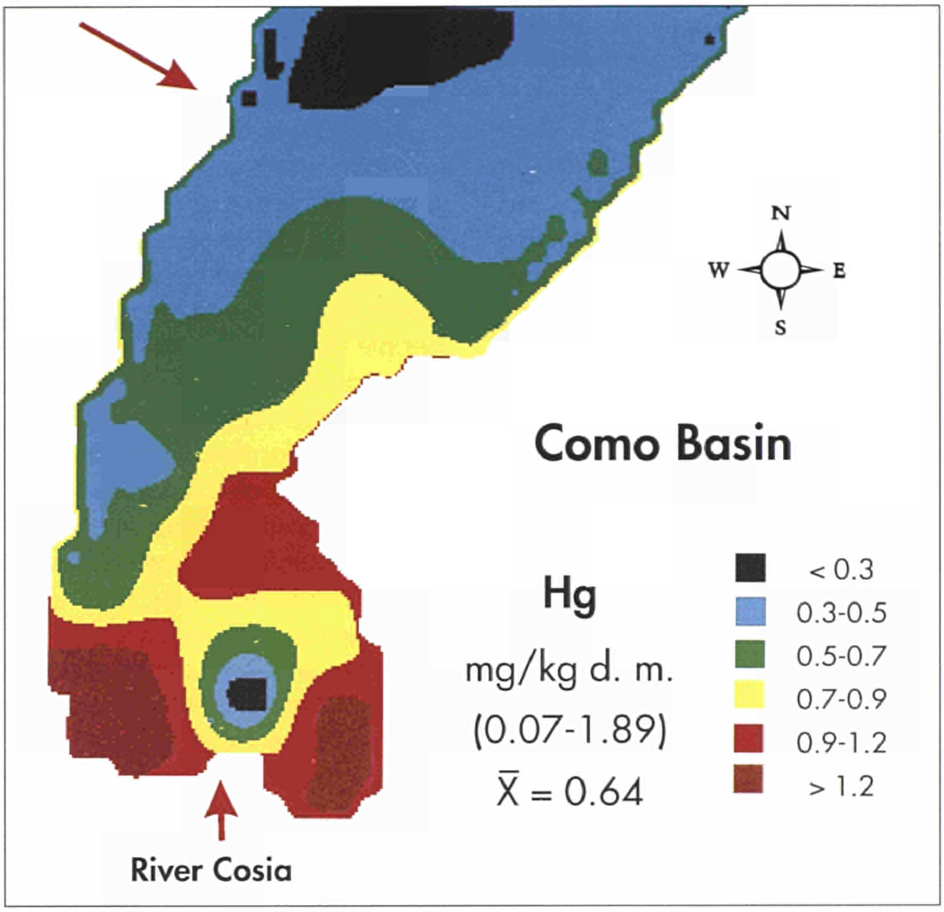

Fig. 75. Spatial distribution of Hg in the Southern-west part of lake Como.

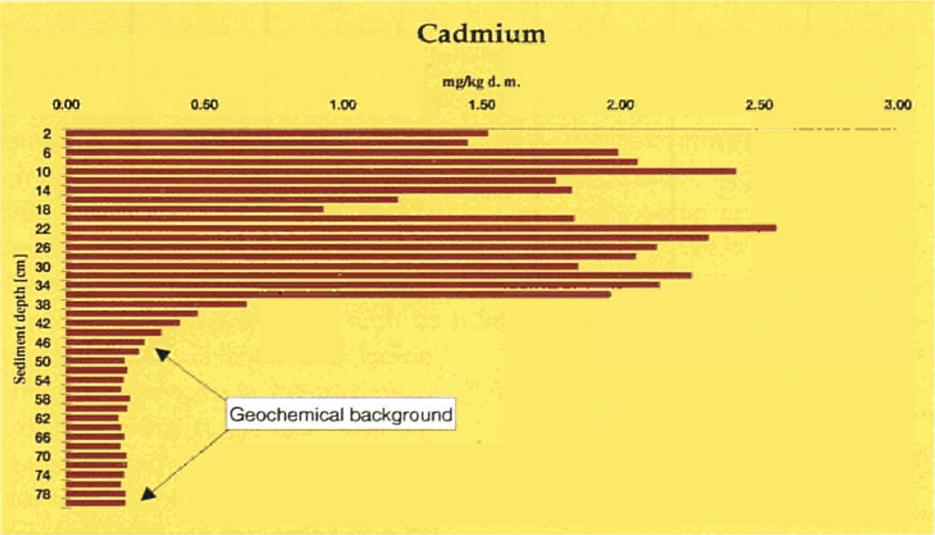

Fig. 76. Temporal development of metal deposition on the lake bottom.

This prediction model should contribute to a revision of the intermediate and final objectives of the 1984 Water Clean-up Plan of the Lombardy Region, which used, with the "cold" planning approach, to indicate an intermediate objective of 14.1 mg m^{3} and a final objective of 9.4 mg m^{3}.

Work in the context of the contract agreed in 1992 with Azienda Comasca Servizi Municipalizzati di Como, has been completed. The inventory-taking of harmful substances present in the southern-west part of Lake Como, included the monitoring of the two major feedings rivers, the spatial distribution (Fig. 75) as well as the temporal development of metal deposition on the lake bottom (Fig. 76), and the assessment of metal and nutrient fluxes across the sediment-water interface.

In the framework of the contract agreed in 1992 with the Italian Research Council regarding the Venetian Lagoon Project, work has continued to analyze the spatial distribution of metals, nutrients and organic micropollutants, such as persistent organochlorine compounds, in the sediments of the Venice city channels.

Surprisingly high concentrations of mercury up to 12 mg kg^{1}, cadmium up to 17.4 mg kg^{1}, and zinc up to 2,889 mg kg^{1}, were found, as well as DDT and DDE, up to 233 and 76 µg kg^{-1}. PCBs were also present at remarkably high concentrations in several areas of the city.
Numerous requests to assist national laboratory groups in their attempts to improve measurement quality were received.

The contract agreed 1992 with

Regione Emilia Romagna for the organization of proficiency testing exercises of drinking water analysis entered into its second phase. Two further exercises were organized for some metals, such as Hg, Cd, Pb, As, Cr, Cu, Zn, and other compounds, such as nitrates, sulphates, chlorides, phosphates and ammonium. Laboratory responses were satisfactory for some of these, while others (Hg, Pb, Cd, As, NH_4^+) need further study.

Ente Autonomo del Flumendosa, Cagliari agreed with the EI a contract for the organization of internal quality control for its own laboratories and the first exercises have been run.

The competence of the EI in the field of environmental reference material production prompted further requests. Two sludge materials and three soil materials were produced for different customers, intended for the certification of metal contents. One sediment material intended for the testing of the European Procedure for sequential metal extraction has been produced for the University of Barcelona.

The preparation of lichen reference material has been completed for the IGB Bern.

The Research Council Institute of Pallanza requested the analysis of a second batch of 28 fish samples for mercury and other trace elements. This work was sponsored by the "Commissione Italo-Helvetica per la protezione delle acque comuni".

Analytical Measurements and Quality Control

In the context of international collaboration concerning the BOREX experiment at the Gran Sasso Underground laboratories, the specfic task of the EI is the determination of ultratrace impurities in various materials. During this year, some of the measurements have been performed by using the ETV-ICP-MS technique. The advantage of the method is the possibility of the direct determination of the impurities in organic liquids and solid samples, without any treatment (chemical or preconcentration). In this way, the risk of contamination of the material is greatly reduced.

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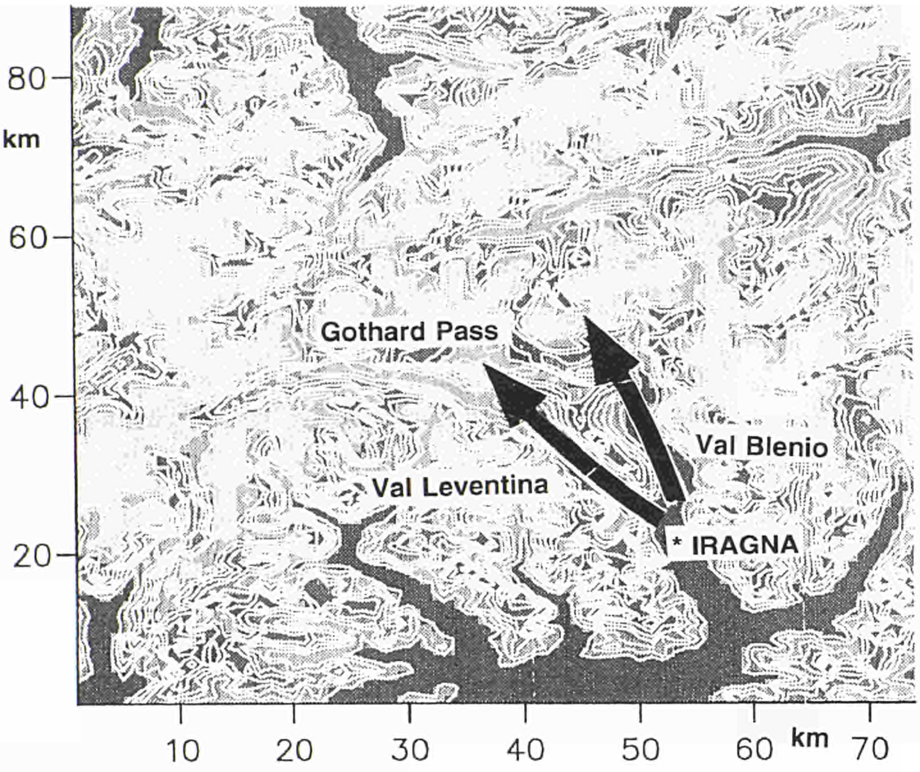

Fig. 77a. The 1989 campaign.

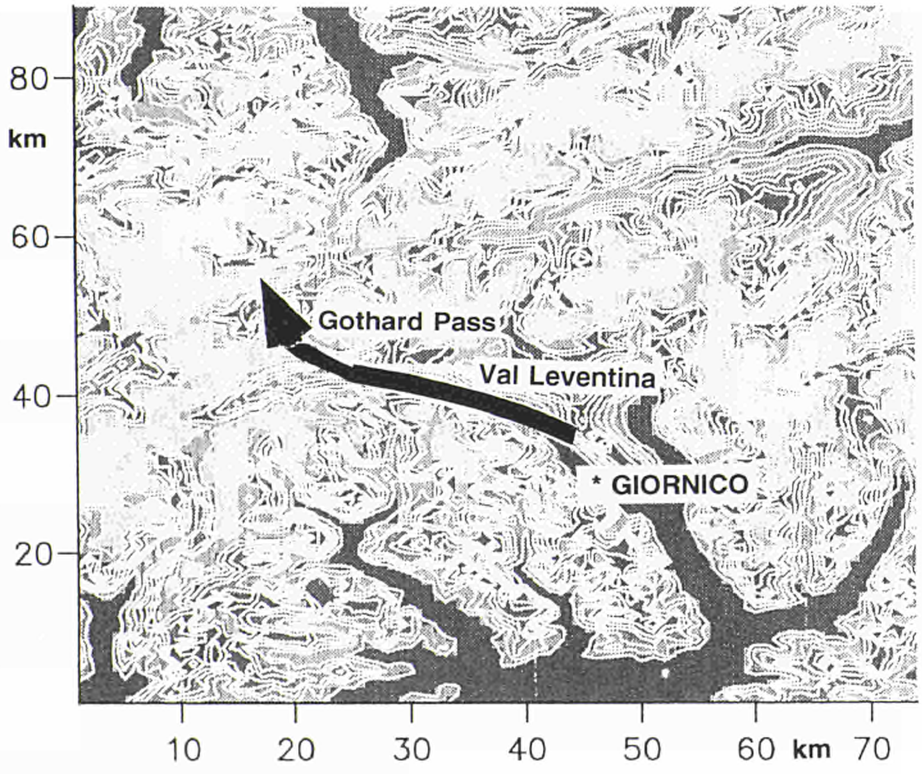

Fig. 77b. The 1990 campaign.

Activities related to EUREKA environmental projects have been continued. These have mainly concerned EUROTRAC and EUROENVIRON, i.e. the joint european research project on the impact of human activity on tropospheric chemistry, and the wide scope european project for the development of new technologies and processes for the protection of the environment. In the following sections, the most significant achievements for the subprojects EUROTRAC /TRAC, EUROTRAC / LACTOZ and EUROENVIRON/MOBILE ANALYTICAL LABORATORY will be summarized.

EUROTRAC/TRACT - TRANSALP

Activities under the EUREKA-TRACT programme on atmospheric transport on complex terrains continued. No tracer release was carried out in the Transalp project (to test transport over the Alps), and activities were essentially devoted to organizing the database of the three earlier Transalp releases and data interpretation by mesoscale models.

The data base, including the topography, meteorological observations, measurements from aircraft and tracer concentrations at the ground samplers, has been completed for the three TRANSALP campaigns (October 1989, September-October 1990 and September 1991) and is now available to the scientific community. It is hoped that this will encourage interpretative use and modeling work on the complex problem of mesoscale air mass circulation in elevated mountainous areas. In Figs. 77a, b and c, the geographical domain where the three campaigns were conducted is shown, together with

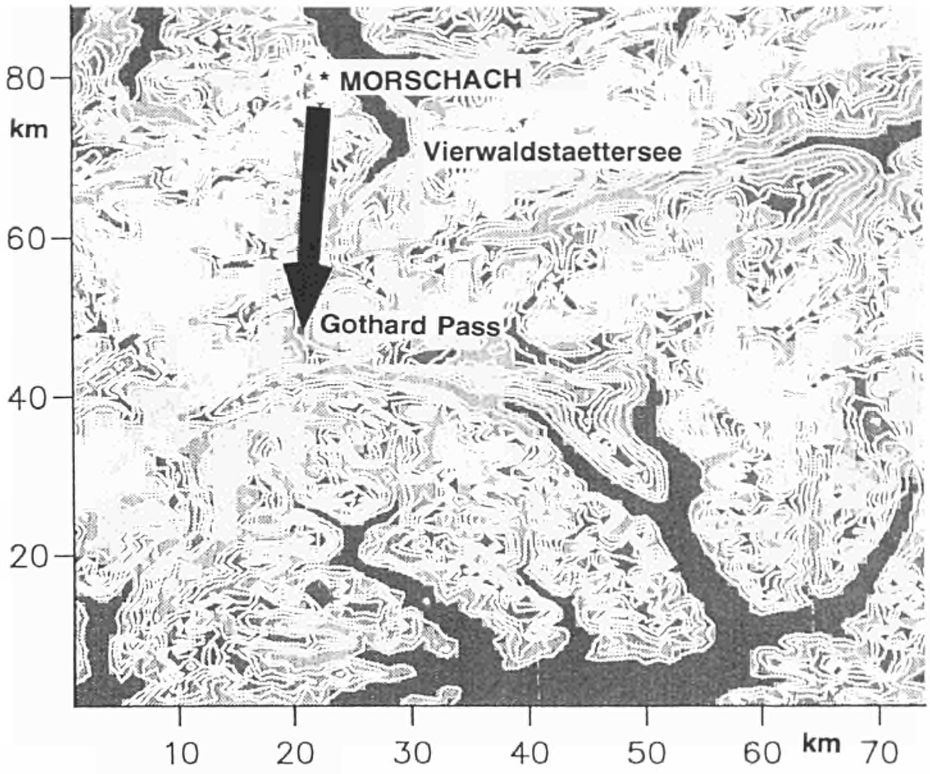

Fig. 77c. The 1991 campaign.

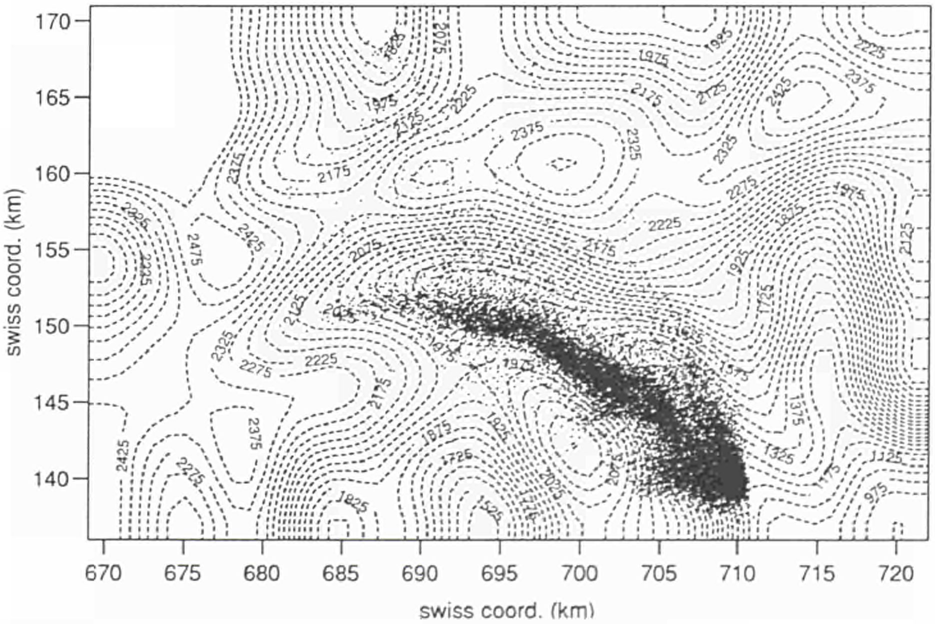

Fig. 78. Tracer cloud evolution at 11:00 UTC, 29.9.1990.

the tracer release locations and the main direction for tracer displacement.

In order to determine the flow over the terrain during the experiment, use was made of information obtained in the meteorological measurements at ground level and of the wind profiles from the two SODAR. These data were introduced in a diagnostic mass consistent model, CONDOR. The results of CONDOR are windfields satisfying the mass conservation equation and the boundary conditions.

The dispersion of the tracer was obtained by the recently improved model, MONTECARLO, which is a Lagrangian particle model for complex terrain that is based on a recent quasi-homogeneous solution of the Langevin equation, suitable for convective atmosphers. The inputs for the model are the windfields produced by CONDOR, the orography of the domain considered, and information on turbulence that can be deduced from measurements.

Preliminary calculations have been performed that indicate that the main features of the cloud evolution are simulated by the coupled use of the two models. Figure 78 shows the position of tracer particles in the Leventina valley, two hours after the beginning of the release and just after the end of emission period.

EUROTRAC/LACTOZ

The main objective of this project is to provide kinetic and mechanistic data for modelling the chemistry of the troposphere. Laboratory studies have been continued on the oxidation of isoprene and aromatics.The results for 1993 are described in the fisrt section of this report (Tropospheric Chemistry).

EUROENVIRON/Mobile Analytical Laboratory

Within the framework of Eureka Project EU674 (Advanced Mobile Analytical Laboratory (AMAL) belonging to EUROENVIRON, two mobile units have been constructed for participation in monitoring campaigns early in 1994. The AMAL combines the latest in analytical techniques with sophisticated new methods of sample collection, sample holding and data transfer.

The first field campaign, near Milan (Brembate), will provide the first test of the complete system under field conditions.

The targets of the Brembate campaign are:

- in-field tests of transportable instruments and of the mobile vans;
- in-field comparison of various analytical methods, in particular XR and ICP-MS for elements, GC and GC-MS for organic pollutants;
- preliminary tests of *in situ* organic pollutant measurements, in particular the use of membrane introduction mass spectrometry;
- verification of the teamwork, with special reference to the Quality Assurance procedures and their application to the AMAL staff.

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6. Appendices

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Glossary of Acronyms and Abbreviations

ACE
Aerosol Characterization Experiment

ALVPD
Air-to-Leaf water Vapor Pressure Deficit

AMAL
AdvancedMobileAnalytical Laboratory

ASE
Amplified Spontaneous Emission

ATC
Anatonical Therapeutic Code

BEMA
Biogenic Emissions in the Mediterranean Area

BIBEX
Biomass Burning Experiment

BOD
Biologic Oxygen Demand

BTX
Benzene, Toluene, Xylene

CAS
Chemical Abstract Service

CB
Chlorinated Biphenyl

CCD
Charge Coupled Device

CCN
Cloud Condensation Nuclei

CD
Criteria Document

CD-ROM
Compact Disc - Read Only Memory

CDS
Coding Decoding Software

CEN
European Standardisation Committee

CF-FAB
Continuous Flow - Fast Atom Bombardment

CF-FAB-MS
Continuous Flow - Fast Atom Bombardment - Mass Spectrometry

CFN
Swedish National Board for Laboratory Animals

CIS
Confederation of Indipendent States

CMC
Critical Micellar Concentration

CN
Condensation Nuclei

CNR
Italian National Research Council

CNRS
French National Scientific Research Council

COLIPA
Committee of the Association of Perfume, Cosmetic and Toiletry Industries

CPN
Cloud Processed Nuclei

CSTR
Continuous Stirred Tank Reactor

DDE
Dichloro Diphenyl - Ethylene

DDT
Dichloro Diphenyl - Trichloroethane

DMS
Dimethylsulphide

DOAS
Differential Optical Absorption Spectrometry

DOC
Dissolved Organic Carbon

DOM
Dissolved Organic Matter

DU
Dobson Unit

DTA
Differential Thermal Analysis

EASOE
European Arctic Stratospheric Ozone Experiment

EC
European Community

ECA
European Collaborative Action

ECB
European Chemicals Bureau

ECDIN
European Chemical Data Information Network

ECITTS
ERGATT/CFN Integrated Toxicity Testing Scheme

ECPHIN
European Pharmaceutical Information Network

ECURIE	European Community Urgent Radiological Information Exchange system
ECVAM	European Centre for the Validation of Alternative Testing Methods
ED	Electro Dialysis
EI	Environment Institute
EINECS	European Inventory of Existing Chemical Substances
EFTA	European Free Trade Area
EIPO	European IGAC Project Office
EMEA	European Medicinal Evaluation Agency
EMEP	Evaluation Monitoring European Pollution
ENEL	Italian Electricity Board
ENRESA	Empresa National de Residuos Radioactives S.A.
EOWAS	European Office for Wine Alcohol and Spirit drinks
EPA	Environmental Protection Agency
ERGATT	European Research Group for Alternatives in Toxicity Testing
ETEX	European Tracer Experiment
EUCLID	European Chemicals Inventory Database
ETV-ICP-MS	Electro Thermal Vaporisation - Inductively Coupled Plasma Mass Spectrometry
EU	European Union
EWC	European Waste Catalogue
EXAFS	Extend X-ray Fine Structure
FAB	Fast Atom Bombardment
FAB-MS	Fast Atom Bombardment - Mass Spectrometry
FAO	Food Agricultural Organisation
FCM	Flow Cytometry
FRAME	Fund for the Replacement of Animals in Medical Experiments
GC-ECD	Gas Chromatography - Electron Capture Detector
GC-MS	Gas Chromatography - Mass Spectrometry
GIS	Geographic Information System
GLOCHEM	Global Atmospheric Chemistry survey
HA	Humic Acid
HEDSET	Harmonized Electronic Data Set
HPLC	High Performance Liquid Chromatrography
HS-GC	Head Space - Gas Chromatrography
HS-SPME	Head Space - Solid Phase Micro Extraction
HTAB	Hexadecyl Trimethyl Ammonium Bromide
HTO	Tritiated Water
IAEA	International Atomic Energy Agency
ICSE	International Chemical Safety Card
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
IDA	Interchange of Data between Administrations

IGAC
International Global Atmospheric Chemistry

IMAD
Integral Model for Aerosol Dynamics

IR
Infra Red

ISO
International Standards Organisation

IT-MS
Ion Trap - Mass Spectrometry

JRC
Joint Research Centre

KIAE
Kurchatov Institute of Atomic Energy

LDH
Lactate Dehydrogenase

MAGE
Marine Aerosol and Gas Exchange

MBL
Marine Boundary Layer

MF
Micro Filtration

MILOX
Mid - Latitude ecosystems as sources and sinks for atmospheric Oxydants

M ITO
Microphyte Toxins

MS
Mass Spectrometry

MSA
Methane Sulphonic Acid

NACE
General Nomenclature of the Economical activities of the European Community

NARE
North Atlantic Regional Experiment

NCD
New Chemical Database

Nd-YAG
Neodymium - Yttrium Aluminium Garment

NH
Northern Hemisphere

NILU
Norsk Institut Luftorskning

NMR
Nuclear Magnetic Resonance

NR
Neutral Red

NRU
Neutral Red Uptake

OA
Okadaic Acid

OECD
Organisation for Economic Cooperation and Development

OEL
Occupational Exposure Limit

OPC
Ordinary Portland Cement

OSI
Open System Interconnection

PAN
PeroxyAcetyl Nitrate

PCB
Poly Chloro Biphenyl

PEG
Polyethilene Glicol

PFC
Per Fluoro Carbon

PM
Particulate Matter

POM
Particulate Organic Matter

PUF
Polyurethane Foam

PVA
Poly Vinyl Alcohol

QSAR
Quantitative Structure Activity Relationship

REM
Radioactive Environmental Monitoring

RF
Relative Fluorescence value

RNA
Ribonucleic Acid

RO
Reversed Osmosis

SDS
Sodium Dodecyl Sulphate

SERS
Surface-Enhanced Raman Scatterring

SESAME
Second European Stratospheric Arctic Mid-latitude Experiment

SFE
Supercritical Fluid Extraction

SPC
Summary of Product Characteristics

SPM
Suspended Particulate Matter

SPME
Solid Phase Micro Extraction

SVOC
Semi Volatile Organic Compound

TDL
Tunable Diode Laser

TRAGEX
Trace gas exchange

TVOC
Total Volatile Organic Compound

UF
Ultra Filtration

UHT
Ultra High Temperature

UNEP
United Nations Environmental Program

UV-B
Ultra Violet- B

VOC
Volatile Organic Compound

VSC
Volatile Sulphur Compound

WHO
World Health Organisation

WRAC
Wide Range Aerosol Classifier

XRD
X-ray Diffraction

European Commission

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The Annual Report of the Environment Institute of the Joint Research Centre summarizes the major achievements in the projects developed in the course of the year 1993 as a part of the three year (1992-1994) multiannual research programme of the Joint Research Centre.

The Institute's efforts have been addressed essentially to the implementation of the specific programme "Environmental Protection" with emphasis on issues related to Global Change and to Environmental Chemicals, and have concerned air and water pollution, indoor air pollution, chemical waste, food & drug analysis, evaluation of chemicals.

Large space is reserved to the description of the progress accomplished in the activities as scientific and technical support to the Commission's Services which are assuming a steadily increasing significance in the Institute's programmes for what it concerns the support to the General Directorate XI (Environment, Nuclear Safety and Civil Protection).

This has concerned the areas of chemicals, air and water pollution, chemical waste, radioactive environmental monitoring and the validation of toxicity testing methods alternative to those implying the use of animals.

The report is completed by sections summarizing the achievements in the framework of the exploratory research, of the participation into EUREKA projects as well as of the contractual work for third parties, and with most relevant data concerning the Institute structure and financial resources.

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