ANNUAL·REPORT·91

Environment Institute

JOINT
RESEARCH
CENTRE

COMMISSION OF THE EUROPEAN COMMUNITIES

EUR 14631 EN

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Contents

The JRC Environment Institute

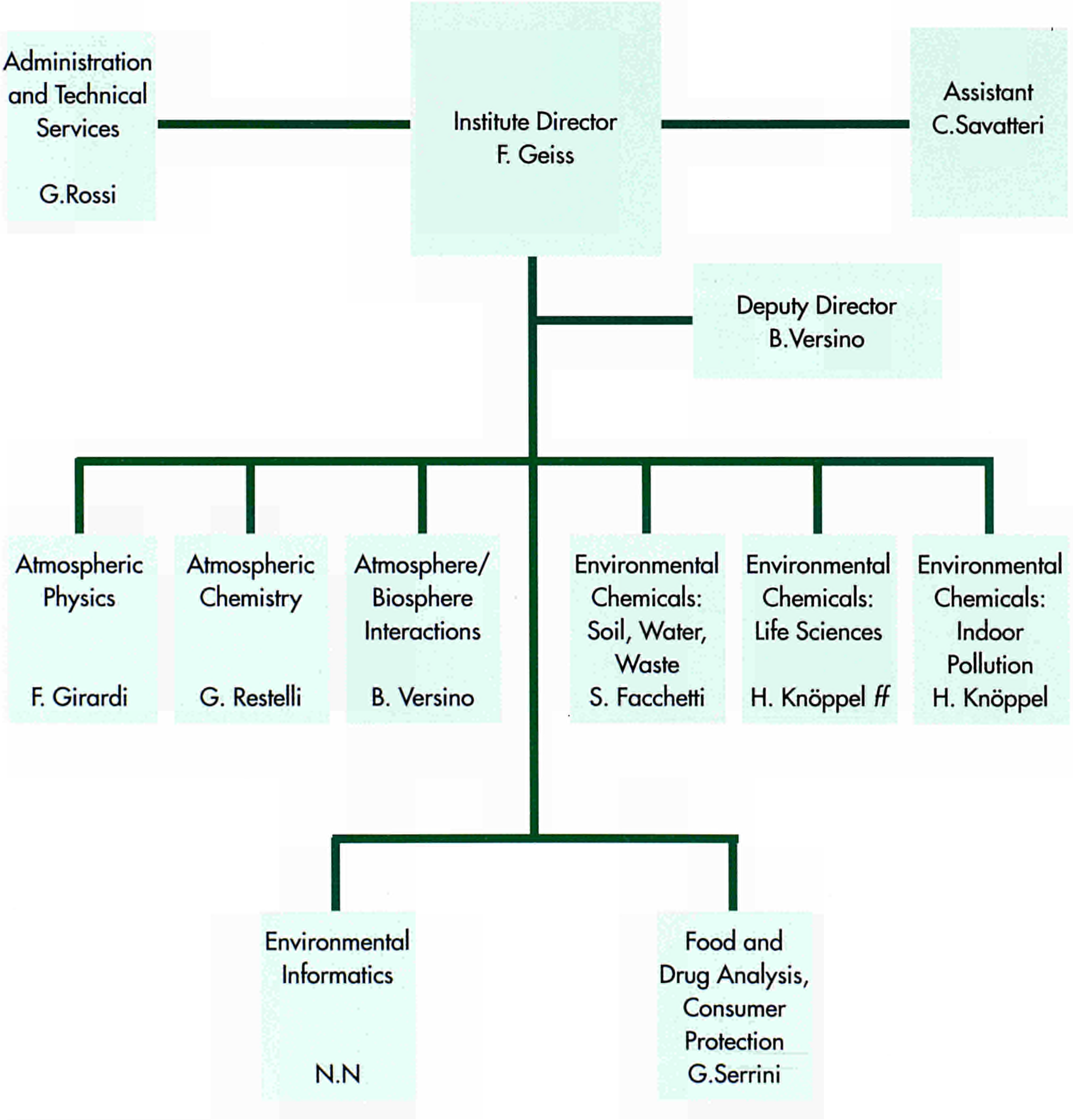
The Environment Institute has a total staff of 245 of which 66 have university degrees.

The broad array of disciplines represented, including chemistry, chemical engineering, physicis, meteorology, soil science, geology, botany, ecology, toxicology, mathematics, informatics, nuclear engineering, reflects the interdisciplinary setting of the Institute and its research projects. It is structured in eight scientific units:

- Atmospheric Physics
- Atmospheric Chemistry
- Atmosphere-Biosphere Interactions
- Environmental Chemicals: Soil, Water, Waste
- Environmental Chemicals: Life Sciences
- Environmental Chemicals: Indoor Air Pollution
- Food & Drug Analysis
- Environmental Informatics

plus a unit comprising the administrative and technical services.

A scheme of the Institutes organization is given below.



Institute organigramme

The Environmental Informatics unit has not yet been set up, the appropriate staff are expected to be available in 1992.
Some twenty five percent of the Institute activities has been geared to scientific and technical support to other Commission services, in particular to the the Directorates General Environment, Agriculture, Internal Market, Consumer Protection and Social Affairs/Health.
The research activities have been focused on the programme "Environmental Protection", proper emphasis being given to topics closely linked within the framework of the more general theme "Global Climatic Change" which is going to constitute a major research area for the Institute in the coming years.

Of equal significance have been the topics included in the area of the "Environmental Chemicals" and of the "Food and Drug Analysis". The latter fits well to the Institute physionomy because of its long-standing focus on and broad experience in all fields of analytical chemistry.

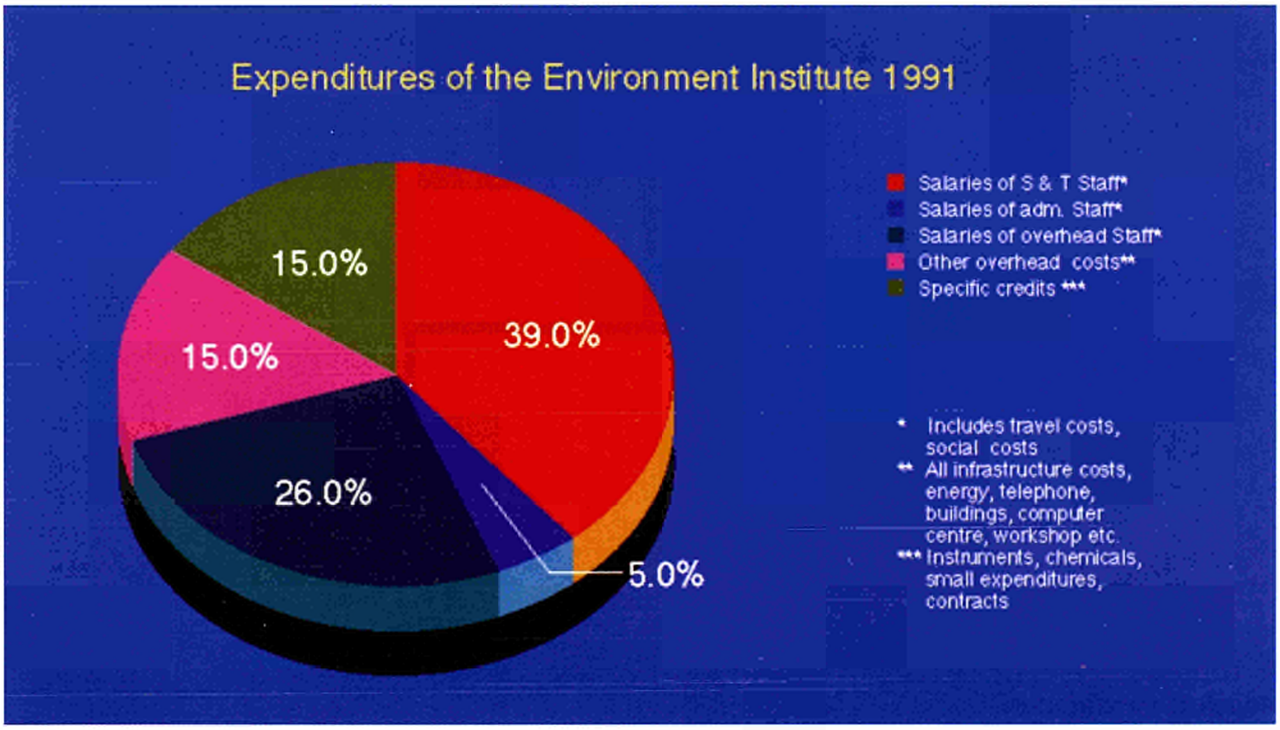
Research activites in the field of nuclear waste have been further decreased to the extent that it can be confidently affirmed that the shift of the relevant competences towards soil conventional pollution problems has been completed.

As the multiannual programm 1988-91 of the JRC has been concluded by 31 December 1991, the annual report has kept the same structure as for the preceeding years, the activities which are presented here being the logical follow up.

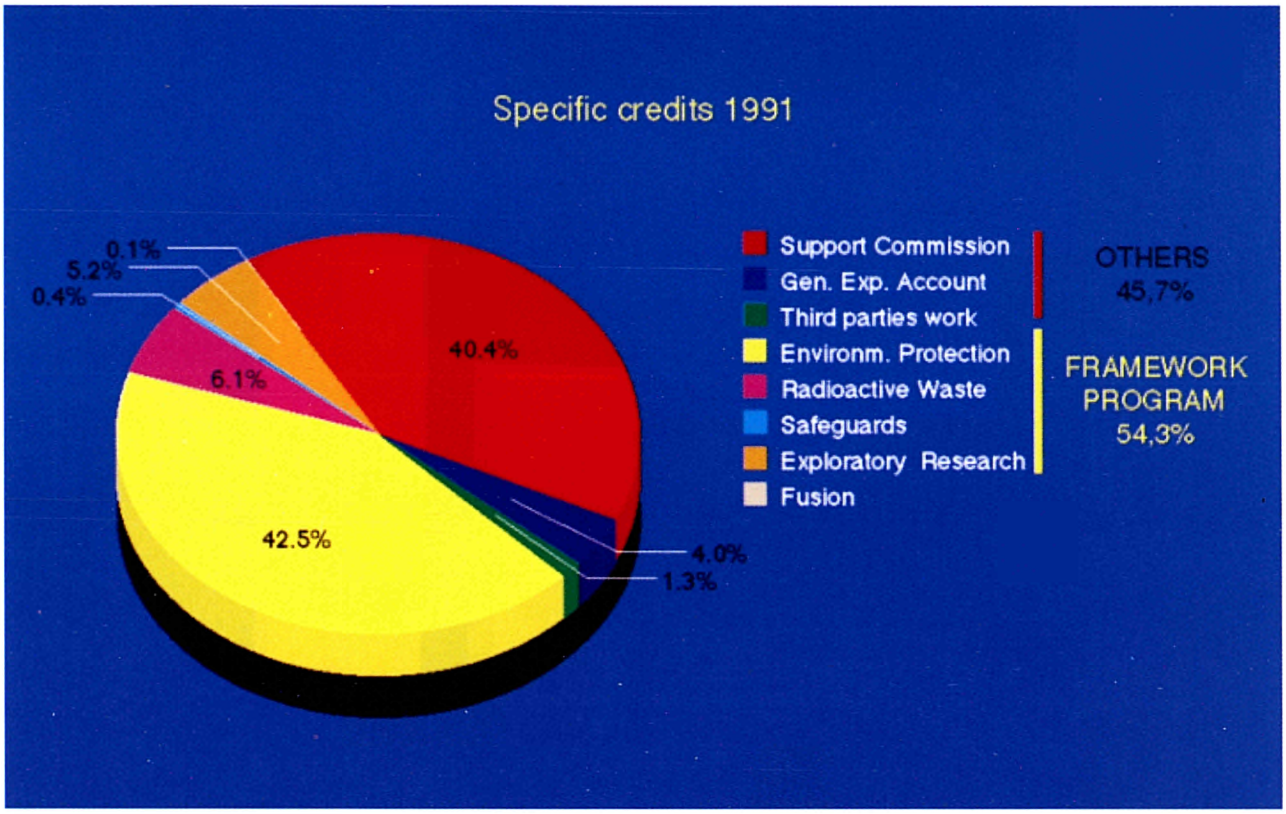
Thus the results and the progress accomplished for the various projects are presented according to the research areas in which they are included rather than to the scientific units where they are tackled.

Section 1 summarizes the achievements for the projects included in the Specific Research Programme, while relevant information concerning the scientific and technical support to the Commission Services are presented in Section 2. Section 3 and 4 are dedicated to the progress accomplished in the projects included in the Exploratory Research and to the contract work for third parties respectively.

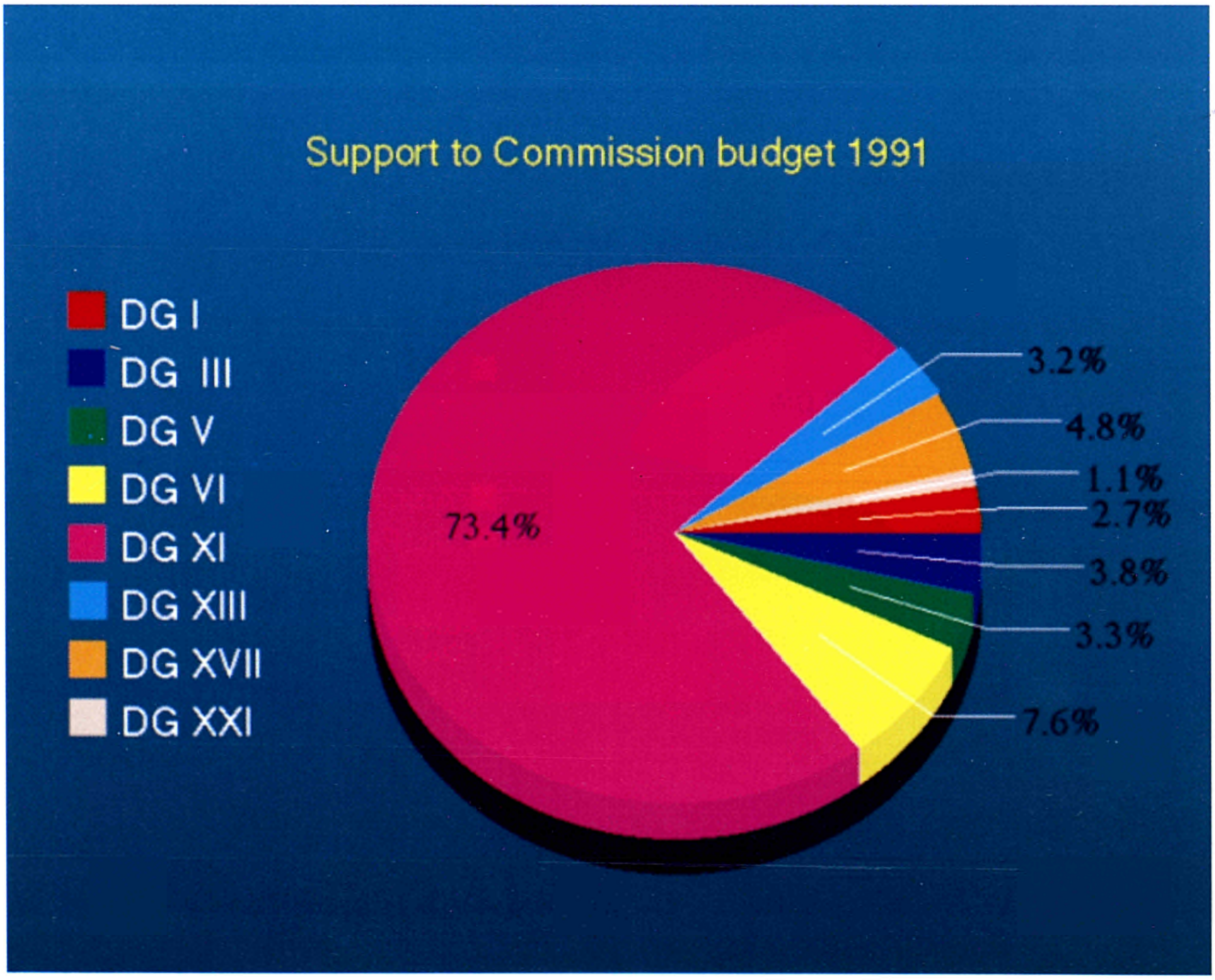
For sake of completeness some statistics concerning the staff, the research activity and significant budget data are given prior to the description of the scientific results. It is hoped that this will help in assessing both the Institute capabilities and the value of its research output.

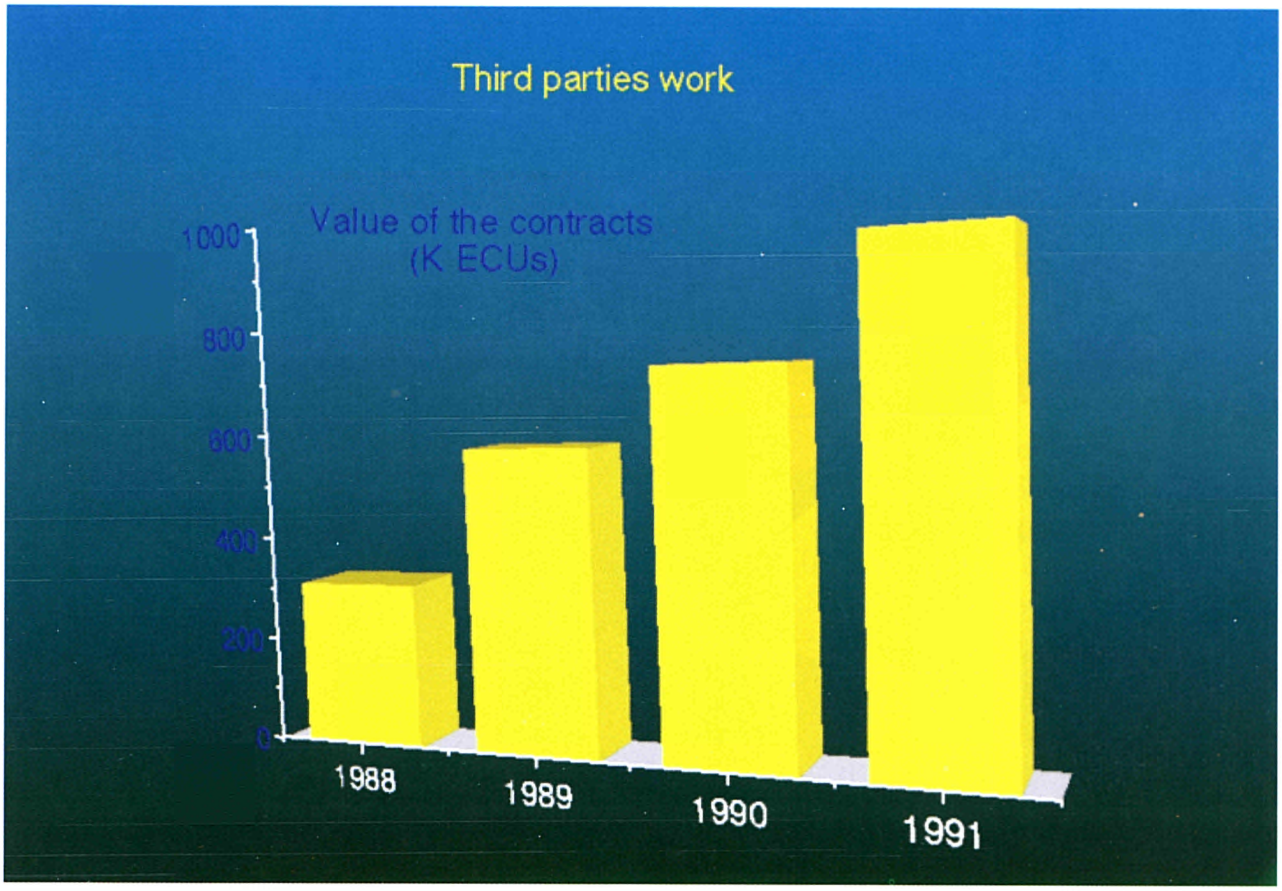


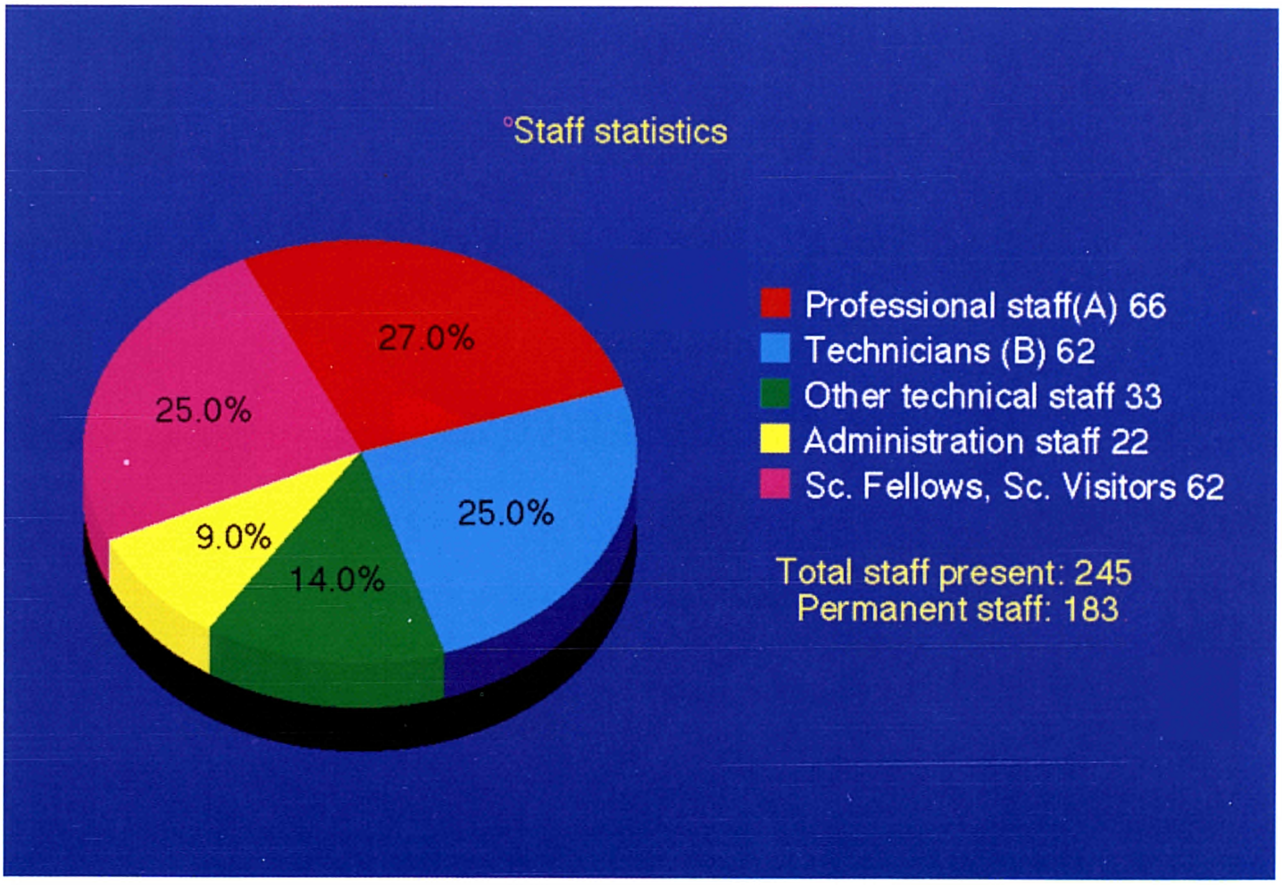
Specific credits 1991



Support to Commission budget 1991




Third parties work


Staff statistics

🟥 Professional staff(A) 66
🟦 Technicians (B) 62
🟩 Other technical staff 33
🟨 Administration staff 22
🟪 Sc. Fellows, Sc. Visitors 62

Total staff present: 245
Permanent staff: 183

Executive Summary

1

Specific Research Programmes

This report summarizes the main achievements in the research activities of the Environment Institute in the course of 1991. As this has been the last of the four-year programme (1988-91), the results are still presented following the same scheme of the preceeding annual reports.

Thus, Chapter 1 summarizes the results of the Specific Research Programmes according to the main research areas included in them and to which the Institute has been contributing, i.e. :

- Environmental Chemicals;
- Air Pollution;
- European Monitoring Network;
- Water Quality;
- Chemical Waste;
- Environmental Studies of the Mediterranean Basin;
- Food & Drug Analysis;

included in the Environmental Protection programme, and

- Safety of Final Storage in Geological Formations;

included in the Radioactive Waste Management programme.

1.1 Environmental Protection

ENVIRONMENTAL CHEMICALS

This research area includes three activities:

- **ECDIN,**
- **Indoor Air Pollution,**
- **Trace Metal Health Effects.**

As regards **ECDIN** (Environmental Chemical Data and Information Network), the content of the data bank has been expanded by the addition of an existing data base on water solubility of about 4.000 organic compounds while several data files - in particular concerning toxicology, waste legislation and chemical economy - have been updated and improved.
A first CD-ROM version of ECDIN (1.800 compounds) for use with personal computers has been made available.

The Institute's research activities on **indoor air quality** problems are focused on organic indoor pollution. Work performed in 1991 was aimed at validating a chamber method for the determination of emissions of volatile organic compounds (VOC) from indoor materials and products, and models for describing the concentration vs. time profiles of the emitted compounds. In addition work for validating sampling of polar and unpolar VOC on hydrophobic sorbents has been continued. The development of a method for the determination of semivolatile organic compounds (SVOC) in indoor air has been initiated.

The activity **trace metal exposure and health effects** has been re-oriented to include:

- the EURO TERVIHT project (Trace Element Reference Values in Human Tissues), developed to establish and compare baseline values of trace elements in inhabitants of the EC;

- the TRACY project, developed in the framework of EUREKA (EUROENVIRON EU 618) with the aim to establish trace element reference values in body fluids;

- new approaches in occupational health-related studies including the aspect of multiple trace metal exposure in workers in hard metal industry (Co,W,Cr,Ta,Nb,V,Mo,Ni) and studies on possible relations between microexposure to metals and certain diseases occurring in the later stage of life (cardiovascular, neurological, immunological diseases, effects on reproductive system).

- in vitro toxicity testing - aimed at reducing the number of animal tests - which includes the use of subcellular preparations, isolated cellular components and cell culture systems for the screening tests on cytotoxicity and morphological transformation of metal compounds in relation to their uptake, intracellular distribution and biotransformation (dose-effect relationships).

AIR POLLUTION

In continuation of the previous work on the **atmospheric chemistry of terpenes** the activities in 1991 were focused on the study of selected terpenes with regard to their ability to form ozone in the NOx-photochemical system. Preliminary results indicate, that at the concentrations levels used in these studies (terpenes: 80-250 ppb, NO:10-20 ppb) terpenes suppress ozone formation. Moreover, changes in NO-concentration influence the formation of ozone rather than changes in the concentration of the hydrocarbons used in the experiments.
At [HC] / [NO] constant ratio, about 100% increase of [NO] results in about 100% increase of [O_3]. Relative humidity plays only a minor role on the amount of O_3 formed during the irradiation of terpene / NO mixtures.

The experiments on **trace gas exchange of tree canopies** in Continuous Stirred Tank Reactor (CSTR)-systems focused on simultaneous monitoring the mass balance of photosynthetic gas exchange, of biogenic hydrocarbon emissions, and of pollutant deposition. Preliminary results demonstrated that trace gas exchange is dominated in dry conditions by stomatal conductance, which in turn is controlled by radiation and soil water supply. After technical improvements the studies were then focused on low level, continuous exposure of spruce canopies (cloned Picea abies), in dry conditions, to SO_2 and O_3, either alone or in combination, to investigate methodical aspects and the biological/physical relation between photosynthetic gas exchange and pollution deposition.

Laboratory studies of **kinetics and mechanisms of tropospheric reactions** controlling the chemical fate of biogenic and anthropogenic emissions as well as the oxidative capacity of the polluted troposphere have led to further steps in the analysis of NO_3-initiated reactions. The nighttime oxidation of **isoprene** by NO_3 leads to the predominant formation of organic nitrates, contrary to the daytime OH-initiated degradation of isoprene, which has unsubstituted carbonyl compounds as principal products. In particular, the nitrate radical adds preferentially to the 1- position and 3-methyl-4-nitroxy-2-butenal appears to be the main product. The nighttime oxidation of isoprene by NO_3 may then have consequences for the tropospheric NOy budget.

Studies of the reaction of NO_3 with a series of **organosulphur compounds** with the structures RSH, RSR', RSSR' (R=H, CH_3, C_2H_5) in air, show that alkylsulphonic acids, SO_2 and H_2SO_4 are the main sulphur containing products and that relatively stable peroxy-nitrate intermediates (tentatively: $RS(O)O_2NO_2$) are always formed. The peroxy-nitrate intermediate reacts with liquid water to form the alkylsulphonic acid as the main product, thus modifying the partitioning between the oxidized sulphur products as resulting from the gas phase reaction only.

The operation of the pilot plant for the **Ispra Mark 13A** process for flue gas desulphurisation in Sarroch (Sardinia) has been temporarily suspended due to organizational and financial problems of the main contractor. During 1991 an extensive search for a new partner with a strong chemical engineering background began.
In the bench scale plant at the JRC Ispra studies about aerosol formation and about the effects of impurities on the performance of the electyrolysis were successfully carried out. The work on the removal of nitrogen oxides from waste gases resulted in the development of a new denoxing process, which produces a concentrated stream of NO and H_2, suitable as a starting product for the production of hydroxylamine. A patent application was filed and laboratory scale work performed. As a side line of the work on electrolytic denoxing, a

new process for the electrolytic removal of nitrates from waste waters was identified. This new process was tried out in a bench-scale equipment with promising results.

EUROPEAN MONITORING NETWORK

A 26-year (1868-1893) data series of **daily ozone observations** made by the Schönbein technique at Moncalieri, near Turin, has been discovered. Data have been converted to present day concentration following an ad-hoc developed procedure. From these data it could be concluded that: (1), in agreement with the Montsouris data series, the present-day levels are 2-3 times as large as one century ago and (2), an increase in ozone levels of the same order of magnitude is also observed in the free troposphere.The analysis of historical data has been expanded to observations made around 1880-1890 in South America. From this study it could be infered that one century ago at 30-40°S the surface ozone level was comparable to that observed at Montsouris and Moncalieri. Furthermore, the present-time ozone level observed at remote sites of that latitude of the southern hemisphere is about twice as large as one century ago; this increase is lower than that observed at about 45-49° latitude (Turin, Paris) in the Northern Hemisphere.

Atmospheric tracer techniques utilized at EI to study atmospheric dispersion are being improved to meet the requirements of future campaigns : the release rate of perfluorocarbon (PFC) tracers has been increased, and new sampling devices are being studied, to allow a pre-concentration of PFCs on absorption columns, thus allowing a collection of PFC from at least 100 liters of air.

Models describing the microphysics and chemistry of **aerosol formation** (AERO2, IMAD, OCCAM) have been upgraded, and techniques of uncertainty and sensitivity analysis were applied to these models to ascertain their adequacy to interpret aerosol dynamics as observed in controlled laboratory experiments.

A new project on the **environmental sulphur cycle** has been initiated, in collaboration with other JRC Institutes. The project aims at studying the effects of dimethylsulphide emissions from phytoplankton on the earth temperature : dimethylsulphide is oxidised in the atmosphere with formation of H_2SO_4 aerosols, which increase the atmosphere albedo, both directly and by formation of cloud condensation nuclei.

A new facility is being constructed to study aerosol processes at a larger scale than in the classical atmospheric research laboratory : it comprises a 70 m^3 environmental chamber and 10 m. high vertical flow reactors where aerosol formation and growth and aerosols-gas interactions can be studied in strictly controlled laminar flow conditions (flowrate down to 2 cm s^{-1}, implying interaction times up to 140 s in the reactor, and a temperature control of ± 0.1°C). The facility will become operational in early 1992, and will open to international cooperation.

CHEMICAL WASTE

Studies on **pollutant-soil interactions** have been pursued. Sorption/desorption of 3,4,5-trichloraniline and 3,5 dichloraniline on seven different soil horizons has been investigated and the organic carbon distribution coefficient Koc has been derived. In order to assess the contribution of earthworms to the transport of polychlorinated biphenyls (PCBs) through soil, PCBs uptake by earthworms (lumbricus rubellus) has been determined.

Soil sorption of atrazine was studied in 110 different soil horizons from 24 different soil profiles. It was found that clay did not correlate with soil sorption of atrazine.

The influence of humic substances on the transport rate of selected trace metals (Hg, Cr, Co) in soils and aquifer systems has been investigated by applying a combination of spectroscopic techniques and column migration experiments.

The stochastic model FEMSUN has been applied to study and quantify the uncertainties due to the high varibility and scarse knowledge of parameters used for **modelling pollutant migration** through soil porous media. Based on stochastic simulations performed by the FEMSUN model the relative importance of the various parameters on the contaminant transport has been investigated on an hypothetical waste repository site.

In the frame of **waste management** techniques the granulation technique with cement or clay has been applied for the stabilization of chromium. Leach tests indicated a very good immobilization of the chromium(III) contained in the spherical particles.

ENVIRONMENTAL STUDIES OF THE MEDITERRANEAN BASIN

Activities on the joint European **MITO Project** have been focused on:

- the development of fast and easy-to-use monitoring systems for surface waters using the possibilities of modern technology, - i.e. flow cytometry- to characterize and quantify algal blooms;
- the development of alternative bioassays to study the impact of toxin-producing phytoplankton on the ecosystem;
- the application of biochemical indices of the physiological state of algae to understand the fate of algal toxins in the aquatic environments, and;
- the development of hydrodynamic, transport and biological process models to predict toxin occurrence and distribution.

A simple protocol to preserve algal samples for bivariate cytometric analyses has been developed.The preservation procedure, based on a 0.1% paraformaldehyde treatment, does not affect chlorophyll autofluorescence and cell size volume.The method has been employed during the experimental campaign in Corfu Sea (Greece), aiming at quantifying horizontal and vertical distribution of phytoplanktonic communities and their pigments.
A second Project on **Analytical QUAlity CONtrol and Measurement Assessment Studies** (AQUACON) is aiming at the identification, quantification and reduction of errors in environmental analysis, sampling procedures included.

FOOD AND DRUG ANALYSIS

This activity is focused on the study of methods to check food adulterations or fraud in their trade in view of supporting the EC directives.
"**Detection of wine sugaring by NMR**" has been pursued to improve the EC reference method (purity of the wine distillate, stability of the internal standard used in the NMR analysis) and to evaluate the reproducibility and the preparation of the samples (round robin exercise). This constitutes the basis for the validation of the future NMR results to be included in the 1991 European wines data bank.
As for as **dairy products** are concerned, several methods have been investigated to detect fraud; the presence of cow's milk in ewe cheese, the presence of alien fats in milk fat, the attempt to establish the origin of milk fats by their triglyceride profiles and the research of some chemical indicator for the heating of the milk. Within the framework of the just started activity of microbiological laboratory, some research on aflatoxins in one African beer and its ingredients and a systematic control of cosmetics have been performed.

1.2 Radioactive Waste Management.

SAFETY OF FINAL STORAGE IN GEOLOGICAL FORMATION

The contribution of the EI to this programme has been concluded with the year 1991. Gradual shift and merging of competences towards research activities on transport and behaviour of toxic chemicals in soils and groundwaters took place.
In the course of 1991, the awareness that the geochemistry, as well the bioavailability of metals are both dominated by their **speciation**, rather than just total concentrations, has urged the development of analytical techniques which are both sensitive and selective for molecular chemical forms. Non-invasive X-ray and Laser induced spectroscopic techniques were applied to examine

sorption equilibria and kinetics involving radionuclides at mineral surfaces.

Long-term laboratory migration experiments with Np and Pu through columns loaded with sediments collected at the Gorleben salt dome have been concluded. The output of these experiments will be used, in cooperation with the Technical University of Munich, for the development of the **long term transport model of Transuranium Nuclides.**

A pilot in-situ diffusion experiment using the Autolab probe lowered in a well drilled at the JRC-Ispra has been successfully performed in collaboration with the CEN-Cadarache. The purpose of this field trial was twofold: first, to demonstrate the handling and mechanical operation of the probe on site in an actual borehole, and second, to test the feasibility of conducting **radionuclide migration studies** under field conditions. In the framework of a collaboration agreement with OECD/NEA, the critical assessment of literature thermodynamic data of Americium has been performed according to guidelines developed within the **Thermochemical Data Base Project.**

2

Scientific/Technical Support to Community Policies

As for the preceeding years of the programme (1988-91), the Environment Institute has provided technical and expertise assistance to the following Directorates General :

DG I
External Relations :
Support to IAEA's Pact programme;

DG III
Internal Market and Industrial Affairs:
Pharmaceutical data-bank;

DG V
Employment, Industrial andSocial Affairs:
Biological data in occupational health;

DG VI
Agricolture:
Data-bank of NMR fingerprints of european wines;

DG XI
Environment, Nuclear Safety and Civil Protection:
Chemicals, Waste, Water Quality, Atmospheric Pollution, REM (Radioactivity Environmental Monitoring);

DG XIII
Telecommunications, Information Industry and Innovation:
Ispra Mark 13A flue gas desulphurisation pilot plant;

DG XVII
Energy:
Control of fissile materials;

DG XXI
Custom Union:
Characterization of imported goods.

However, as the largest part of the effort has been devoted in support to DG XI, only the main achievements referred to that Directorate General are summarized in the following.

2.1 Chemicals

Technical/scientific support for the implementation and the updating of the EC **Dangerous Substances** Directive (79/831/EEC) has been continued, with special emphasis on the classification, packaging and labeling of organic peroxides.

The applicability of the **Structure-Activity Relashionship** to predict the environmental distribution and fate of industrial chemicals has been investigated with the aim of introducing groups of similar structure in the EINECS inventory.

As far **testing methods** are concerned, experimental work has been focused on the preparation and standardization of six european reference soil samples to be used in adsorption tests.

2.2 Waste

An analytical method for the fast determination of **PCBs in waste oils** has been set up and it will be tested by an international interlaboratory comparison with the participation of specialised laboratories of the Member States.

2.3 Water Quality

JRC scientific expertise was made available to DG XI to contribute in the development of a new directive on **surface water ecological quality**, and of a possible lake classification system.
The impact of trace elements from point and non-point sources on aquatic systems has been further studied.

2.4 Air Pollution

Within the framework of the harmonization programme for the **NO2 Directive** (85/205/EEC), an intercomparison has been performed of different NO_2 primary calibration methods , namely:

- permeation method (ISO 6349-1979)
- Griess-Saltzman wet chemical method (ASTM D 1607-1976)
- Griess-Saltzman wet chemical method (VDI 2453-1989)
- static volumetric dilution method (VDI 3490-1985).

The results of the permeation and static volumetric dilution methods match very closely, confirming the validity of the Directive reference method. On the contrary, the ASTM and VDI Saltzman methods are to be rejected because of the variable stoichiometry of the reaction (Saltzman factor).

In the frame of a convention between DG XI and the Madrid City Hall (Ayuntamiento), an evaluation of the Madrid **air quality survey network** was performed by means of passive NO_2 samplers and mobile laboratory measurements.The study proved that this combination constitutes a successful approach to air quality evaluation in different areas under different conditions (season, day, meteorology..), providing a number of informations on the characteristics of the urban network (station location and performance), on the existence of areas at risk, and on the need for NO_2 control measures.

The **EMEP** Station at JRC Ispra has pursued with the daily measurements of air, atmospheric particulate and precipitation samples following the extended EMEP programme. The obtained results are distributed at regional, national and international level.
Other tasks included the participation in the intercalibration exercise for **PAN measurement** organized by NILU and sponsored by EC and the technical and scientific support for revising and

updating the analytical method for determining **asbestos in air** samples of the Directive EC 87/217.

2.5 Radioactivity Environmental Monitoring (REM)

The **REM data bank** has been extended to include more than 400.000 data from the EC as well as other European Countries for environmental and foodstuff samples. A user manual for the access to the new version of the data bank has been prepared to be made available early in 1992.

The **Occupational Exposure Data bank** has been transferred from the Sun 386i/Unix workstation under ORACLE v.6.0 to a PC/MS DOS computer under ORACLE 5.1 C. At the same time the data base structure has been revised and updated to support all new requirements deriving from the increased complexity of the gathered information. A tool implemented under MS DOS has been developed to store all the unstructured information (comments and qualitative considerations).

Within the framework of the cooperation with IAEA for the harmonization of the **early warning and exchange of information systems** developed by EC (**ECURIE**) and IAEA, respectively, decoding software has been prepared to be integrated with encoding one prepared by IAEA. An ORACLE data bank containing incoming ECURIE messages will be set up.

The **Atmospheric Transport Methods Evaluation Study** (ATMES) has been concluded and has allowed useful conclusion to be reached as far as regarding the applicability and reliability of 21 models considered in the study. While most of them were able to describe the arrival time of the radionuclide cloud, only few of them are apt to correctly describe the cloud position and the soil contamination. In addition the model performances were found to dramatically deteriorate when the forecasted windfields were employed.

Fractal analysis has been performed on deposition data sets referred to Federal Republic of Germany, Greece and Ireland showing that they were of multifractal nature.

Within the framework of the **harmonization of measurement and reporting of environmental radioactivity** the proposals made by the Environment Institute have been adopted by the national experts. In collaboration with the International Reference Centre of the WHO an intercomparison campaign has been launched, to which 12 national laboratories took part for the analysis of 137 Cs, 90 Sr and H_3,. the results being expected by the first half of 1992.

3

Exploratory Research

Three projects, all being the continuation of projects selected in 1990 for exploratory research, have been further developed, i.e. :
- Innovative Laser Technology for Chemical Analysis
- Laboratory for Separation Science
- DNA Adducts

3.1 Innovative Laser Technology for Chemical Analysis

The complete characterization of a "flame ionization detector", in terms of quantum efficiency and ion yield, the evaluation of a low pressure dicharge lamp as ionization detector, and the conceptual development of a laser induced fluorescence approach to absolute chemical analysis were the goals to be achieved with the project. It was shown that the flame detector indeed approached a unity quantum efficiency: however, the experiments performed with a commercially available glow discharge lamp were not promising. In the absolute analysis approach, an intensified diode array detector, which allows the simultaneous coverage of several spectral regions, was successfully tested.

3.2 Laboratory for Separation Sciences

A continuous liquid sample introduction system has been developed and installed on a high resolution mass spectrometer for fast atom bombardment (FAB-MS) studies in combination with micro-liquid chromatography and capillary electrophoresis systems. The performance of such an interface was evaluated with modified nucleic bases and nucleosides, amino acids and peptides.On the other side, the application of crossflow membrane techniques in the treatment of wastewater has been investigated.

The aims of this approach are:
- to study the performance of the most recent membrane process techniques with regard to the treatment of environmentally important waste- waters, such as those containing organo- chlorinated compounds, following in particular the removal of chlorophenols and phenols.
- to study the role of ultrafiltration as a pre-treatment technique for the removal of suspended matter or toxic compounds, prior-for instance-to reverse osmosis or a biological treatment.
- to identify the fouling agents, which are responsible of important flux drops of the membrane plants;
- to establish the scientific basis for the design and construction of a pilot plant in cooperation with an industrial partner attempting to work on a "real world" environment test case.

A pilot plant has been designed and delivered in November 91; it should allow for combining different types of micro and ultra filtration membranes in a most versatile way, processing wastewater quantities well above the laboratory bench scale; easy transport, in view of "on the spot" utilization.

3.3 DNA Adducts

The efforts have been particularly devoted to the optimization of the methods for the characterization and the detection of DNA adducts formed by metabolic intermediates of 1.3 Butadiene, and to the development of a comprehensive approach for the evaluation of the exposure of fish to environmental genotoxic chemicals, DNA adducts serving as the selective biomarkers. Epoxybutene (EB) and Diepoxybutane (DEB) are the two genotoxic intemediates in the metabolism of 1.3 Butadiene in mammals, selected for their capability to induce different types of adducts. HPLC separation followed by MS and NMR have been applied for the purpose. For DNA adducts of DEB the 32 P-Post labelling Technique (32 PPL) proved to be successful.The overal exposure of fish to genotoxins can be derived from the levels of DNA adducts in fish liver which gives an indication of the biologically-effective dose. DNA adducts in different species of fishes exposed to Benzopyrene have been detected by HPLC and 32 PPL.

Main Achievements

1

Specific Research Programmes

1.1

Environmental Protection

In this section the most significant progress achieved in the following research areas is presented :

- Environmental Chemicals ;
- Air Pollution ;
- European Monitoring Network ;
- Water Quality ;
- Chemical Waste;
- Environmental Studies of the Mediterranean Basin;
- Food & Drug Analysis .

All the above items were included in the Environmental Protection Programme ending on December 31st 1991.
As no new action or project has been launched in the course of the year, what is presented constitutes the follow up of activities started in the preceeding years the aims and targets of wich has been already described in the Annual Reports 1988,1989 and 1990.

ENVIRONMENTAL CHEMICALS

This area includes three activities, i.e: the ECDIN databank, Indoor Air Pollution and Trace Metal Health Effects.

ECDIN Data Bank

ECDIN is a factual databank, set up and developed by the Environment Institute within the framework of the Environmental Research Programme of the Joint Research Centre.

The primary aim of the ECDIN databank is to present a comprehensive collection of validated data on potentially hazardous chemical substances and pollutants in order to facilitate the evaluation and control of environmental and health risks.

In total, ECDIN includes information or data on more than 120,000 substances.
The databank also contains the "European Inventory of Existing Commercial Chemical Substances" (EINECS) comprising more than 100,000 compounds.

A public version of the ECDIN databank is accessible through DIMDI ("Deutsches Institut für Medizinische Dokumentation und Information, Cologne). In addition, extracts of certain data files are available on CD-ROM for use with personal computers.
Records are updated continously in collaboration with specialists and research Institutes throughout the world
Thus, in 1991 the data content of the ECDIN databank was extended substantially by the addition of an existing database on water solubility (more than 10,000 records for about 4000 organic compounds). In addition, updating and significant improvements were made in the toxicological, and waste legislation files as well as in the chemical economic sector file. A new file on abiotic degra-dation of chemicals has also been introduced.
On-line use of the ECDIN databank is increasing steadily and the number of regular users has nearly doubled in 1991.

A first CD-ROM version of ECDIN data for use with personal computers has come on the market in Europe, focusing on 1,800 compounds of primary commercial, environmental and occupational importance. An appreciable number of discs was sold already in Italy. Agreements for distributing CD-ROM versions abroad (USA, Japan) are under negotiation.
In collaboration with the Community Bureau of Reference (BCR) and expert laboratories in the member states, the 3rd volume of the series "Spectral Atlas of Polycyclic Aromatic Compounds", containing newly measured data on molecular spectra and literature data on physico-chemical and biological properties was compiled and published in October, 1991.

Indoor Air Pollution

Indoor air pollution receives increasing attention because of the potentially high exposure of the population (high residence times indoors, concentrations of many pollutants higher indoors than outdoors) and the prevalence of susceptible groups (children, elderly, unhealthy people) in the non industrial indoor environment. Moreover the problem of complaints on indoor air quality in large buildings (mostly office buildings) with sealed structures and typically equipped with air conditioning systems, is of increasing concern to public and private administrations.

The JRC's contribution in this field consists in:

- the management and scientific coordination of the Concerted Action "Indoor Air Quality & Its Impact on Man" (see chapter 5);

- research activity aimed at an assessment of organic indoor pollutants and their sources;

and

- work for Third Parties (see chapter 4).

The Institute's research activities are focused on indoor air quality problems related to organic indoor pollution. This activity is motivated by the specific competence which has been developed over the past twenty years in the field of organic environmental analysis and by the European commitment to provide harmonized and validated methods. Most importantly, however, organic indoor pollutants are of particular concern since many of them are known or suspected to cause carcinogenic, neurotoxic, allergenic, immunotoxic, irritating or sensory effects. In particular volatile organic compounds (VOC) are often suspected and sometimes have been shown to play a role in complaints about inadequate indoor air quality in office buildings or other indoor environments. Building and furnishing materials, household and hobby products are important indoor sources of these compounds.

Work performed in 1991 was aimed at validating a chamber method for the determination of VOC emissions from indoor materials and products, and models for describing the concentration vs. time profiles of the emitted compounds. In addition work for validating sorbent sampling on hydrophobic sorbents has been continued and the development of a method for the determination of semivolatile organic compounds (SVOC) in indoor air has been initiated.

Validation of a chamber method for the determination of VOC emissions

The most appropriate means of controlling indoor pollution by VOC is to reduce source emissions, e.g. by the choice of low emitting materials and products. Prerequisite conditions are validated standardized methods for emission measurements. In 1991, the Institute launched an interlaboratory comparison experiment in order to validate a guideline for emission measurements issued in 1990 by the Concerted Action "Indoor Air Quality & Its Impact on Man". Twenty laboratories in Europe and in the USA are participating. The experiment includes three steps of increasing complexity, requiring the determination of the emission rate of:

- a single compound source (n-dodecane) the emission rate of which could also be accurately determined by weighing (constant emitting source);

- the four main compounds and the total volatile organic compounds (TVOC) emitted from a PVC tile sample (slowly decreasing source);

- a few compounds and TVOC emitted from a wax sample (rapidly decreasing source).

The samples for the first two steps were distributed in 1991. Only the results of the first step are already available from most laboratories and are summarized in Figure 1. In this figure quotation marks set at the laboratory identifier refer to different characterization procedures with the same chamber, whereas letters a and b refer to the same procedure with different chambers. The results show that agreement between the measured and expected emission rate is far from being acceptable for several laboratories. The discrepancies, except for two laboratories, are all negative, i.e., the emission rate determined from the measured concentration is less than the emission rate expected on the basis of the weight loss. An unequivocal explanation for this discrepancy has still to be found; among the possible hypotheses adsorption on some chamber sites (sinks) is the most probable one and should be investigated.

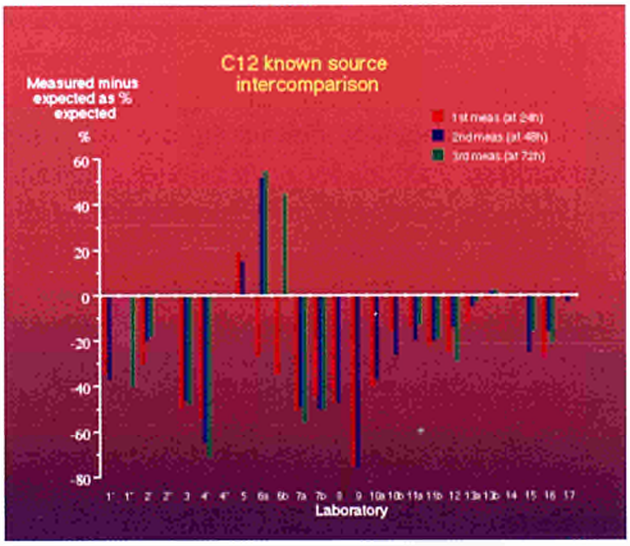


Fig. 1: Results of an intercomparison of a known source of n-dodecane in small environmental test chambers.

Comparison of models used to estimate parameters of organic emissions from materials tested in small environmental chambers.

Two models, physical and empirical, have been applied to the characterization of emissions from cleaning/conservation products as thin films and tested in small environmental chambers. The models have been compared in terms of the agreement between measured and calculated emission and ease of use. Both models provide emission parameters through non-linear regression of chamber concentration vs. time data.

The physical model is subdivided into four submodels of increasing algebraic complexity called Dilution, Vapour pressure, Sink and Full model, respectively. As it is based on equations with coefficients bearing a physical meaning, the physical model is, in principle, more informative than the empirical one. However, it is uncertain whether it always gives accurate and unambiguous results. Moreover, in order to be exploited in a reasonable amount of time, it requires the use of non-linear regression routines implemented on mainframes and, even then, it is often quite difficult to handle.

The empirical model exists in a simplified and a basic version and does not rely explicitly on physical effects. Though by definition it can only

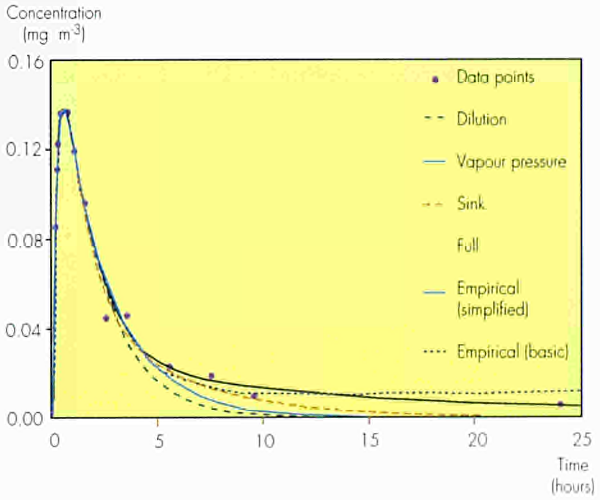


Fig. 2: Best fits of concentrations of dicyclopentadiene alcohol emitted from a liquid floor detergent applied to a ceramic tile using different models.

describe but not interpret the experimental data, it did estimate parameters describing the emission with an accuracy comparable to that of the physical model. It was easier to handle than the latter because it could be run with non-linear regression routines implemented on personal computers. The most complex submodel of the two models provided the best results in general. An example of a non-linear regression fit is given in Figure 2 for a source with decreasing emission, a so-called thin film source.

Quality assurance of VOC sampling

Tenax and Carbotrap are the most widely used sorbents for sampling volatile organic compounds (VOC) in indoor air. Contradictory results have been published on the reliability of sampling with these sorbents. Therefore the performance of Tenax and Carbotrap samplers has been tested with 10 apolar and polar (mostly lipophilic) hydrocarbons. The tests include: accuracy and reproducibility of the measured concentrations, background or blank emission of the samplers, stability upon storage of clean samplers and of samplers loaded with VOC, and the performance stability after many sampling-desorption cycles.

Both sampler types were shown to be suitable and reliable for use under the testing conditions. In particular they may be stored for one month before and after use and they may withstand several tens to hundreds of analyses without discernible deterioration. The sampler background is only significant for benzene and toluene and somewhat higher for Carbotrap than for Tenax. At a sampling volume of 0.5 l the relative standard deviations of repeated measurements are, for both sorbents, higher than at a sampling volume of 2 l. However, at the lower sampling volume the deviations are significantly higher for Carbotrap samplers whereas Tenax samplers show slightly higher scatter at 2 l sample volumes. Occasionally artifacts have been observed for Carbotrap, like partial decomposition of bromoalkanes. These artifacts appear to be limited to some batches. Alpha-pinene has turned out to be a sensitive indicator of potential reactions in the sampling-desorption system.

Development of a method for the determination of semivolatile organic compounds (SVOC) in indoor air

The knowledge of semivolatile organic compounds (SVOC) in indoor air is still very limited although they encompass potentially dangerous substances such as pesticides, plasticizers or polynuclear aromatic hydrocarbons.

Available analytical methods are time consuming and require sampling of large air volumes which may create problems in small indoor environments. Therefore the development of a more appropriate method has been started.

Combined supercritical fluid extraction (SFE) gas chromatography offers high sensitivity so that air sample volumes can be reduced from some 100 m^3 as required by presently used methods to about 1 m^3. Using the determination of the terpene content of conifer needles and scales as an example it was shown that the extraction time can be reduced from 24 hours using Soxleth extraction to 20 minutes using SFE and that the amount of sample to be extracted may be reduced from 5g to few mg, i.e. by a factor of 1,000.

A commercial SFE-GC combination where the extracted compounds are concentrated in a cryo-trap before thermal injection into a gas chromatograph has been tested.

The cryotrap has been modified, in order to achieve a more homogeneous temperature distribution during the cooling phase.

This distribution is critical because at "cold spots" carbon dioxide (the supercritical solvent) may condense and block the cryotrap, whereas a temperature as low as possible is required in order to avoid breakthrough of more volatile SVOC. Figure 3 shows the temperature distribution in the coldtrap before and after the modification.

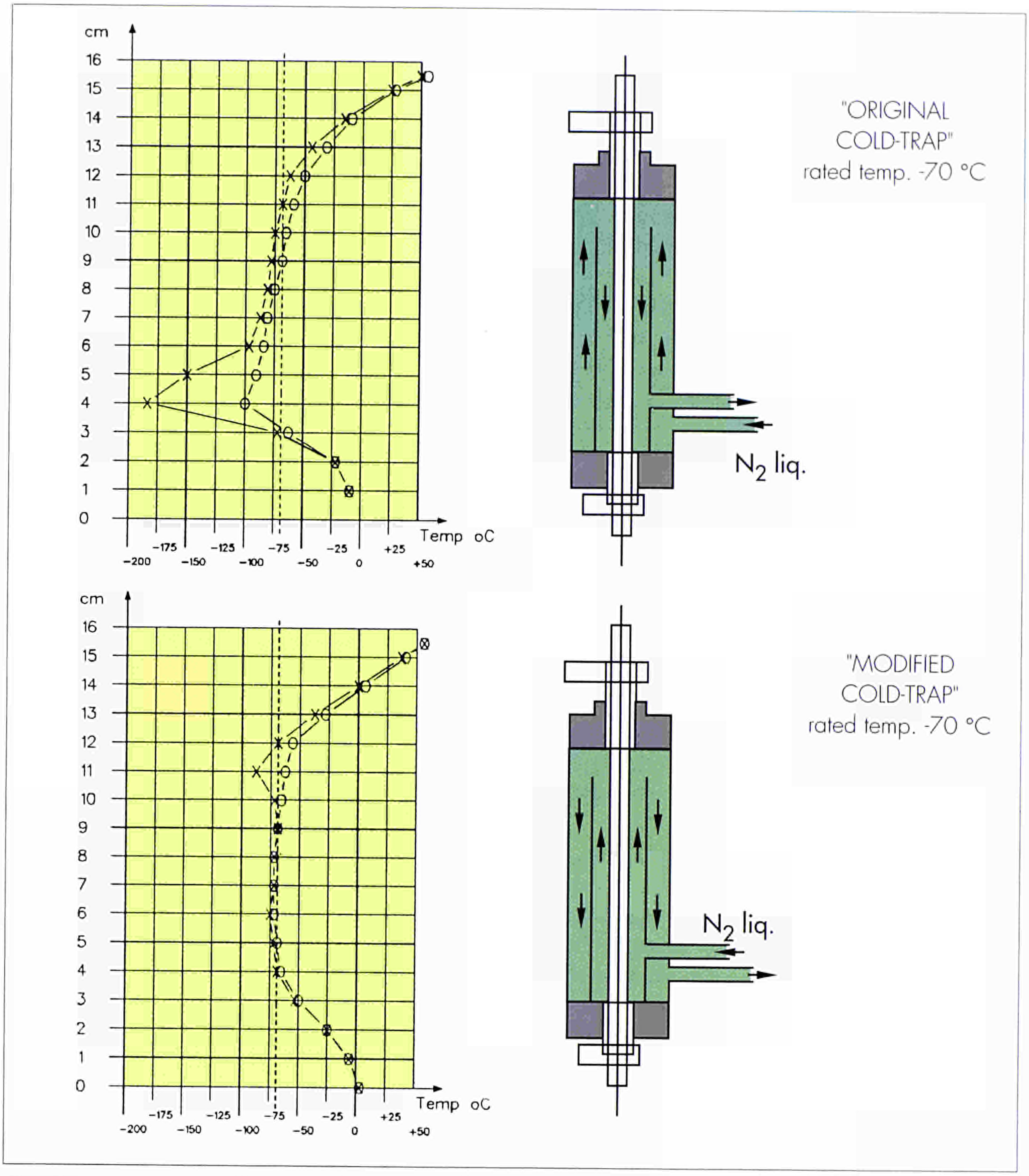


Fig. 3: Temperature profiles along the cryotrap of a commercial on-line SFE-HRGC instrument before and after modification.

Biological tests of indoor pollutants

This activity is being revised and it will be merged into that of the European Centre for Alternative Testing Methods (ECVAM) which is going to be set up in the Environment Institute.

Emphasis has been put on genotoxicity studies of constituents of environmental tobacco smoke (ETS) and on the production of transgenic mice to be used in genotoxicity studies.

Genotoxicity studies of ETS constituents.

As reported in previous scientific reports by the JRC as well as by other laboratories, the composition of tobacco smoke is characterized by more than 3,500 chemical compounds. Although it is well known that ETS is noxious to human health, it is not clear how the adverse biological effects are induced by the chemicals present in this complex mixture. In particular, it is not known whether NNK, {4-(N-Methyl-N-nitrosoamino)-1-(3-pyridyl)-1-butanone}, a tobacco specific nitrosamine and BP {benzo (a) pyrene}, have any synergistic or antagonistic effects. In addition, the role of the microsomes in the genotoxicity of these two compounds has so far not been investigated in detail. These issues have been studies in vitro measuring the unscheduled DNA synthesis (UDS) induced in hepatocytes isolated from CD-1 male mice.

The following major conclusions were reached :
- Both NNK and BP were confirmed as genotoxic compounds.
- The genotoxicity of NNK was not enhanced by the presence of BP. On the contrary, the resulting DNA repair synthesis promoted by the mixture of these two chemicals seems to be lower than the sum of the repair syntheses induced by the single xenobiotics added to the cell cultures.

The induction of the microsomal activity resulting from 10-15 days in vivo treatments of mice with phenobarbital (PB) and ethanol (Et-OH) and diazepam has also been studied. The in vivo induction by diazepam and by phenobarbital resulted in an in vivo enhanced genotoxicity for NNK, but in a lowered DNA repair synthesis for BP. Nevertheless, the antagonistic effect already observed in non-induced hepatocytes was confirmed. Moreover, the treatment for 12 days of mice with Et-OH or with diazepam increased the frequencies of the cells that enter the S phase, thus suggesting a possible role of these compounds in different stages of carcinogenesis.

Diazepam and ethanol are of widespread use. Therefore experimental approaches like the ones described appear to be important for a proper assessment of the genotoxic risk of ETS and it's constituents.

Transgenic Mice.

Within the framework of a collaboration with the Italian National Research Council (CNR), during the last two years the entire procedure for the production of transgenic mice has been implemented at the JRC.

Although not yet clarified in detail, it is well known that oncogenes play an important role in the postulated multi-step theory of carcinogenesis. For this reason, it is supposed that the insertion into the murine genome of oncogenes should be of great benefit in understanding carcinogenic mechanisms. In the last few years, many scientific reports suggested that transgenic mice may represent ideal short term test models for investigating interactions between environmental chemicals and genetic material. It is also recognized that their use can contribute significantly in reducing the number of animals in these kind of investigations. As a final consideration, the early phenotypic expression and the (relative) simplicity of the analyses that must be carried out after treatment of transgenic mice with xenobiotics, contribute to reduction of pains experienced by the experimental animals.

Along this line, a nucleotide sequence of 12.4 Kb, that contains a truncated myc oncogene and its 5′ regulatory regions, have been inserted into the murine genome.This construct has been recovered from a cell line (Hut-78) of a man affected by Sézary syndrome, a promyelocytic leukemia. Another feature of this construct is the fact that the oncogene has a deletion of 61 bases in its 3′ region. The introduction of the exogenous DNA has been carried out by the classical procedure that consists of the microinjection of mouse zygotes and their reimplantation in foster mothers. The litters born from these experiments (50 mice) were analyzed for the positive insertion of the construct. Three animals resulted transgenic {2 males of which 1 mosaic (transgenic in somatic cells, but not in germ cells) and 1 female}. The transgenic male mouse was mated with normal CD-1 female mice in order to expand the line. The analyses of the RNA from different transgenic mouse tissues confirm that the introduced sequence expresses a myc-HUT 78 specific transcript. More than 100 transgenic mice are presently available, 50 out of them having been treated with a known genotoxic compound (Ethyl-Nitroso Urea) to confirm the usefulness of this animal model for the search of the genotoxic properties of the chemical compounds.

Trace Metal Exposure and Health Effects

The aims of the activity consist essentially in establishing, on a scientifically sound basis, dose-effect relationships in view of preventing potential health hazard from the exposure to trace metals.

To achieve this goal, two topics, linked to each other and covered by this more com-prehensive theme, are being investigated, i.e.:

- trace metal levels in human tissues of EC general population and occupationally exposed workers;

- metabolism and biochemical effects of trace metals.

Trace Metals in Human Tissues

This first topic is addressed, on one side, to establish baseline values in general population as the fundamental parameter for the assessment of the biological effects of trace metal exposure on humans. In particular, the availability of accurate trace element reference values in human tissues represents an important indicator in relation to the health status of a population and the quality of the environment:

- to understand appropriately the pathological states in connection with environmental factors and to identify anomalous trends of essential/toxic elements in the general population;

- to verify and eventually reconsider legal limits of exposure for the protection of the general population.

In this context three projects are being developed:EURO TERVIHT, TRACY and HAMBIHT.

EURO TERVIHT

Trace Element Reference Values in Human Tissue), in collaboration with the EC Directorate General V Employment, Industrial and Social Affairs, Health and Safety Directorate, Luxembourg.

The project is aimed at establishing and comparing trace element reference values in tissues from inhabitants of the European Community as baseline values for clinical/toxicological assessment studies. The project foresees an international cooperation of specialized chemical/toxicological EEC laboratories.

So far the major achievement consists of the definition of the strategy adopted including guidelines for the selection of subjects as "reference groups" and the analytical quality controls. Aspects investigated are related to the risk of contamination during blood collection and the use of anticoagulants; the risk of losses during storage and freeze-drying as well as the possible risk of contamination arising from trace elements in airborne particulates of the laboratory environment.

For the analysis of Al, Ba, Cd, Co, Cr, Mn, Mo, Ni, Sb, W, V and Zn in blood, teflon cannula is the method of choice. Contaminations were experienced for Co, Cr, Mn due to the addition of anticoagulants.

Twenty-four radiotracers in "metabolized form" (radiolabelled rat or rabbit tissues from animals administered with radioisotopes) showed that samples stored for 1 month at -20°C have no significant trace metal losses. Strict ambient air quality standard has to be respected (continuous monitoring) to avoid any risk of sample contamination inside the laboratory.

- In addition, the concentration levels of 37 elements in lymph nodes of "normal subjects" were determined. The results allowed to propose indicative values for 26 elements analyzed in more than 25 subjects (Ag, As, Au, Ba, Cd, Ce, Co, Cr, Cs, Eu, Fe, Hg, Ir, Lu, Ni, Rb, Sb, Sc, Se, Sn, Ta, Tb, Th, U, Yb, Zn).

- In a similar way the concentration levels of 37 elements in cerebrospinal fluid of subjects with non neurological diseases were established. Iron and bromine were the elements with the highest concentrations (318 and 259 $\mu g\ l^{-1}$) followed by Rb, Sr, Zn, Ba, Sn, Mo, Cr, Cd, Ce, Se, Nd. All other metals ranged from 0.84 ng l^{-1} (Cs) to < 0.007 $\mu g\ l^{-1}$ (Ir).

The statistical treatment of the data of trace elements in blood (see Annual Report 1990) was improved by using a computer-based Lilliefors test. The distribution of Pb in whole blood of 350 subjects (163 ± 68 $\mu g\ l^{-1}$) is better defined by log-normal function rather than the normal distribution. In this case the recalculation by the log-normal statistical model gave 147.9 ± 15.1 $\mu g\ l^{-1}$, 9% lower in comparison to the Gaussian model.

TRACY (Database of Toxic Metals in Human Tissues and Fluids).

The project will be developed in the framework of EUREKA (see Section 5).

HAMBIHT (Hard Metal Biomonitoring In Human Tissues)

The project is aimed at determining hard metals (Co, W, Ta, Cr, Nb, Ti, Ni, Mo) in tissues of professionally exposed subjects. In this framework the three following experimental studies have been carried out.

Four subjects working in sharpening and grinding of hard metal tools were examined. Only a 37 year old female exposed for 7 years to hard metal dusts, developed hard metal pneumoconiosis, which rapidly progressed to death. Cytology of the bronchoalveolar lavage (BAL) showed a high number of eosinophils amounting to more than 30% of the cell population(Figure 4A). Biopsy of the lung revealed interstitial fibrosis with hyperplasia of the pneumocytes of the second type and inflammatory cellular infiltration of the interstitium (Figure 4B). High W and Ta concentrations were determined by neutron activation analysis in the admission BAL and in the biopsy 4 months later while Co levels were near to normal values. The content of Co and W in blood (9 and 60 $\mu g\ l^{-1}$ respectively) and urine (8 and 1,000 $\mu g\ l^{-1}$) and particularly in pubic hair (4,200 and 18,000 ng g^{-1} wet w.) and toe nails (31,560 and 105,000 ng g^{-1} wet w.) of the patients was significantly higher than the normal values. This suggests that these biological specimens could be used as indicators of chronic exposure to hard metal dusts.

Co, Ta and W were determined in total bronchoalveolar lavage (BAL) and its subfractions

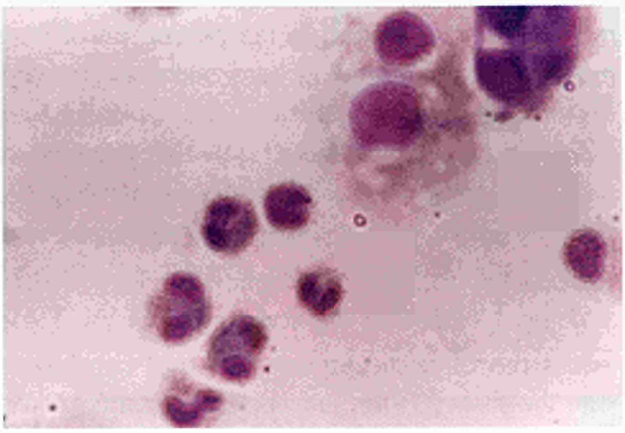


Fig. 4A: BAL cytology showing the presence of macrophages, lymphocytes and numerous eosinophil granulocytes.

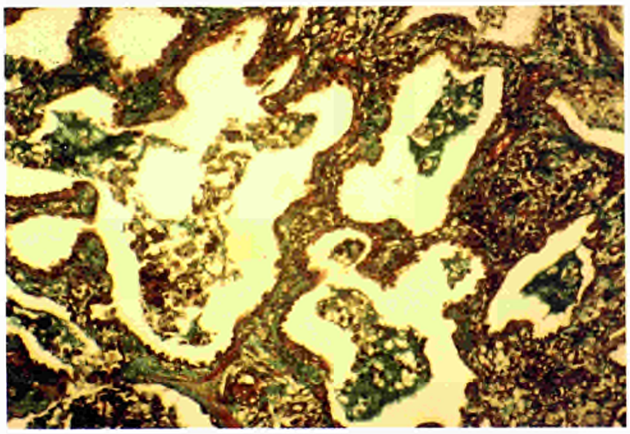


Fig. 4B: Histological examination of the lung biopsy showing interstitial fibrosis.

(supernatant and cellular fraction) from 26 hard metal workers engaged in the production of hard metal tools or in grinding hard metal components of tools by diamond-cobalt discs. Cobalt (0.7 - 13.4 $\mu g\ l^{-1}$) was distributed between supernatant and cellular fractions in a ratio nearly to 1:1. W (2.5 - 3,680 $\mu g\ l^{-1}$) was almost incorporated into the cellular fraction (macrophages). Ta (<0.05 - 167 $\mu g\ l^{-1}$) followed the same trend of W. These results are of particular interest and compatible with the theory of an immunological origin of the hard metal disease as well as of a possible role of Co as hapten.

Co and W were analyzed in urine of hard metal workers. A correlation at $p<0.001$ ($r = 0.72$) was found to exist between Co and W in urine confirming previous observations related to another group of workers occupationally exposed to hard metal dust.

Trace Metal Metabolism and Biochemical Effects

For the development of the second topic, studies on metabolic pathways and on the toxicological effects of low doses of trace metals are required being performed both in vivo on laboratory animals and by in vitro toxicity testing as alternative to animal testing.

The in vitro activity was focussed on bioassays which involved the use of subcellular preparations, isolated cellular components and all culture systems.

Subcellular preparations were employed to study the incorporation of $^{58}Co^{2+}$ and $^{187}W^{6+}$ at concentrations of 1 mg l^{-1} into pig spermatozoa and seminal plasma.
Both metals were incorporated, after 16 hrs of incubation, into the germinal cells. More than 10% of the cellular Co was associated with the heads of the spermatozoa while the remaining 90% was bound to tails. More than 98% of the W was present in the seminal plasma. These findings are of particular interest to assess the potential effects of the abnormal amounts of Co and W found in the sperma of hard metal workers (see Annual Report 1989).

The following conclusions were reached using isolated cellular components. A competitive inhibition pattern was found for vanadate ions on the activity of horseradish peroxidase. No significant inhibitory effects were found when vanadium (V) was tested with catalase and glutathione peroxidase. A lack of a direct inhibitory effect of vanadate on the activity of the main antioxidant enzymes, superoxide dismutase, was also observed. It suggests that many biological and toxicological effects of V may be mediated more by oxido-reduction reactions of the metal with physiologically relevant biomolecules than by a direct modulation of enzymatic activities.

As regards the use of cell culture systems, a previous in vitro study had shown a morphological transformation in the mouse embryo cell line BALB/3T3 exposed to vanadate salts. A mechanism of detoxification based on a glutathione-dependent biotransformation of the toxic V to less toxic IV was demonstrated. The continuation of the study showed that the depletion of GSH in the cell led to an increased morphological transformation frequency suggesting that cytotoxicity and morphological transformation in the BALB/3T3 are strictly related to the capacity of the GSH-mechanisms in reducing the toxic V (pentavalent) ions to tetravalent V specie.

As far as it concerns in vivo experiments, the following results are worth of mentioning:

Biliary excretion of barium was studied in bile-duct-cannulated rats injected intravenously with 1.8 mg $^{133}Ba^{2+}$/rat. The results suggest that biliary excretion is of little quantitative importance in the elimination of barium by the digestive tract. Physiological routes other than bile must contribute to the elimination of barium in the feces as observed in humans.

The distribution of low doses of ^{75}Se-selenite in rat tissues including testicles and its subfractions has been verified. At 16 hrs post injection the amount of selenium in the testicles was of the same order of magnitude of that when the element is administered by intraperitoneal injection or per os (0.6 and 0.8 of the dose respectively). The epididymus contained 0.14% and 0.11% of the dose in both cases while the Se in the deferens was 0.026% and 0.02% of the dose respectively. In the testicles more than 55% of the ^{75}Se was associated with the nuclear fraction and about 25% with the cytosol components. Subfractionation of the purified nuclei showed that more than 60% of the nuclear selenium was bound to the nuclear membranes and 40% to the chromatin, essentially in association with non histone proteins.

AIR POLLUTION

This research area includes Air Chemistry and the Ispra Mark 13A flue gas desulphurization process.

Air Chemistry

The activity is characterized by a priority given to chemical substances released by biological sources and to their interaction with anthropogenic pollutants.
Various aspects of the impact of these species on atmospheric chemistry have been investigated, namely in:

- the contribution to transformation processes leading to acidic compounds using simulated atmospheric conditions (teflon bag experiments);

- the atmosphere/biosphere interactions by means of exposure chambers;

- the kinetics and mechanisms of chemical and photochemical reactions through laboratory studies;

- the evaluation and distribution of sources by means of field campaigns.

Terpenes photochemistry:teflon bag experiments.

Special emphasis was put on the ability of terpenes to form ozone in the NOx-photochemical system. For the purpose teflon bags as chemical reactors and sunlight conditions are utilized.
An approach to show the efficiency of the selected biogenic compounds in generating O_3 is to ratio

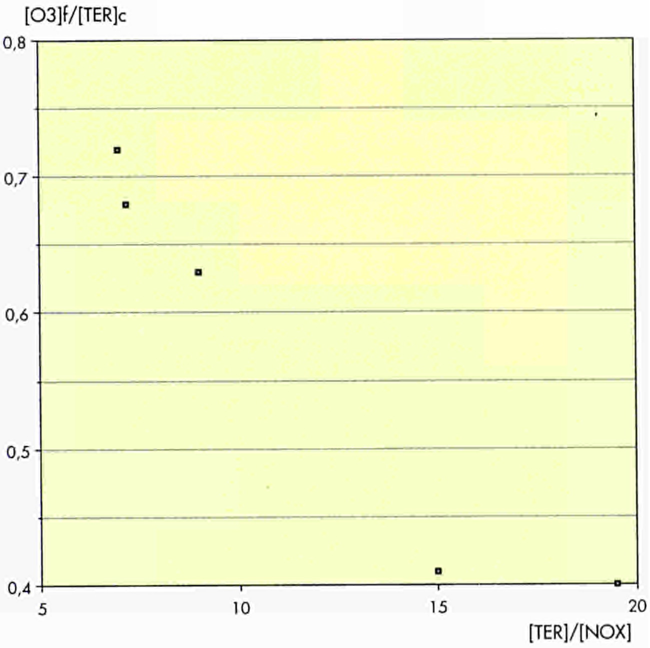


Fig. 5: Ozone formation efficiency vs HC/NOx ratio.

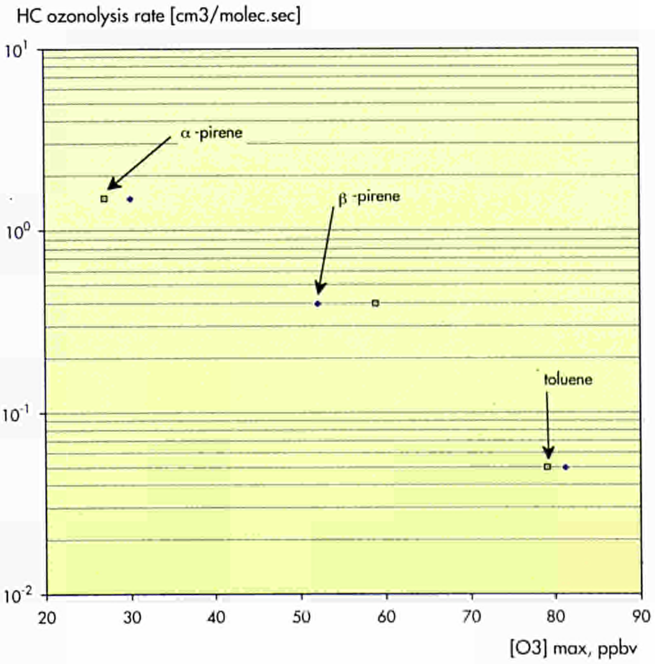


Fig. 6: Ozone maximum concentration in relation to the hydrocarbon reactivity.

Date	Hydrocarbon	$[HC]_o$ [ppb]	$[NO]_o$ [ppb]	t min	T °C	r.h. %	$[O3]_{max}$ [ppb]	$\frac{[HC]_o}{[NO]_o}$
28.6.91	β-pin	223	10	180	22.2	46.8	31	22.3
28.6.91	toluene	239	10	180	22.8	44.9	58	22.9
23.7.91	β-pin	140	10	180	23.7	5	21	14.0
23.7.91	β-pin	149	10	180	23.1	59.2	25	14.9
30.7.91	β-pin	279	20	180	20.4	5	53	13.99
30.7.91	β-pin	218	20	180	21	62.2	51	10.9
2.8.91	β-pin	246	19	180	23.6	58.3	58	12.9
2.8.91	β-pin	238	19	180	23.7	56.1	51	12.5
6.8.91	α-pin	257	20	180	20.1	6	27	12.8
6.8.91	α-pin	245	20	180	20	72.8	31	12.2
9.8.91	toluene	235	21	180	20.6	6.5	79	11.1
9.8.91	toluene	243	21	180	207	66.5	82	115

***Table 1**: Results for the irradiation of α-pinene, β-pinene and toluene under simulated atmospheric conditions (teflon bag, sunlight).*

the O_3 max-concentration to the concentration of the monoterpene reacted at that point. As an ewample in the case of β-pinene, the ozone formation efficiency (i.e. ppb O_3 produced vs. ppb terpene reacted) varies from 0.4 to 0.72 and is higher at lower HC/NOx-ratios (Fig.5).

At the concentrations used in our studies terpenes in fact suppress ozone formation. Changes in the initial NO-concentration influence significantly the ozone formation rather than changes in the concentration of the hydrocarbons. Changes in relative humidity had a small effect on the amount of the O_3 formed during the irradiation of the terpene/NO-mixtures (Table 1).

By comparing the data obtained for terpenes (α–, β-pinene) with those for other hydrocarbons of anthropogenic origin (e.g. toluene) it can be seen, that compounds with the highest reactivity towards ozone are the most effective at suppressing ozone build up (Fig. 6).

Tree exposure chambers

The experiments on trace gas exchange of tree canopies in Continuous Stirred Tank Reactor (CSTR)-systems focussed on simultaneous monitoring the mass balance of photosynthetic gas exchange, biogenic hydrocarbon emissions, and pollutant deposition.

CSTR-systems are designed to give ideal and instantaneous mixing of components entering and present in the chambers, mixing being independent from air flowrate and residence time of the components.

The canopies of cloned spruce tree (Picea abies) are enclosed and the soil containers separed outside. The chambers are housed in a cooled greenhouse, where climate (air temperature, relative humidity, light intensity) follows ambient conditions.

Work was initially concentrated on methodical aspects and on the measurements of the physical parameters needed to investigate trace gas exchange with enclosure techniques.

Preliminary results demonstrated that trace gas exchange is dominated in dry conditions by stomatal conductance, which in turn is controlled by radiation and soil water supply.

After some technical improvements, studies were then focussed on low level, continuous exposure of spruce canopies (cloned Picea abies) in dry conditions to the gases SO_2 and O_3, either alone or in combination, to investigate methodical aspects and the biological/physical relation between photosynthetic gas exchange and pollution deposition.

The work is being done in collaboration with the Meteorological Institute of Munich University (Dr. Dlugi), to develop process-level modelling for the mass balance of trace gas exchange on the basis of experimental manipulations with the CSTR-enclosure-technique. The final scope is to describe the physical chamber characteristics with micrometeorological methods and models in order to compare enclosure- and tower- based flux measurements.

A second activity was addressed to improve VOC-sampling and analysis with respect to the special conditions in dynamic CSTR-chambers (Fig. 7) and cuvettes. Previous measurements of biogenic emissions showed too high variability that could be due to:

- water condensing in the absorber tubes,
- possible ozone/VOC reactions in the tube,

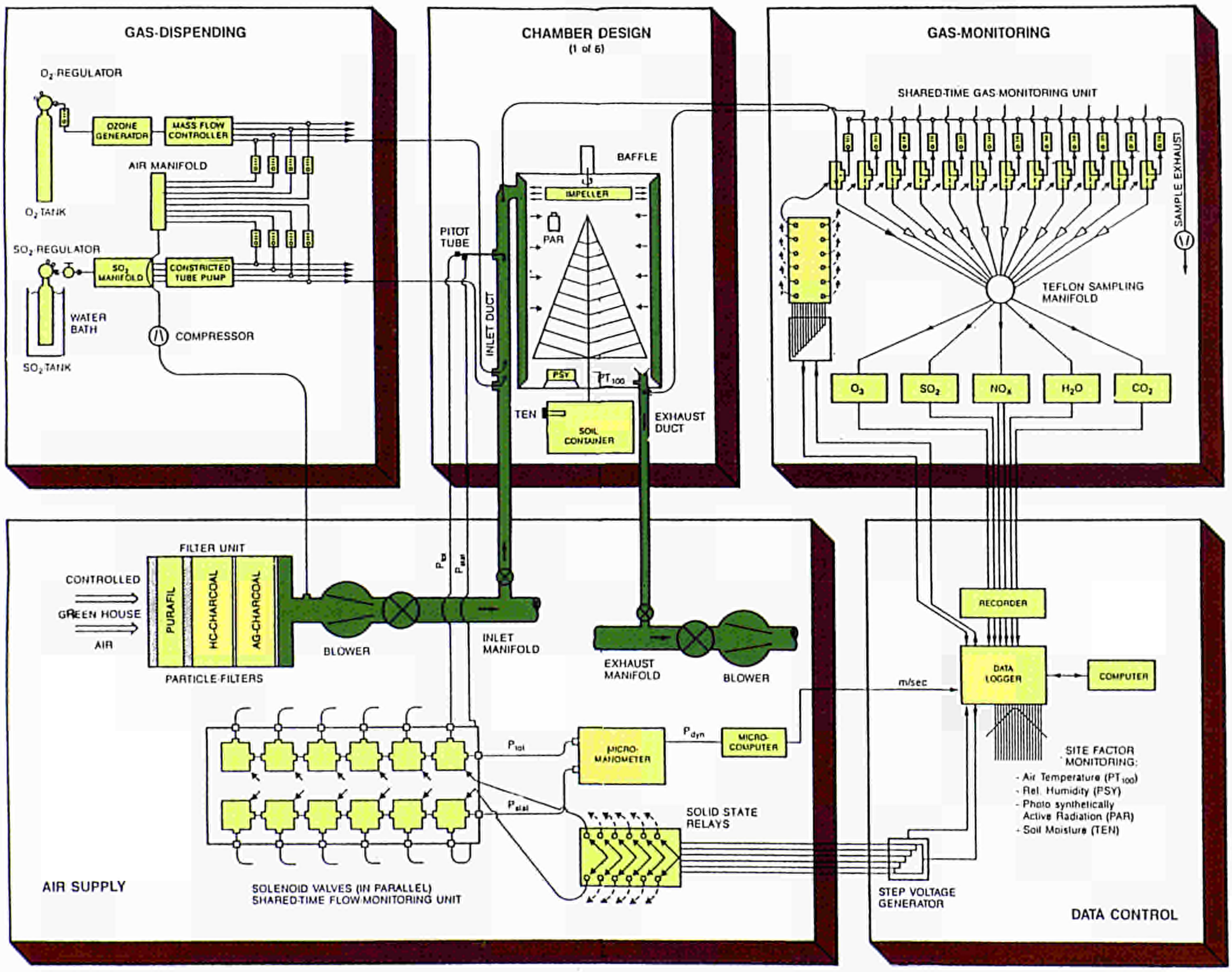


Fig. 7 : Technical design of the CSTR-plant exposure system in the greenhouse for simultaneous monitoring of the mass balance of photosynthetic gas exchange (H2O, CO2), of pollutant deposition (O3, SO2, NO, NO2) and of biogenic hydrocarbon emissions.

- unstable and not enough low airflow provided by membrane pumps and flowmeter.

To solve these problems, a sampling device for simultaneous VOC-sampling at 8 measuring points was mounted. It consisted of a cooling trap for water, an O_3 scrubber (if necessary), a by-pass-fitting for the Tenax tube by solenoid switching and a mass-flow controller with totalizator.

In addition the development of an independent, dynamic, gas phase calibration device was started by temperature controlled weighing of terpene diffusion tubes, the dilution gas being provided through massflow controllers. The system is now used to

- test different sampling procedures in the lab to control in an independent way other calibration methods for GC-analysis, to provide an internal standard in the chambers and to fumigate plants with an artificial tracer terpene.

Laboratory studies of reaction mechanisms and kinetics

The OH radical concentration is expected to be much lower at night than during the day, because the main known sources are photochemically driven reactions. The reactivity of the polluted troposphere is however not proportionally reduced at night due to the presence of the nitrate radical NO_3, formed by the reaction between NO_2 and O_3. In these last years, an increasing accent has been put on the nighttime chemistry, with a special regard to the oxidation of biogenic species. The reaction of NO_3 with unsaturated hydrocarbons and with reduced organic sulphur compounds is in fact demonstrated to be fast enough to provide scavenging pathways to important atmospheric species alternative to those photochemically driven and predominant during daytime.

Nighttime oxidation of isoprene

Isoprene is emitted from vegetation in amounts that on a global scale exceed considerably the emissions of anthropogenic non- methane hydrocarbons: ca. 450 Tg/year aginst ca. 100 Tg/year. Its main fate in the troposphere is the daytime oxidation by the hydroxyl radical;

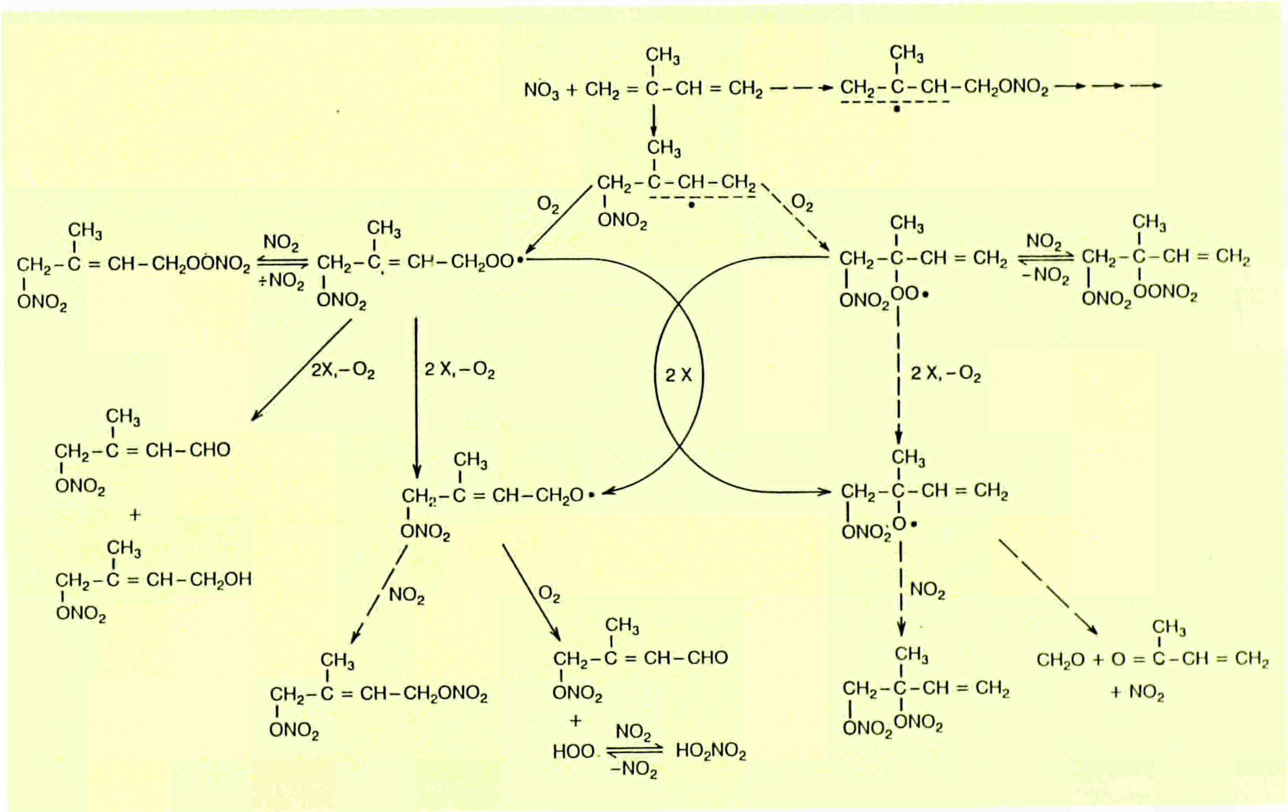


Fig. 8: Mechanism of the NO_3 initiated oxidation of isoprene in air; broken lines indicate pathways of secondary importance.

however the reaction with the nitrate radical is considered of importance under some conditions.

Isoprene, in fact, is also found at night and its degradation by the reaction with NO_3 follows mechanisms which differ from those typical of the OH radical oxidation which has unsubstituted carbonyl compounds as principal products.

According to the results of this study, the nighttime oxidation of isoprene by NO_3, contrary to the daytime OH initiated degradation of isoprene, leads to the predominant formation of organic nitrates. To clarify the reaction pathways, information about the structure of the products has been obtained through synthesis of isotopically labelled (partially deuterated) isoprene and other dienes. By reacting these species with NO_3 the position of functional groups could in fact be clarified by IR spectroscopic techniques. In particular,evidence has been obtained that the nitrate radical adds preferentially to the 1- position; 3-methyl-4-nitroxy-2- butenal appears to be the main reaction product.

The addition to the 4- position appears to be a minor, but not neglibile (about 20%) pathway (Fig.8).

Considering the high yield of organic nitrates, the nighttime oxidation of isoprene by the nitrate radical may significatively perturb the tropospheric NO_y budget on a local/regional scale (e.g. forested areas).

Tropospheric oxidation of organo-sulphur compounds

Studies on the tropospheric reactions of biogenic organic sulphur compounds with main emphasis on the reactions with the NO_3 radical were started some years ago in this laboratory. The species of main interest is dimethylsulphide (DMS), emitted in large quantities from marine phytoplankton and accounting for about one quarter of the total, natural plus anthropogenic, sulphur flux to the troposphere. The oxidation of DMS by the NO_3 radical has been the subject of previous studies. To get a better insight into the mechanism controlling this process, the reaction of the NO_3 radical with a series of compounds with the structures RSH, RSR and RSSR, for R being CH_3 or C_2H_5, has been investigated. All the compounds follow a similar degradation mechanism producing SO_2, H_2SO_4, alkylsulphonic acids (R-SO_3H), CH_2O, R-CHO, R-CH_2ONO_2 as main reaction products (Table 2).

Reactant / Reaction Products	CH_3SCH_3 (DMS)	CH_3SH	CH_3SSCH_3	CH_3CH_2SH	$(CH_3CH_2)_2S$	$(CH_3CH_2)_2S_2$	$CH_3CH_2SCH_3$
$CH_3CH_2SO_3H$	–	–	–	17±1	20±2	34±14	10±2
CH_3SO_3H	48±16	45±11	53±20	–	–	–	18±2
H_2SO_4	12±8	4±2	14±9	11±2	15±2	36±18	14±1
SO_2	14±4	20±5	35±17	35±1	37±2	72±11	25±5
CH_3CHO	–	–	–	26±3	141±6	66±6	62±5
CH_2O	100±11	13±7	37±22	–	–	–	60±3
$CH_3CH_2ONO_2$	–	–	–	6±1	6±1	<2	<d.l.*
CH_3ONO_2	6±3	10±4	11±3	–	–	–	<d.l.*

Table 2. *Product yield of the reaction between NO_3 and the seven reduced organic sulphur compounds,$CH_3CH_2SCH_3$ (DMS), CH_3SH, CH_3SSCH_3, CH_3CH_2SH, $(CH_3CH_2)2S$, $(CH_3CH_2)_2S_2$ and$CH_3CH_2SCH_3$. The experiments were performed in purified air and under similar NOx rich conditions.*

The product yield is expressed in % of consumed reactant. HNO_3 was also identified as a main end product, but it could not be quantified, because additional HNO_3 was produced in the system by the N_2O_5 + H_2O reaction.

Uncertainties are given as one standard deviation of the experimental measurements and do not include possible systematic errors

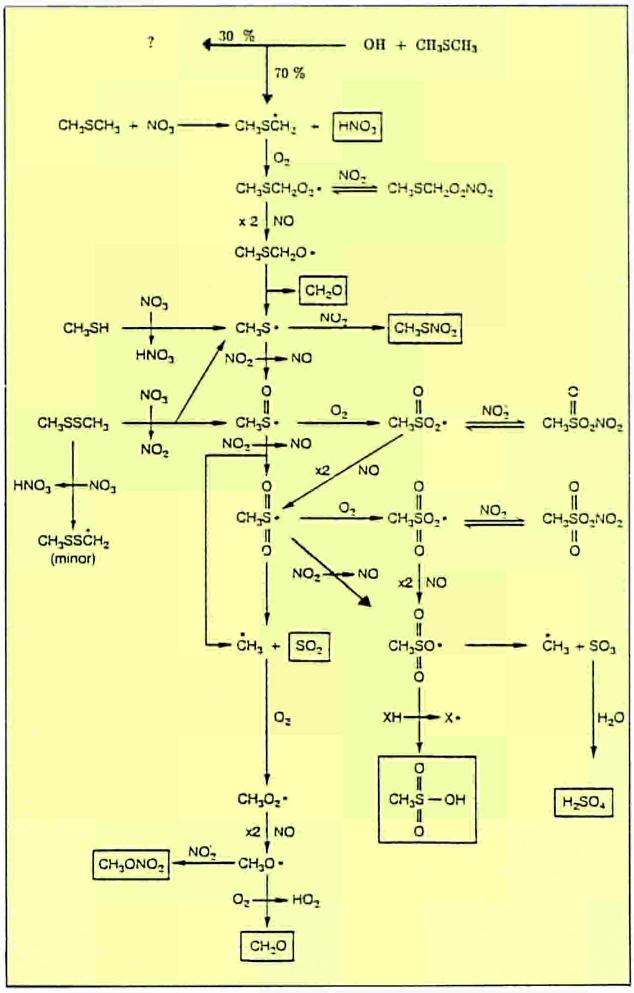


Fig. 9 : Suggested mechanisms for the reactions between NO_3 and CH_3SCH_3 (DMS), CH_3SH and CH_3SSCH_3.

The mechanism, except for the initial step, should be valid also for the OH initiated degradation of DMS. Experiments performed at 298 and atmospheric pressure show (Hynes A.J., Wine P.H. and Semmes D.H. (1986). J. Phys. Chem., 90, 4148. that 70% of the oxidation pathway for the DMS + OH reaction proceed by H-atom abstraction as indicated in the figure.

In addition, the formation of relatively stable peroxynitrate-intermediates with the tentative formula $RS(O)O_2NO_2$ was always observed. After the initial reaction step, which may be H-atom abstraction (R-S-R, R-S-H) most probably following NO_3 addition, or addition followed by decomposition (R-S-S-R), the degradation proceeds through the reactions of the three key intermediates, R-S°, R-S(O)°, R-S(O_2)° (Fig.9). Kinetics, products and mechanisms of the reaction of these species with their potential tropospheric reaction partners (O_2, O_3, NO and NO_2), as well as the rates of the unimolecular thermal dissociation, determine the yield of oxidized sulphur products. It must be stressed that this situation holds also in the case of the OH initiated daytime degradation of these species.

A climatic impact of DMS emission is understood to derive from gas-to-particle conversion of the oxidized sulphur products ($H2SO_4$, $CH3SO_3H$) and the contribution of these species to the formation of aerosols and, indirectly, to the modification of clouds lifetime and optical properties. The interaction between chemistry and aerosol dynamics of DMS and oxidation products is then of paramount importance.

A series of experiments were then performed in collaboration with the 'Atmospheric Physics' Unit using large Teflon bags as reaction chambers. Although the main objective was the study of the formation of particles by DMS oxidation (see section on 'Aerosol Science and Technology') useful information about the chemistry in a NOx-rich atmosphere was obtained. A particularly interesting result of these experiments is the observation that the peroxynitrate intermediate previously mentioned, apparently reacts with liquid water to form methane-sulphonic acid (MSA) as the main product. This pathway may modify the partitioning among the oxidized sulphur products, as resulting from the gas-phase reaction only, with consequences on the overall gas-to-particle conversion process.

Field measurements of the DMS oxidation product MSA, used as tracer of DMS emission, have been carried out during a cruise by the end of May around the Italian peninsula on the research vessel 'Minerva'. The measurements, performed with the collaboration of the analytical group of the Institute, showed an average MSA to non-sea-salt sulphate ratio of 0.9%. On this basis a very crude estimate of the contribution of DMS emissions to the total marine tropospheric sulphur budget on these sites in this period of the year can be made. By taking into account the typically observed product distribution by the oxidation of DMS under ambient tropospheric condition this contribution is estimated as approximately 13 %.

The reaction between NO_3 and HO_2.

In the chemical reactions system which controls the formation and the fate of the nitrate radical, a considerable importance has been recently attributed to the reactions between the nitrate radical and the hydroperoxyl radical:

a) $NO_3 + HO_2 \longrightarrow HNO_3 + O_2$

b) $NO_3 + HO_2 \longrightarrow HO + NO_2 + O_2$

and in particular to the second branching reaction. This reaction has been reported to be fast and in a recent paper (Platt et al., Nature, 1990, Vol. 348, 147) it has been suggested that it may be, under some conditions, an important source of OH radicals in the troposphere at night. The only existing value of the rate constant of reaction b) has however been measured at low pressure.

A study has been performed at atmospheric pressure reacting in a 480 L chamber HO_2 and NO_3 obtained by the thermal dissociation, respectively, of HO_2NO_2 and of N_2O_5. The OH radical was determined from the oxidation rate of isotopically labeled carbon monoxide, $C^{13}O^{18}$, added to the system and forming $O^{16}C^{13}O^{18}$, measured by second derivative tunable diode laser infrared spectroscopy (Fig. 10). Preliminary results of this study appear to indicate a reaction rate constant for the branching b) at atmospheric pressure and room temperature, slower (by one order of magnitude) than the value measured under the low pressure condition hitherto applied.

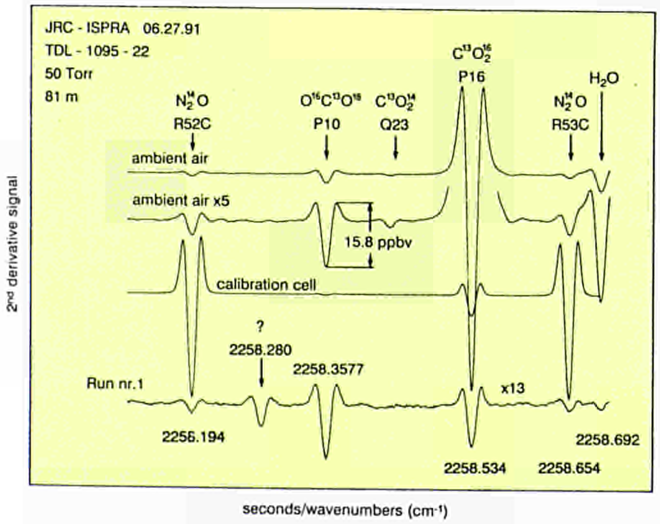


Fig. 10: Esperimental second derivative tunable diode laser absorption spectrum. From top: ambient air; reference cell containing CO_2 and N_2 O; gas mixture at the end of the reaction between HO_2 and NO_3 in presence of $C^{13}O^{18}$. The "?" indicates a spectral feature for which no attribution has been found.

Reaction of NO_3 with aromatics.

The NO_3 initiated oxidation of aromatic hydrocarbons must be considered a minor sink for these species; however the increasing concentrations of aromatics observed in urban areas demands a better description of the rates, mechanisms and products of all the degradation reactions of these hydrocarbons, also in regard to the possible formation of noxious compounds (nitro-derivatives).

The gas-phase reaction of NO_3 with aromatics has been subject of continuing study in collaboration with the University of Milan. Methyl-substituted benzaldehydes, benzyl-nitrate and benzyl-alcohols were observed and quantified as reaction products, by gas chromatographyc analysis; only aldehydes groups were positively identified by infrared spectroscopic analysis of the reaction mixture. The results of the experiments aimed at clarifying the mechanism holding in the gas phase reaction do not allow to conclude in favour of a predominant mechanism between direct atom abstraction from the methyl group or NO_3 addition to the aromatic ring followed by elimination of HNO_3. A third mechanism consisting of electron transfer with formation of a radical cation appears to be excluded.

Reaction of NO_3 with halogenated alkanes.

Hydrogen-containing halogenated alkanes (hydro-chloro-fluoro- carbons, HCFC and hydro-fluoro-carbons, HFC) have been proposed as substitutes for the CFC compounds.

Injection of these chemicals into the troposphere, while certainly releases the problem of stratospheric ozone depletion, is however matter of concern from two points of view, namely, their chemical degradation pathways and their global warming potential in relation to the accumulation in the atmosphere (see this report at "European Monitoring Network").

In the year, the investigation of the rate constants of the reaction of the NO_3 radical with a series of these compounds has been continued, confirming that these reactions are slow (ca 10 - 18 cm^{3} molecule^{1}s^{1} at 296°K), and that this degradation pathway is of minor importance with respect to the OH initiated oxidation.

Studies are now in progress of the mechanisms involved in the OH- initiated oxidation of these species.

The Ispra Mark 13A process for flue gas desulphurization

The pilot plant project

This flue gas desulphurization process has been invented at the JRC Ispra in 1980. Laboratory and bench-scale development work was carried out in the period 1980-1988. The Commission is supporting the final stage of the project i.e. the operation of pilot plant to desulphurize a flue gas throughput of 32,000 Nm^{3}/h at the SARAS Refinery in Sarroch (Sardinia Italy). The project is administratively under the responsibility of DG XIII Luxemburg and JRC Ispra bears the responsibility for the technical supervision.

The pilot plant in Sarroch was completed during the year 1988 and operation started in the first months of 1989. The first year of operation was dedicated to the testing of components (flowmeters, pumps, piping, etc.). The plant was in full operation for more than 2,000 hours. Several problems with components were encountered during this phase. The solving of the problems caused considerable delays in the execution of the experimental programme. In turn these delays originated caused, on their turn, financial and organizational problems to the main contractor, Ferlini Technology, who decided during 1990 that he needed a financially strong partner with chemical engineering experience for a successful termination of the contract. Work on the pilot plant project was temporarily suspended and new organization forms for the project were sought.

It must be stressed that the impasse was reached for reasons which are not connected in any way with the technical merit of the process.

During 1990, an Italian company, in co-operation with two partners, expressed the willingness to push forward the project , but neither they nor the Commission were ready to underwrite the debts incurred. To search for a way out of this impasse, the Commission organised during 1991 an exploration of the willingness of one or more leading European chemical or process engineering companies to enter into the project. This explorative research was carried out on a contract basis by the London based firm Pax Technology Transfer. The JRC Ispra collaborated very actively in the preparation of the necessary documentation and the dissemination of technical details. Final results of the study are expected to become available during the first months of 1992.

There still exists a strong interest of the US company General Atomics to commercialise the Ispra Mark 13A technology in the USA and to take over the activities of Ferlini Technology in Europe. However, a prerequisite condition for transfer of licence rights from the European Community to a USA company is that no European firm is likely to be interested. This condition will be fulfilled should no candidate result from the exploratory study in course. No legal obstacles will then exist for a partecipation of an American company in the project.

Bench scale work

A bench scale plant of the Ispra Mark 13A process is in operation at the Environment Institute. This plant is at present used to study specific problems occurring in the development of the process. During 1991 two of such problems have been tackled, namely:

- the aerosol formation and the effect of orimulsion fly ash;
- the removal of nitrogen oxides from flue gases

The Aerosol formation and the Effect of Orimulsion Fly Ash

During pilot plant operation an emission of HBr in the purified flue gas was observed (approximately 150 mg/m^3), most probably caused by the formation of a stable aerosol during the condensation of saturated water vapour in the presence of gaseous HBr. HBr concentrations in the exit gas of more than 50 mg/m^3 were observed also in the bench-scale plant

The possible formation, prevention and abatement of aqueous hydrogen bromide aerosols was studied, including a systematic study of the effect of scrubber temperature. It resulted that in the bench-scale plant the main cause of aerosol formation was a temperature drop in the section between the pre-concentrator and the reactor.

By taking adequate measures to avoid condensation at that spot, very low values of HBr vapour concentration at the scrubber exit were obtained. Typically, these values were ranging from 0 to 5 mg/m^3. The study was concluded by a test of a Koch aerosol filter, installed downstream of the scrubber. By the combination of prevention and abatement measures it was possible to reduce the HBr concentration in the gas outlet systematically at values below 1 mg/m^3.
The applicability of the Ispra Mark 13A process for the desulphurization of flue gases produced by the combustion of Orimulsion, a bitumen-water emulsion based fuel, was also investigated in the bench-scale unit.

The combustion of Orimulsion produces a fly ash, rich in magnesium and vanadium, which could have negative effects on the electrolysis of HBr, a principal step of the Ispra Mark 13A process. The performance of the electrolysis was studied in correlation with the dissolved fly ash concentration. Standard desulphurisation runs were carried out, voltage-current density relationships were established and rate constants of the cathodic back reaction were determined.

The results show that in all cases there is no significant difference between the results obtained with and without dissolved fly ash. The conclusion is that apparently there are no objections for the application of the Ispra Mark 13A process for the desulphurization of flue gases originating from the combustion of the new fuel.

Removal of nitrogen oxides from flue gases

Besides the abatement of sulphur dioxide, the researches for the extension of the Ispra Mark 13A process to a combined desulphurisation-denoxing process are carried out.

During 1991 work was focused on the development of a process based on the absorption of NO and the preparation of a concentrated stream of NO and H_2 suitable as a raw gas for the production of hydroxylamine.

The process thus combines the denoxing of waste gases (necessary for environmental reasons) with the production of a precious chemical, an intermediate product in the manufacture of nylon-6. The removal of the nitrogen oxides takes place by absorption and complexation in an aqueous solution of an iron chelate complex (e.g. Fe(EDTA)).

The NO is then desorbed from the complex by thermal stripping using hydrogen as a secondary scavenger gas. The hydrogen needed for this purpose is directly obtained in the process, from electrolysis of the aqueous Fe(EDTA) solution. Oxidation of the ferrous to ferric iron occurs when the complex comes into contact with oxygen containing gases and electrolytic (cathodic) reduction of Fe(III) to Fe(II) is necessary.

The desorption is carried out in such a way that a mixture of hydrogen and nitric oxide of about 35 vol% of NO and 65 vol% of H_2 is obtained. This gas mixture is suitable for the production of hydroxylamine according to well-known and industrially applied processes. During 1991 laboratory scale work was performed and a patent application filed.

Electrolytic removal of nitrates from waste waters

A new method for the removal of nitrates from waste water streams was tested. The process takes place in an electrolytic cell. In the cathode of the cell nitrates are reduced to ammonium ions, which in the anodic compartment can be decomposed into nitrogen.

The process was tried out with a simulated regeneration waste solution from the denitrification of drinking water by ion exchange. The work was carried out with a cell of a surface area of 500 cm^2. The effects of acidity of the solutions, current density etc. were investigated.

The work was continued with a number of once-through experiments at a low liquid flow rate. In these experiments, the liquid was first passed through the cathode and then through the anode of the electrolytic cell. The applied current density was 1.6 kA/m^2.

In one pass and a residence time of about 3 minutes, more than 50% of the nitrates were cathodically converted into ammonia. In the anodic compartment more than 80% of the formed ammonia is converted into nitrogen. However, there is still a large margin for process improvement.

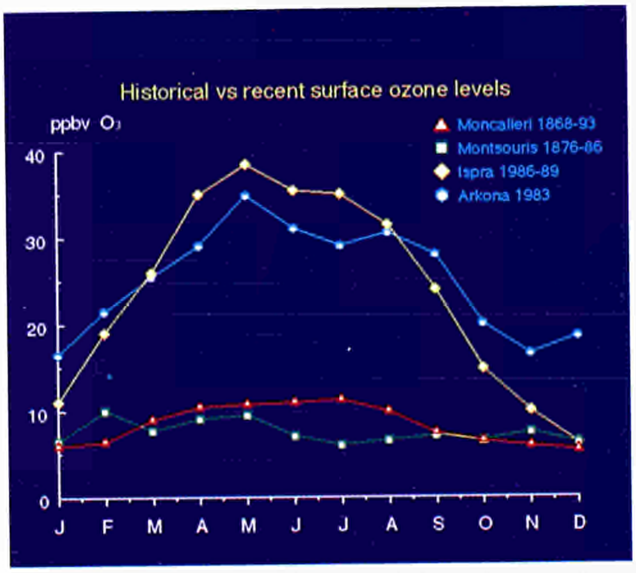


Fig. 11: Reconstruction of historical data of tropospheric ozone in the Northern Hemisphere: Moncalieri (1868-1893) and Montsouris (1876-1886) vs Arkona (1983) and Ispra (1986-89).

The results obtained up till now are considered very interesting and promising. Contacts with the specialised industry will be taken up during 1992.

EUROPEAN MONITORING NETWORK

Ozone Distribution in the Pre-Alpine and Alpine Region

As follow-up of previous studies on the mechanisms responsible of influencing the tropospheric ozone patterns in the pre-Alpine region, ozone measurements available in the pre-Alpine and Alpine regions since 1987 have been collected and assembled in a database.

Historical ozone data

Recently a 26-year (1868-1893) data series of daily ozone obervations made by the Schönbein technique at Moncalieri, near Turin, has been discovered. Data have been converted to present-day concentration following an ad-hoc developed procedure. From these data it could be stated that, in agreement with the Montsouris data series, the present-day levels exceed by 2-3 times those of one century ago and that an increase of the same order of magnitude is observed in the free troposphere (Fig.11).

The increase is most evident in the warm season indicating the predominant photochemical contribution.
The analysis of historical data has been expanded to observations made around 1880-1890 in South America. From this study we could derive that one century ago at 30°-40°S the surface ozone level was comparable to that observed at Montsouris and Moncalieri. Furthermore, the present-time ozone level observed at remote sites of that latitude of the Southern Hemisphere is ca. twice as large as one century ago; this increase is lower than that observed at ca. 45°-49° latitude (Turin, Paris) in the Northern Hemisphere.

Brewer Spectrophotometer

A Brewer ozone spectrophotometer, on demand and on-loan of the Italian Ministry of the Environment has been put in operation in the second half of the year. It should provide an ozone (stratospheric plus tropospheric column) monitoring station in the northern part of Italy, to be integrated in the European Brewer Net (BEN). The instrument (Mark IV) is specified for measuring, besides the total ozone column, the SO_2 and the NO_2 column, and in suitable conditions, the ozone vertical distribution (umkehr measurement). The instrument can operate unattended for days, but several aspects still demand careful investigation for a reliable interpretation of all the data supplied. The instrument participates in the WMO global ozone observation campaign, started at the beginning of October in correspondence with the European Arctic Stratospheric Ozone Experiment (EASOE).

Application of Spectroscopic Techniques

Halogenated alkanes HCFCs and HFCs, likewise CFCs, strongly absorb radiation in the 8-12 μm atmospheric window. Their global warming potential must then be evaluated to provide correct inputs to the atmospheric radiative transfer models.

A study has been performed to increase the scarce number of data available in the literature for the absorption cross-sections of these compounds, in particular concerning their temperature dependence.
The absolute infrared absorption strengths of five hydrohalocarbons (HFC-152a, HFC- 134a, HCFC-22, HCFC-123 and HCFC-142b) have been measured in the wavenumber region 600-1,500 cm^{-1} at 293K, 273K and 233K. A weak temperature dependence is apparent for all the halocarbons investigated, showing a slight increase of the band strengths at decreasing gas temperature.

In a parallel way, problems related to the detection of OH radicals in the troposphere using laser-based methods have been analysed through a detailed literature survey. Considering both laboratory and in-flight measurements, the following major conclusions have been reached:

- both Long Path Absorption (LPA) and Laser Induced Fluorescence (LIF) techniques used in various European and American laboratories are capable of detection sensitivities in the range 10^5 - 10^6 OH radicals cm^{-3}, which is considered to be adequate for testing fast tropospheric photochemistry;
- the problem of spurious generation of OH radicals, as a consequence of the photolysis of ozone caused by the UV laser beam, can be eliminated in the LIF technique by a two-colour excitation process (one infrared and one near-UV laser) since in this case neither laser photolises the ozone. The problem can also be minimized by using short excitation pulses, by expanding the laser beam to decrease its photon irradiance and by working at reduced pressure.

A fluorescence set-up, consisting of an excimer-pumped, pulsed tunable dye laser, frequency doubled in the UV, a reference hydrocarbon flame and a multichannel analyser has been assembled in the laboratory, in view of its potential use in the study of the excitation and fluorescence spectrum of the OH radical and in analytical applications in the frame of laboratory studies of atmospheric chemistry.

Atmospheric Tracers

Development and application of atmospheric tracer technology

Field experiments in which known amounts of an inert tracer are released into the atmosphere and measurements of the air concentration are carried out at various downwind locations are well known tool for studying meteorological processes. Evaluation, verification and improvement of transport model calculations are also important aspect of such field experiments.

At the Environment Institute field experiments are performed using perfluoro-carbon tracers (PFCs).

A well equipped mobile unit for tracer release and tracer analysis allows fast operation in the field. For the collection of air samples more than 100 battery powered samplers with 8 separate lines each are available. Air is sampled into special plastic bags. The determination of the tracer concentration is performed in a modern laboratory by GC analysis with an electron capture detector. The tracer technique has been successfully applied in several field experiments.

During 1991 new chemical compounds were tested to assess their suitability as atmospheric tracer. This need arose as the perfluorocarbon tracers used so far are no longer manufactured. A new tracer release unit was built to perform small scale experiments.

The present system allows for perfluoro-carbons to be detected at the pptv level. But in future experiments (e.g. ETEX, see section 4.6.) it will be necessary to detect the tracer at even lower concentrations levels. Therefore a pre-concentration of the tracer has to be made by increasing the sampled air volume by a factor of 100 or more. A well known technique is to sample the tracer in absorption tubes. However for our purposes suitable material for absorption of the tracer had to be found and tested. For the analytical part a thermal desorption unit including a 50 sample carrousel has been installed. First performance tests have been carried out.
Tracer experiment to study air flow across the Alps the results are reported in section 5.

The tracer technique will be used to study the main processes of pollutant transport in the mesoscale over complex terrain and the handover of pollutants from the planetary boundary layer to the lower troposphere. The application of the tracer technique is envisaged in various field experiments. For example in the new project "Biogenic Emissions in the Mediterranean Area" the tracer may be used to check deposition velocities derived by the gradient method. A major part of our future activity is dedicated to the needs of ETEX, a "European Tracer Experiment", described in section 4.6. In particular sampling devices have to be modified and the chemical analysis system upgraded.

Modelling of atmospheric transport

In the course of 1991 a great deal of activities has been performed in developing and testing atmospheric transport and dispersion models.
The availability of data from tracer release experiments at short and mesoscale range makes this activity particularly promising , also in view of the generally perceived needs for standardization of models for nuclear and chemical pollution episodes and, more generally, for environmental impact assessment. This requirement has produced the launching in Europe of various initiatives and projects, with which connections have been established.

Comparison of concentration fields obtained by using different models has been carried out for the short range. The analysis was continued for the mesoscale including the comparison with the tracer releases data from the 1989 TRANSALP campaign using a mass consistent model for the determination of the windfield . The results indicated that in slightly complex orographies good agreement is achieved between measurements and model results. This is not always true in alpine regions where valley bifurcations exist and altitude gradients are often larger than 20% .

For what concerns regional circulation models, which include such phenomena like sea and lake breezes or mountain-valley circulation, two different models have been made available during the period:

- T.V.M. (Three dimensional Vorticity Model), developed at Louvain-la Neuve University.
- R.A.M.S. (Regional Atmospheric Modelling System) , which includes also a non-hydrostatic version and is therefore more suited for the complex alpine terrains .

These models are been compared with the data of the air pollution remote sensing campaign performed at Fos on 1983.

Aerosols and Global Climatic Change

Modelling

Model development and applications proceeded along three lines:

- zero-dimensional models of the microphysics and chemistry of aerosol formation (models AERO2, IMAD, OCCAM)
- uncertainty analysis of the aerosol model AERO2
- three-dimensional global modelling of the sulphur cycle (MOGUNTIA).

AERO2 describes the formation of H_2SO_4-H_2O aerosols from the gas phase treating the processes of nucleation, condensation, coagulation and deposition. It calculates the evolution of the full size distribution of the aerosol. The thermodynamics of H_2SO_4-H_2O solutions embedded in AERO2 has been extended to allow calculations in a wide range of atmospheric conditions : i.e. temperatures between - 80 and 100 °C and relative humidities between 0 and 100 %.

In a first application, AERO2 has been calibrated against a set of smog chamber experiments with SO_2-NOx mixtures.
The constant k1 of the reaction SO_2+OH H_2SO_4 came out to be in the range 7.8×10^{-13} and 1×10^{-12} molec^{-1}.cm^{3}.s^{-1}, which is smaller than and within the range of the literature. It also followed that the nucleation rates (Jaecker-Voirol and Mirabel, Atm. Env. 23 (1989) p.2053) used in AERO2 should be multiplied by a factor tn between 10^4 and 10^7, which is near the upper bound of the range in the literature. In the light of the remaining uncertainties on k1 and tn, the uncertainty on the accommodation coefficient ($0.04 < \alpha < 0.09$) becomes important.

In a second application AERO2 was calibrated with a number of field observations of new aerosol formation near the top of marine stratus clouds (Hegg et al., JGR 95 (1990) p.13917). AERO2 could reproduce these observations only when for the nucleation tuner tn a value of 10^4 was taken and for the accommodation coefficient a value between 0.04 and 0.3. These values are consistent with those obtained from the smog chamber experiments.

Our values for tn are in large contrast with a recent (and only) set of experiments on nucleation in H_2SO_4-H_2O mixtures yielding a value for tn of about 10-12 (Wyslouzil et al., J.Chem.Phys. 94 (1991) p.6842). It was concluded that in the smog chamber either 1) H_2SO_4 and H_2O are not the only species participating in the initial phase of the nucleation process, or 2) that the reaction between SO_2 and OH initially leads to intermediate sulphur or sulphur-nitrogen complexes that nucleate more easily than H_2SO_4.

IMAD is the name of a family of models that describe aerosol formation and growth in terms of a limited number of parameters: the gas phase concentration of the condensable species, the total number and the total mass concentration of the aerosol. Although IMAD gives less size information than AERO2, it more easily allows for the description of multi component systems. IMAD2 and IMAD3 were developed to describe H_2SO_4-H_2O and H_2SO_4-MSA-H_2O aerosols respectively. IMAD2 was successfully compared with AERO2 and will probably be implemented in the MOGUNTIA model. IMAD3 was developed in particular for interpreting a set of smog chamber experiments dealing with formation of aerosols from the reaction of NO_3 with DMS.

In the frame of the development of IMAD3, the possibility of ternary nucleation in the H_2SO_4-MSA H_2O system was investigated.
It was found that, at 298°K, at least 100 pptV gaseous MSA should be added to the system in order to induce a noticeable increase in the nucleation rate with respect to the binary case. This suggests that ternary nucleation is not relevant in the marine boundary layer where much lower MSA concentrations occur.It might however occur in smog chamber experiments.

Aerosol production from the DMS + NO_3 reaction

The laboratory experiments on aerosol formation from the night time chemistry of DMS were completed. (For a description of the experimental set up and experimental method see previous Annual Report). The goal of the last set of experiments was to obtain experimental evidence for the large stability of a peroxynitrate intermediate, something that was hypothesized after the previous experiments.

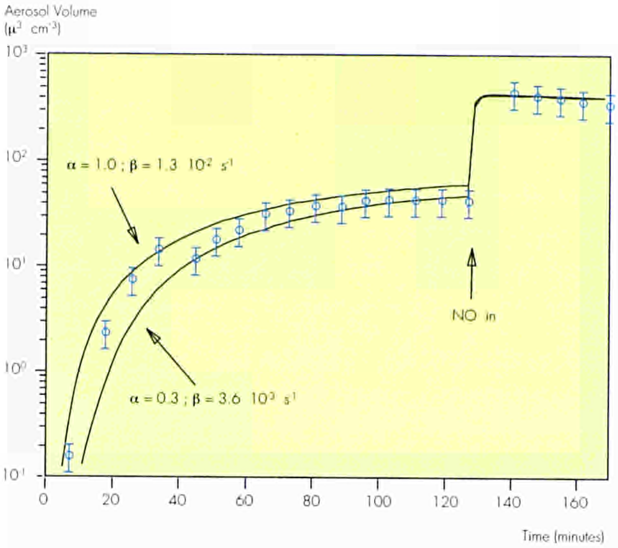


Fig. 12a: The aerosol volume resulting from the DMS + NO_3 reaction in the 1.4 m^3 teflon bag reactor, for one typical experiment. Lines represent model calculations with IMAD3. The figure shows the extreme acceptable cases for the MSA accommodation coefficient within the uncertainty on the vapour deposition rate β.

The experimental conditions were the same as before, except for the addition of excess NO to the system after 2 hours. This should lead to the immediate conversion of the peroxynitrate to MSA which should be found back in the aerosol.

Fig 12.a shows the aerosol volume as a function of time during one experiment. The volume sharply increases upon addition of NO; simultaneously, the ion-chromatography of the aerosol shows an increase of MSA. This is taken as evidence that peroxynitrate was present at the moment of adding NO. It also shows that the peroxynitrate is fairly stable under the conditions of the first two hours of the experiment. This observation triggered more detailed experiments on the stability of this peroxinitrate in the photochemical cell of the Atmospheric Chemistry Unit. The fact that the volume increases quasi instantaneously after addition of NO also suggest a high accommodation coefficient for MSA on the

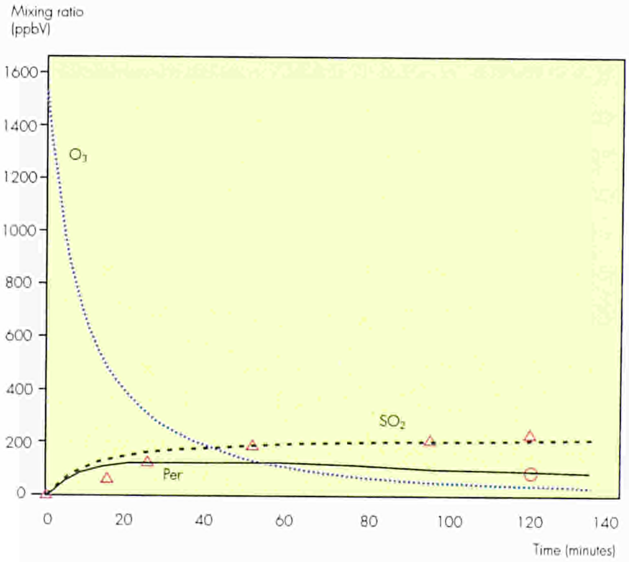


Fig.12b: Measured concentrations of SO_2, O_3 and Peroxynitrate for the same experiment as in Fig. 1a. Lines represent the fitting by the chemical kinetics model CHEMFIT

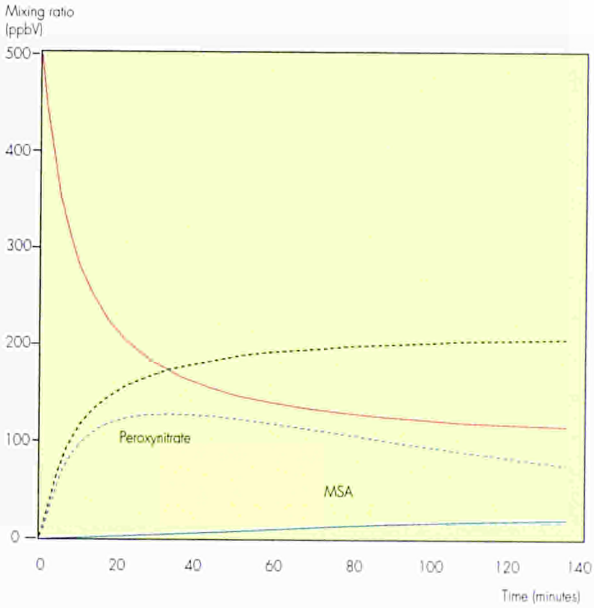


Fig.12c: Partitioning of the sulphur compounds resulting from the night-time chemistry of DMS, calculated with the chemical model for the conditions of the experiments.

aerosol. Quantitative information on the MSA accommodation coefficient was obtained by fitting in an iterative way a chemical kinetics model and IMAD3 (Fig.12.b) to the measurements of the gas phase and aerosol phase. The fitting procedure is shown in Fig. 13. The final fits are shown in Fig. 12a and 12b. Compared to the previous modelling attempt, in which the peroxynitrate was not included in the chemical model, a substantial improvement in the agreement between modelled and measured aerosol parameters is achieved. For the MSA formation rate given by the chemical model, and within the uncertainty on wall deposition rates of MSA and H_2SO_4, a sticking probability between 0.3 and 1 gives excellent agreement for the aerosol volume over the 3 hours run, including the "jump" caused by adding NO (Fig. 12a). Figure 12c shows the partitioning of the sulphur compound. It is shown that before adding NO, aerosol particles contain only a minor fraction of the sulphur compounds resulting from the DMS + NO_3 reaction: 4% is a maximum for the yield of MSA + H_2SO_4 in the aerosol with respect to initial DMS. The remaining 96 % being SO_2 and peroxynitrate.

The experiments show the importance of the peroxynitrate intermediate as a buffer for sulphur, prior to its conversion to condensable products. The peroxynitrate is a PAN-like compound with a strong temperature-dependent decay-rate. Hence, it should be taken into account in the atmospheric sulphur balance and in evaluating global transport properties of sulphur.

The MSA sticking probability obtained is not restricted to this particular chemical system, but is also applicable to the daytime chemistry, were larger yields ofH_2SO_4 and MSA are observed. The value of the MSA sticking probability is essential in modelling aerosol growth rates, in particular for predicting CCN concentrations. Because of the low nucleation potential of MSA (compared to H_2SO_4), and because of its higher sticking probability, MSA is not likely to contribute to new particle formation over remote oceans. On the other hand, it has a higher "particle growth" potential than H_2SO_4, and thus can significantly contribute to the formation of CCN.

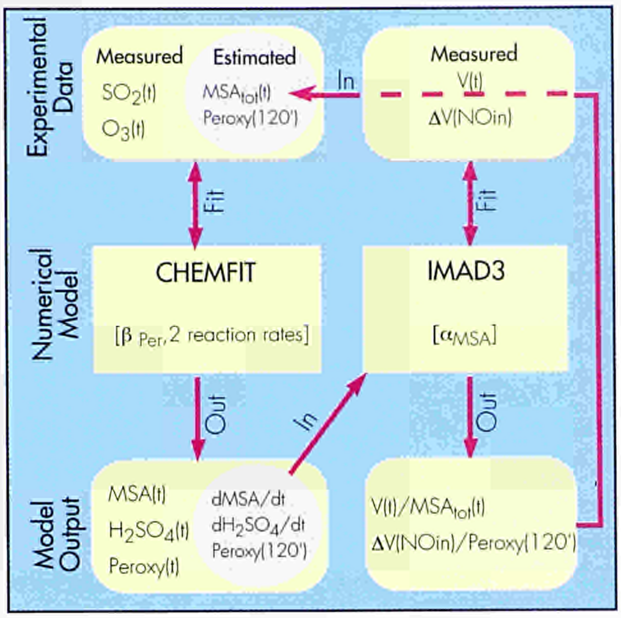


Fig. 13: *Scheme of the fitting procedure. The deposition rate of peroxynitrate, β_{Per}, and two reaction rates are adjustable in the chemical model CHEMFIT, whereas the accommodation coefficient of MSA, α_{MSA}, is the only adjustable parameter in the aerosol model IMAD3. The procedure starts with an estimation of the time profile of total, MSA $MSA_{tot}(t)$ (inferred from the aerosol volume profile V(t)) and with an estimation of the Peroxynitrate concentrations at 120 min (inferred from the measured jump in V when NO is introduced (.V(NO in). CHEMFIT then calculates formation rates of MSA and H_2SO_4, which are introduced in IMAD3 to calculate new values for $MSA_{tot}(t)$ and Peroxy(120').*

Environmental Sulphur Cycle: a new project

In an attempt to merge existing activities related to the environmental sulphur cycle an inter-institute research activity was started in 1991. The initiative was promoted by a number of researchers, after they realized that they were tackling different sides of the same issue. In particular:

- The Air Chemistry Unit at the Environment Institute studies the complex kinetics of the dimethylsulfide (DMS) oxidation, responsible for SO_2, methanesulfonic acid and excess sulphate levels observed over oceanic areas.

- In the same Institute, the Atmospheric Physics Unit studies the aerosol growth from sulphate particles and the evolution of the size distribution of the aerosol, with the formation of Cloud Condensation Nuclei (CCN).
- The Institute for Remote Sensing Application (IRSA) has an on-going activity on the modelling of the DMS production rate in relation to the ocean phytoplankton biomass cycle.
- The Institute for Safety Technology (IST) has an interest in fluid dynamics modelling, in collaboration with IRSA, aiming to couple ocean modelling with atmospheric modelling to investigate global climatic changes.

The sulphur cycle project was finally boosted into life from Prof. M. Schlesinger, who spent a short sabbatical at JRC in summer 1991 discussing with all the involved scientists and their management, and drafting a proposal for a set of Global Change related activities (Schlesinger M.E. "Recommendation for global change research to be performed by CEC/JRC Establishement" Ispra 1991). It will be peculiar of this project, if successful, the bottom-up process which led to its birth.

The rationale for the study stands on the following considerations.

The sulphur cycle is summarily described in Fig.14. DMS from the ocean biota is related to the density of cloud concentration nuclei, which in turn influences cloud coverage and albedo, both affecting ocean insolation. The cycle is closed by the influence of insolation on the DMS productivity from the biota. A description of the evidence and the assumptions behind the cycle concept is found in Bates S. T., Charlson R. J. and Gammon R. H. - " Evidence for the climatic role of marine biogenic sulphur"; Nature, 329, September 1987; and in Foley J. A. , Taylor K. E. and Ghan S. J. - "Planctonic dimethylsulfide and cloud albedo: an estimate of the feedback response"; Climatic Change, 1-15, 1991.

The rationale for studying this cycle is twofold. On one hand it is relevant to the study of the climate evolution to quantify the response of the DMS cycle to external forcing. The forcing being considered is a doubling of the CO_2 concentration and the parameter to be estimated is ΔT_{2x}, the change in mean temperature resulting from a doubling of CO_2, including the feedback response. On the other hand a validated model for the sulphur cycle would allow that part of the uncertainty on ΔT_{2x} which is due to antropogenic sulphur to be reduced (See the above mentioned report by Schlesinger).

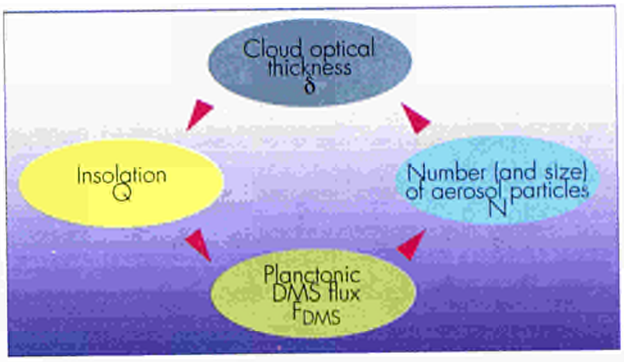


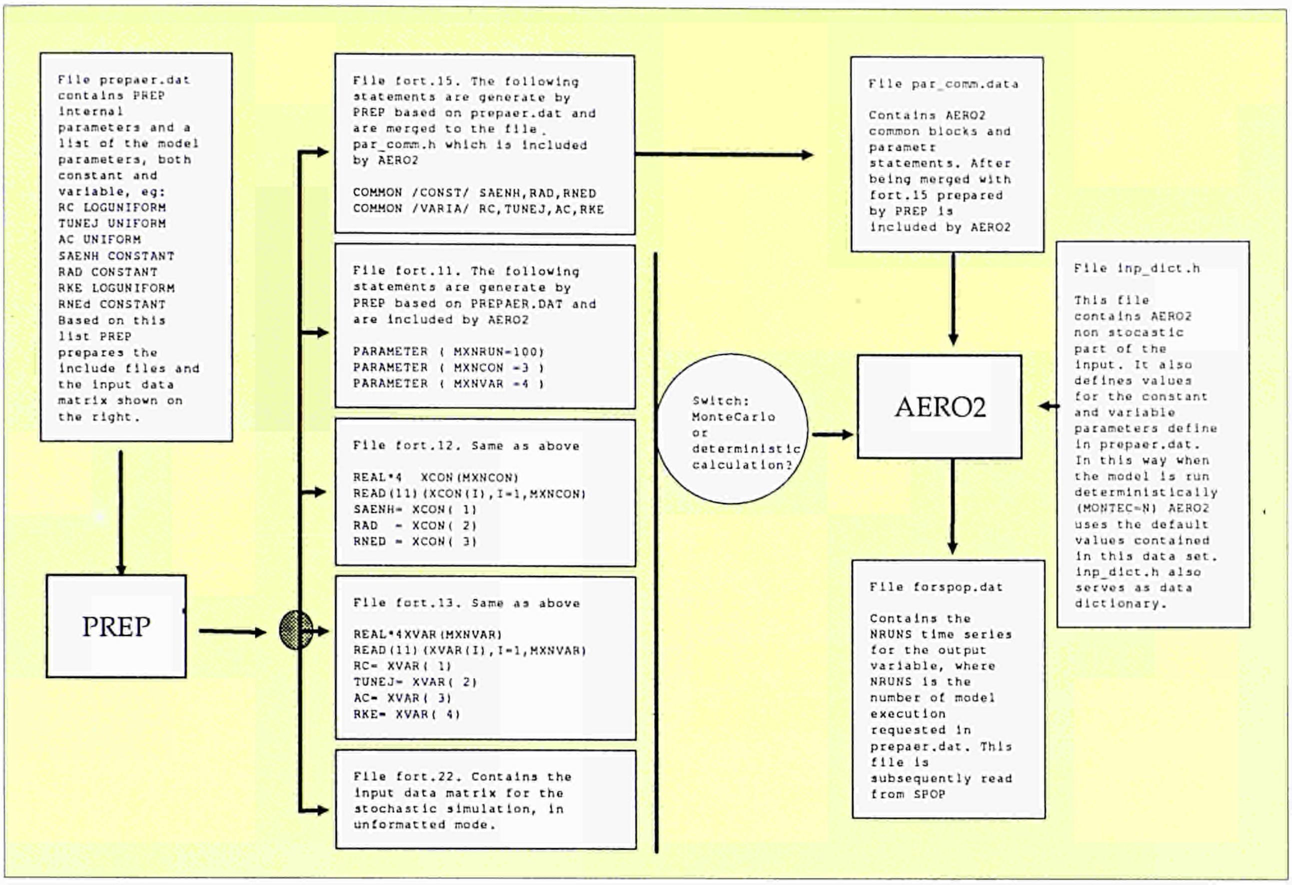
Fig. 14: DMS cycle Bates (1987) and Foley, (1991) FDMS is sensitive to Q and influences N. N affects δ which governs Q.

A global model of the sulphur cycle is bound to be affected by uncertainties of various kind, both in the models and in the input parameters. Modelling climate response to external forcing is a typical case of prediction under uncertainty.

Computational tools have been developd at EI which can be used at the various stages of the analysis. In particular the PREP and SPOP codes allow an individual system model to be run stocastically (Fig.15). This is useful in a number of instances, namely:

- When performing uncertainty analysis (how uncertain is the prediction ?)
- In sensitivity analysis (which parameter has most impact on output uncertainty ?)
- When tackling aggregation problems (how many aerosol classes should be used; how many layer the ocean model should have)
- When balancing computer code cpu versus accuracy.

In its above mentioned report, Prof. Schlesinger



```
File prepaer.dat
contains PREP
internal
parameters and a
list of the model
parameters, both
constant and
variable, eg:
RC LOGUNIFORM
TUNEJ UNIFORM
AC UNIFORM
SAENH CONSTANT
RAD CONSTANT
RKE LOGUNIFORM
RNEd CONSTANT
Based on this
list PREP
prepares the
include files and
the input data
matrix shown on
the right.
```

```
File fort.15. The following
statements are generate by
PREP based on prepaer.dat and
are merged to the file.
par_comm.h which is included
by AERO2

COMMON /CONST/ SAENH,RAD,RNED
COMMON /VARIA/ RC,TUNEJ,AC,RKE
```

```
File fort.11. The following
statements are generate by
PREP based on PREPAER.DAT and
are included by AERO2

PARAMETER ( MXNRUN=100)
PARAMETER ( MXNCON =3 )
PARAMETER ( MXNVAR =4 )
```

```
File fort.12. Same as above

REAL*4   XCON(MXNCON)
READ(11)(XCON(I),I=1,MXNCON)
SAENH= XCON( 1)
RAD  = XCON( 2)
RNED = XCON( 3)
```

```
File fort.13. Same as above

REAL*4XVAR(MXNVAR)
READ(11)(XVAR(I),I=1,MXNVAR)
RC= XVAR( 1)
TUNEJ= XVAR( 2)
AC= XVAR( 3)
RKE= XVAR( 4)
```

```
File fort.22. Contains the
input data matrix for the
stochastic simulation, in
unformatted mode.
```

```
File par_comm.data

Contains AERO2
common blocks and
parametr
statements. After
being merged with
fort.15 prepared
by PREP is
included by AERO2
```

```
File inp_dict.h

This file
contains AERO2
non stocastic
part of the
input. It also
defines values
for the constant
and variable
parameters define
in prepaer.dat.
In this way when
the model is run
deterministically
(MONTEC=N) AERO2
uses the default
values contained
in this data set.
inp_dict.h also
serves as data
dictionary.
```

```
File forspop.dat

Contains the
NRUNS time series
for the output
variable, where
NRUNS is the
number of model
execution
requested in
prepaer.dat. This
file is
subsequently read
from SPOP
```

Fig. 15 :This flow diagrams is part of PREP/SPOP documentation and illustrates how PREP organizes the stocastic simulation for AERO2. The user defines in prepaer.dat (left) all the variables for which a distribution of values might be used. In the example above it has been decided that eg RAD is a CONSTANT, and RKE is a variable with a LOGUNIFORM distribution. For a subsequent analysis the user may revert this choice changing only the keywork for RAD and RKE in the file prepaer.dat. PREP takes care of things such as : generating the appropriate commmon block and parameter statements for AERO2, assigning the appropriate element of the stocastic input matrix to the variable (eg RKE=XVAR(4)), counting the number of variables and so on. Based upon the value of the switch MONTEC in inp_dict.h(see right) AERO2 selects whether including fort.12 and fort.13 and reading the matrix in fort.22 (MONTEC=Y) or going on with the values which are in any case given in inp_dict (MONTEC=N). In other words, RKE and RAD are also defined in inp_dict, these values being overidden for MONTEC=Y.

suggested for the integrated model of the sulphur cycle the acronym OBCAAM, the Ocean Biology Chemical Atmosphere Model; in an attempt to euphonize, the term OCCAM was also put forward.

Different modules of the OCCAM code are already available at JRC, though at different stages of development. In particular:

- Kinetics of DMS oxidation are modelled at EI Air Chemistry Unit using the package FACSIMILE (Mainframe and Personal Computer versions).
- Aerosol growth is modelled at EI Air Physics Unit, using the FORTRAN code AERO2 (running on workstation).
- A global model for tracer transport (MOGUNTIA) has been received from the University of Mainz and is being tested on a workstation at the ITS.
- A model is available at IRSA for the ocean biota system (SMALLTALK package, on workstation).
- An ocean transport model is available at IST (ISPRA-MIX).

A description of the how those models can be interlinked can be found in Prof. Schlesinger's report .

Source work has been already done toward OCCAM during 1991. In particular OCCAM related activities include:

- A re-coding of AERO2 meant to accelerate the

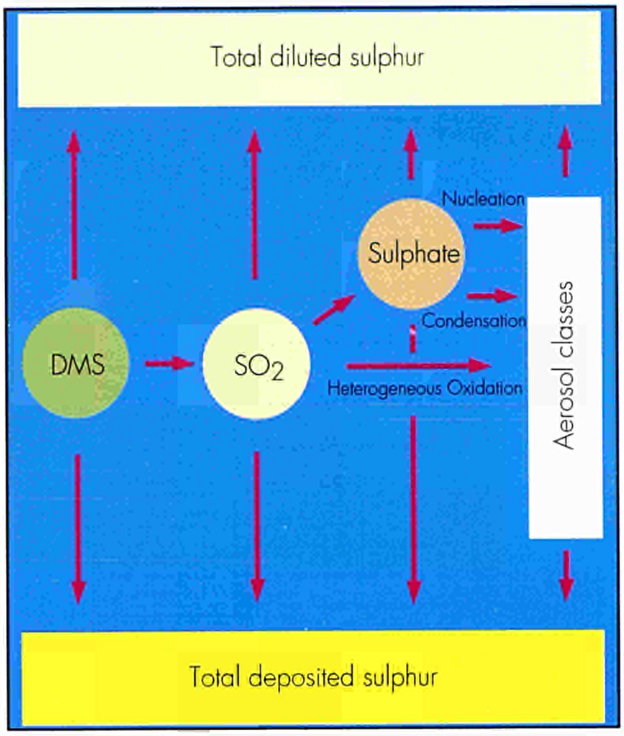


Fig.16: Processes considered in the DMS kinetics-aerosol formation model AERO2. The arrows indicate deposition, dilution, nucleation, condensation, homogeneous and heterogeneous oxidation of SO_2.

execution time and to ease the interfacing of this code with the other modules of OCCAM; the re-coding also allowed AERO2 to be run stocastically, in conjunction with the processors PREP and SPOP described previously. During 1991 AERO2 was also migrated from mainframe computer to workstation.

- Inclusion of simplified DMS oxidation kinetics in AERO2, in collaboration with the Atmospheric Chemisty Unit. The following processes were included: homogeneous (gas phase) oxidation of DMS to SO_2; homogeneous oxidation of SO_2 to sulphate; heterogeneous oxidation of SO_2 to sulphate (within the aerosol particle. See Fig.16).

- Uncertainty, Sensitivity and Regression analysis on the AERO2 model. With uncertainty analysis the range of the model prediction (total aerosol particle number and volume) was quantified as function of the uncertainty in four selected input parameters. Sensitivity analysis allowed the order of importance of the parameters in generating uncertainty in the output to be ranked. Using regression analysis the parameters were calibrated against three sets of experimental results.

WATER QUALITY

Lake Orta

The trace metal studies, designed to support the development of predictive metal dispersion models for freshwater systems of the EC and realized on lake Orta (Italy), selected as suitable test site, considered besides the most important element Cu, a number of trace elements (EC Directive 76/464 List II) during the analytical steps of the project.
One of these, Ni, was found at surprisingly high concentrations in the dissolved state (average lake concentration) which are explained by irregular and high discharges observed in four out of the seven monitored tributaries (Table 3).
On the basis of the analytical figures the following conclusions were drawn: lake Orta receives from tributaries 3640 kg/year and from other external sources (precipitations, surface runoff) 350 kg/year of Ni, 2203 kg/year being transported by the out-flowing river and 645 kg/year removed from the water column and deposited along with settling particulate matter.
Assuming zero internal Ni loading by remobilization from settling and settled particles a rather unrealistic assumption, taking into account the general mobility of Ni compounds observed in the aquatic environment, the remaining 1038 kg/year would lead to an estimated yearly Ni concentration increment of about 1 mg/m3 in the dissolved phase, and considering the already high present Ni concentration of 17 mg/m3, critical concentrations could be reached rather soon. External river loading therefore needs to be reduced drastically.
Modelling studies have mainly concerned a refinement of numerical results as for the evolution of Cu concentration in the lake.
For heavy metals other than Cu (i.e. Ni, Cr, Zn), for which historical data are rather scarce, the calculation programme is somewhat reduced with respect to copper, being limited to the evaluation of metal characteristic times and asymptotic concentrations, both in the mixed reactor and in the two vertical box approximations.

These results will be included in the Lake Orta project final report.

As the conclusion of Water Quality project activities during 1981-1991, modelling studies carried out in this period were collected in a monograph, published by the Commission.

CHEMICAL WASTE

Soil-Pollutant Interaction Studies

3,4,5-Trichloraniline (3,4,5-TCA) has been used as a model compound for chloroanilines which are found in waste streams from tanneries and pesticide industries. Sorption/desorption experiments were set up for 7 natural soil horizons having a broad range of organic carbon content (0.15 - 6.13%) and 3,4,5-TCA distributions between soil and soilwater (Kd) were measured. Linear and Freundlich sorption isotherms were derived for concentrations in the ppm range. The organic carbon distribution coefficient was determined (Koc=2766± 126 L/kg). The water solubility and the octanol/water partition coefficient of 3,4,5-TCA were measured at pH 3, 5, 7 and 9. Soil sorption (Koc) of chloroanilines can be predicted reasonably well from experimental models based either on the compound water solubility or on the octanol/water partition coefficient.

In order to evaluate potential groundwater pollution originating from vinclozolin (a broadly used pesticide) application, the degradation intermediates and 3,5-dichloroaniline (3,5-DCA) had also to be considered. Vinclozolin showed higher mobility in the soil-water system than did 3,5-DCA, suggesting that a possible source of 3,5-DCA groundwater contamination could derive from the degradation of vinclozolin in the deeper soil horizons rather than from direct migration of 3,5-DCA from the top soil.

Uptake of polychlorinated biphenyls (PCBs) by earthworms (lumbricus rubellus) from a soil contaminated with a commercial PCB formulation (Askarel at 150 μg/g) and later release of PCBs by the contaminated earthworms into a low contaminated soil (1.5 ug/g) have been studied. The uptake and release rates were similar for all PCB congeners notwithstanding their different chlorine substitution pattern, suggesting that bioaccumulation of PCBs in earthworms is governed by passive, possibly diffusion controlled processes. The soil to earthworm bioconcentration ranged from 4 to 20 for tetra- to octachlorinated biphenyls and was weakly dependent on the octanol-water partition coefficient.

Soil sorption of atrazine was studied in 110 different soil horizons from 24 different soil profiles all deriving from granodioritic materials. The soil

	n	Nickel concentration (dissolved) [mg/m^3]			n	Nickel concentration in particulate matter [mg/kg]			KD [m^3/kg]		
		Mean	Max	Min.		Mean	Max	Min.	Mean	Max	Min.
Whole lake	386	17	91	3	404	193	1602	0.2	15	223	0.7
Lake outlet	33	15	32	2	33	136	358	12	12	50	0.7
Feeding rivers	28	34	259	0.2	28	908	5229	58	438	9288	0.4
Background river (Toce)	40	3	20	0.2	40	89	233	23	100	469	6

Table 3. Nickel input and output to lake Orta.

sorption was statistically correlated by multiple linear regression analysis with organic matter of the soil, aluminium oxides and iron oxides. Clay did not correlate with soil sorption of atrazine. It is speculated that coating of the clay by organic matter may mask sorption sites in the clay.

The influence of humic substances on the transport rate of selected trace metals (Hg, Cr, Co) in soil and aquifer systems was investigated by using a combination of spectroscopic techniques and adsorption measurements under static and dynamic conditions.

Reduction of hexavalent Cr to the trivalent state is considered as a safe strategy for the disposal of Cr containing wastes. This is based on the lower solubilities of Cr(III) compounds with respect to Cr(VI). However, complexation of trivalent Cr ions with naturally occurring organic substances may increase transport rates and bioavailabilities of Cr compounds. Time Resolved Laser Fluorescence was used to investigate the possible binding of Cr(III) to the humic acid employed in the column experiments. Spectroscopic measurements were made in the system Cr/HA/Eu by looking at the decrease of the fluorescence signal of the pre-formed EuHA complex with increasing concentrations of the non-fluorescent Cr(III) ions. Fig. 17 compares the fluorescence titration curves obtained by reporting the intensity of the signal as a function of the humic acid concentration. The observed decrease can only be ascribed to a chemical competition effect leading to the formation of a CrHA adduct. Formation of CrHA microcolloids was observed at high Cr concentrations.

Column migration experiments showed a considerable enhancement in the mobility of Co when 10 ppm of a lower molecular weight humic acid (HA) were added in the flowing groundwater. This may be due either to the saturation of sorption sites on the sand by HA, or to the formation of unreactive CoHA species. Similar observations were made for Cr(III). In this case, however, the migration experiment was performed in the open atmosphere, where an oxidation process of Cr(III) to Cr(VI) due to dissolved oxygen was observed. Although Cr(III) is relatively stable under oxidizing conditions for kinetic reasons, the redox transformation, probably accelerated by undetected impurities in the heterogeneous system, was fast enough to prevent an unambiguous interpretation of the column experiment. This will be repeated under strictly controlled redox conditions by using anoxic chambers better simulating subsurface environments.

Concerning Hg interactions with humic substances, the investigation was started under static conditions using alumina particles as a model of main inorganic components of soils and sediments.

Environmental Informatics Studies

In the context of pollutant migration in porous media the stochastic model FEMSUN (Finite Element Model coupled with Sensitivity and UNcertainty analysis) has been applied to study and quantify the uncertainties due to the variability and scarse knowledge of the parameters and to a lesser extent to study uncertainties resulting from incomplete model description or approximation.

The parameters required in the implementation of the stochastic concept by the FEMSUN code along with their ranges of variability have been determined by laboratory and field investigations,

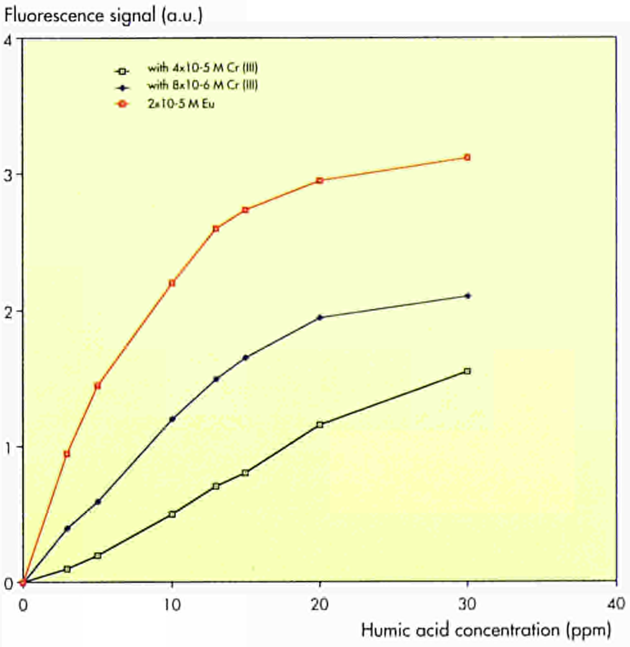


Fig. 17: Fluorescence titration curves in the system Cr(III)/HA/Eu

including:

- soil hydrodynamic characterization employing gamma-ray attenuation measurements during column experiments (performed at Grenoble University);
- soil chemical characterization, employing neutron activation analysis and radioisotope techniques in batch and column experiments.

For those parameters for which site-specific data were lacking representative data have been compiled from literature.

Based on stochastic simulations performed by the FEMSUN the relative importance of the various parameters on the contaminant transport has been investigated on an hypothetical chemical waste repository site. For the assumptions used, the system studied, and the range of parameters tested, the distribution coefficient Kd, the longitudinal dispersivity DL and the coefficient L of the van Genuchten's model have been identified as the most sensitive parameters contributing most significantly to the uncertainty in contaminant redistribution. In addition, it was demonstrated that the FEMSUN code can be useful in optimizing requirements for spatial and temporal sampling parameters suitable for a monitoring network. This can be accomplished by:

- diagnosing areas at low and high sensitivities
- ranking the model parameters with respect to their relative influence on the model output in space and time.

The parameter vector estimation procedure concerning the van Genuchten's model which describe the hydrodynamic soil properties in the unsaturated zone, came from employing a

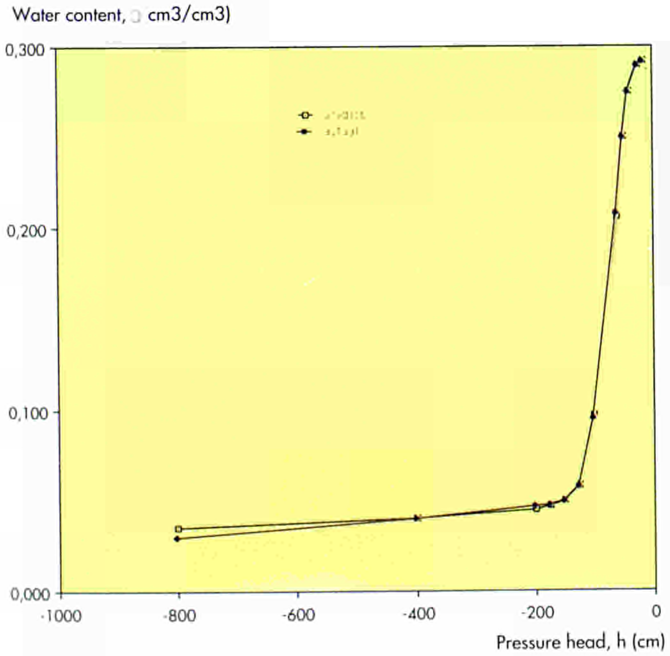


Fig.18: *Hydraulic properties function 1: water content-pressure head relationship.*

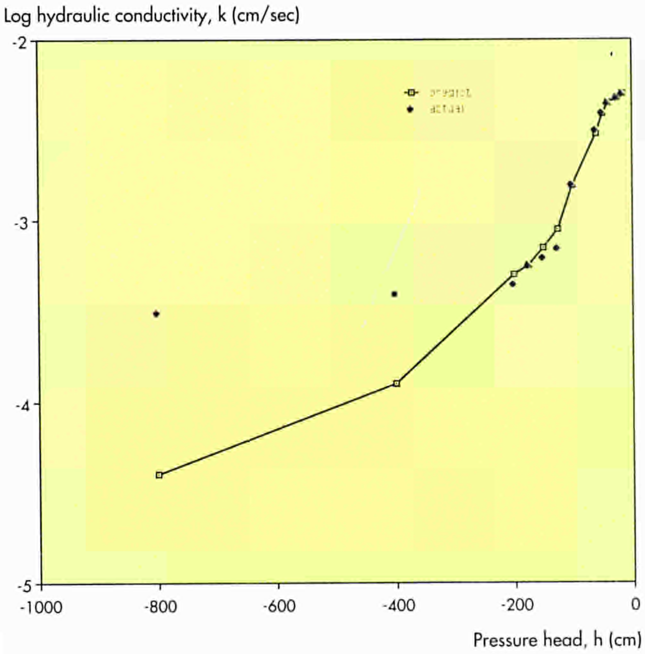


Fig.19: *Hydraulic properties function 2: hydraulic - pressure head relationship.*

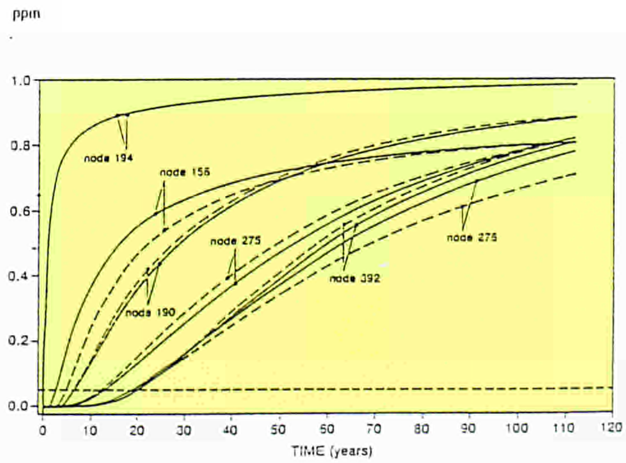


Fig.20: *Calculated increase of Cr(VI). concentration at different locations of the saturated and unsaturated zones.*

nonlinear least squares optimization scheme based on the Levenberg-Marquardt algorithm. The parameter values, along with their confidence intervals and the correlation matrix of the parameters estimates from the estimation procedure, were used jointly with the chemical data in the stochastic simulations by the FEMSUN code.

Figures 18 and 19 compare the fitted retention and hydraulic conductivity curves with the experimental data. The actual points were predicted very well for the $\theta(h)$ water control, but less accurate predictions were obtained for the hydraulic conductivity $K(h)$. In this latter case the actual data were still predicted near to saturation but considerably underpredicted in the highly unsaturated zone (i.e. $h<-200$ cm). It is expected that the uncertainty in the prediction of the low hydraulic conductivity values is transformed into uncertainty in predicting the Cr^{6+} time-dependent concentration profiles.

A comparison between the predicted Cr^{6+} concentrations, as obtained by employing van Genuchten's model (dashed lines) and by the hydraulic properties in a tabular form (solid lines) respectively, at different locations of the saturated and unsaturated zones are represented in Fig. 20.

Finally, as far as the apparatus for the soil hydrodynamic characterization is concerned, this is now in the calibration phase.

Waste Management

In alternative to the waste solidification /stabilization technology applied for cement sludges mixtures, the granulation technology seems to meet the requirements of easily handling, transport by pneumatic convoyer and heating treatment in view of improving the leaching resistance and the decomposition of organic hazardous wastes.

Granules of cement or clay containing Cr simulating a waste generated in a tanning or electroplating manufactory have been prepared by a new recent fabrication method starting from the aqueous phase. Powders or aqueous suspension are blended with methylcellulose. The drops of slurry are formed in a column containing an alkaline hydroxide solution.

The spheres have been calcined on N_2-H_2 gas to stabilize Cr^{3+} compounds.

The material has been submitted to a leach test. The chemical analysis of the liquid fractions indicated a very good immobilization of the Cr contained in the spherical particles.

ENVIRONMENTAL STUDIES OF THE MEDITERRANEAN BASIN

The MITO Project

The expected increase in temperature and the changes in precipitation patterns will certainly affect the development of algal blooms, both in salt and freshwaters, i.e. their frequency, intensity, species composition and toxicity.

The effect of algal blooms on the quality of drinking water (for water reservoirs) and of food (the sea), and even the direct effects on the health of humans (irritation by contact with water drops) could be substantial. The progress of these expected changes should be monitored adequately.

For these reasons the JRC-Ispra has developed, in close collaboration with institutions in five Member States, a joint European Project on algal blooms, i.e the MITO (Microphyte Toxins) project.

Special emphasis is placed on the following objectives:

- the development of fast and easy-to-use monitoring systems for surface waters, using the capabilities of modern technology, i.e. flow cytometry, to characterize and quantify algal blooms:

- the development of alternative bioassays to study the impact of toxin-producing phytoplankton on the ecosystem;

- the application of biochemical indices of the physiological state of algae to understand the fate of algal toxins in the aquatic environments, and

- the development of hydrodynamic, transport and biological process models to predict toxin occurrence and distribution.

The main topic areas of the Project are:

- Analytical cytology of phytoplankton
- Aquatic biotoxins
- Algal taxonomy and physiology
- Modelling

In the course of 1991 the following progress has been achieved.

As regards the characterization of phytoplanktonic populations by flow cytometry (FCM), a simple protocol to preserve algal samples was developed in the first half of 1991 to perform a bivariate cytometric analysis of pigment autofluorescence and light scatter.

The protocol consists of immediate fixation with 0.1% methanol free paraformaldehyde (final concentration). In this way, samples can be conserved at 4°C up to 4 months without loss of their characteristics (size and chlorophyll autofluorescence). The material tested was a Gymnodinium corii culture in stationary conditions, which is a very fragile alga and, therefore, a good example for a preservative method. Five samples of Gymnodinium were fixed with five different final concentrations of methanol-free paraformaldehyde; afterwards, the effect of fixation procedures on pigment autofluorescence and size over time was followed by FCM.

Preserved samples were analysed immediately after fixation by a PAS III flow cytometer (PARTEC) for chlorophyll autofluorescence and compared with same unfixed samples. The autofluorescence histograms (fig. 21) were compared with an internal standard (10 μm DNA immunocheck beads, Coulter) vs control instrument variations.

The fluorescence of the standard is unaffected by paraformaldehyde. Paraformaldehyde concentrations of 5 and 3% respectively were checked at first.

The ratio between the mean chlorophyll fluorescence of the Gymnodinium population and the mean standard fluorescence was calculated for each histogram (Table 4).

Using 5% paraformaldehyde concentrations, a slight degradation of chlorophyll autofluorescence was immediately observed, this process showing a

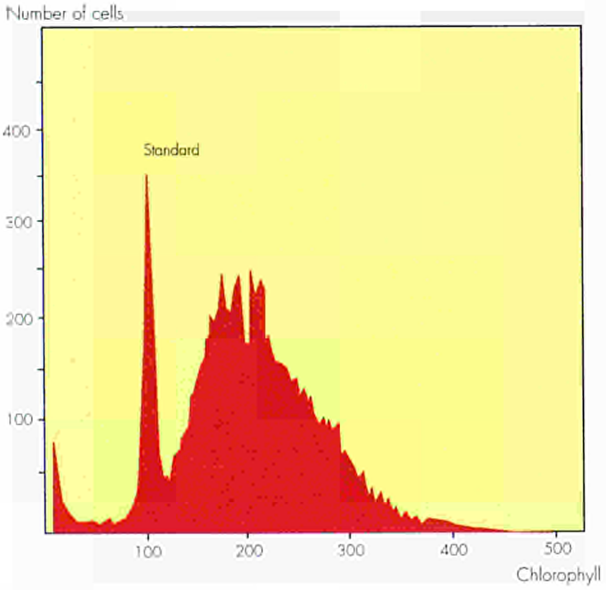


Fig. 21: Chlorophyll fluorescence distribution of Gymnodinium population (life sample).

Sample (Paraformaldehyde final concentration)	**Mean Chlorophyll Fluorescence** Mean Standard Fluorescence			
	Immediately	two weeks	two months	four months
fresh sample	2.0			
5%	1.8	0.6		
3%	3.3	0.5		
1%	3.3	1.3		
0.5%	2.0	2.0	2.0	1.8
0.1%	2.0	2.0	2.0	2.0

Table 4: *Ratio between the mean chlorophyll fluorescence of the Gymnodinium population and the mean standard fluorescence.*

marked increase after two weeks (Fig. 22a ,Table 4). On the contrary, when 3% paraformaldehyde concentrations were used, an increase of chlorophyll autofluorescence was observed within few hours, following the same degradation effect experienced with 5% paraformaldehyde after two weeks (Fig.22b). Paraformaldehyde concentrations of 0.5, 0.1, and 1% respectively were also tried. As with 3% fixation, 1% caused an immediate increase of chlorophyll fluorescence, but with a lower pigment degradation after two weeks. Optimal final paraformaldehyde concentrations

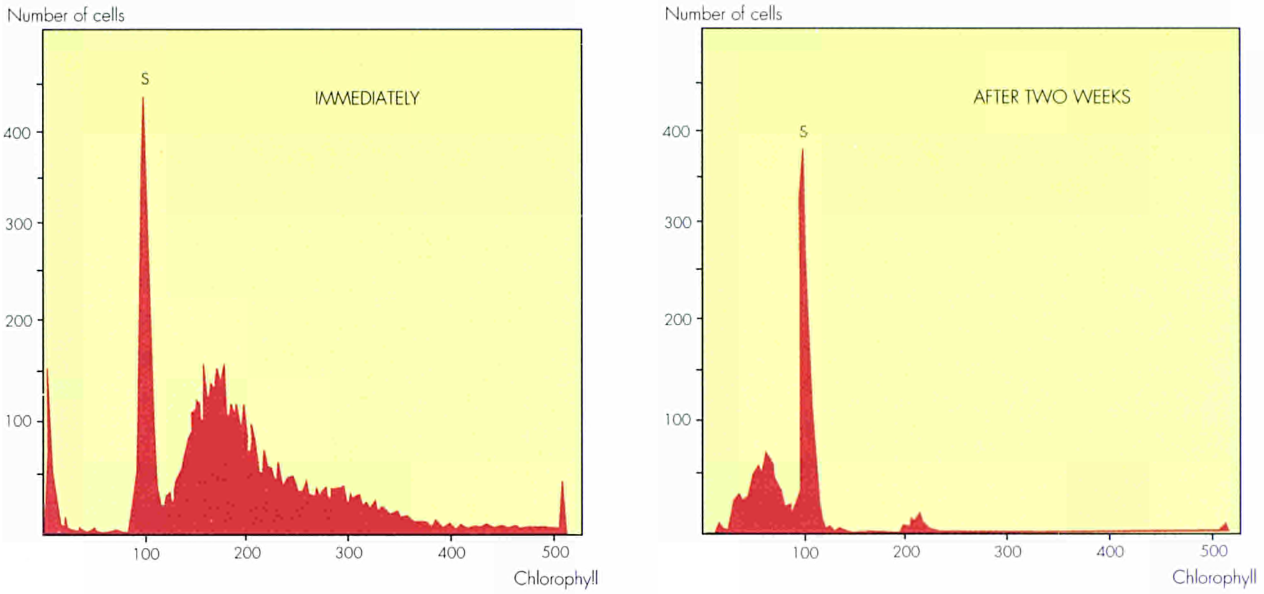


Fig. 22a: Chlorophyll fluorescence distribution of the Gymnodinium population (5% Fixed sample).

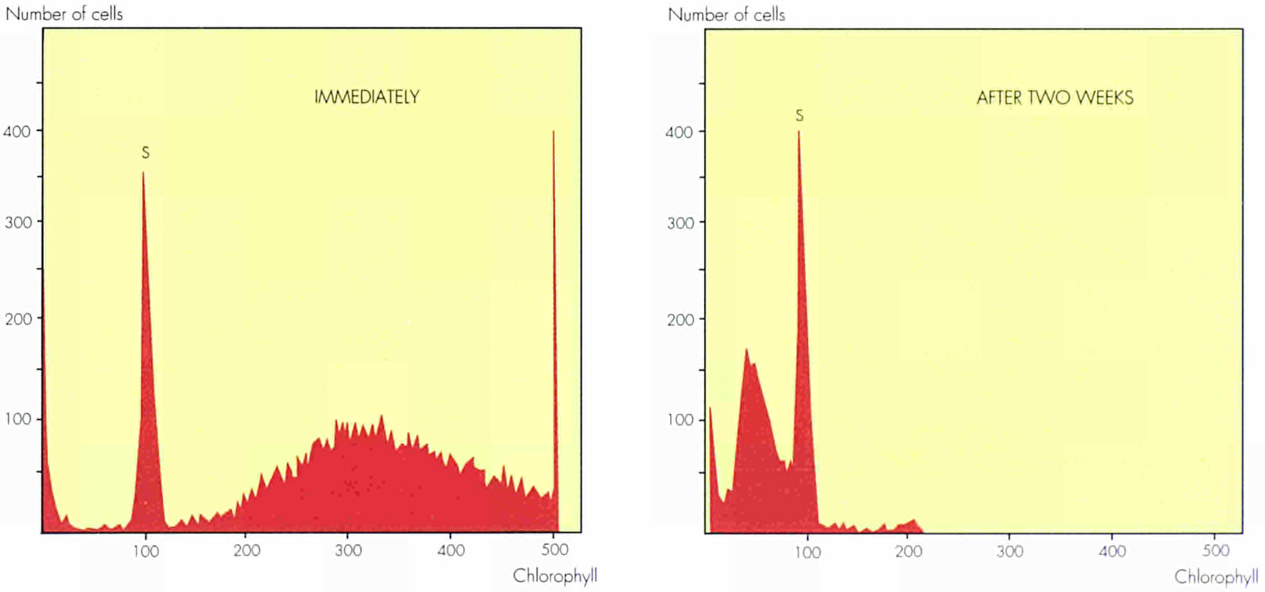


Fig. 22b: Chlorophyll fluorescence distribution of the Gymnodinium population (3% Fixed sample).

were found to correspond to 0.5 and 0.1%; both these concentrations are able to preserve the chlorophyll autofluoescence of Gymnodinium population up to 2-4 months (Fig.23 a and b). Further, it was observed that also the cell size (measured with a coulter counter) was unaffected by the above paraformaldehyde concentrations during the same period of time. In fact the coulter size distribution of 0.1% fixed sample was found to be the same as that of the fresh sample. Therefore, it can be concluded that the sample fixation with 0.5 or 0.1% paraformaledehyde is a very appropriate procedure for the preservation of algal characteristics of interest and it is easily applicable on board ship. This method will allow the collection of a quantity of samples during oceanographic campaigns and to analyze them more carefully in the laboratory.

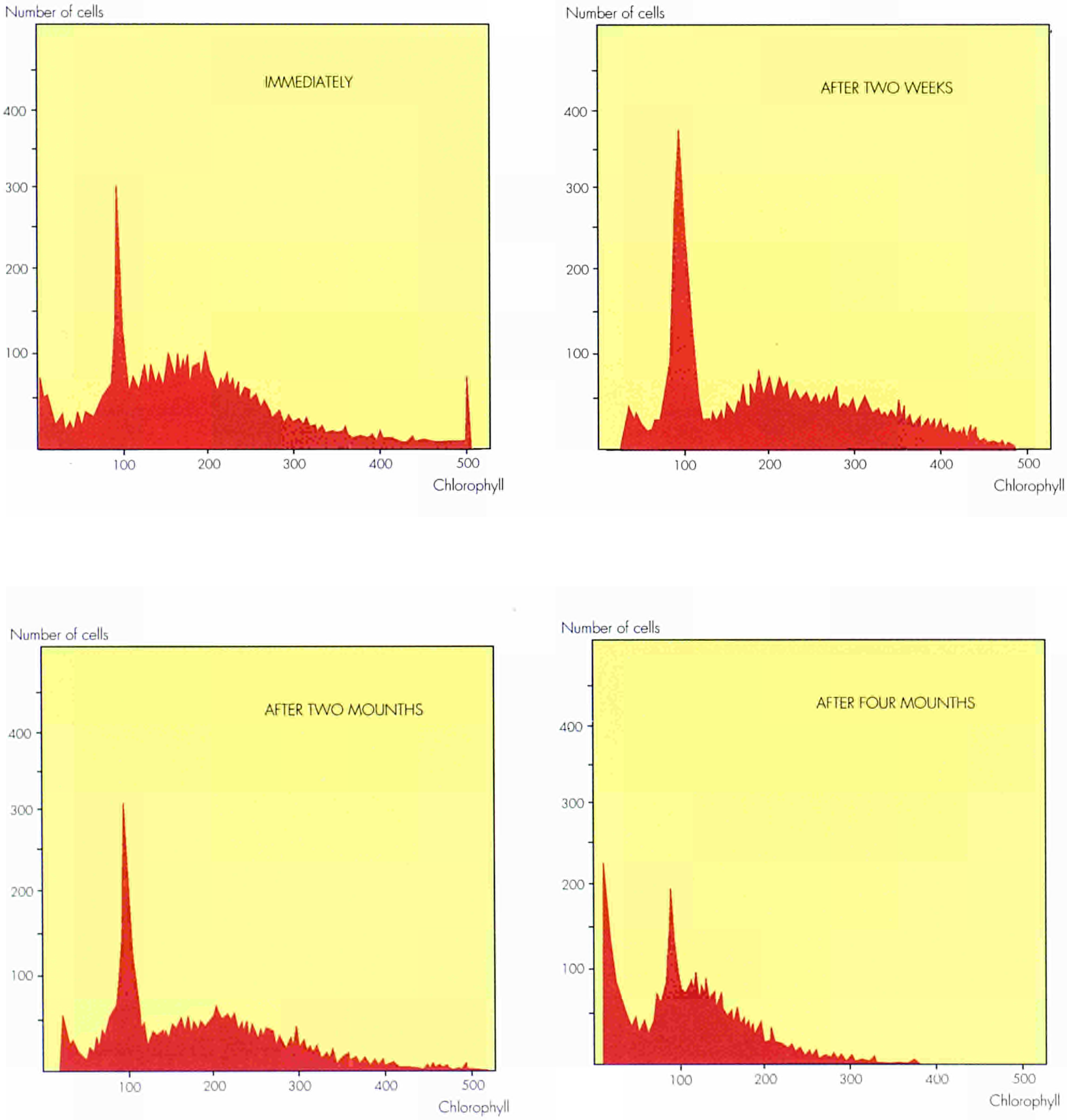


Fig. 23 a: Chlorophyll fluorescence distribution of the Gymnodinium population (0.5% Fixed sample).

A field exercise was organized by JRC at Corfù (Greece) in September, 1991 during a cruise of the research vessel AEGAIO of the Greek National Centre for marine research. The participants included experts from Italy, the Netherlands and Greece.

The main goal was the study of the horizontal and vertical distribution of phytoplanktonic communities and their pigments in a dense net of stations, comparing classical (microscopic inspection) and innovative (FCM) methods of analysis.

The quantification and identification of phytoplankton were carried out on fresh (live) and fixed samples. Preserved samples were analysed

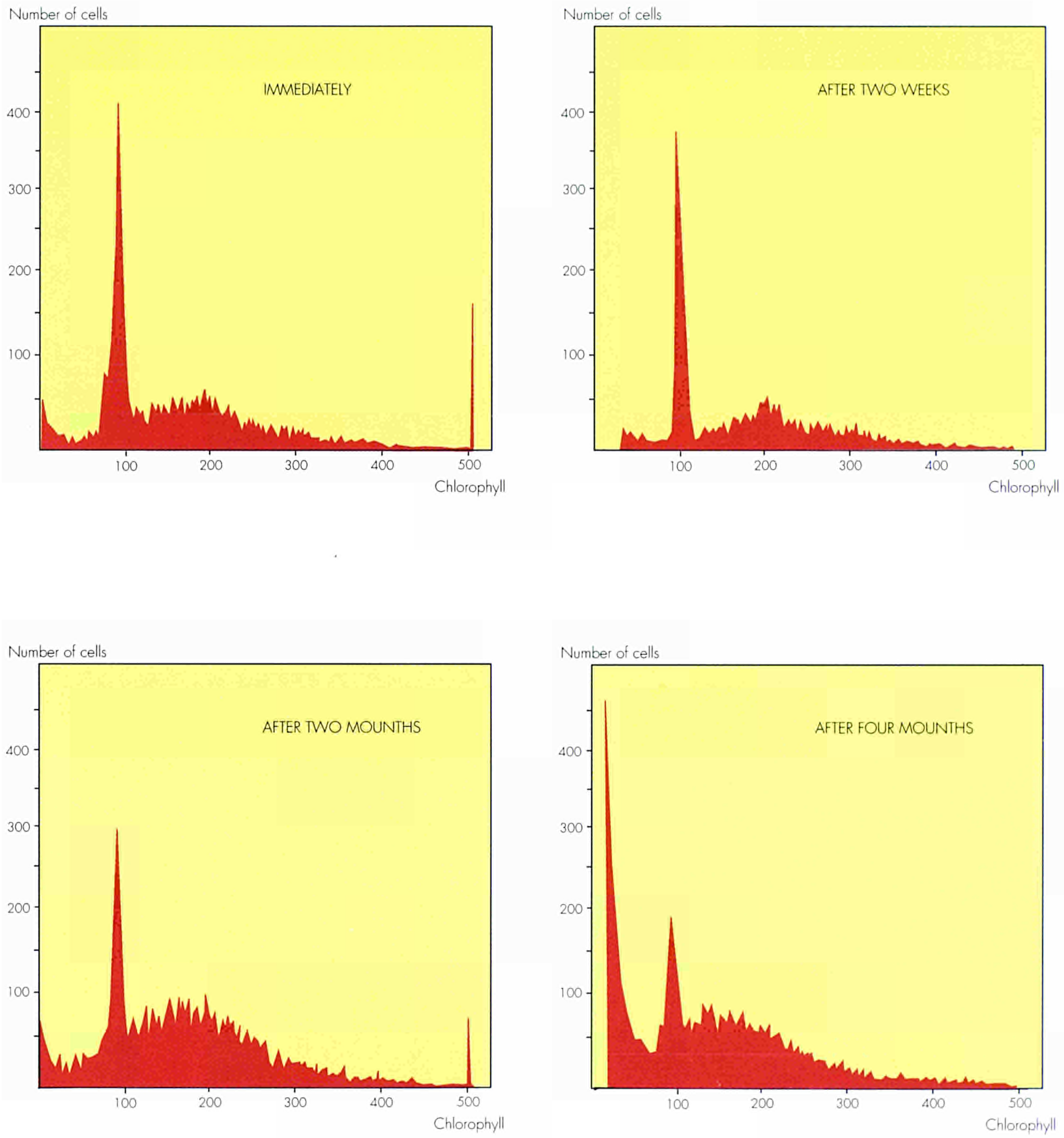


Fig. 23 b: Chlorophyll fluorescence distribution of the Gymnodinium population (0.1% Fixed sample).

at JRC and TNO (the Netherlands). laboratories, using FCM, fluorescence microscopy and optical plankton analyser. The field work included physical measurements (CTD), high resolution spectra of up- and downwelling light, chemical (nutrients) and biological (chlorophyll, phytoplankton counting) parameters and the use of a flow cytometer on board.

The analyses are completed and the results will be published at the beginning of 1992.

The AQUACON Project

The JRC decided to develop in close cooperation with national laboratories of the mediterranean area (Italy, Greece, Spain, Portugal and France) a project aiming at the identification, quantification and reduction of measurement errors in environmental analysis, i.e. AQUACON (Analytical Quality Control and Measurement Assessment Studies) project.

Agreement was found with representatives of the above mentioned EC Member Countries on a number of high-priority study items, all closely related to the implementation of EC-directives: Hg and other toxic trace metals, persistent organochlorine compounds and pesticide residues and polyaromatic hydrocarbons in a number of critical matrices, such as water (from drinking water to waste water),seafood, as well as substrates acting as "interim hosts" for environmental chemicals, like the sediments.

It has been widely recognized that sampling procedures constitute major error sources.in environmental analysis and that error components due to the varying influences of sampling equipment and handling, but also due to unknown spatial variabilities of the contaminants, might lead to incomparability of results.

The JRC Ispra offered therefore opportunities to national laboratories to check and evaluate their present sampling and analysis procedures in the

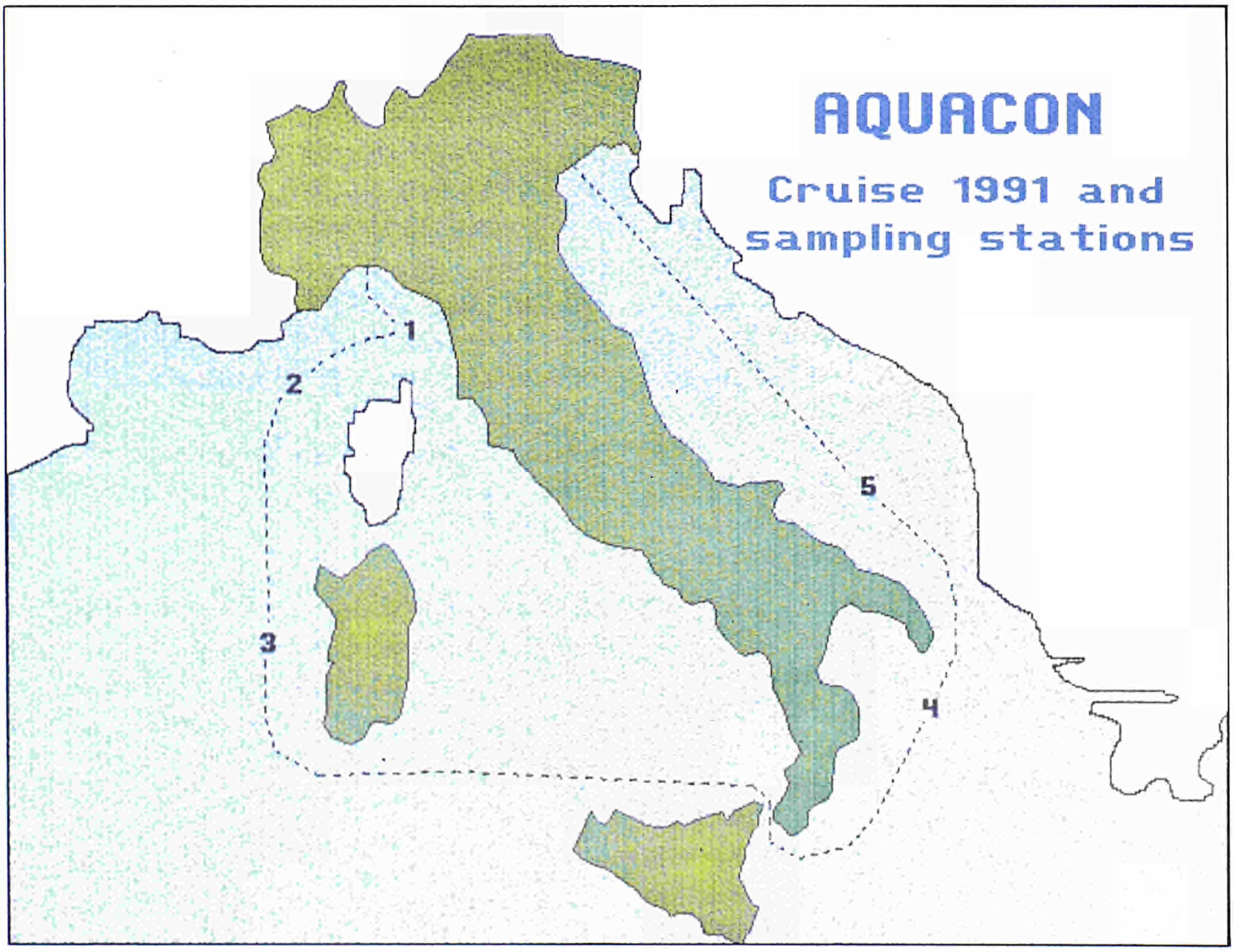


Fig. 24: Metal sampling error assessment study: sampling campaign 1991 and sampling stations.

framework of field-related and laboratory collaborative studies.

A number of subprojects, to be developed during the 1991-1994 "Protection of the Environment" Programme, were designed and are at present at different stages of progress.

A first field study has been organized within the framework of the collaborative sampling error assessment study related to "Trace metals in sea water" . The campaign took place from May 21st to June 3rd 1991 in the form of a cruise of CNR research vessel "Minerva".

Due to the restricted laboratory space, only one laboratory from each participating countries could be admitted.

Sampling was performed at La Spezia Gulf, at Lyon Gulf, off Sardinia coast, at Taranto Gulf and low Adriatic sea. (Fig. 24).

The study aimed at the sampling error assessment of trace metal determination in seawater taking Pb and Cd as examples as well as the determination of suspended matter, employing eight different sampling systems. Immediate analysis of all samples for Pb and Cd was performed aboard the ship in a mobile class-10-laboratory, owned by the Department of Environmental Chemistry of the Venice University, which acted as reference laboratory.

To summarize, the results of this first field exercise showed that the different sampling devices, employed during the experiment, although all being widely used commercially available, yielded largely different results.

While the analytical method (rotating glassy carbon-disc-differential-pulse-anodic stripping-voltammetry), designed for the sub-ppt concentration range applied in the clean laboratory aboard the ship by the staff of the reference laboratory showed a variability of 8 to 12% for both metals, which is only slightly above the normal performance level at the "ground" based laboratory, the variability obtained for the group of samples varied between 100 and 200%.

As a first conclusion it can be stated that one special type of sampler yielded much more stable results compared to the mean while another type yielded in all cases scattered results.

Additionally, experiments were conducted on the multisampling of particulate matter (basic sample variability) using an Ispra-designed multisampler.

The sampling errors found for carbon, nitrogen and chlorophyll taken as indicators of the particulate matter variability ranged from 30 to 70% while the method errors amounted to 5%.

A study concerning "Total mercury and organic mercury species in fish and seafood" has been started. As a first step two test materials (tuna fish and mussel tissue), which undergo at present the homogeneity evaluation, have been prepared. To date 58 laboratories have stated their willingness to participate in the first laboratory intercomparison.

Three subprojects, namely "Trace metals in sediment", "Persistant organochlorine compounds in sediments", and "Organic trace compounds in water" are in an advanced stage of definition and planning.

As far as it concerns the subproject "Acid rain analysis", the first interlaboratory comparison exercise has been completed.

70 Laboratories out of 125 laboratories who had requested the 4 samples (simulated rain water), delivered the full set of results.

The parameters to be measured included pH value, conductivity, sulphate, nitrate, chloride, calcium, magnesium, sodium, potassium and ammonium content. Widely scattering results were observed in particular for pH (data between 3.90 and 6.05; target value: 5.02 + 0.02 and between 3.46 and 4.22; target value: 3.88 + 0.02), but also for nitrate, chloride, calcium and ammonium.

New Project "Biogenic Emissions in the Mediterranean Area"

It is generally accepted that understanding the role played by biogenic emissions (mostly NMHCs and their chemical and photochemical transformation products) in the atmospheric chemistry is becoming increasingly important, in particular with reference to their relation to ozone and hydroxyl radical tropospheric budget, acidic compound formation and modification of the radiative properties of the troposphere.

For many years now, the Environment Institute of the JRC has been involved in such studies.

In fact it is firmly believed at the JRC/EI that, a special effort has to be made to understand the role of biogenic emissions in the Mediterranean area.

This area has quite a peculiar type of vegetation including shrubs such as rosemary, lavander, sage, etc.) and it's contribution to the tropospheric chemistry should be evaluated.

In collaboration with the Italian National Council (CNR) Atmospheric Pollution Institute (IIA) at Monterotondo (Rome) headed by Dr. I. Allegrini, the feasibility of one or more new project focused on the Mediterranean area and centred around the location of an instrumented experimental test sites was examined. The test site should become the focal point for joint intercomparison measuring exercises and joint measuring campaigns.

The major goals of such a project should be:

- Identification of major types of vegetation in the Mediterranean area on which to focus emission experiments;
- In-field evaluation (qualitative, quantitative) of the organic emissions under different, known, defined meteorological conditions (e.g. temperature, relative humidity, solar radiation, soil moisture, soil temperature, etc.);
- Identification of major reaction products. Field measurements to be backed by laboratory experiment (e.g. teflon bag, reaction chamber experiments with O_3, OH, and NOx).
- Micrometeorological measurements to provide data on fluxes of trace gases such as O_3 and NOx.

Intercomparison measuring exercises (in the laboratory and in the field) aiming at defining analytical methods for volatile organic compounds (VOCs) and their reaction products will obviously be of paramount importance and part of the project.

One of the experimental test sites which, for the time being, has been identified as a possible and suitable one is located 15 km south of Rome between the port of Ostia and the beach of Torvaianica. The size of the area is ca. 4,800 hectares extending from the suburban area of Rome to the Tyrrenean sea on a gradient of natural origin where typical Mediterranean vegetation is well represented. It has a rectangular shape of about 4 x 15 km where the shorter side is that following the sea shore. It is surrounded by the pine (Pinus pinea) forest of Castelfusano and Ostia so that the anthropogenic emission is further reduced. The site is one of the biggest and oldest protected areas in the Mediterranean basin.

CNR/IIA and the JRC/EI will guarantee the operation of the experimental test site throughout the year and will also perform measurements outside the joint measuring campaign periods.

Moreover, the CEC Environmental Programme (DG XII/E) and the JRC/EI could consider the possibility of partially contribution towards costs for the joint measuring campaigns and for co-ordination meeting.

Several European research laboratories have already expressed their interest in developing such a joint project, and the JRC/EI intends to convern a meeting at the beginning of 1992 to discuss and define:

- the content (scope, goals, timescale, etc.) of the project;
- the roles of the different participating laboratories;
- the financial possibilities, constraints and needs;
- the opportunity of having additional experimental test sites in other Mediterranean countries
(e.g. Spain, Greece, France);
- the opportunity of linking the new project to the existing ones
(i.e. BIATEX, IGAC, STEP 0060, etc. ...).

In view of this joint project, the EI has started some preliminary work focussed on:

- literature evaluation and mapping of major, common vegetation types in the Mediterranean, based mainly on CORINE data and maps;
- cultivation of some of the most common Mediterranean species rich in volatile oils (e.g. Lavandula, Cistus, Laurus, Myrtus) in its greenhouse;
- screening these species for leaf oil contents and for biogenic emissions, using a minicuvette-system;
- development of large mobile cuvettes (up to 400 l)

to measure the mass flux of trace gas exchange in the field.

One type of cuvette is designed to determine the mass balance of gas exchange at wooden Mediterranean scrub-species rich in volatile oils (e.g. Rosmarinus, Cistus, Thymus, Lavandula, Salvia) with the soil being included or excluded. A second type is designed to expose branches of mature trees. Both types will be used in the course of the in-field campaigns as well as for screening of biogenic emissions from different species in the greenhouse.

Based on the Continuous Stirred Tank Reactor (CSTR) principle, both types of cuvettes fulfill the following requirements:

- provide ideal and instantaneous mixing of components entering and present in the cuvettes;
- are made of material having (Teflon, Plexiglass) low absorption characteristics and more than 90% radiation transmissability;
- allow for the airflow, supplied through Teflon tubing, to be adjusted with mass flow controllers to give up to one air change per minute with accuracy better than 1%;
- allow for the air in the cuvette to be cooled to ambient temperature even in mediterranean summer midday conditions;
- the cuvettes to be portable and easy to handle with respect to field campaigns;
- their size to be adjustable to get optimum volume/surface ratio for the different species: the branch type varies with D=40 cm; H=40/60/80 cm; the scrub varies with D= 40/60/80 cm, H=40/60/80 cm.

As regards the air- surface exchange field observation campaign was conducted in May 1991 at the agrometeorological site of S. Pietro Capofiume, in the Eastern Po plain, aimed at investigating exchange processes between the atmosphere and the surface. Several groups from various European countries (Germany, Belgium, France, Italy) participated in that campaign, which was organized by the JRC.

Vertical fluxes of ozone, nitrogen oxides and aerosol particles were measured by the eddy-correlation method. The interpretation of data obtained requires the knowledge of the characteristics of atmospheric turbulence; for that reason the vertical heat fluxes and other turbulence parameters were measured.

Examination of the data reveals several features of interest. Ozone always undergoes deposition during daytime and the time evolution of that process follows the behaviour of the turbulent heat fluxes. Further, the experiment took place on bare soil and it proves that ozone deposition occurs also in the absence of vegetation.

The vertical NO_2 fluxes were bidirectorial, but mostly directed upwards; this is due to the emission of NO generated by denitrification processes in the humus layer. The NO molecules are rapidly oxidised to NO_2 by the ozone present, resulting in the upward fluxes observed at the 7.5-m level.

A full analysis and interpretation of the data is still underway.

FOOD AND DRUG ANALYSIS

The aim of this activity is the development of analytical competences to support EC sectorial policies in agriculture, internal market and consumer protection. Work is mainly focussed on identification of adulteration, on fraud origin of food, on harmonisation of analytical methods or expertise. In many cases the use of complex analytical instrumentations or the presence of a neutral or Communitary Laboratory (activation of an EC working group, harmonisation of the national methods, training of the EC inspectors, creation of EC data banks etc.) is mandatory.

In collaboration with EC Directorates General VI (Agriculture), III (Industrial Affairs and Internal Market) and the Consumer Policy Service (CPS), detailed programmes for the period 1992-94 have been established.

The analytical facilities of this laboratory have been already described in the 1990 Annual Report.

The activity in food chemistry started at the end of 1988, the control of sugaring of wine (chaptalization) has been the first problem tackled.

The determination of the site specific natural D isotope concentration in wine distillate by NMR (Martin method) allows the detection of alien sugar addition. Since this concentration varied with latitude, climate, type of grapes, ripeness etc.. a data bank of reference wines, renewed every year, is necessary to improve the applicability of the method. By virtue of EC Directives 2048/89, 2347/91 an 2348/91 a reference laboratory for the validation and collection of the NMR data of the European wines has to be set up at JRC Ispra.

To gain experience at European level, a small scale pilot experiment using Greek, Italian and German wines of known origin and preparation had been performed in 1990. A particular effort had been directed to improve the NMR method taking into account the purity of the wine distillate (ethanol) and the stability of the tetramethylurea (TMU) employed as internal standard.

In view of testing the reproducibility and repeatability of the method, a round robin exercise involving 18 laboratories has been recently carried out; the results will be ready early in 1992.

About 1400 samples of 1991 European wines have been prepared by various laboratories of the Member Countries for the data bank and will be analysed in the next year. Further the JRC NMR laboratory can also support laboratories of the Member Countries not yet properly equipped for this kind of control for wines, spirits or ethanol used as fuel additive.

HPLC has been employed to investigate the adulteration of citrus fruit juice with beet invert sugar and high fructose corn syrup. Improvement of this method has been obtained using a special heartcut technique.

As regards milk and dairy products the following activities are included:

- regular participation at the meetings and the various interlaboratory activity organised by the communitary experts group (D.G. VI);
- determination of some denatured whey proteins in sterilised and UHT milk (this work has been launched by Prof. Resmini to found a chemical indicator of the heat treatment of milk);
- determination of the fatty acid and triglyceride profiles and sterols in milk fat samples to verify their possible adulteration (these determinations have been extended to some vegetable fats) and tentatively their origin;
- participation in the final round robin to establish the reference method for the detection of cow's milk in ewe cheese

The activity of the Microbiological Laboratory has involved the following items:

- research on aflatoxins in one African beer and its primary ingredients and on microbial pathologies to which freshwater and farmed fish are subjected;
- microbiological control of new and used cosmetics (primary and secondary contamination). Research on origin of these microbial contamination and on efficiency for the most common preservatives;
- research on the origin of corrosion of the JRC water pipelines feeded with lake water (possible bacteriological corrosion).

Analytical work

A number of about 7000 samples (25.000 data) originating for the most part (73%) by E.I. research activities has been analysed in 1991. The wide ranging nature of the analysed samples included water, clay, soil, fly ash, air and water particulate, leachings, liquid wastes, metals, alloys, gaseous mixtures, corrosion products, food etc.. The requested controls varied from the determination of major to minor or trace compounds or structural composition. The most applied analytical techniques have been: IC, XRF or XRD, GFAAS, AAS, UV-VIS, elemental analysis, classical wet chemistry, electrochemistry.

1.2

Radioactive Waste Management

The 1988-91 Radioactive Waste Management Programme of the JRC, adopted by the Council on 14 October 1988 (O.J.No. L286/29, 20.10.88), was divided in four Research Areas:

1. Operation of the PETRA facility
2. Actinide Monitoring
3. Characterisation of Radioactive Waste
4. Safety of final storage in geological formation

Research areas 1 and 2 were entrusted to the Institute for Safety Technology and Research area 3 to the Institute for Transuranium Elements. They are described in the annual reports of the concerned Institutes.
The Environment Institute participated in the Research area 4, which included three activities:
- Risk Assessment,
- Analytical Development and
- Radionuclide Migration in the Geosphere.

The contribution of the EI to this programme finished in the year 1991. Gradual shift and merging of competences towards research activities on transport and behaviour of toxic chemicals in soils and groundwaters took place. Main achievements obtained in the 1991 and specifically related to Radioactive Waste are summarized below.

Risk Assessment

Within the field of probabilistic code development for Risk Assessment, and its application to geological disposal of Radioactive Waste, the LISA package (Long-term Isolation Safety Assessment) has been completed and the User Guides published as external Euratom Reports.
The great international interest this code attained through the OECD/NEA distribution to more than twenty European and non-European Institutes or organizations concerned with radioactive waste disposal should be noted.

Analytical Development

Awareness that the geochemistry (as well the bio-availability) of metals are dominated by their speciation rather than just total concentrations, has urged the development of analytical techniques which are both sensitive and selective for molecular chemical forms. Non-invasive X-ray spectroscopic techniques and Laser induced fluorescence were applied to examine sorption equilibria and kinetics involving Eu and Ce at mineral surfaces.
The usefulness of lanthanide elements as analogues for modelling dispersal and migration processes of transuranics from nuclear waste geological repositories stems primarily from two factors. The first is the recognized analogy of chemical behaviour between lanthanides and actinides in identical valence state, the second is their sensitivity to changes of solution composition and to the redox status of the environment.
Considering the importance of manganese oxides as controls of transuranic concentrations in natural waters, radiochemical techniques, together with spectro-fluorimetry and X-ray absorption spectroscopy, were used for the study of ^{144}Ce(III) adsorption on synthetic δ-MnO_2(s). Parallel experiments used ^{152}Eu(III) as reference element for trivalent lanthanides.
X-ray absorption measurements using synchrotron radiation indicated that the uptake of Ce on MnO_2 is the result of an electron transfer reaction occurring at the oxide-water interface, causing oxidation of Ce(III) to Ce(IV) after adsorption, rather than a redox reaction in oxygenated homogeneous solutions (Fig. 25).
The above results not only confirm that surface mediated redox processes in aquatic environment provide an alternative reaction pathway at lower activation energy, but clearly demonstrate the applicability of X-ray Absorption Spectroscopy to

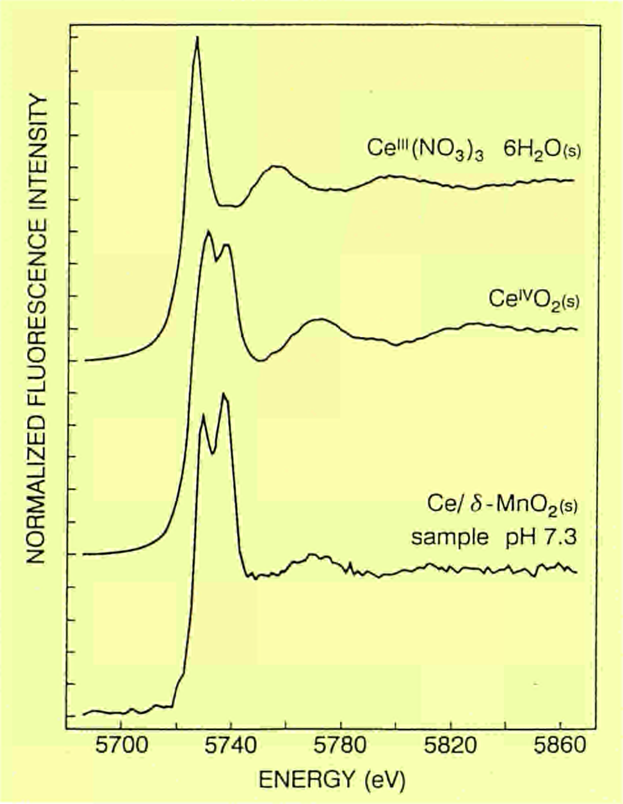


Fig. 25: XANES spectrum of Ce on δ-MnO_2(s) from a 0.1 M $NaClO_4$ solution at pH 7.3. This is compared with the experimental L_{III}-XANES spectra of reference Ce compounds.

study mineral-water interfaces.

Because of their very low solubilities, the phosphate-based minerals are attractive as additional components to be included in the backfill material for nuclear waste repositories. A combination of Radiochemical techniques and TRLIF (Time Resolved Laser Induced Fluorescence) was therefore applied to investigate the rate and extent of Eu(III) interaction with the hydroxylapatite structure.

TRLIF allowed the identification of a two step kinetic process which was highly dependent on the type of surface bound Eu species. During the first step, Eu aquo ions adsorb rapidly at the highly polar apatite surface. This step is then followed by a slower isomorphous substitution of Ca in the mineral lattice.

TRLIF appears to be a powerful tool to address problems of REE interactions at mineral-water interfaces. The advantage of this technique is the sensitivity to small concentrations and to the lattice disorder caused by ions interacting with the surface.

Radionuclide Migration in the Geosphere

Long-term laboratory migration experiments with Np and Pu through columns loaded with sediment collected at a depth of 140 m above the Gorleben salt dome (candidate site for High Level Radioactive Waste disposal in Germany) have been concluded after 4 years of percolation. Sectioning of the columns for determining the accumulation profile of radionuclides will start at the beginning of 1992. These data, together with spectroscopic analysis of the glass leachate and column effluents to be performed in cooperation with the Technical University of Munich, will be used for the development of the long-term transport model of Plutonium and Neptunium.

A pilot in-situ diffusion experiment for ^{85}Sr, using the Autolab probe lowered to a depth of 40 m in a well drilled on site at the JRC-Ispra, has been performed. The Autolab probe was developed at the CEN Cadarache (France) in the framework of a contract with the CEC.

The purpose of the field trial was twofold:

(1.) to demonstrate the handling and mechanical operation of the probe on site in an actual borehole.

(2.) was to test the feasibility of conducting radionuclide migration studies under field conditions. On the basis of both geochemistry and safety considerations, ^{85}Sr was chosen as the tracer. During the trial, an identical diffusion test was run parallel in the laboratory both to monitor the undisturbed in-situ diffusion and to provide a direct comparison for the field results. The in-situ and laboratory runs each comprised two columns, open at both ends, prepared with the same geologic material coming from the borehole (fluvio-glacial sediment). In both cases identical ^{85}Sr spikes were used, each was initially sealed in a glass ampoule and anchored inside the respective groundwater reservoir during a preliminary equilibration period of about one month. In both cases diffusion was commenced by ampoule breakage. After a second month, the probe was recovered and allowed to decompress slowly in

the laboratory prior to opening. On removal the columns were then sliced into thin sections and specific activity and cummulative thikness (by weighing) of each slice determined. Symmetrical diffusion profiles into both ends of each column were obtained from laboratory and in-situ runs however, whilst in the laboratory run a distance of about 2 cm separates the two diffusion fronts, in the field version the two fronts have coalesced. Clearly the in-situ diffusions were unexpectedly more rapid compared to those in the laboratory. Symmetry between profile pairs for individual columns shows porosity was consistent along their lengths. Moreover, monotonicity amongst all the curves suggests the presence of only one diffusing species with a single or dominant control mechanisms in each case. However, the apparent differences of Sr mobility indicates alternative behaviour in the two experimental locations.
Dissolved CO_2 could be the key factor in accounting for the apparent difference of Sr mobility. In the absence of carefully calibrated measurement of in-situ CO_2 concentration, it is not possible at this stage to account for the different mobilities more specifically. However, the difference of behaviour between the two sets of data emphasize two important points. First, laboratory data require field validation and secondly, field experiments require laboratory controls to verify procedures.

In the framework of a collaboration agreement with the OECD/NEA we have contributed to the review of thermodynamic data of Am. The objective of this review is a critical assessment of literature data according to guidelines developed within the OECD/NEA Thermochemical Data Base (TDB) project. The book on the Am review will be published as the second volume in a series including various actinide elements.

2

Scientific/Technical Support to Community Policies

As for the preceeding years of the programme, the largest part of the effort in support to Community Policies has been spent in favour of the Directorate General XI (Environment, Nuclear Safety and Civil Protection).

This has covered the areas of Chemicals, Waste, Water Quality, Atmospheric Pollution and Radioactivity Environmental Monitoring, major achievements being presented in sections 2.1 to 2.5.
Although the expertise and scientific support provided to other Directorates General (I, III, VI, XVII, XXI) or services (CPS) of the Commission are not to be considered of lesser significance, the 1991 achievements related to these activities are merged and summarized in section 2.6.

2.1

Chemicals

In the last decade, public awareness and regulatory activities related to hazards and risks posed by industrial chemicals for the environment and human health have increased steadily. For instance, the 6th amendment of the Dangerous Substances Directive (EC 79/83) introduced the obligation for chemical manufactures and importers to provide a basic data set for new chemicals, permitting a hazard and risk evaluation, and necessitating the registration of existing chemicals", available on the EC market before 18/9/81. As the result the "European Inventory for Existing Commercial Chemical Substances"- EINECS - had been prepared. At present a Council regulation is expected for 1992 aiming in the first step at the hazard and risk assessment of existing chemicals produced in relevant quantities.

In this context the sector "Chemical Evaluation" carried out the following activities:

- technical / scientific support for the implementation of directives;
- scientific coordination;
- participation in meetings with Competent Authorities of Member Countries;
- organisation, participation and chairing of expert meetings.

In the framework of the above activities, the sector participated actively in the updating of Annex 1 of the Dangerous Substances Directive (EC 79/831), for instance with respect to the classification, labelling and packaging of hazardous chemicals.

A meeting was held with national representatives and industry experts in July 1991 at Ispra to classify organic peroxides which are on the market in the EC.
Comments received from competent authorities after the publication of the EINECS Inventory in the EC Official Journal have been evaluated and the necessary modifications were introduced.
Work concerning the application of Structure-Activity Relationships has been continued with the aim to introduce groups of similar structure for the EINECS Inventory and to predict environmental distribution and fate of industrial chemicals .
A Eurocourse was held in June 1991 at Ispra on the subject of "Multivariate Analysis in SAR and Environmental Studies" and the proceedings were published.
In the area of Testing Methods, work on the six European reference soils was continued.
The final version of the European interlaboratory comparison concerning the adsorption/desorption of three test chemicals (atrazine, lindane and 2, 4-D) was drafted and will be added to the Final Project Report, presently in preparation.

The six EURO-Soils are in rising demand by European research laboratories for use as reference substrates in the testing of chemical-biota systems, e.g., biodegradation and chemicals recovery. 200 kg EURO-Soils 3, 4 and 5 from the French, British and German reference sites have been stocked and EURO-Soil 1 and 2 shall be collected this year again. Long-term storage stability testing of adsorption capacity toward the test chemicals shall be continued this year.

2.2

Waste

The first phase of a study on the rapid screening of polychlorinated biphenyls in waste oil has been completed.

A three-step approach was recommended:

(1.) the screening of the samples (in-field) for their total chlorine concentration using commercially available test kits based on either colorimetric or electro-chemical chloride detection.

(2.) the screening of positive samples are screened for PCBs by fast gaschromatography electron capture detection. This may be carried out in the laboratory or with a portable GC in-field.

(3.) positive samples confirmed by gas chromatography-mass spectrometry at the laboratory.

The procedure was established by thorough analysis of each step starting from the evaluation of test kits and alternative screening methods, of the methods for sample preparations for GC analysis and fast GC screening up to the final confirmation by specific isomer analysis of PCBs.

The second phase foreseen an interlaboratory comparison exercise to organized with national experts of the EC member Countries.

2.3

Water Quality

A major study was completed on monitoring, sampling frequency and reference methods of analysis for drinking water quality in connection with EC Directive 80/778.

It was suggested that for the following points there is room for improvement and revision:

- strategies and procedures of sampling;
- location of sampling points;
- principle/methods of analysis;
- standardization and quality assurance.

JRC scientific expertise was made available to contribute to the development of new directive on ecological quality of surface waters.

A proposal for the possible lake classification system to be used throughout the Community, based on physico-chemical and biological features, was prepared. This allows for the description of lentic systems in complying and uncomplying waters, establishing basic (ecological) and minimum (managerial) objectives for lakes.

Work was carried out for the preparation of the "International Conference on River Quality Ecological Assessment and Control" held on the December 1991 in Brussels.

The work on the impact of trace elements (EC Directive 76/464, list I and II substances) has been continued, by studying the non-point sources and non-point discharges of Sb, Be and Tl and the discharges from point sources of Cr, As, Mo and B.

Non-point sources of Sb, Be and Tl were estimated, for the EC, to about 39, 13 and 26 t/y, respectively, surface runoff and deposition being the largest sources.

Some data was available on discharges of As, Mo and B yielding a fragmentary picture for a country-by-country evaluation, whereas Cr data allowed a more complete picture suggesting discharges of about 740 t/y in the Community (Table 5).

NACE	Sector (process)	B	DK	F	FRG	G	IRL	I	L	NL	P	SPA	UK
161	Electric power production	0.02		3					0.2				
22	Production Processing of metals	***		***	***			***	***	6.4		***	***
232	Mining of Potassium			50									
24	Manifacture of non-metallic mineral products	*		**	**	*	*	**	*	*	*	**	**
25	Chemical industry:												
	TiO_2 production (1)			230				70				100	70
	Phospate fertilizers	3		20	1			9		14.6	2		5
31/27	Manifacture of metal products	2	0.1°	20	30	0.3	0.1	10	0.1	0.2°	0.4	5	8
41/42	Food, drink and tobacco industry	0.1	0.1	0.4	0.7	0.02	0.1	0.2	0	0.06°	0.03	0.1	0.6
43	Textile industry	0.7	0.1	2	3	0.2	0.03	5	0	0.1°	0.1	0.8	1.6
441	Leather, tanning and dressing of leather	0.6	0.5°	5	6	0.8	0.4	25	0	0.2°	2	9	6
	Miscellaneous	0.2	0.1	1	2	0.02	0.01	0.6	0	0.6°	0.03	0.4	1

Table 5 : *Estimates of annual gross chromium discharges (tonnes per year) per EC country and per process in the period 1985 - 1989*

Note: **** > 1t/y; 0.01 t/y < ** > & t/y; * <0.01 t/y*

(1) E.C. directive concerning the TiO_2 industry (89/428/EEC) obliges to terminate discharging waste by mid-1993

° Net discharges

2.4

Atmospheric Pollution

CENTRAL LABORATORY OF AIR POLLUTION

In the framework of the harmonization programmes for current directives the following achievements are worth of mentioning.

SO_2 Directive.

Following the conclusion of the preceeding programme, the implementation of harmonized procedures in the EC networks will be promoted by the publication of Instruction Manuals for sulphur dioxide and black smoke measurements.
Their contents include the following headings:

- Purpose and Overview;
- Monitoring Systems;
- Monitoring Procedures;
- Quality Control;
- Quality assurance;
- Strategy for EC monitoring networks;
- Appendices.

NO_2 Directive.

In collaboration with the Member Countries, a common measuring programme for the harmonization of the Directive 85/205 EEC had been launched in 1990 and further developed in 1991. The programme consisted of the following actions:

Definition of a common EC performance test procedure for air NO_2 analysers.

The intercomparison of the different performance test procedures will be conducted in 1992 by two different laboratories in the Member Countries. It is expected that the practical outcome of this intercomparison will be the agreement on a common test procedure to be further submitted to the CEN.

Intercomparison of different NO_2 primary calibration standards.

The intercomparison was performed among the following primary calibration methodologies:

- permeation method (ISO 6349-1979);
- Griess-Saltzman wet chemical method (ASTM D 1607-1976);
- Griess-Saltzman wet chemical method (VDI 2453-1989);
- static volumetric dilution method (VDI 3490-1985).

From the exercise it appears that the results of the permeation and of the static volumetric dilution methods match very closely, confirming the validity of the Directive reference method. On the contrary, the ASTM and VDI Saltzman methods were rejected because of the variable stoichiometry of the reaction (Saltzman factor).

Quality assurance of NO_2 routine measurements in the EC networks.

The first intercomparison, scheduled to take place in September at the Landesanstalt fur Immissionsschutz, Essen, had to be postponed to 1992 for technical reasons.

Quality assurance of NO_2 calibration procedures implemented in the Member Countries.

The test atmosphere generator previously developed to evaluate the efficiency of the sampling collectors in the monitoring stations has been operated in field conditions. The tests, conducted on two measuring stations in Northern Italy, have shown that the absorption effects along the air sampling line, were about 5% for NO_2 measurements, but up to 40% for SO_2 measurements.

In view of a future ozone directives, sampling and measurement of volatile organic compounds (VOC) were performed. Following the results of the working group of experts on VOC sampling and measurement techniques managed by the Institute, an EC wide intercomparison had been decided in 1990. The exercise, organized in collaboration with the National Physical Laboratory in the UK which provided the standard hydrocarbon mixture, took place in September-October 1991 and involved 21 participants selected among leading laboratories in the field of VOC measurements. The participation was extended to scientific organizations outside the EC, currently dealing with VOC measurements in Europe, such as EMEP and TOR.

The exercise consisted in the measurement of a dilute mixture of hydrocarbon gases simulating an urban atmosphere. The mixture contained 26 individual hydrocarbons (C_2 to C_9), with concentrations ranging from 5 to 100 ppb by volume. The list of hydrocarbons, as defined by the VOC working group, comprised those species relevant to the formation of photo-oxidants. Evaluation of the results is underway.

MONITORING NETWORK DESIGN

In collaboration with the local air quality office (Alpa-Remappa, now Airnormand), a monitoring campaign has been performed to map the NO_2 distribution over the Rouen-Le Havre region. The campaign has been successfully completed in 1990, and critically evaluated with respect to the Directive guidelines, have been analysed in view of an extension and redesign of the Airnormand air pollution network.

The annual average concentration over the area was found to be 23 $\mu g/m^3$, i.e. much lower than the 47 $\mu g/m^3$ obtained in the former survey performed in Paris. Areas in which the NO_2 concentration approached the directive limit value, *at risk* for the population, have not been found in Le Havre. In Rouen however, two sites showed average values higher than 65 $\mu g/m^3$, hence presenting a risk to exceed in the future the limit value of the directive (80 $\mu g/m^3$).

In the framework of a convention between DG XI and the Madrid City Hall (Ayuntamiento), an evaluation of the Madrid air quality survey network was performed by means of passive NO_2 samplers (two campaigns performed on 27/6-17/9/90 and on 27/11/90 - 26/2/91 respectively) and mobile laboratory measurements (14-25/11/90). The data collected were used to construct NO_2 isoconcentration curves for the greater Madrid area. Evidence of higher average concentrations in winter was obtained, but peaks higher than 75 μg NO_2/m^3, were only noticed in summer due to increased photochemical activity. The values have been compared with the limit value of the Directive, reported to the annual average for the passive measurements and to the 99th percentile for the mobile measurements. The results showed, for a 8/10 days pollution episode, the breach of the Directive 99th percentile limit value (230 μg NO_2/m^3) at the kerbside of heavy traffic roads. No background site showed the breach of the annual limit value (80 μg NO_2/m^3), nevertheless 11 sites with values between 60 et 80 $\mu g/m^3$, were at risk. Measurements made with the mobile unit along selected circuits (pedestrian-commercial centre, industrial outskirts, etc..) allowed the elaboration of detailed maps of pollutants distribution under different meteorological conditions. The analysis of the results (see e.g. Fig.26) led to important conclusions on the network performance, on the pollutants distribution during different conditions (weekday, time and meteorology), and on the contribution from the different sources (industry, traffic, heating). The study concluded on the necessity of NO_2 abatement measures, the revision of the siting of some stations and the survey of the airport area, where the guide value were exceeded.

The study proves that the combination of passive sampling techniques with mobile measurements constitutes a successful approach for air quality evaluations and for network design.

EMEP MONITORING PROGRAMME

The Evaluation and Monitoring of the European Pollution (EMEP) is a cooperative programme for the evaluation of the long range transport of atmospheric polllutants in Europe. Its main objective is to provide Member Countries with information on the deposition, concentrations and fluxes of atmospheric pollutants across national boundaries.

Following of article 9 the Council Resolution Nr. 81/462/EEC, and upon request by DG XI JRC Ispra is operating an EMEP monitoring station at the Ispra site since November 1985.

The following parameters are measured:

- in air: SO_2, NO_2, NO, O_3 and PAN continuously, non methane hydrocarbons, methane and NH3, occasionally;
- in atmospheric particulate: SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, TSP and H^+ on regualar basis, heavy metals in 7 days sampling periods;
- in precipitation samples SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{++}, Mg^+, pH, electrical conductivity and strong acidity;
- meteorological parameters.

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

Considering the monthly average concentrations from 1986 on, it was observed a negative trend for SO_2 (from 12 to 5µg /m³) and a positive trend for NO_2 (from 23 to 30 µg /m³). Fig. 27,

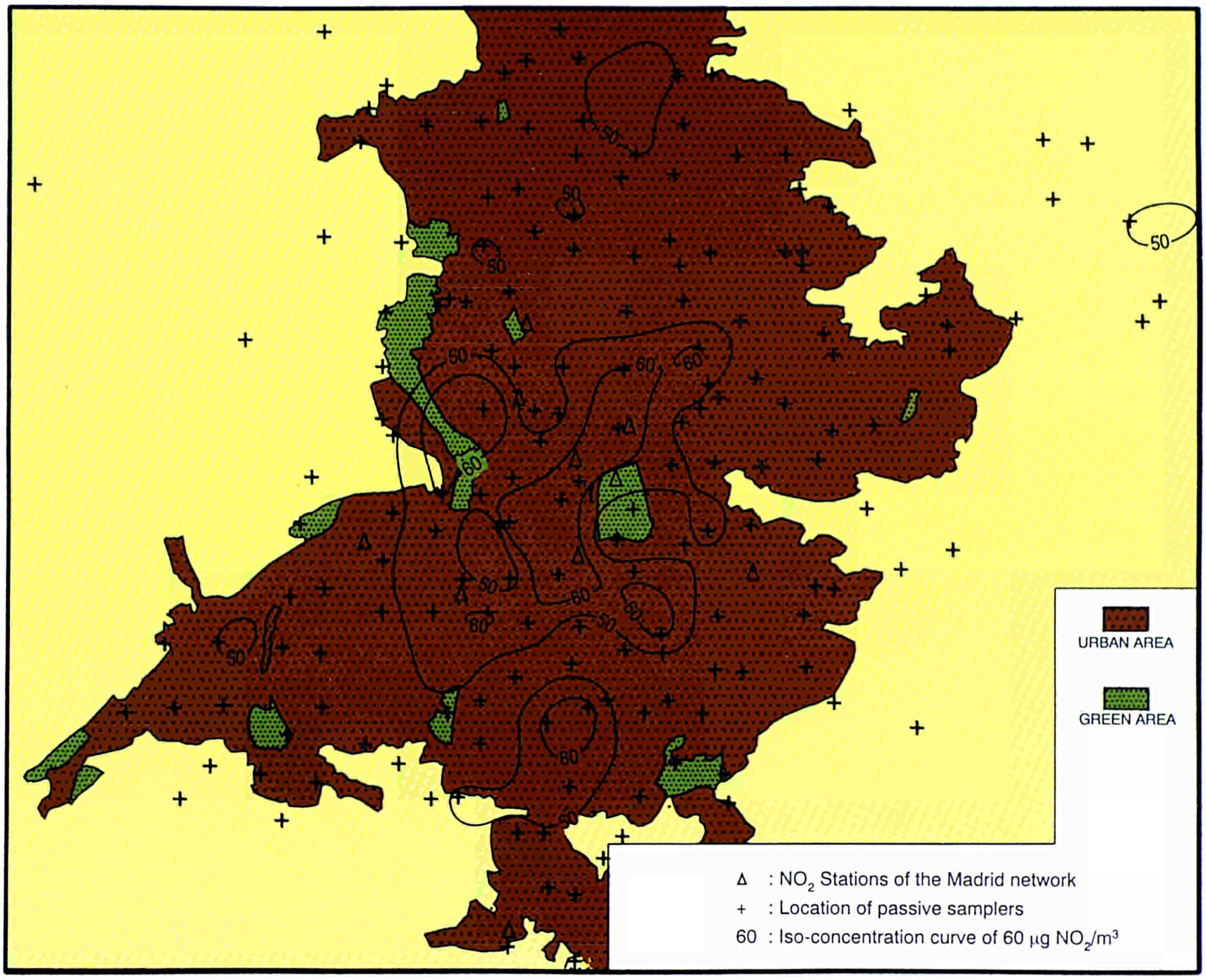


Fig. 26: Map of isoconcentration curves of NO_2level in the greater Madrid area, reported to the main annual value, prepared on the basis of the result of measuring campaigns (3 months in winter and 3 months in summer) by passive samplers.

The isocurves "50" mark the boundary of areas (inside) where the NO_2 level exceeds the EC-Directive "guide value" (50 µg cm³) . The isocurves "60" define the areas at risk with respect to breaching the "limit value" of the EC-Directive (8Oµg cm³).

represents the monthly averages concentrations, measured at this station during the last five years, of O_3, NO_2, and SO_2 in air; H^+, SO_4^{2-}, NO_3, in atmospheric particulate and pH, NO_3 , NH_4^+ and SO_4^{2-}, in rain.

In 1992 the EMEP programme intend to start a discontinuous measurement of VOCs in air, in ten sampling sites over Europe. NILU and JRC Ispra will be responsible for the analytical control of air samples from these selected sites.

The Environment Institute is participating in the intercalibration programme on PAN measurement organised by NILU and sponsored by EC, in which eleven European laboratories are taking part. The first round robin exercise on circulated liquid standards has been concluded on December 1991. Three new intercalibration exercises are scheduled for 1992. In view of overcaming some difficulties due to the thermal instability of PAN, special care has been devoted to the detection of more stable substitutes.

PREVENTION AND REDUCTION OF ENVIRONMENTAL POLLUTION FROM ASBESTOS

In view of the implementation of the Directive EC 87/217, JRC Ispra contributed to the development of a ISO standard method for the determination of the asbestos fiber concentration in air. The set up of the standard method has reached its final stage of development.

As a part of an intercomparison exercise organized by the Asbestos International Association (AIA), 25 asbestos samples have been analyzed, the results being now evaluated.

Close contacts with national experts have been pursued in view of evaluating the performances of different existing analytical procedures. As a result, the feasibility of an intercomparison exercise is being considered and suitable plans established.

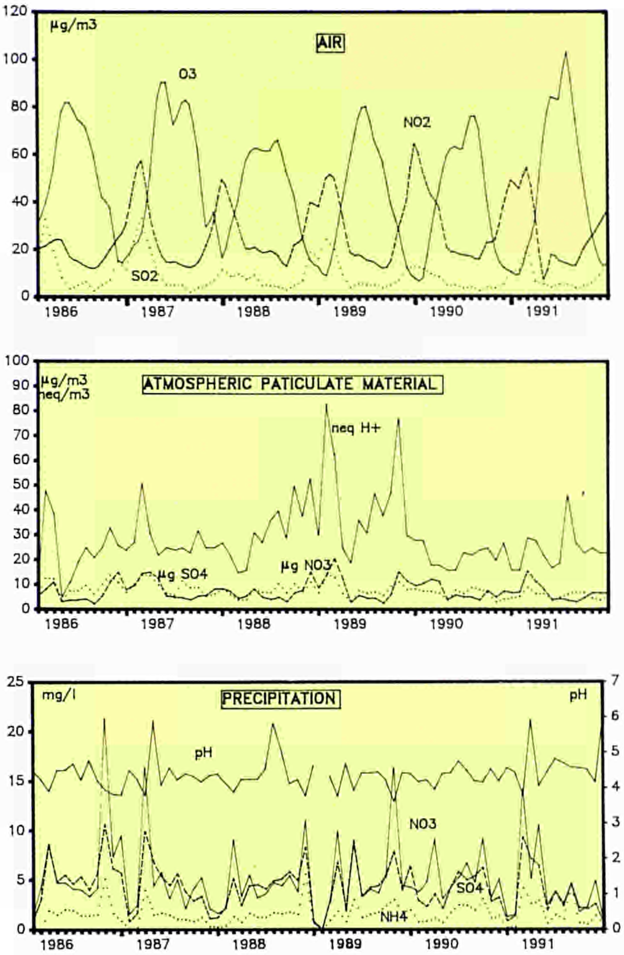


Fig. 27: Monthly average concentrations of polluants. Jan.1986 - Dec. 1991 JRC Ispra EMEP Station

2.5

Radioactivity Environmental Monitoring (REM)

DATA BANK DEVELOPMENTS

REM Data bank

The current total number of data records stored in REM exceeds 400,000. Data are available to external users via the network connection to REM (X.25). Information held by the bank covers data from the twelve EC Member Countries, as well as other European Countries for both environmental samples and foodstuffs from 1984 onward (Tab.6). The REM project aims to promote the integration of this information on a European-wide basis and to make the data widely available in a coherent form for scientific study and analysis.

As the bank is periodically updated new releases are made available to users. The new version, REM 4.0 has been released in August 1991 (only for internal use). A user manual describing how to access and query the new version of the data bank has been prepared and will be available by February 1992. Also the REM data bank reference manual is under preparation.

Following a study of air measurements (published in EUR report 12269), REM data describing fallout and cumulative radioactive deposition due to the Chernobyl accident, have been thoroughly examined. The results have been published in EUR report 12800. Because of their importance for the atmospheric transport models, the data sets have been regularly updated (additional data for Poland, Norway and Rumania have been added) (Fig.28).

Sample Type	B	D	DK	E	F	GR	I	IRL	L	NL	P	UK	non-EC	TOTAL
Air	2041	4659	1278	1211	17995	469	7120	60	371	1500	42	3023	4332	44102
Deposition	428	1636	1092	257	2920	8782	13110	146	282	1389	57	1418	3230	34747
Surface water	481	165	116	293	1819	82	3487	-	115	507	8	2046	121	9240
Drinking water	80	15	24	82	200	61	3487	24	21	7	-	42	42	4085
Milk	582	234	615	219	6732	16	39634	-	1042	769	240	6894	28716	85693
Meat	172	-	36	-	-	-	10532	-	78	6	5	1320	8274	20423
Vegetables	-	94	164	320	-	-	17591	-	113	133	95	1206	1675	21391
Fruits	-	6	180	-	-	-	5827	-	44	-	7	12	3426	9502
Cereals	-	-	160	-	-	-	5131	-	30	-	5	36	2444	7806
Fish	-	9	-	-	-	-	3698	-	32	15	7	268	215	4244
Other	816	340	113	30	719	-	54573	-	22	1896	249	5568	23205	87531
TOTAL	4600	7158	3778	2412	30385	9410	164190	230	2150	6222	716	21833	75680	328764

Table 6: *Survey of Chernobyl measurements in REM DB (number of measurements)*

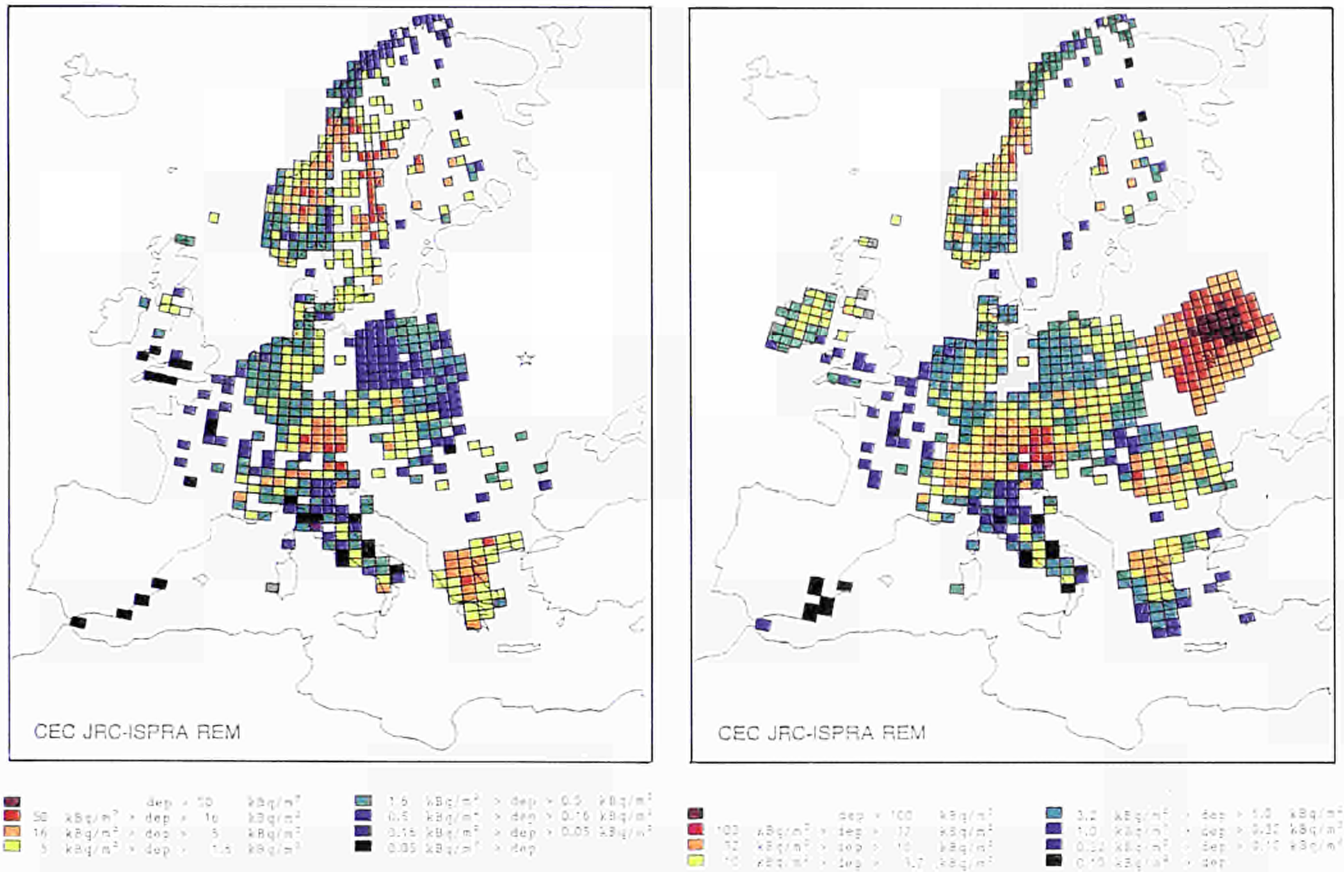


Fig. 28: Caesium cumulative deposition measurements related to the Chernobyl accident, taken from report EUR 12800, averaged per ATMES cell (0.5° latitude, 1.0° longitude).

The meeting of the group of experts of art. 35 - 36 of the CEEA treaty, held at Luxembourg, 6-7 September 1990, to discuss the Radioactivity Environmental Monitoring Report 1984-86, resulted in the establishment of two working groups:

- Working Groups I : to discuss problems related to data transfer, dense monitoring network and preparation of the next monitoring report.
- Working Group II : to set up a sparse scientific measurement network and an intercomparison study.

The first meeting of the Working Groups, held in Brussels - 19-20 June 1991, resulted in the approval of reporting limits as well as on additional sample types, such as sea and lake water and mixed diet. The next Monitoring Report will cover the years 1987-1990, and will be published in 1992. From then onwards, the Monitoring Report will become a yearly bulletin describing the radioactivity in the Member States during the preceeding year.

The input/output interface of the REM data bank, PROTEO, has been tested thoroughly and has been improved. The program permits manual data input and checks the contents of most data fields against tables. Once inputted, the data can be exported into the REM card image format. Data in this compressed format can directly be up-loaded in the data bank.
To make the data bank more accessible to applications, the software will be extended with an option to transform the card image format of off-loaded data into an ASCII formatted table of data fields chosen in advance.

Monitoring data from the Member States should preferably be sent to the REM data manager in a uniformly digitised format. This even becomes indispensable for yearly reporting. Therefore a simplified input interface, called EASY PROTEO, adapted to the requirements of monitoring data, is under preparation. and will be proposed as the favoured data input tool for the annual updating of REM.

Occupational Exposure data bank

The complete data base has been transferred from the Sun386i/Unix workstation under Oracle v.6.0 to a PC/MS-DOS computer under Oracle 5.1C. This implied recreation of the database objects under the RDBMS version 5, loading of all the data stored on the RDBMS version 6 and importing of the Data Administration Tool.

The information already stored in the data base (1981 to 1988) has been validated through a direct comparison with the data written in the questionnaires. This set of data is stored in the data base according to the data format defined by the previously used questionnaire. It has been decided to keep these data exactly as they have been supplied by the utilities, without giving any interpretation aiming at a conversion from the old to the new format.

Exposure data for 1989 and 1990, supplied with the new questionnaire have been introduced in the data base.

The format of the exposure data proposed in the new questionnaire has been put into operation starting from 1989. Due to the fact that the requested information is much more complex and differentiated than it was before, the utilities have encountered some difficulties in filling in the items; as a consequence, important information has been supplied without respecting completely the format of the questionnaire. Furthermore, the analysis of the data requested by the Commission has made it necessary to enrich the information originally contained in the database. The database structure has therefore been revised and updated in order to support all the new originated requirements. The Data Administration Tool has been updated to reflect changes made in the data structure. The Data Administration Tool User Manual will be supplied together with the Final Report.

In the framework of the project, it was decided to supply the utilities not only with the annual analysis of the data (i.e. giving interpretations of elaborated data), but also with the full set of original data. Instead of providing to the utilities data printouts, it was decided to support them onto magnetic media. Keeping in mind two main requirements, user friendliness and very little software & hardware requirements needed to examine the data, it was decided to distribute the files to the users in Dbase format and to develop a tool able to implement some very basic query functions. "The "Browser" application has been developed under the MS-DOS operating system and distributed to the data suppliers.

Another tool was developed to store all the unstructured information (such as comments andqualitative considerations) very often contained in the questionnaires. Again, the requirements were to be user-friendly and small SW & HW needs for running it, due to the fact that this information will have to be used directly by the utilities. The tool ("comment manager") was implemented under MS-DOS and will be put into operation from next year.
In order to simplify the data input, it was also decided to prepare an "electronic questionnaire", with the same structure of the questionnaire on paper. The electronic questionnaire is being implemented in six languages, for use on personal computers under the MS-DOS operating system.

The annual meeting of data suppliers was held in december in Luxembourg. An overview of ten years of records of occupational exposure of plant operators, giving trends on collective doses, individual dose distribution, job-related doses and team-related doses was given by a DG XI expert, based on records of the data bank.
The 1992 programme of the bank was also agreed, having as a main objective (in addition to input of 1991 records) : - the implementation of the electronic questionnaire, - the implementation of the bank on the IBM 550 database server of the Environment Institute for on-line access through X-25 lines, - the transfer of an operational copy of the bank to DG XI-Luxembourg for CEC use.

ECURIE

After the nuclear accident at Chernobyl, a system to meet the requirements for early warning and exchange of information was set up by IAEA (under the Early Notification Convention -27 October 1986 and the Early Assistance Convention -26 February 1987). A similar system was set up by EC (under the Council Decision of 14 December 1987). This further developed and finally resulted in the European Community Urgent Radiological Information Exchange (ECURIE) system, developed in close collaboration with the Member States.

The system consists of a telex communication network between the CEC and the Member States for the transmission of radiological emergency messages. Since Member States belonging to both the IAEA and the European Community have to fulfill similar obligations it was decided between IAEA and CEC to cooperate, what resulted in an identical code (Convention notification and Information Structure, CIS), by which messages will be sent through the communication systems.

Encoding/decoding software has been prepared by IAEA (decoding part) and by JRC-Ispra (encoding part). Both programmes have been integrated and were distributed to the EC Member States. At present an English version is available, though translation in all EC official languages is foreseen. The software is still being improved by addition of a message manager, format consistency checks, and connection to automatic telex device.

In order to become and remain operational, different levels of exercises between CEC and the Member States exist to test different aspects of the emergency system:
-levels 0 - 1: communication test only (held three times in 1991)
-level 2: contact of radiological duty officer (held three times in 1991)
-level 3: exchange of simulated accident data in CIS (first exercise is foreseen to be held in November 1992)

An automatic telex communications device will connect the telex network with a SPARC-2 workstation at JRC-Ispra to automatically receive and send ECURIE messages. The same device will also be connected to a PC for use in the Member States: software is being developed. Interconnection of the system to other ways of communication, e.g. automatic fax and E-mail, are under investigation.

An Oracle data bank, externally accessible by X25, containing incoming ECURIE messages will be created. To further develop ECURIE into a rapid information system, it is needed to interface the data bank with aggregation programs for fast reporting and with long range transport models to provide Member States with adequate radiological predictions.

MODELLING

ATMES

The "Atmospheric Transport Models Evaluation Study", ATMES, has been terminated by a Workshop held in Belgirate on 11-14 March 1991. ATMES used the data of radioactivity in air and depositions resulting from the Chernobyl accident to evaluate the capability of existing models to predict the atmospheric transport of radionuclides. The main conclusions of the study were :

- Most of the 21 models participating in the study were able to predict the arrival times of the cloud at the two selected sites within a few hours, using the analysed windfields .
- Eight models were capable to describe correctly the cloud position and contamination levels in various days, when using the same wind values .
- When dealing with cumulated deposition, only seven models were able to describe the soil contamination satisfactorily .
- A dramatic deterioration in model performances was found when using the forecasted windfields .
- No tendency was found that the model complexity improves its performances.

The statistical package used in ATMES has been extended to general use for atmospheric model comparison .

Among the recommendations of ATMES, the necessity was stressed for the use of a correct simulation of mixed layer growth in lagrangian models. For this reason, the computer model LORAN has been prepared and tested. LORAN is particularly suited for emergency calculations, due to its shorter computer times and to its reduced input requirements .

Fractal analysis was performed on deposition data sets of (West-)Germany, Greece and Ireland and were found to be multi-fractal. Important applications, especially during a radiological emergency situation, are to reconstruct realistic deposition fields from a limited number of data points and to use a more appropriate interpolation technique considering fractal nature of the deposition process, to localize eventual hot spots.

In collaboration with the University of Pavia, the establishment of a statistical fractal model describing the cumulative deposition field after a nuclear accident is under study.

HARMONIZATION OF RADIOACTIVE MONITORING TECNIQUES

The proposals made by the Environment Institute with respect to harmonizing the measurements and reporting of environmental radioactivity in the EC Member States have been adopted by the national experts of the EURATOM Treaty Articles 35 and 36.

In order to implement them, two working groups have been created:

The first group is dealing with transfer of data between member states and the CEC, and with the establishment of a dense network of monitoring stations

The second one is dealing with the establishement of a sparse network of sensitive monitoring stations and with the organization of intercomparison exercises of measuring techniques of environmental radioactivity.

The intercomparisons are performed in collaboration with the International Reference Centre of the WHO at Le Vésinet (F). In the fall of 1991 water samples were prepared by the IRC-WHO and sent to laboratories in the 12 Member Countries for analysis of ^{137}Cs, ^{90}Sr and ^{3}H. The results of this exercise are due in May 1992.

2.6

Other Miscellaneous Contributions

DG I

In support to the agreement between DGI and IAEA, technical assistance to the Agengy's Pacts Programme through the training of scientific staff in analytical and structural chemistry has been provided. During 1991 SCIENTISTS from Senegal (2), Sri Lanka (1) and Nigeria (1) have been trained.

DG III

European Pharmaceutical Databank (ECPHIN)

The creation of a databank on pharmaceutical products was requested by the European Parliament as an additional measure of market transparency in response to a Commission proposal for a Council Directive (EC 89/05) related to market transparency and regulating prices of human medicines.

As a result of a meeting organised with national experts at Ispra in July 1991 it was agreed that existing pharmaceutical databanks of the Member Countries will participate in the construction of a European Pharmaceutical Databank (ECPHIN) by contributing their data. Collection and formating has commenced and data have been received from 11 national authorities in 9 member states.

On occasion of the 2nd meeting with national experts at Ispra in November 1991.a demostration of ECPHIN was given based on the first phase of a display system which allows access to complete data records as well as summaries of related products on specification of product/speciality name, company name, authorisation number or ingredient name with optional secondary specification of member state or pharmaceutical form.

Access to the data by the contributing member states will be available from February 1992 when a number of changes improving the retrieval record on specification of partial names will have been effected. A number of indexes will also be available to facilitate searching which will subsequently be complemented by dictionaries of equivalent terms.

DG V

Renal insufficiency and trace metals

Forty-four elements have been determined in dialysate fluids for hemodialysis, fluids for hemofiltration and continuous ambulatorial peritoneal dialysis.

The data point on the pivotal role of dialysis fluids in contributing to trace metals imbalance in dialysis patients. The exposure for several trace metals appears to be 50 to 12,000 fold higher than the corresponding values on the amounts absorbed via gastrointestinal tract via diet (hemodialysis: Au, Ba, Be, Ce, Ga, La, Sc, Ta, Th, V, Zr; hemofiltration: Be, Ce, Ta, Th, V, Zr; continuous ambulatory peritoneal dialysis: Au, Be, Ce, Ga, V, Zr).

It has been suggested that the beneficent deferoxamine (DFO) therapy applied in uremic patients, which has traditionally been assigned only to the chelation of aluminium, could also be the result of chelation of iron.

In vitro experiments on the effect of aluminium alone or in the presence of DFO and/or iron salts on the activity of superoxide dismutase (SOD) do not rule out this possibility; they simply state that aluminium and iron do not mutually interact in order to affect SOD activity directly.

DG VI

Control of wine sugaring

The Support given to DG VI for the control of sugaring of wines and for the implementation of a data bank of NMR fingerprints of european wines has been already described in the section "Food and Drug Analysis" of this report.

DG. XIII

New Antioxidant for Plastics

Development and synthesis work was continued with a view of optimizing a new type of antioxidant for plastics with an improved retention in the polymer structure.

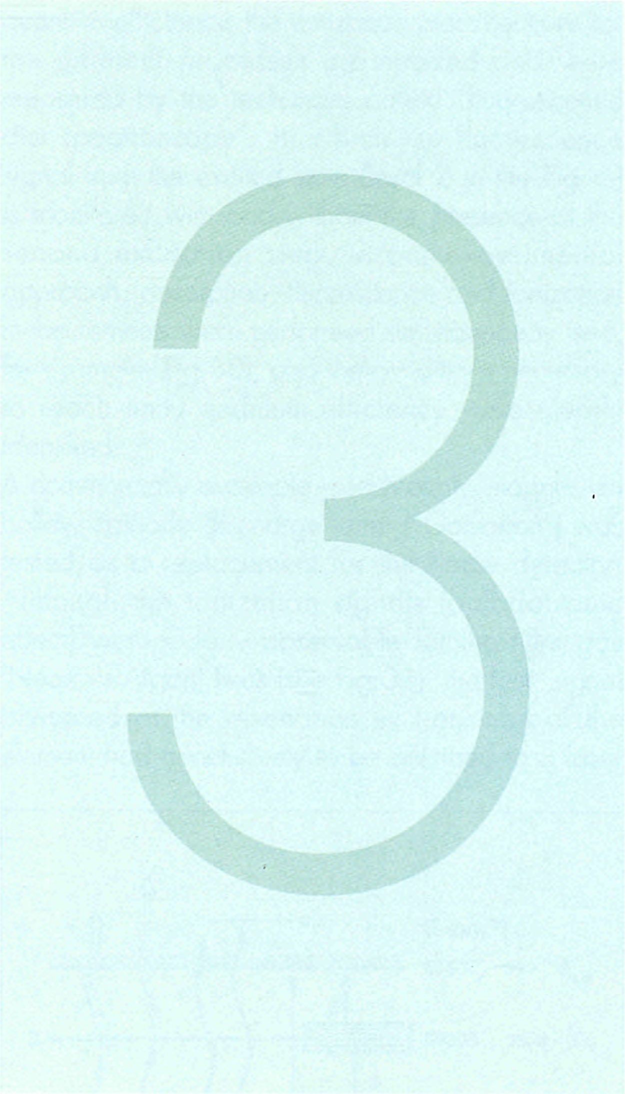
DG XVII

ECSAM

In the frame of the ECSAM support activity to DG XVII, uranium accurate and precise potentiometric determinations have been performed in about 100 UO_2 powder and pellet samples. Furthermore, 5 in-field campaigns of uranium analysis in UO_2 samples and in nitrate solutions have taken place in 4 LEU fabrication plants and in 1 reprocessing plant.

D. G. XXI

Measurements of chemical or structural composition of unknown or not well defined products have been performed and evaluated for chemical products imported in EC in order to apply the correct customs tariffs have been provided.



3

Exploratory Research

3.1

Innovative Laser Technologies for Chemical Analysis

Following previous research, three aspects have been selected:

- evaluation of the quantum efficiency and ion yield of a photon detector, based upon the use of the laser-enhanced ionization technique in a flame;
- evaluation of other atom reservoirs, i.e., low pressure glow discharge lamps, as photon detectors;
- characterization of the laser excited fluorescence technique in a graphite furnace as a potential approach to absolute analysis.

The essential requisites of an ideal photon detector based on ionization can be summarized as follows:

- existence of a suitable scheme, from a selected excited state, capable of unity ionization efficiency:
- absence of ionization background;
- presence of a sufficient number density in the ground state or in the state originating the primary absorption step, to insure total absorption;
- good atomization efficiency and long residence time of the atoms in the interaction volume;
- large acceptance solid angle for the incoming photons; and finally
- availability of a method of charge detection characterized by unity collection efficiency.

It was proven experimentally that a flame system fed with a magnesium solution possesses many of the above requisites. The magnesium energy level scheme pertinent to the ionization process is shown in Fig. 29. Both two-step excitation (followed by collisional ionization) and direct photoionization in the continuum or into an autoionizing level were experimentally evaluated. In order to calculate the quantum efficiency, the ionization cross sections for the different processes are needed and were measured by the technique called "fluorescence dip spectroscopy", in which the fluorescence signal from the excited state (level 2 in the Figure) is monitored with and without the presence of the second excitation step. In our experimental approach, absorption, fluorescence and ionization measurements were performed simultaneously (see, for example, Fig.30), and the conditions necessary to reach unity quantum efficiency were clearly identified.

A commercially available, see-through, magnesium hollow cathode discharge lamp ("Galvatron") was tested as a replacement for the flame detector. Although the ionization signals (optogalvanic effect) were clearly observable for the filler gas (Neon or Argon) lines (see Fig.31), the fast signal observed at the resonance uv transition of the element had conclusively to be ascribed to a laser

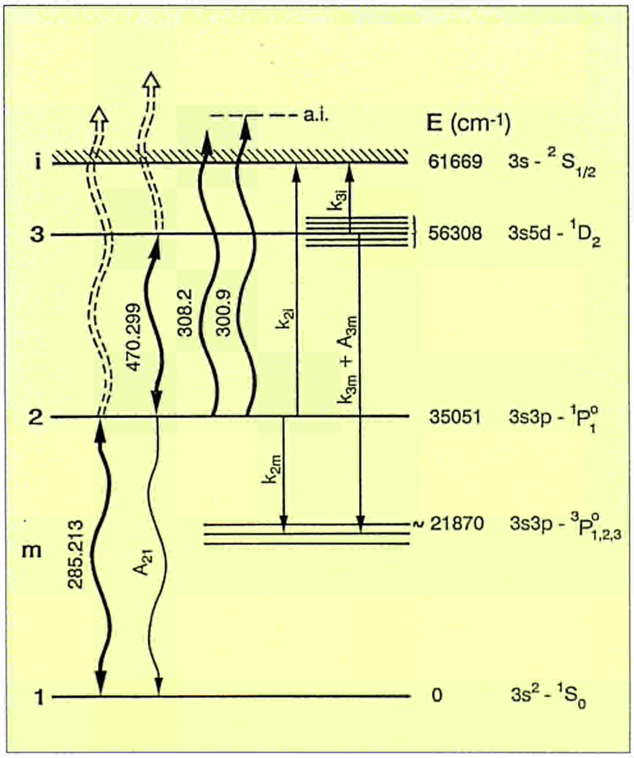


Fig.29: *Energy level scheme pertinent to the magnesium system used as photon detector. The energy and the spectroscopic notation of the levels are given on the right. The wavelengths of the transitions are indicated in nanometers. m, i, and a.i. represent the metastable levels, the ionization continuum and the autoionizing level, respectively. Both radiative (A's) and collisional (k's) rate coefficients are indicated.*

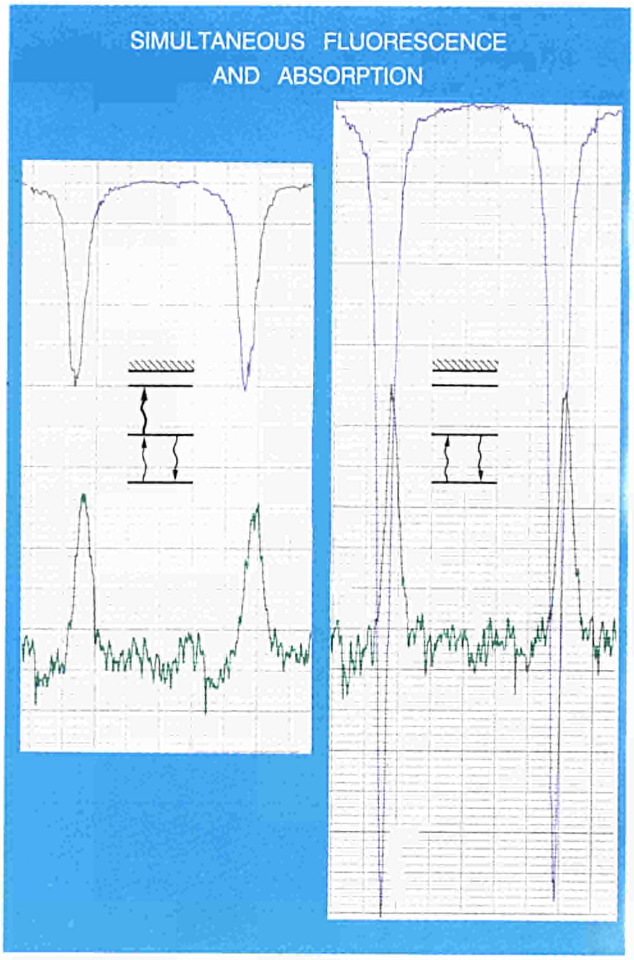


Fig. 30: Experimental traces showing simultaneously monitored absorption (noisier trace) and fluorescence signals for the magnesium transition at 285.213 nm. The insert indicates whether the second excitation step was present (left part) or absent (right part) during the measurement. As expected, both the absorption (monitoring the ground level population) and the fluorescence (monitoring the first excited level population) signals decrease when the second excitation step removes the atoms from the excited level.

induced artifact, possibly due to the impinging of the laser beam on the cathode and to the resulting photoelectric emission. Therefore, the magnesium lamp cannot be considered, at the moment, a suitable ionization detector based upon the magnesium scheme. More work is needed if other schemes, involving the filler gas lines, have to be evaluated.

The concept of absolute analysis is essentially based upon the theoretical knowledge of the functional dependence between a measurable physical quantity and the concentration producing that quantity. During the last decade, the technique of atomic absorption coupled with electrothermal atomization has been shown to fulfill the basic requirements of an absolute analysis method, i.e., elimination of matrix interferences, stabilization of the calibration over time and theoretical

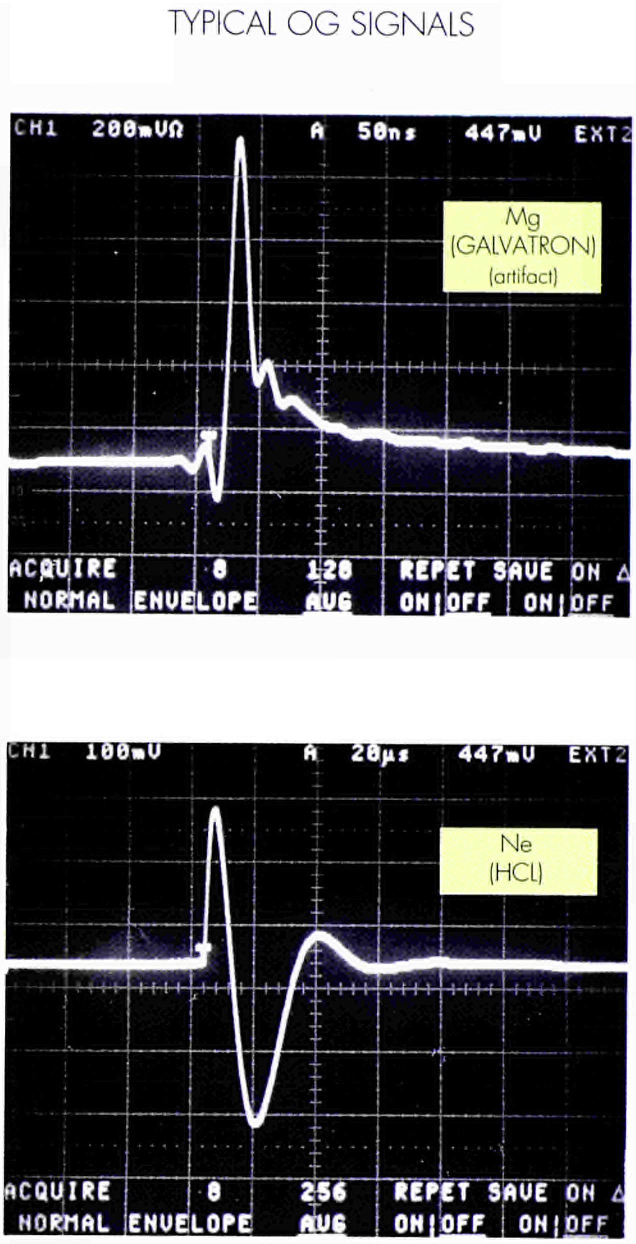


Fig.31: Typical oscilloscope traces of optogalvanic signals in a low pressure hollow cathode discharge. The upper trace is an artifact, due to the uv laser beam impinging on the cathode. The lower trace is a true optogalvanic signal observed when the population of the metastable neon levels is perturbed. Note the different time scales on the oscilloscope.

knowledge of the calibration function. We have performed a detailed theoretical evaluation of the laser induced fluorescence technique in a graphite furnace as a viable approach to absolute analysis, and have identified an analytical protocol to be followed in order to validate such approach.

The basic processes and the fundamental relations are shown in Fig. 32. The key parameter is the "sensitivity factor" (Volt/atom pulse). Its evaluation requires the knowledge of:

- the relation between the total number of atoms and those fluorescing (ionization losses);
- the optical collection efficiency and
- the detection parameters.

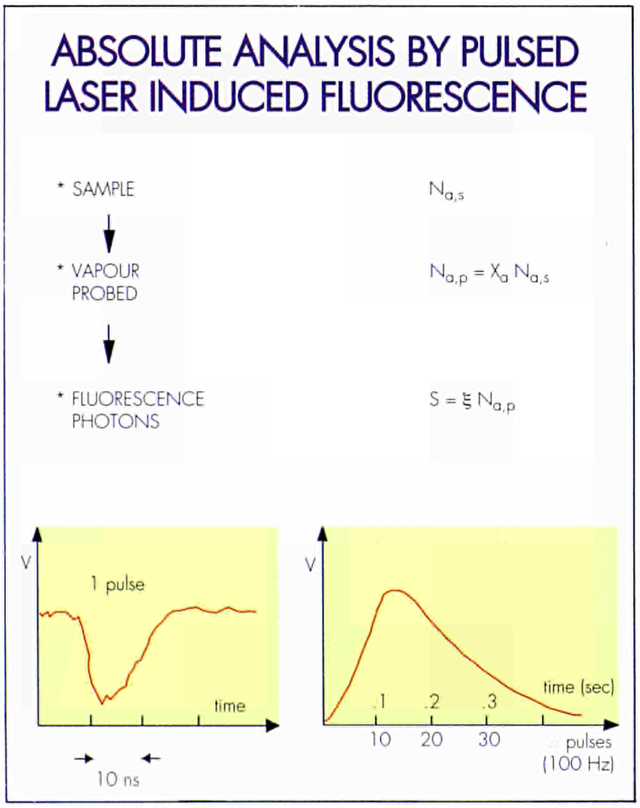


Fig. 32: Simplified flow chart, indicating the basic processes and relations pertinent to the absolute analysis approach.

By taking thallium as a test element, a relationship was derived between the time-integrated fluorescence pulse and the number of emitting atoms (Fig.33). In order to evaluate, as accurately as possible, the background under the analytical line, a fluorescence set-up using an intensified diode array as detector was successfully tested.

SIGNAL EVALUATION

* V_{max}(Volt/atom)= sensitivity (ξ)

* S ⇒ evolution of atom pulse in the furnace

$$S=\int_0^{\infty} V_{max}\,(t)dt = \xi\,\left(\frac{m_A N_A}{M_A}\right)\,\chi_a\,\left(\frac{l^2}{8D}\right)\,\left(\frac{g_1 \exp(-E_1/kT)}{Z(T)}\right)$$

$m_A = c_A V_A$ =analyte mass (g), given by the product of the analyte concentration,c_A(g/l) and the sample volume, V_A(L)

N_A = Avogadro number, (atoms/mole)

M_A = analyte atom weight, (g/mole)

$\chi_a = (\eta_a \eta_p)$= atomization and probing efficiency

$$\eta_a = \frac{2\tau_2^2}{\tau_1^2}\left\{\frac{\tau_1}{\tau_2} - 1 + \exp\left(-\frac{\tau_1}{\tau_2}\right)\right\}$$

$\eta_p = (V_p / V_a)$, where V_p is the laser probe volume, V_a is the atomizer volume (cm^{-3})

l = lenght of the cuvette, (cm); and
D = atomic diffusion coefficient, ($cm^2\,s^{-1}$)

Fig. 33: Relation between the time-integrated fluorescence pulse (Volt second) and the emitting thallium atoms in the furnace. τ_1 and τ_2 appearing in the definition of χ_a are the atomization time and the residence time, respectively. The last factor represents the fraction of atoms in the initial absorbing state (a Boltzmann distribution is assumed, with Z (T) being the partition function).

3.2

Laboratory for Separation Sciences

A continuous liquid sample introduction system has been installed on the VG70SEQ mass spectrometer. The objectives were to develop a new system more suitable for:

- Interface micro LC to FAB-MS, in particular for the analysis of modified bases and nucleosides.
- Interface capillary electrophoresis system with FAB-MS for large molecule analysis.

The system was put together with a VG Universal FAB source, the main distinguishing feature of which is a heated copper block that permits the heating of the probe tip thus preventing freezing of eluent and matrix.

Preliminary considerations had shown that a Valco internal loop valve should be simplest to mount and operate with the system. It allowed to optimize a matrix composition and flow rate. The most satisfactory matrix composition was found to be 46% CH_3OH, 46% H_2O and 8% glycerol. It was observed that flow rates of up to 3.0 μl/min can be tolerated by the vacuum system. The most satisfactory operation was obtained at flow rates of 1.5-2.0 μl/min.

The valve was connected to an ISCO syringe pump with a 1/16" o.d. (0.2 mm i.d.) stainless steel tubing, a 0.4 mm o.d. (50 μm i.d.) fused silica tubing served as the transfer line between the valve and the probe tip. The position of the tubing at the probe tip was critical. To improve the positioning of the fused silica at the tip, a modified tip for the dynamic FAB probe was made and installed. The tip design not only allow one to maintain the capillary position during introduction and removal of the probe, but also prevents the pooling of the matrix in the tip. All component parts of the tip are of the same diameter as the probe, thus permitting a smoother introduction and removal through the vacuum lock.

The performance of the dynamic FAB was evaluated with modified nucleic bases and nucleosides, amino acids and peptides. The system was found to be very stable over periods ranging up to 6 hrs; the total ions counts showed a change of ±6%. "Clean" spectra can be readily obtained with the system even at relatively low concentrations of 2 nanomoles.

Several butadiene monoxide and dioxide adducted bases, and monoxide reacted DNA hydrolyzates were analyzed. The presence of guanine adduct in a LC-fraction of DNA hydrolyzate was confirmed with the detection of pseudo molecular ion for the adducted guanine (m/z 222) and guanine (m/e 152). Similar confirmation was obtained for another fraction by the presence of m/z 198 resulting from cytosine reaction with the dioxide.

In order to evaluate the performance of system with buffered LC eluents and matrix modifiers, various matrix compositions were tested; these included matrices with NH_4Cl or $HCOONH_4$. The system can tolerate up to 5mM concentration of salts, the tube plugging problems were less severe with formate than NH_4Cl. However, the most stable conditions were obtained in the absence of salts: the salts tend to plug up the fused silica tubing at the probe tip resulting in excessive sputtering and associated vacuum instabilities. The most suitable matrix had the following composition CH_3OH/H_2 45/45-glycol 10% with 5 mM salt. The high methanol concentrations seem to leave the probe tip dry, resulting a noticeable drop in the sensitivity, whereas the higher concentrations of water tend to freeze at the probe tip.

The system evaluation was carried out with 9-ethyl adenine as the model compound. Detection limits down to 1 ng were achieved. The response was reasonably linear over 2.5 to 100 ng concentration range, (correlation coefficient 0.998).

The system yielded good quality background corrected spectra at low concentration, as shown in the case of 1/50 dilution of the LC fraction for guanine monoxide adduct. Spectra for several amino-acids and oligopeptides were also obtained.

Finally the identification of zinc bound species was accomplished. The primary objective was to identify zinc amino acid complexes, the secondary objective to determine the yield of such species in equimolar zinc gluconic acid/aminoacid formulations. The chromatograms have shown that most of the arginine in a neutersol sample is present as free arginine. These findings were confirmed by MS analysis i.e. only 10% of the arginine is bound to zinc as zinc arginate or zinc glucoarginate. No zinc complex was found in the case of the zinc gluconate taurine formulation. In another set of experiments conducted with a mixture of neutersol and lysine, a lysine argine Zn complex was detected (m/z 385, 387, 389), clearly indicating that under suitable conditions zinc binds readily with the amino acids.

The Application of Crossflow Membrane Techniques in the Treatment of Wastewater

The application of the different crossflow techniques to a variety of wastewater types requires a pilot plant which should allow:

- combination of different types of micro and ultra filtration membranes in a most versatile way.
- processing of wastewater quantities well above the laboratory bench scale.
- easy transport, thus allowing its employment later on directly "on the spot".

Our pilot plant has been realized in collaboration with SEPAREM, Biella (Italy); it combines eight tubular membrane modules and a spiral ultrafiltration module. Its total size of about 1.8x11.6x1.0 m and its high mobility will allow a later employment in the field.

The plant has been delivered in November 1991 and following to the test runs, the membranes are being at present tested for their separation power characteristics.

The membrane unit was planned to be as much versatile as possible with the purpose of running simultaneously comparative studies of the performance of various types of membrane systems on wastewater treatment.

The tubular group can be equipped with all types of micro and ultrafiltration membranes of 1.5 m length. The first tests were run using membranes of polvinyldenofluoride (PVDF), nominal pore class of 100,000 and total active area 0.9704 m^2 (0.1213 m^2 each module). The operation conditions are: maximum inlet pressure = 2.5 bar; optimum operating range 1.5-2.0 bar; maximum working temperature 60°C; operating pH range1-12. Before starting working with a real wastewater several tests were run with a standard solution of 100 ppm Dextrane (110,000 Dalton) in order to characterize the membranes. With these membranes we obtained a 43% product rejection and a permeate flux of 48 l/h (working conditions: pressure = 1.5 bar; temperature = 25°C; pH = 7 and axial flux = 200 l/h, indicating that these membranes will work in the microfiltration range.

The spiral group is prepared for working with all kinds of 4" spiral wound membranes. In this case two different types of membranes were studied.

The first tests were run with a polysulphone membrane, with a nominal pore size of 60,000 and a total active area of 6.5 m2. The operation conditions are: maximum inlet pressure 4.5 bar; optimum operation range 3.0-3.5 bar; maximum working temperature 50° C; pH range 1-12. The first tests run with a standard solution of 100 ppm Dextrane (40,000 Dalton) gave a product rejection of 89% and a permeate flux of 750 l/h (experimental conditions: pressure = 1.5 bar, temperature = 25°C axial flux 3,700 l/hh and pH = 7).

It was tested also a second type of spiral membrane with a nominal pore size of 15,000 in order to extend as much as possible the range of the removal rate. This membrane was of the composite type (Polyamide) with a total active area of 8.7 m^2. In this case the operation conditions are; maximum inlet pressure 4.5 bar; optimum pressure range 3.5-4.0 bar; maximum working temperature 50° C; pH range 2-11. With a standard solution of 100 ppm Dextrane (40,000 Dalton) we obtained a product rejection of 95% and a permeate flux of 270 l/h at the following experimental conditions; pressure = 3.0 bar,

temperature = 25°C, axial flux = 16,000 l/h and pH = 7.
Simultaneously the physical-chemical characterization of a textile industrial wastewater was started. Until to now the parameters measured were: Total Organic Carbon (TOC); Dissolved Organic Carbon (DOC); Chemical Oxygen Demand (COD); Total carbon, nitrogen, hydrogen (CHN); AOX (Adsorbable Organic halogen). These waters will be used for testing the plant.

3.3

DNA Adducts

The formation of DNA adducts is a primary event in chemical carcinogenesis. The detection of DNA adducts in lymphocytes provides direct evidence of human exposure to environmental genotoxins and makes possible individual risk esimation as well as the identification of goup at risk.

The detection of DNA adducts in their tissues of wild animals constitues a novel approach in the assessment of exposure to environmental chemicals and permits the identification of sensitive sentinel species to select as specific bioindicators (e.g. fish and water quality).

However, methods to detect DNA adducts in microsamples of genomic DNA are only in a early stage of development. There is a need for reference physico-chemical methods for validation of high sensitive biochemical assays under optimization. The multidisciplinary approach followed in the present reseach responds to these requirements.Major efforts were devoted to the optimization of:

- Methods for the characterization and detection of DNA adducts formed by metabolic intermediate of 1.3 Butadiene.
- Development of a comprehensive approach to evaluate the exposure of fish to environmental genotoxic chemicals using DNA adducts as selective biomarkers.
- DNA adducts of 1.3 Butadiene metabolites.

Epoxybutene (EB) and diepoxybutane (DEB), are the two genotoxic intermediate in the metabolism of 1.3 butadiene in mammals. These two chemicals were chosen in our studies as model compounds for mono and bifunctional agents which are expected to induce different types of adducts. For the methodological development, two approach were followed:

- physics-chemical characterization of the reaction products of EB and DEB with nucleobases and nucleotides using uHPLC, CE, MS and NMR.
- development and optimization of a sensitive biochemical method based on HPLC-TLC and 32P-PostLabelling technique. (In collaboration with the School of Biological Sciences, University of Swansex, UK)

Reaction of EB with nucleotides, polynucleotides, calf-thymus DNA and human blood lymphocites "in vitro" were studied by HPLC separation and characterization of the isolated products by MS. The MS analysis assigned to these adducts structures corresponding to N7 Guanine. The formation of the two major adducts the structure of which has been reported in previous report, was dose dependent in human lymphocites.

These two guanine derivatives were also detected after depurination of ply(dG-dC) reacted with EB. The formation of AP sites is being studied using different enzymatic digestion and 32P-PL.

An O^6 adducts was identified and characterized using MS and NMR (in collaboration with the University of Missouri, USA). Fig. 34. Derivatives of O^6 Guanine explain the presence of fragments of m/e 203, 178 and 151 ions in the EI-MS spectra. Such adducts are of fundamental importance in supporting the strong mutagenic properties on k-ras-protooncogene in mice exposed by inhalation to 1.3 Butadiene.

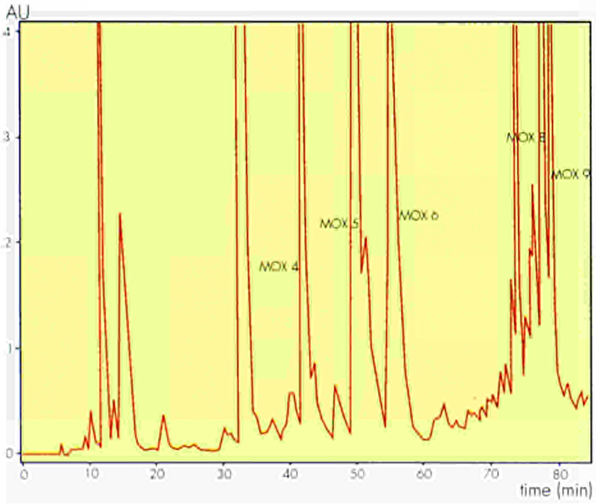


Fig. 34: *GUANOSINE + EPOXYBUTENE (MOX).*

In the study of DNA adducts of diepoxybutane (DEB), major efforts were concentrated on the ^{32}P-PostLabelling technique to detect adducts in the liver of mice treated with DEB. Exposure to DEB gave rise to the formation of Adenine and Guanine adducts which were also found in "in vitro" exposed polynucleotides and DNA. The structure of these adducts is under clarification.

There is evidence that fish living in polluted rivers and estuaries exibit relevant incidence of tumours. Bottom fish grown in areas known to contain high levels of PAH, PCB and pesticides in sediments show higher liver neoplasia than fish from clean waters.

Laboratory studies have demonstrated that the hepatic cellular response in fish exposed to chemical carcinogens is similar to that of many mammalian species. Fish metabolize carcinogens very efficently and some metabolites can bind covalently to DNA contributing to the neoplastic initiation of cells by mechanisms qualitatively similar between various species. Indeed, certain

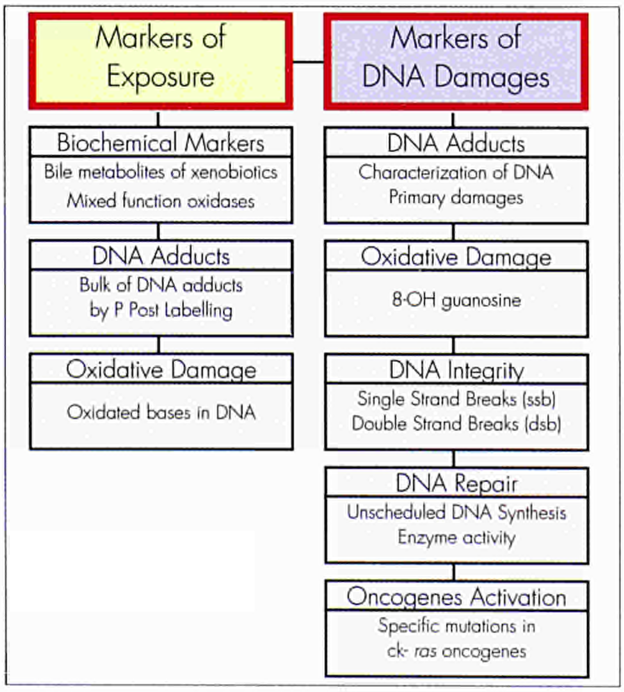


Fig. 35: *Molecular - Genetic strategy for the assessment of genotoxins in water quality .*

hepatic conditions of feral fish most probably reflect the quality of their environment, particularly in terms of exposure to xenobiotics.

A novel strategy based on molecular and genetic biomarkers was developed in support to studies on the water quality (Fig.35).

The overall exposure to genotoxins is evaluated by assays on DNA damages and oncogenes activation. It is expected that correlating these molecular biomarkers in fish with the level of pollutants in tissues, water and sediments, a better estimation of the overall intake from food, water and absorption from sediments and particulate. Fig.36 shows the HPLC detection of bile metabolites in cat-fish exposed to Benzopyrene.

The levels of DNA adducts in fish liver can be considered an indication of the biologically effective dose and clearly highlights exposure to specific genotoxins. These measurements can then be used as useful molecular dosimeters. Fig.37 shows the detection ³² PPL and HPLC of DNA adducts in the liver of different species exposed to BP.

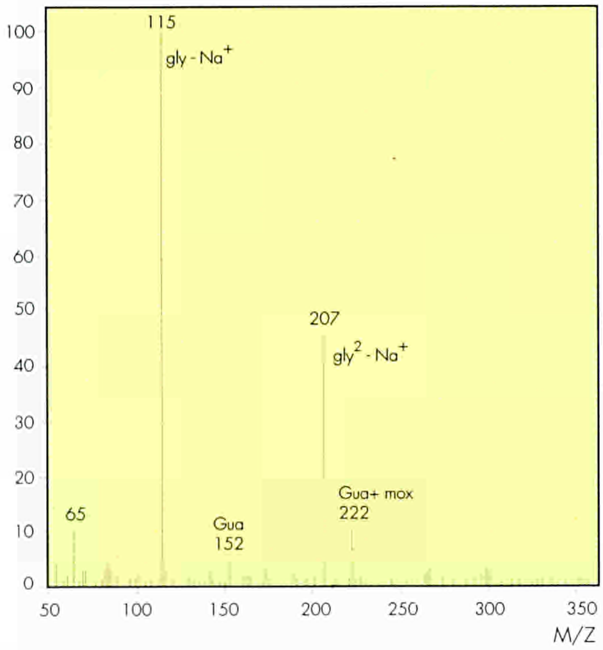


Fig. 36: Characterization of guanine adducts in calf-thymus DNA and DNA from human lymphocytes exposed to epoxybutene.
MS analyses confirmed the presence of guanine adducts in HPLC fractions of de-purinated DNA. Molecular ion of the adducted guanine (m/e 222) was detected by FAB-MS. Using EI ionization, fragment ion at m/e 191, characteristic for MOX 5, was present.

Single Strande Breaks (ssb) and Double Strande Breaks (dsb) can occur in DNA as a result of interaction with chemical and/or physical agents. These lesions can be repaired by DNA enzymes even if some breaks can remain in the polynucleotide chains. The detection of permanent or transient populations of broken DNA provides a direct testing for genotoxic events. The measurement of DNA repair in fish hepatocytes can be taken as an indirect index of induced genotoxic events (Fig.38)

Cellular protooncogenes can be activated by chemical carcinogens-DNA interaction. Specific mutations in the ck(ras) oncogenes have been

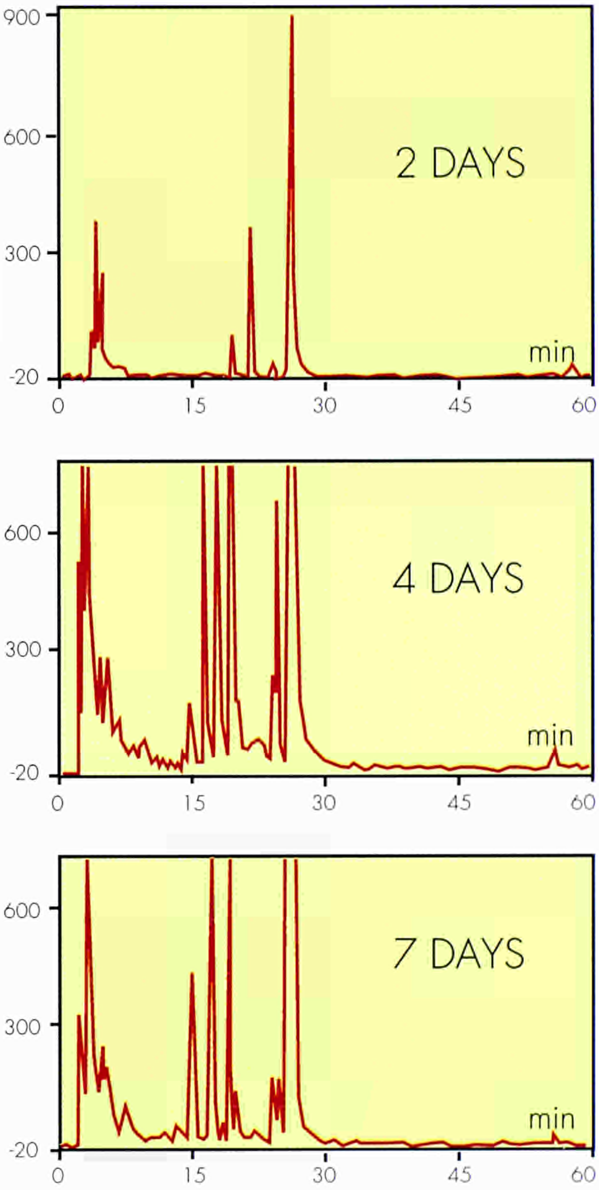


Fig. 37: HPLC separation of total bile from catfish exposed to a single i.p. injection of 0,1 mMole BaP:Kg body weight.

founded in the liver tumours of fish living in highly polluted areas. Association of DNA damage with particular mutate alleles would improve the assessment of chemical risk.

The relationships between the levels of DNA adducts and activation of oncogenes following exposure to PAH is presently under investigation. Fig.39 shows the PCR (Poly Chain Reaction) products of k-ras in the liver DNA of different fresh and seawater fish.

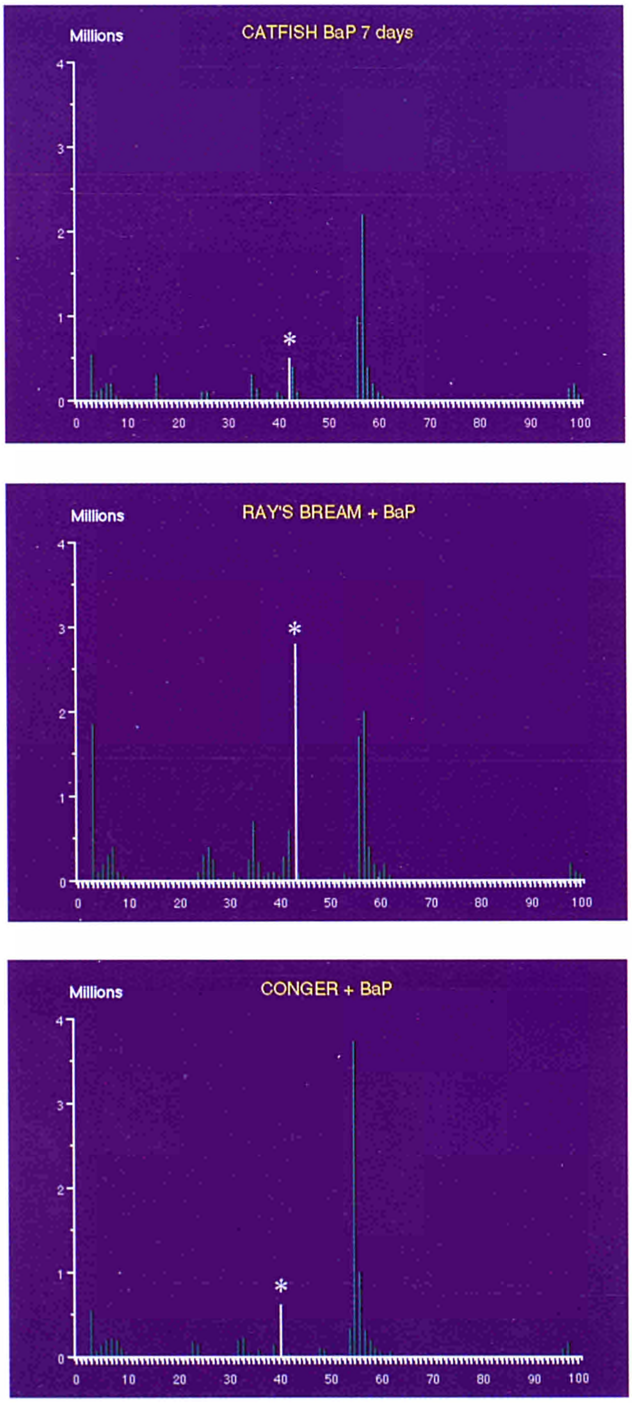


*Fig. 38: Detection of DNA adducts in the liver of different fish exposed to Benzopyrene. Peaks * correspond to significative differences when compared to unexposed DNA.*

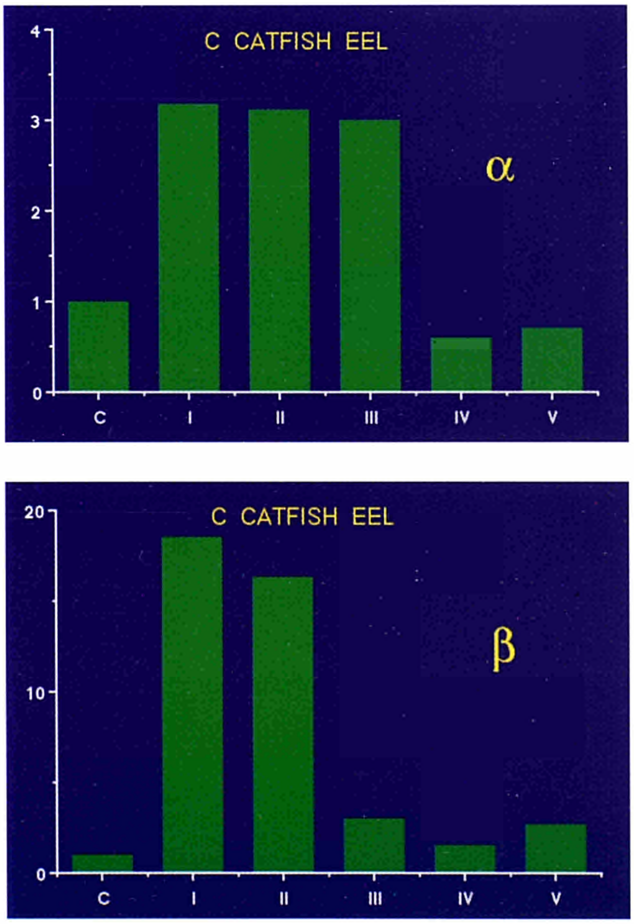


Fig. 39: Activity of DNA Polymerase in the liver of catfish and eel at 4 days after the exposure to a single i.p. injection of 0,1 mMoleBaP / Kg body weight..

4

Third Parties Work

As for the preceeding annual reports, this chapter includes a variety of activities performed in 1991 which have yielded a total income of about 500,000 ECUs.
In the following only the most relevant of them are mentioned. These have concerned the areas of Environmental Chemicals, Indoor Air Pollution, Water Quality, the Long Range Atmospheric Transport (ATMES) and Radionuclide Migration in Geochemical Bodies.

The collection of data on 150 priority chemicals has been the subject of a first contract with the German Ministry of the Environment/German Federal Environmental Agency, to be followed by a new contract focused on 200 new priority substances.
A comprehensive study has been performed for the Italian Association of Wallcovering Producers (Assoparati) aimed at identifying a series of pollutants contained and/or emitted by their products. Emission rates were assessed by means of dedicated environmental test chambers.
A european quality standard has been proposed by Assoparati on the basis of the achieved results.

The indoor air quality in 11 schools in Milan has been investigated. The results showed that in all but one case the indoor Total Volatile Organic Compounds (TVOC) was higher than outdoor the highest concentrations having been experienced in nursery schools.

Within the framework of a contract with Lombardy Region a contribution to define a manual of procedures for the operators of subnetworks of air monitoring stations was given.
A research contract with the Italian Electricity Board (ENEL) and with the National Research Council (CNR) has dealth with the physical-chemistry of photoxydants and their precursors. The study has involved the acquisition of data for troposferic ozone at different sites and altitudes and the study of troposferic chemical reactions in NOx rich atmosphere.

In the frame of the EC PHARE project a contract has been established with the Polish Ministry of the Environment to investigate the transboundary transport of air pollution in Upper Slesia.

The water quality of the reservoirs of the drinking water supply system of southern Sardinia has been investigated in the framework of a contract with the Ente Autonomo del Flumendosa (Cagliari).
The spatial and temporal distribution for a number of elements and compounds has been assessed.

A joint field study on Lake Stechlin (Federal Republic of Germany) has been started under contract with GSF Neuherberg entailing extensive sediment sampling and measurements of trace elements and nutrients.

Interlaboratory exercises (proficiency testing) for the control of drinking water by regional and district laboratories have been organized in the framework of a contract with the Emilia-Romagna Region.

Ultratrace impurities determinations in deionized and re-distilled water as well as in the trimetylborate have been performed by mass spectrometry in support to Borexino detectors to be built at the Gran Sasso underground laboratory for real time observation of ^{7} Be solar neutrinos.

As the follow up of the ATMES study a "European Tracer Experiment" (ETEX) has been launched to verify the feasibility of real time evaluation of the evolution of clouds of atmospheric pollutants in emergency conditions. The work is a part of a contract with the World Meteorological Organization

The studies related to the contract with ENRESA (Empresa National de Residuos Radioactivos S.A.) aimed at clarifying the process and the dynamics of radionuclide migration in granite formation has been concluded.

4.1

Environmental Chemicals

In the framework of third party work, a first contract concluded with the German Ministry of Environment / German Federal Environment Agency (UBA) aiming at the data collection for 150 priority chemicals was completed and a second contract is being prepared, focussing on 200 new priority substances.

Data were collected and evaluated for the 150 priority substances on physico-chemical properties aquatic toxicity, mammalian toxicity, biodegradation and bioaccumulation, abiotic degradation and environmental concentrations. Data were delivered in both ECDIN and CHEMIS format.

Revenues were obtained also from the on-line distribution of the ECDIN databank through the host organization in Germany.
More recently, a new contract was concluded with a host in America (TDS) for on-line distribution of ECDIN in the USA.

Several contracts were concluded also for the distribution of ECDIN on CD-ROM.

4.2

Indoor Air Pollution

The Italian Association of Wallcovering Producers (Assoparati) requested an investigation into specified pollutants which might be released by their products. The emission and/or content of the following has been determined: formaldehyde, vinyl chloride, chlorofluorocarbons, plasticizers, dioxins, total volatile organic compounds (TVOC), heavy metals, fungicides and radioactivity.For the determination of some of them specified methods (e.g. Euro Norms) had to be used. For others such as plasticizers and dioxins, methods had to be developed in order to comply with the high sensitivity requested. Except metals, fungicides and radioactivity, for which the content was quantified, the emission rate was assessed through small environmental test chambers. The results of the investigation show that some of the products emit formaldehyde and TVOC at a non negligeable rate during the initial phase, but after 2-4 days the concentration has decreased below guideline or recommended values. Based on the results of our work Assoparati has proposed a European quality standard.

In the framework of an investigation into indoor air quality in a sample of 11 schools in Milano conducted by the University of Milano (Istituto di Medicina del Lavoro) several chemical, microbiological and climatic parameters have been determined. The EI was requested to carry out the determination of volatile organic compounds (VOC). The results showed that, with one exception, the TVOC concentrations indoors are always higher than outdoors and in some cases much higher. The schools with the highest concentrations (up to 13 mg/m^3) are nursery schools, apparently because of the use of various products used for playing and cleaning.

4.3

Air Pollution

In the framework of a three years (1990-1993) contract with the Regione Lombardia, a contribution was given to define a manual of procedures for the operators of the sub-networks and 14 air quality stations were validated. Since last December the above-mentioned manual is an official document of the Regione Lombardia. The activity is in progress and to December 1991 twenty stations have been validated.

A research contract with CNR/ENEL has concerned the physical-chemistry of photooxidants and of their precursors.

Ground-level ozone data recorded at 15 stations distributed at different altitude in the pre-Alpine and Alpine regions in Italy, Switzerland (Ticino) and Austria (Tyrol) have been collected and stored in a database. The ozone patterns at different sites and altitude as well as the observed episodes will be analysed. The data acquisition is continuing.

The results of the studies performed on kinetics, mechanisms and products of NO_3 radical reactions relevant to the budget of photooxidants and their precursors are described in the Air Chemistry section pertinent to the Specific Programme.

A study contract with the Polish Ministry of the Environment, in the frame of the EC PHARE project was focused on pollution monitoring of the Upper Silesia (Katowice region) and on the transboundary transport of air pollution from Czechoslovakia to Poland. The start of this study, initially planned for October 1990, has been shifted to early spring 1992.

4.4

Water Quality

Two contracts with the Italian Ministry of the Environment are in preparation. They foresee the availability of the JRC scientific know-how in setting up safeguarding plans and prevention pollution schemes for the rational management of surface water resources.
In particular:
- assessment of trophic levels of lakes Como and Garda (the largest lake of the European Commmunity);
- ecotoxicological evaluation of the impact of the environmental chemicals in these systems;
- quantification of internal nutrient loadings;
- definition of water quality objectives for management purposes, and
- prediction of lake recovery times.

The Ente Autonomo del Flumendosa, Cagliari, requested the assistance of EI to their investigation of the water quality of reservoirs Flumendosa, Mulargia and Simbirizzi, which form the basis of the drinking water supply for southern Sardinia.
In particular, the release of harmful elements and compounds from the sediments of the three reservoirs should be estimated.
The spatial and temporal distribution of a number of elements and compounds in the three reservoirs has been assessed and visualized (distribution mapping).
Lake Flumendosa showed particularly high toxic metal concentrations in its sediments, for example 40 mg/kg of Cd, which is the highest concentration of this element, we ever encountered in a freshwater lake.
The elevated metal concentrations are related to manifold surface mineralizations in the northern part of L. Flumendosa (Pb, Zn, Cu, Fe ores). Also L. Mulargia shows some evidences of metal ore presence in its area.

Following tthe inventory of trace metals and nutrient elements in the sediments, field-based studies aiming at the contaminant flux estimation at the sediment-water interfaces, were started in a seasonally structured sequence and are due to be concluded spring 1992.

In the framework of the cooperation contract between GSF Neuherberg and the EI, a joint field and laboratory study on Lake Stechlin (former DDR) has been started.
This lake has been used as cooling water source for a nuclear power station for many years and the study aims at a pollution status assessment in view of the future use of the lake.
Extended sediment sampling was performed July 1991 in cooperation with the Institut für Ökosystemforschung Berlin-Halle und Institut für Gewässerforschung Neuglobsow. Pollutant measurements, including trace elements and nutrients (Ispra) and organic substances (Neuherberg), are in progress.

The EI receives at a growing rate requests to assist groups and associations of national laboratories in their attempts to improve their analytical measurement quality.
One contract of this kind has been concluded with Regione Emilia-Romagna. The request is to organize on a regular basis interlaboratory exercises (proficiency testing) for the drinking water control by the regional and province laboratories.
The first exercises has been completed in September and included three simulated drinking water samples for the determination of Cu, Zn, As, Cd, Cr, Hg, Ni, Pb, SO_4^{2-}, NO_3^-, NH_4^+, Cl^- and P.

4.5

Analytical Services

The competence of EI collected in the last 15 years of reference material production led also to request of national organizations to produce candidate reference materials and proficiency testing samples. Such proposals were received and contracts concluded with ENEA Casaccia, COPES, Milano, University of Osnabrück and University of Strasbourg.

A contract with the italian Electricity Board (ENEL) of Cagliari for the chemical identification of major, minor and trace components of various fly ash samples has been concluded.

The process of energy production by the sun (fusion of four protons into a helium nucleus) is accomplished by a chain of nuclear reactions (the "pp" chain) starting with the weak interactions $p+p—d+e^{+}\nu e$ and making progressively heavier element up to ^{8}B. The only way to test this fundamental theory of stellar process is to detect at the earth the only reaction product that can escape the sun, the weakly interacting neutrino. A rich spectrum of neutrinos is predicted for the p-p chain. The dominant part of the flux (98%) is emitted at energies ≈1 MeV. A large international scientific collaboration (BOREX) proposes to accomplish this task with a new type of detector, BOREXINO to be built at the Gran Sasso Underground Laboratories in Italy. The key technical ingredient is the detection medium: a scintillation liquid of ultrahigh radioactivity purity [10-15 to 10-16 g (U, Th) /g]. It leads not only to the very low background needed but also to a high signal sensitivity stemming from the high luminosity of the scintillator. Borexino will be able to observe neutrinos signals of energy ≈0.25 MeV. With such a threshold Borexino will focus on the specific real time observation of ^{7}Be solar neutrinos using ν-e

scattering as the detection reaction.
The impurity levels of interest to Borexino and the variety of contaminant species in question necessitate a wide ranging program using several ultrasensitive analytical techniques.

The specific task of J.R.C. Ispra is the determination and measurement of the ultratraces impurities in Borexino materials. In order to satisfy these demands both ultrasensitive mass spectrometry and suitable preconcentration methods were developed.
After preliminary determinations of U and Th in deionized and redistilled water, significative data concerning the radiopurity of the scintillator liquid (TMB: TriMethylBorate) were obtained. (Table 7).

To improve both the final detection limit and the contribution of the blank different aspects are being studied.

Sample	Number of repetitions	Number of counts	U conc. in preconc. sample g/g	U conc. in original sample g/g
II residue	6	439±27	$0.6X10^{-13}$	$5X10^{-16}$
II residue	6	489±32	$0.65X10^{-13}$	$5X10^{-16}$
Blank	6	126±7	$0.1X10^{-13}$	

***Table 7**: Radiopurity data of a scintillator liquid (TMB: TriMethylBorate) obtained after determina-tions of U and Th in deionized and redistilled water.*

4.6

ATMES - ETEX

The ATMES study, described in section 2.5 was co-sponsored by the World Meteorological Organization (Genève) and by the International Atomic Energy Agency (Vienna), which paid part of its cost .
The models participating in the study were 21 from various institutions, such as Universities, Nuclear Safety Centres and meteorological Offices from 14 different Countries. The participants were not only from Europe, but also from USA, Canada, Japan, South Africa and Israel.
As a follow-up of ATMES a "European Tracer Experiment (ETEX)" has been launched by the three sponsoring Organizations (CEC, IAEA, WMO) to verify the capability of forecasting the evolution of a cloud of an atmospheric pollutant in conditions of emergency (real-time evaluation). In the exercise, a release of a perfluorocarbon tracer (PFC) will be performed during daytime at selected sites in Western Europe .
The participants to the project will be informed of the occurrence, location, characteristics of the release only at the time of its occurrence. They should then acquire the necessary meteorological input and carry on model evaluation to predict the cloud evolution as if it were a real accident, thereby informing at the fastest rate the national and international emergency management authorities.
The forecasted atmospheric concentration of PFC will then be compared with the actual concentration measured at approximately 200 sampling stations located at national meteorological sinoptic station in Europe.
WMO and IAEA will participate financially to the project. A special fund has been granted by EC to support the participation of central and eastern European countries in the project.

4.7

ENRESA

The contract with ENRESA (Empresa Nacional de Residuos Radioactivos S.A.) on geochemical investigation carried out in situ at "El Berrocal" uranium mine as well as with laboratory experiments at the JRC-Ispra, finished in the course of 1991.

Intact and fractured granite cores from the El Berrocal mine were used for the column migration tests together with groundwater samples from the same site.

Prior to the migration experiments, the association of various actinides with the natural organic matter was investigated. The behaviour of Pu, Np, Am and Tc was studied at variable concentrations of organic substances. No association of Technetium /Neptunium with colloidal particles of 1 - 1,5 nm size, occurred upon the addition of natural organics to the groundwater. This preferential interaction was found to occur for Plutonium. The effect of the redox environment was investigated by performing experiments both under oxic and anoxic conditions.

Exploratory batch experiments on granite /radionuclide interactions using U, Np, Pu, Se, Tc, Sr and Cs isotopes and crushed granite were performed. These tests intended to provide input data for a preliminary evaluation of the average residence times in granite columns of given length. This helped to design the laboratory experimental setup for migration experiments. Kd measurements showed Neptunium to be a suitable element for column migration studies on a reasonable time scale. The much higher retardation factor exibited by Plutonium suggested for this element a too long residence time in the granite columns.
A pressure apparatus for flow-through experiments, using granite cored columns, was built and installed in the alpha glove-boxes. The hydrodynamic characterization of the columns used in the migration tests was performed making use of tritiated water. Under oxic conditions, and in the absence of organic substances, Neptunium was completely retained in both type of granite columns (crushed and cored). In accordance with the static Kd measurements, a more rapid breakthrough of some Np-species was instead observed in the presence of natural organic matter. This eluted fraction represented, however, only a small percentage ot the total pulse activity.

Under anoxic conditions, the Neptunium pulse through intact cores was found to move faster than under oxic conditions, with a 0.2% cumulative recovery. The addition of 5 ppm of humic substances produced an even more rapid breakthough (about 0.55% recovery) almost indistiguishable from the tritiated water peak (Figure 40).

Selenate ions were found to move through granite columns without retardation but with incomplete recovery. This was interpreted as a surface mediated redox transformation due to selenate interactions with fracture filling materials. A stronger affinity of selenite ions for granite was observed.

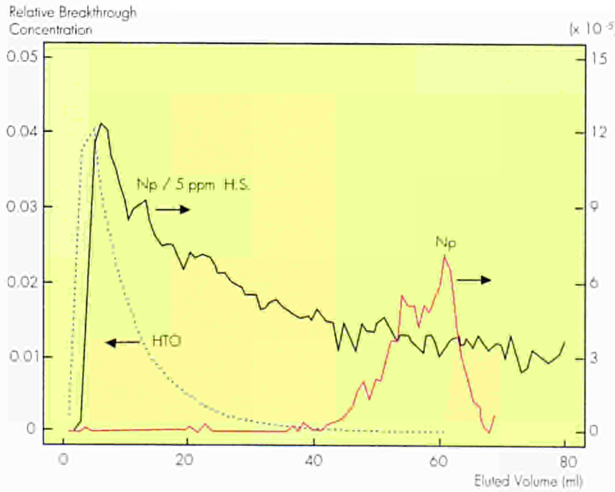


Fig. 40: Anoxic breakthrough concentration of Np and Tritiated Water (HTO) from a granite cored column. The influence of 5 ppm Humic Substances (HS) is also shown.

A second contract for the execution of an in-situ migration experiment has been signed on 24th July 91. In the framework of this contract a preliminary cross-hole migration test was performed between two boreholes, known to be connected by a fracture in the Berrocal mine, using a conservative, non-radioactive isotopic tracer. 79-Br was injected into borehole n° 7 (S7) as ground waters marker at a 39 m depth and recovered from borehole n° 1 (S1) seven meters away. Groundwater was forced to move by pumping from the recovery well, where several samplers have been located at different depths. This test was carried out after some preliminary experiments with packers to precisely locate the fracture intersection with the two holes. The field activity lasted from September 23th to October 4th, the migration itself taking the last four days.

This experiment, intended to demonstrate the feasibility of the isotopic marker technique, is a preparation step for further tests with reactive tracers. Tracer arrival was noticed in the range of 26-28 hours after the injection and one 50th of the spike was recovered. This preliminary test provided useful suggestions for the improvement of procedures, equipment and timing, in order to set up the best configuration for further experiments.

5

Participation to EUREKA and COST Concerted Actions

5.1

EUREKA

Further developments have been achieved in the course of 1991 in the activities carried out in the framework of the participation of the Environment Institute to EUREKA projects in the environmental field i.e. EUROENVIRON and EUROTRAC.

It is recalled here that EUROENVIRON is aimed at developing processes, systems, services and technologies for the protection of the environment while EUROTRAC has been devised as a joint european effort to elucidate the impact of human activities on the tropospheric chemistry.

The projects are subdivided into a series of sub-projects each one dealing with a special aspect of the more comprehensive problem covered by the project itself. In the following the progress accomplished in the sub-projects in wich the Institute is actively engaged is summarized.

EUROENVIRON MOBILE ANALYTICAL LABORATORY

The Environment Institute has finalised a proposal for the development and the exploitation of a mobile laboratory for in-field sampling and analysis of waste, soil and water contaminants.

This facility is expected to be relevant for the monitoring activities in the following areas:

- preventive pollution control of soils and waters (surface and underground),
- long term analytical support to rehabilitation of contaminated sites,
- fast analytical screening in emergency situations.

The project has gained the Eureka status (EU 674,Mobile Analytical Laboratory) in June 1991 and it is carried on with the collaboration of fifteen European laboratories. The project coordination is under the responsibility of the JRC Environment Institute assisted by a Steering Committee consisting of participant representatives.

In the definition phase of the project (up to December 1991) two meetings were organised at Ispra (June 1991) and in Copenhagen (October 1991), during which the criteria of participation, the general working plan and the various contributions were discussed. Besides that, seven technical working groups have been established with competences in different fields such as sampling, inorganic and organic analysis, data evaluation, construction and exploitation of the mobile unit. The next meeting will be held in Bergamo on February, 27-28, 1992.

TRACY

The project (Database of Toxic Metals in Human Tissues and Fluids) has been jointly developed by Norway (Dag Brune Consultant), Swedish (University of Umea and National Institute of Occupational Health, Solna) and CEC Joint Research Centre - Ispra in close cooperation with the Scientific Committee on the Toxicology of Metals within the International Commission on Occupational Health (ICOH) and has been further recognized by the International Union Pure and Applied Chemistry (IUPAC) - Commission on Toxicology.

In the fields of occupational and environmental health there is an increasing use of biological monitoring of toxic metals in human tissues and fluids. Unfortunately, the huge amount of data published concerning concentrations in human tissues and fluids of toxic metals is of varying quality and it is difficult to find adequate "reference values" in literature since the qualities and conditions of the studies vary. There is a great need to have easy access to reliable "normal (or reference) values" for persons without occupational metal exposure in order to establish wheter or not occupational exposure causes metal levels that exceed the "normal range" for each metal.

The aim of TRACY is the systematic collection and critical evaluation of the published information concerning trace metals in human tissues and fluids. The data will be stored in a computerized data file for the derivation of "reference values", making retrival of desired accessible to users. The published data will be judged and graded according to criteria established in accordance with an IUPAC expert group, prior to the assessment of selection of data for reference value production. Elements to be implemented in the database subsequent to evaluation comprise e.g. Cd, Co, Cr, Pb, Ni, Se and V.

EUROTRAC

BIATEX

Measuring campaigns have been undertaken within the EUROTRAC-subproject BIATEX (Biosphere/Atmosphere-Exchange) to:

- quantify the monoterpene emissions which might enhance photooxidant formation and
- estimate the concentration of carbonyls, as the result of enhanced atmospheric reactivity in remote and semi-remote areas.

In 1991 a measurement campaign (4.6-12.6) was organized at the experimental tower in the Bavarian Forest. Emission rates of the most important terpenes were estimated and the concentration of low molecular aldehydes and monoterpenes at different heights (below and within the canopy area) were measured.

Emission rates of α-, and β-pinene ranging from 0.37 to 10.2 ng/m^2.s. The concentration of the same at ground and at 18 meter ranged from 0.3 to 2.8 ppb and 0.3 to 4.7 ppb, respectively.

Low molecular aldehydes (formaldehyde, acetaldehyde) were measured at ground level, 21 m and 31 m. Concentrations varied from 0.8 to 1.7 ug/m^3.

For 1992 additional joint fields campaigns are planned including test-sites in the Mediterraneran Region.

JETDLAG

The major objective of this subproject is to promote the technological development and to demonstrate the usefulness of infrared tunable diode laser spectrometers in environmental research and monitoring. In 1991 the 3rd Int. Conference on Trace Gas Monitoring by Tunable Diode Lasers, organized by the Fraunhofer IPM Freiburg and co-sponsored by the CEC-GD XII/E, has provided the opportunity for an update of the situation in the field. The Environment Institute has participated to the Conference with a paper and as co-editor of the Proceedings.

LACTOZ

The main objective of this project is to provide kinetic and mechanistic data for a proper description of the complex chemical processes which lead to ozone formation and destruction in the troposphere.

As described in another part of this report, the contribution of the Environment Institute has been focused on aspects of the nighttime tropospheric chemistry. Further progress has been made in the study of the reaction of NO_3 with isoprene and with aromatics, and a new study has concerned the reaction of the nitrate radical with the hydroperoxyl radical.

TRACT- TRANSALP

Within the subproject TRACT (Transport of Air Pollutants over Complex Terrain) three pre-experiments have been performed to study air flow in complex mountainous terrain, preparing the way to the main experiment, to be performed in 1993.

At first in 1989 the split of the air flow between the Leventina and Blenio valley was investigated.

Next in 1990 the south/north overflow of the alpine barrier (Lucomagno, Gottardo, Nufenen) was studied.

In 1991 the air flow across the Alps was studied in an extended area and in a direction opposite to the previous ones i.e. from north to south. The general layout of this experiment and the first results are given here.

The main goal of the 1991 experiment was to show that the tracer technique can be applied successfully to study long-range transport patterns over the Alps. The channelling of air in the main valleys and the interaction between the general circulation and the local wind systems in the valleys are still not well understood.

The field campaign was planned for September and October 1991. The organisation of this large experiment started with meetings in March and July. The following institutions participated in the Transalp campaign: CNR, Torino (I); ENEL, Milano (I); IMK, Karlsruhe (D); MetAir, Illnau (CH); PSI, Villigen (CH); SMA, Locarno-Monti (CH).

The investigated area stretched from Vierwaldstätter See (CH) in the north to Lago Maggiore (I) in the south (120 km) and in east west direction from Brig to Chiavenna (both CH) (100 km). The area including the release point, the tracer sampling network and the meteorological instruments is shown in Figure 41.

The release point of the perfluorocarbon tracer was situated at Morschach (690 m asl) on the eastern lake shore of Vierwaldstätterr See. This location was chosen because the tracer would be emitted into already channelled air thus making the transport over the main alpine barrier more likely. The time of the release was set for 13 UTC to ensure that by the time of the arrival of the tracer at the Passo del Gottardo, the local wind system in the Leventina valley would already have shifted to the night regime.

The sampling network for the tracer concentration covered the whole area of interest. Ground sampling locations were carefully selected along the main transport routes, on all passes and height profiles across valleys. A total of 90 samplers were set-up at 61 sites including co-located samplers for quality control.
Air sampling was also performed by a motor glider along north-south and east-west traverses at different altitudes.

Since the previous experiments investigated a south to north air flow, a north to south transport situation was favoured for this campaign. For the selection of a favourable weather situation support of the Swiss Meteorological Institute and forecasted forward trajectories from Deutscher Wetterdienst were granted. Meteorological data were available from the routine stations in Switzerland and from 10 masts for wind speed and direction, a sonic anemometer, 3 Doppler sounders, a tethered balloon and a rawinsonde for the vertical profile of the wind in operation during the experiment.

The first tracer release took place on September of 1991. The weather forecast predicted medium to strong northerly winds. Also the forecasted forward air mass trajectories clearly showed a rise of the lowest levels over the main alpine barrier. Temperature data from the 12 UTC rawinsondes at Payerne and Milano show no pronounced stratification of the atmosphere. At Morschach the perfluoromethylcyclohexane (C_7F_{14}) was released from 13 to 14:30 UTC with a source strength of 8 gs-1 amounting to a total of 43 kg.

The sampling frequency and times were chosen to clearly reveal the time of arrival of the tracer plume and to follow its evolution. At selected sites the air samples were taken up to 52 hours after the release. The air samples were taken immediately to our field laboratory and analysed. The tracer concentrations are for 30 min sampling periods.

An example of the tracer plume evolution as it traverses the Passo del Gottardo is shown together with the height profile of the valley base in Figure 43. The valley base at the end of the Reuss valley climbs from 1100 m at Göschenen and 1440 m at Andermatt to 2100 m at the highest point of the pass. Air flowing over the Passo del Gottardo meets the mountain ridge between the Leventina valley (Airolo, 1200 m) and the Sambuco valley. The tracer concentrations along this north-south line are shown for samples collected at six stations between 14 and 21 UTC. The highest concentrations of the tracer measured at these sites range from 0.65 to 1.12 ppt. The arrival time of the tracer plume at Gottardo 2 hours after the start of the release suggests a wind speed of 7 to 8 ms^{-1}. This is in good agreement with the wind measurements of the sodar at the same location (Fig.43). Both the arrival time and the time of the

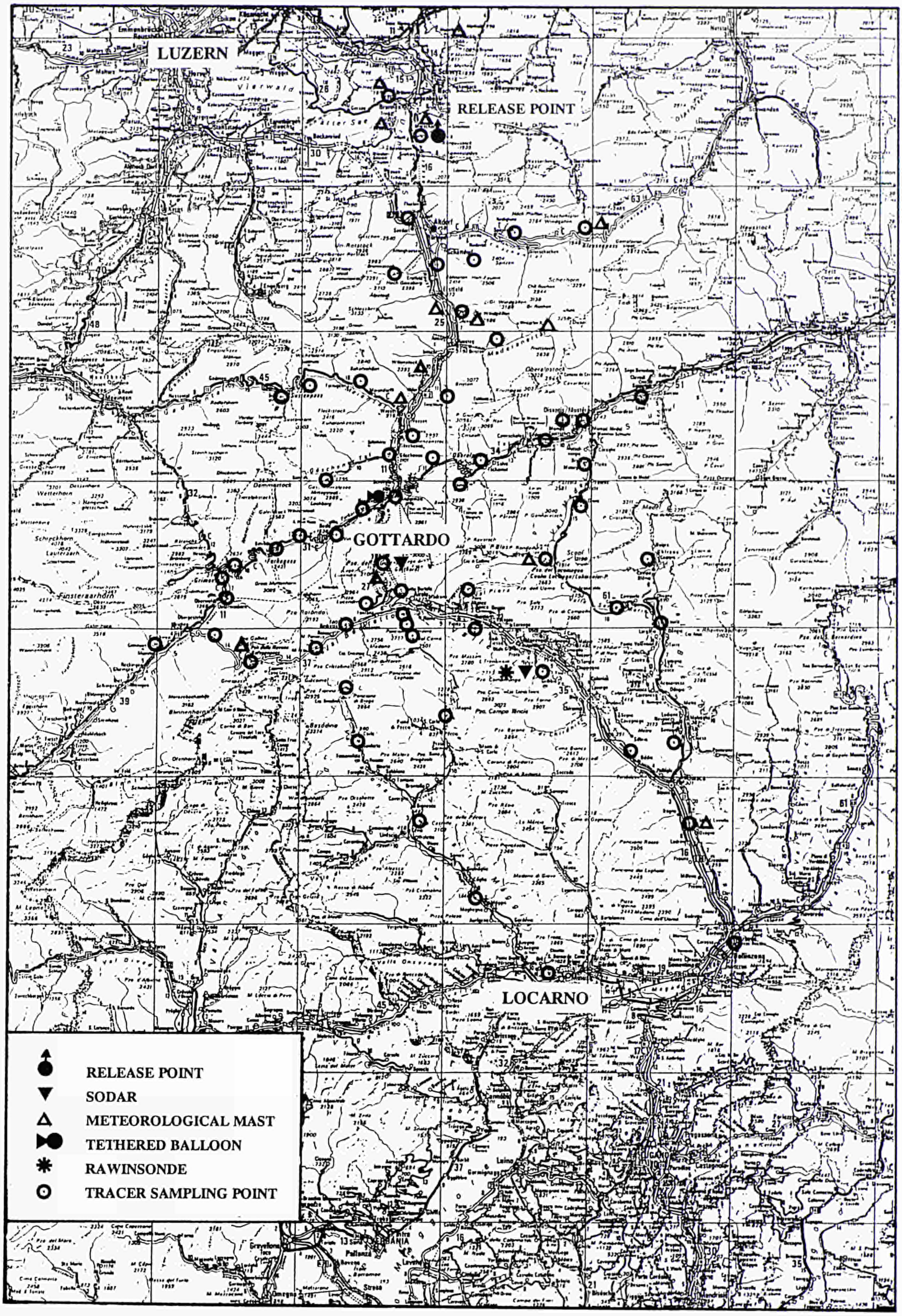


Fig. 41: Area of TRANSALP experiment 1991 showing the tracer release point, tracer ground-level sampling network and meteorological stations.

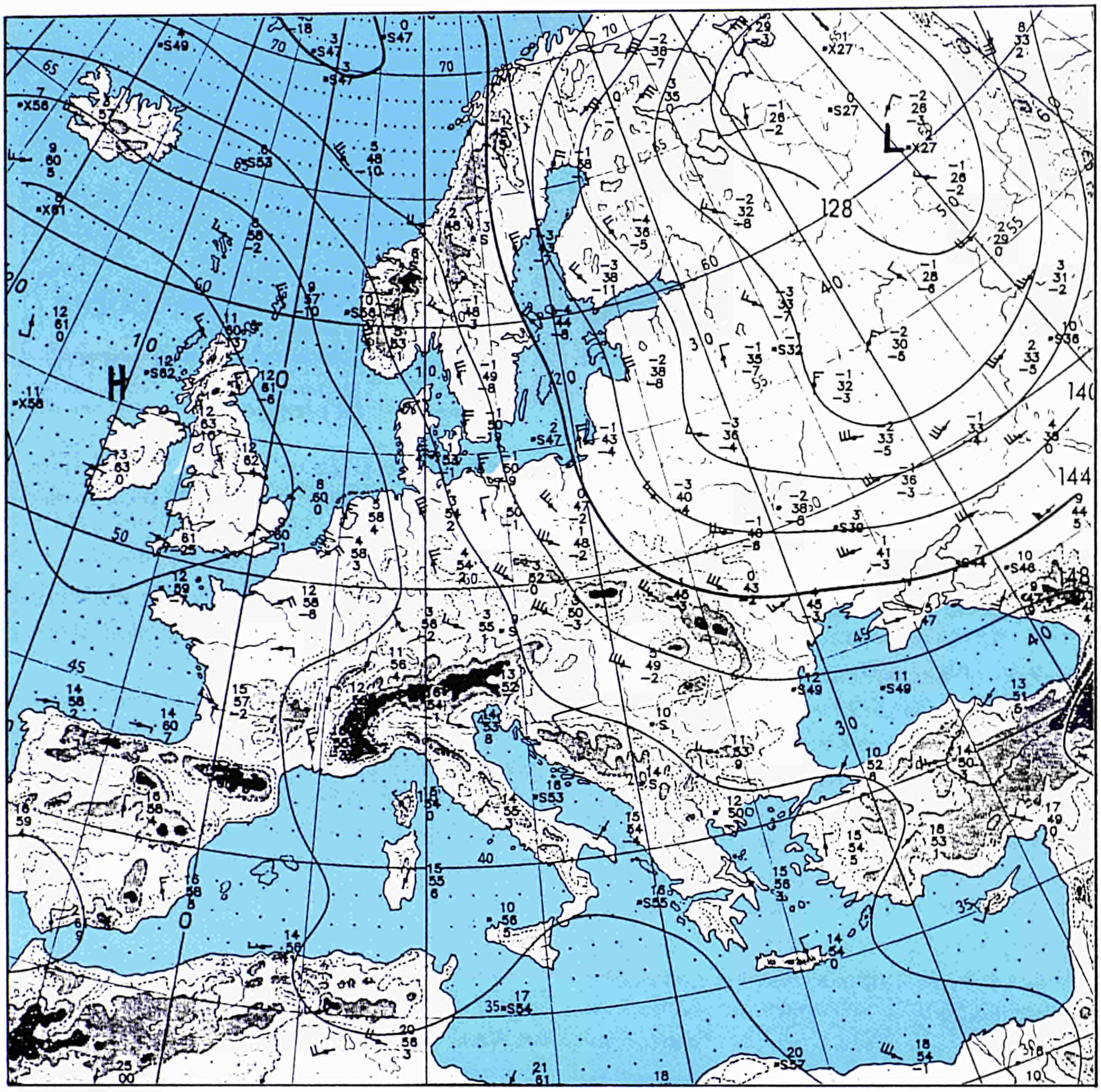


Fig. 42: 850 hPa pressure contours for 12 UTC on 7. September (Deutscher Wetterdienst, Offenbach)

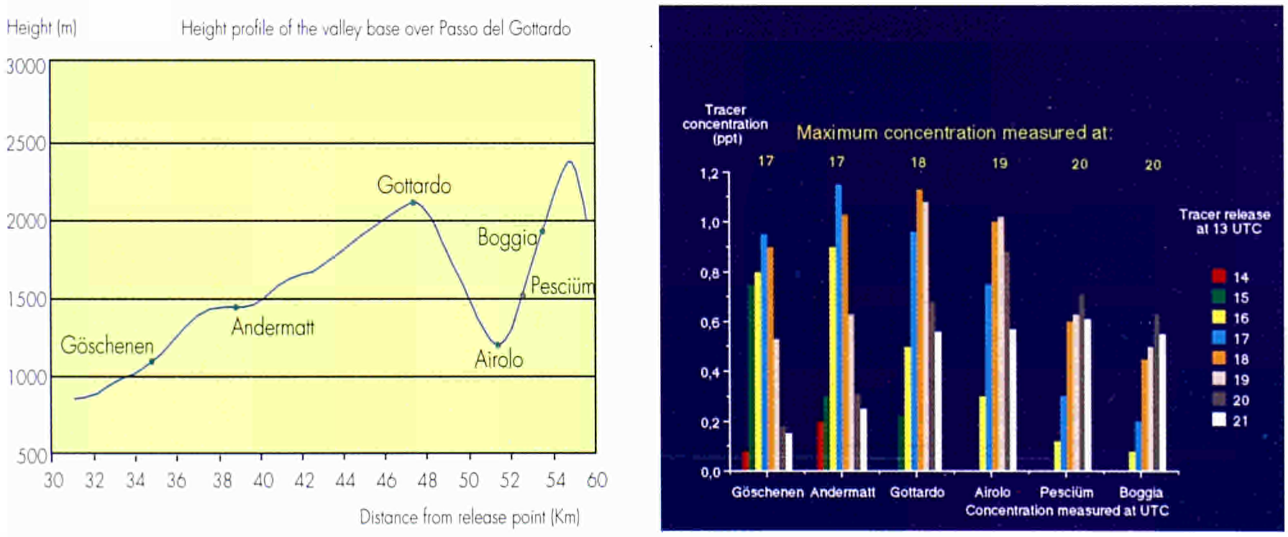


Fig. 43: Tracer plume evolution over Passo del Gottardo as observed at six ground-level sites.

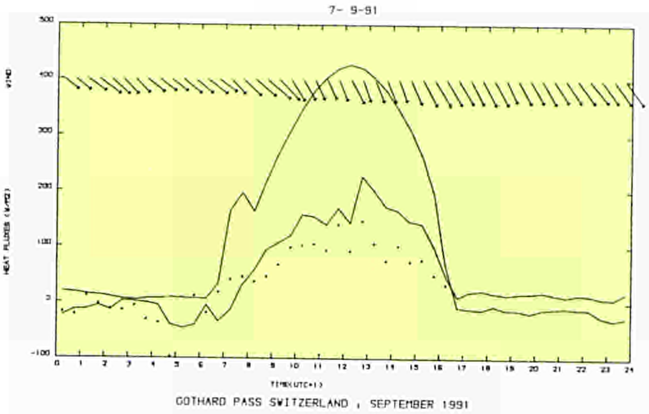


Fig. 44a: Net radiation (upper solid line), sensible heat flux (lower solid line), latent heat flux (point), wind velocity and direction at Passo del Gottardo.

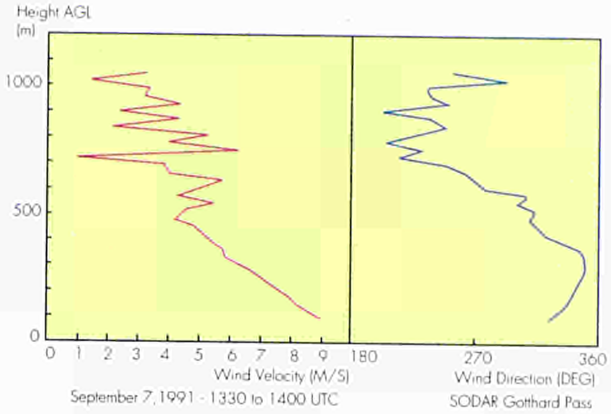


Fig. 44b: Vertical profile of wind velocity and direction measured by a Doppler sounder (SODAR) at Passo del Gottardo.

maximum concentration increases with increasing distance from the release point.

Examination of the meteorological data recorded at the Passo del Gottardo reveals several features characterizing the air mass flow over the Alps. The channelling effect is well apparent (Fig.44a) with the wind blowing steadily parallel to the valley line. Further the stratified structure of the air flow can be seen from the SODAR profile (Fig.44b), where the wind direction is determined by the topography (roughly NW) up to 600 m (a.g.l.). Above that altitude it approaches the geostrophic wind direction (SW).

An interesting phenomenon can be observed by comparing the tracer concentrations at Airolo, Pesciüm and Boggia. The plume maximum arrives at the two elevated stations Pesciüm and Boggia 1 hour later than in Airolo located at the bottom of the Leventina valley. This means the air flowing over the Passo del Gottardo first reaches the bottom of the Leventina valley and then slowly fills it up. This climbing and funnelling effect of the tracer over a pass or a ridge was also observed at two following ridges further south (not shown here).
A second tracer release was carried out on October 3rd 1991 north of Luzern at Althäusern to study the local wind systems induced by thermal heating around the Vierwaldstättersee. First results indicate a very weak influence of the mountains on the wind pattern in the plain around Luzern at that time of the year.

The results showed that the perfluorocarbon tracer emitted north of the Alps was transported over the main alpine barrier.
The tracer was not only detected far south around Lago Maggiore but also at the bottom of the valleys directly behind the main mountain ridges. This means that air travels not only over the Alps, but also finds it ways through the valleys.
Channelling of air through passes and valleys is therefore an important transport mechanism for air masses flowing over the Alps.
This means also that air pollutants from the north side of the Alps are transported southwards over the Alps. And what is even more important: this air flow reaches the bottom of the valleys directly south of the main ridges.

As far as it concerns future experimental activity, theTract A1 Experiment in Baden Württemberg (FRG) is planned for September 1992.

GLOMAC

A collaboration was started with the University of Stockholm and the Max Planck Institute in Mainz to study the role of aerosols in global climate change. This study is part of the GLOMAC sub-project in EUROTRAC. In this framework, the 3-D global tracer model MOGUNTIA has been transferred to the JRC.The aerosol model IMAD2 will be implemented in MOGUNTIA to study new particle formation from SO_2 and its effects on a global scale.

5.2

Indoor Air Quality and its Impact on Man (former COST Project 613)

Indoor air quality in residential and non - indu-strial working environments has received growing attention over the past 20 years from the scientific community, the public and at political level. The Commission of the European Communities started taking an interest in indoor air quality at the beginning of the eighties when a small research activity was included in the Environmental Protection Programme of the Community's Joint Research Centre in Ispra , Italy. This activity has, from the beginning, been accompained by an effort to organize a collaboration of European scientists in this new field of research. At the end of 1986 the formation of the Community Concerned Action "Indoor Air Quality and its Impact on Man" was decided. Practical work started in March 1987. Fourteen countries are partecipating.

The Environment Institute (EI) continued to manage the Concerted Action (CA) "Indoor Air Quality and its Impact on Man". The EI participated in the organization of a seminar on methods of risk assessment of indoor air pollution sponsored jointly by the CA and a NATO-CCMS pilot study. EI experts participated actively in three CA working groups (WGs) - chairing one of them. Two of these WGs concluded their work (WG 4 and WG 8).
After careful review by the Concertation Committee, the summary report prepared by WG 4 on "Effects of Indoor Air Pollution on Human Health" has been published as Report Nr. 10 of the Concerted Action.

The report discusses human health effects linked to indoor air pollution (IAP) in homes and other non - industrial indoor environments. Rather than discussing the effects on health of the many different pollutants which can be founded in indoor air, the approach has been to group broad categories of adverse health effects in separate chapters, and describe the relevant indoor exposures which may give rise to these health effects. The following health effects categories have been considered: effects on the respiratory system, allergy and other effects on the immune system, cancer and effects on reproduction, effects on the skin and mucous membranes in the eyes, nose and throat, sensory effects and other effects on the nervous system, effects on the cardiovascular system, and systemic effects on liver, kidney and gastro-intestinal system. For each of these categories effects associated with IAP, the principal agents and sources, evidence linking IAP to the effect(s), susceptible groups, the public health relevance, methods for assessment, and major research needs are briefly discussed.

The result of the work of WG 8, a "Guideline for the Characterization of Volatile Organic Compounds Emitted from Indoor Materials and Products" has been published as Report Nr. 8.
This guideline represents a first step towards a European standard method. The EI is organizing an international intercomparison experiment for its validation.

The second edition of a "Project Inventory" containing essential information on 326 indoor investigations ongoing or recently concluded in the 14 European Countries participating in the CA and at the EI has been published by the EI. The Inventory and the above mentioned reports have been distributed to several hundred research groups and administrations interested. Requests of seven earlier published CA reports continue to arrive and about 1,000 copies of each of them have been distributed.

A revised draft of a "Guideline for Ventilation Requirements" has been prepared by WG 6 and has been adopted by the Concertation Committee. After some minor redactional changes the guideline will be published as Report Nr. 11 in spring 1992.

A draft report of WG 5 on methods of assessment of microbiological indoor air pollution has been reviewed by the Concertation Committee. A final draft will be prepared for mid 1992.

6

Associated Laboratories

The Environment Institute has mantained and even enlarged and strengthened tight collaboration with a number of laboratories of the Member Countries as well as of the other European Countries. This has been both in the framework of the EUREKA and COST Actions, as well as of the work for Third Parties:

Danish Centre for Atmospheric Research (DCAR), Roskilde, (Denmark) in the context of environmental protection studies, with special emphasis on processes leading to global change.

National Institute of Public Health and Environmental Protection (RIVM) Bilthoven (The Netherlands) in connection with application of ICP/MS in Environmental Analysis

Chemical Engineering Dept., University of Lisbon (Portugal) on the exploratory research

Institut für Ökologische Chemie, GSF Neuherberg (Germany)

In the framework of the MITO Project the collaboration of the following institution is to be mentionad:

Laboratoire Hydrobiologie Marine, Universitè Montpellier II (France)

C.R.E.M.A. de l'Houmeau CNRS-IFREMER B.P. 5 (France)

Institut de Ciències del Mar, Barcelona - (Spain)

Station d'Hydrobiologie Lacustre, I.N.R.A. (France)

Instituto Espanol de Oceanografia, Centro Costero de Vigo (Spain)

Instituto de Ciències Marinas, Vigo (Spain)

Centre d'Ocèanologie de Marseille (France)

Dipartimento di Biologia,Evoluzionistica e Sperimentale,Università di Bologna (Italy)

Ministèrio do Ambiente e Recursos Naturais, Lisboa (Portugal)

Istituto Superiore Sanità, Roma (Italy)

Stazione Zoologica, Napoli (Italia)

Direcciòn Comisionada de Sanidad, Vigo (Spain)

Dep.Ciències e Engenharia do Ambiente, Faculdade de Ciències e Tecnologia, Universidade Nova de Lisboa (Portugal)

Dipartimento di Biologica Cellulare, Università di Macerata (Italy)

Dipartimento di Biologia, Università di Milano (Italy)

IFREMER, Centre de Brest (France)

National Centre for Marine Research, Athens (Greece)

Università di Trieste, Dipartimento di Biologia Trieste,(Italy)

Athens School of Hygiene, Microbiology Department (Greece)

IFREMER, Centre de Nantes (France)

ENEA, CRE Casaccia - Roma (Italy)

In the field of Radioactive Waste Management :

French Atomic Energy Agency (CEA), Cadarache,(France) within the framework of field experiments on the migration of radionuclides in geological formations.

Centro de Investigaciones Energèticas, Medioambientales y Tecnologicas (CIEMAT), Madrid, (Spain) for the studies on radionuclide migration in granite formations

VTT: Technical Research Center of Finland on the "Studies of hetherogenous chemistry of Trace

Metals

and

Royal Institute of Technology, Stockholm (Sweden)
on the Application of advanced analytical
techniques for solution chemistry studies

7

Appendices

7a

Pubblications, Conferences

SPECIFIC RESEARCH PROGRAMME

Environmental Protection

ENVIRONMENTAL CHEMICALS

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H. Schlitt and D. Lenz. '"Comparison of classical soxhlet- with supercritical fluid extraction coupled "off-line" and "on-line" to HRGC". Poster presented at the European Symposium on Analytical SFC and SFE, Wiebaden, Germany, December 4-5, 1991

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Glossary of Acronymes and Abbreviations

AAS	Atomic Absorption Spectrometry
AIA	Asbestos International Association
AOX	Absorbable Organic Halogen
AQUACON	Analytical Quality Control and Measurement Assesment Studies
ASTM	American Society for Testing Materials
ATMES	Atmospheric Transport Models Evaluation Study
BAL	Broncho-Alveolar Lavage
BCR	Community Bureau of Reference
BEN	European Brewer Net
BIATEX	Biosphere Atmosphere Exchange of Pollutants
BOREX	Boron Experiment
CD-ROM	Compact Disk Read-Only-Memory
CFC	Chlorofluorcarbons
CHN	Total Carbon Hydrogen Nitrogen
CIS	Convention Notification and Information Structure
CNC	Cloud Condensation Nuclei
CNR	Italian National Research Council
COD	Chemichal Oxygen Demand
CPS	Consumer Policy Service
CSTR	Continuous Stirred Tank Reactor
CTD	Conductivity Temperature Dissolved oxygen
DIMDI	Deutsches Institut für Medizinische Dokumentation und Information
DMS	Dimethylsulphide
DOC	Dissolved Organic Carbon
EASOE	European Artic Stratosperic Ozone Experiment
ECDIN	Environmental Chemicals Data Information Network
ECPHIN	European Pharmaceutical Databank
ECSAM	European Commission's Safeguard Analytical Measurements Commitee
ECURIE	European Communities Urgent Radiological Information Exchange system
ECVAM	European Centre for Alternative Testing Methods
EDTA	Ethylen Diamino Tetracetic Acid
EINECS	European Inventory on Existing Chemical Substances
EMEP	Evaluation Monitoring European Pollution
ENEA	Italian Board for Alternative Energies
ENEL	Italian Electrical Board
ENRESA	Spanish Agency for radioactive Waste Management
ETEX	European Tracer Experiment
EUREKA	European Research coordination Agency
EUROTRAC	European Experiment on Transport and Transformation of Environmentally relevant Trance Constituents
ETEX	European Tracer Experiment
FAB	Fast Atom Bombardment
FCM	Flow Cytometry
FEMSUN	Finite Element Model coupled with Sensitivity and Uncertainty Analysis
GC	Gas Chromatigraphy
GC-MS	Gas Chromatography-Mass Spectrometry
GFAAS	Graphite-Furnace Atomic Absorption Spectrometry
GLOMAC	Global Modelling of Atmospheric Chemistry
GSF	Gesellschaft für Strahlen Forschung
HAMBHIT	Hard Metal Biomonitoring in Human Tissues
HCFC	Hydrochlorofluorocarbons
HFC	Hydrofluorocarbons
HPLC	High Performance Liquid Chromatography
IAEA	International Atomic Energy Agency
IC	Ion Chromatography
ICOH IGAC	International Commission on Occupational Health

IIA	Italian Atmospheric Air Pollution Laboratory
IMK	Institute for Meteorology and Climatology
IRSA	Institute for Remote Sensing Application
IST	Institute for Safety Technology
IUPAC	International Union Pure and Applied Chemistry
JETDLAG	Joint European Development of Tunable Diode Laser Absorption Spectroscopy for Measurement of Atmospheric Trace Gases
LACTOZ	Laboratory Studies of Chemistry related to Tropospheric Ozone
LEU	Low Enriched Uranium
LIF	Laser Induced Fluorescence
LISA	Long term Isolation Safety Assessment
LPA	Long Path Absorption
MSA	Methane-Sulphonic Acid
MITO	Microphyte Toxins
NATO-CCMS	NATO-CCMS The North Atlantic Treaty Organisation Commitee on the Challenge of Modern Society
NILU	Norsk Institut Luftorskning
NMR	Nuclear Magnetic Resonance
OBCAAM	Ocean Biology Chemical Atmosphere Model
OECD	Organization for Economic Cooperation and Development
PAN	Peroxy Acetyl Nitrate
PCB	Polychlorinated Biphenyl
PCR	Poly Chain Reaction
PFC	Perfluoro-Carbons
PHARE	Poland-Hungary Assistance for the Reconstruction of the Economy
PREP	Pre-Processor
PSI	Paul Scherrer Institut
RAMS	Regional Atmospheric Modelling System
REE	Rare Earths Elements
REM	Radioactivity Environmental Monitoring
SFE	Supercritical Fluid Extraction
SMA	Schweizerischen Meteorologischen Austalt
SODAR	Sound waves Detection And Ranging
STEP	Science and Tecnology for Environmental Protection
SVOC	Semivolatile Organic Compounds
TDB	Thermochemical Data Base
TDS	Technical Data System
TERVIHT	Trace Element Reference Values in Human Tissuee
TMU	Tetramethylurea
TNO	Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek
TOC	Total Organic Carbon
TOR	Tropospheric Ozone Research
TRACT	Transport of Air Pollutants over Complex Terrain
TRACY	Toxic Metals in Human Tissues and Fluids
TRANSALP	Transalpine Transport of Air Pollutants
TRLIF	Time Resolved Laser Induced Fluorescence
TVM	Three Dimensional Vorticity Model
UDS	Unscheduled DNA Synthesis
TVOC	Total Volatile Organic Compounds
UTC	Universal Time Convention
UV-VIS	Ultraviolet-Visible
VDI	Verein Deutscher Ingenieure
VOC	Volatile Organic Compounds
WHO	World Health Organisation
WMO	World Meteorological Organisation
XANES	X-ray Absorption Spettroscopy Near Edge Spectrometry
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

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Environment Quality of Life series

This is the annual report of the Environment Institute of the Joint Research Centre - Ispra Site - of the Commission of the European Communities.

The report summarizes the progress accomplished in the course of 1991 - i.e. the last of the four year (1988-91) Specific Research Programme of the Joint Research Centre - in the projects tackled by the Institute.

The activities were mainly focused on the areas of environmental chemicals, air pollution, water pollution, chemical waste and food & drug analysis, included in the programme **Environmental Protection**, and of safety assessment of nuclear waste disposal in geological formation as a part of the **Radioactive Waste Management** programme.

The scientific support provided to different Commission Services is also described, proper emphasis being given to that provided to the Directorate General XI (Environment, Nuclear Safety and Civil Protection) in the field of chemicals, air pollution, water pollution, chemical waste and radioactive environmental monitoring (REM). The above activities are aimed at the implementation of EC directives in the related fields.

The work for third parties and the contribution of the Institute to various EUREKA and COST projects are also shortly described.

Lastly the report provides essential data concerning the Institute structure and the human and financial resources.