ANNUAL·REPORT·90

Environment Institute

JOINT
RESEARCH
CENTRE

COMMISSION OF THE EUROPEAN COMMUNITIES

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Contents

The JRC Environment Institute

As it had been anticipated in the '89 Annual Report, the newly created Environment Institute in the course of 1990 has undergone a significant re-arrangement of its internal organisation.

The present structure encompassing eight scientific units - shown in the Annex - has been set up in view of a more sinergistic grouping of competences to deal with relevant features of the Institute research programmes.
The units are the following :

Atmospheric Physics
Atmospheric Chemistry
Atmosphere-Biosphere interaction
Environmental Chemicals: Soil, Water, Waste
Environmental Chemicals: Indoor Pollution
Environmental Chemicals: Life Science
Food and Drug Analysis, Consumer Protection
Environmental Informatics,

their denomination being self-explanatory as for the individual area of concern.

Although from the above it would appear that the activity of the Institute is fully dedicated to environmental issues, it has to be stressed that a residual research activity on nuclear waste is still in progress. However the experience and competences acquired in that field are being progressively shifted into conventional soil pollution area where they can be successfully exploited. As the result, the effort in the nuclear field can be considered as minor and not worth of filling a research unit.

Apart from the organisational aspect, no dramatic changes as far as it concerns the research activities of the Institute are to be mentioned. In fact they do represent the natural and logical follow up of those included in the 1988-91 multiannual programme and which have been described in the preceeding annual report.

The close coordination with shared-cost and concerted actions managed by DG XII/E and by DGXII/D doesn't need to be emphasized again.

Section 1 of the report provides a description of the results and achievements for the projects included in the Specific Research Programmes.

More than 30 percent of the Institute effort is directed towards the scientific support to a number of Commission's services. In particular, worth mentioning the support provide to :

DG I	External Relations
DG III	Internal Market and Industrial Affairs
DG V	Employment, Industrial and Social Affairs
DG VI	Agriculture
DG XI	Environment Nuclear Safety and Civil Protection
DG XIII	Telecommunications, Informatics Industries and Innovation
DG XVII	Energy
DG XXI	Custom Union and Indirect Taxation
CPS	Consumer Protection Service.

Relevant information in the progress accomplished in the above area are presented in section 2 of the report.
Although the contract work for third parties is increasing, the rate of increase is still low so that the target value cannot be reasonably expected to be attained at the conclusion of the multiannual programme. Section 4 provides an insigth in the most significant activities performed under contract with a number of national bodies.

The number of persons working at the Institute has been, in average, about 250, 175 out of them being permanent. The reminders - which include scientific visitors, research fellows, auxiliary and seconded staff - have different types of temporary contracts, up to a maximum of three years, thus ensuring an adequate turnover. The professional staff has been at the same level of the proceeding year, i.e. 65. Data on the staff statistics and financial aspects are summarized at the conclusion of the report.

Executive Summary

1. Specific Research Programmes

1.1. Environmental Protection

The report summarizes the progress accomplished in the course of 1990 in the research areas included in the JRC framework programmes 1988-91, namely :

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

ENVIRONMENTAL CHEMICALS

Several data files for **ECDIN** (Environmental Chemical Data Information Network) have been improved and/or updated in particular as far as it concerns toxicity, carcinogenecity, mutagenecity and aquatic toxicity. Substancial progress has been accomplished in the preparation of an ECDIN data subset on CD-ROM available for use in PC.
An agreement has been reached with the Ministry of Health, FRG, for the on-line distribution of ECDIN data through DIDMI (Deutsches Institut für Medizinische Dokumentation und Information).

Within the framework of the COST 613 concerted action **"Indoor air quality and its impact on man"** - which is led by the JRC Environment Institute - the seven working groups have issued:

- final draft of a summary report on health effect of indoor air pollution (WG4);
- draft guidelines for ventilation requirements in buildings (WG6);
- final draft of guidelines for the characterization of VOC emission from indoor materials and products (WG8);

Emission studies of VOC have concerned household products, the building of the European Parliament and the quality assurance of VOC sampling.

As far as **biological tests of indoor pollutants** are concerned, the activity has been focused on :

- Genotoxicity, using unscheduled DNA synthesis (UDS) in hepatocytes both in vitro and in vivo;
- embriotoxicity of 1-3 butadiene diepoxide very pronounced in early stages of pregnancy;
- production of transgenic mice for investigating the environmental chemicals-oncogens interactions and for detecting genotoxic effects.

Within the framework of **trace metals exposure and health effects**, reference values for a large number of elements in human body fluids have been proposed following an extensive analytical campaign on samples from 350 healthy subjects.

Studies on the relationship between Co, Ta and W content and hard-metal pneumoconiosis in various biological samples of workers of hard-metal industry revealed the individual susceptibility as the most probable origin of the disease.

In vitro tests as alternatives to using whole animals in areas of toxicokinetic testing, molecular target toxicity, cytotoxicity and morphological transformation have been carried out by cell cultures, subcellular preparations and isolated cellular components.

AIR POLLUTION

Activities have been focussed on the role of biogenic emissions (e.g. terpenes) in the chemistry of the clean and polluted atmosphere including product identification, ozone forming potential and gas-to-particles conversion processes.

Formation of carbonyls (formaldehyde, acetaldehyde and acetone) upon reaction of ß-pinene and ozone in the gas phase is significantly influenced by the presence of H_2O vapour

At 5 % r.h., depending on the initial conditions e.g. O_3/terpene ratio and SO_2 concentration, 3,6 to 6,8 % and 11 to 54 % of the reacted ß-pinene are converted to formaldehyde and total carbonyl, respectively.

At 50-60 % r.h., the yield of formaldehyde varies between 12 to 15 % and that of total carbonyls between 20 to 65 %.

Aerosol formation is also strongly influenced by r.h. and SO_2 additions. Without SO_2 addition, aerosol yields vary between 2 x 105 particles/cm^3 and 5 x 105 particles/cm^3. SO_2 additions lead to aerosol yields up to 2,5 x 106 particles/cm^3 under our experimental conditions (O_3 = 600 ppb, terpene = 300 ppb).

A novel experimental esposure system has been developed to study under controlled conditions the contribution of plant canopy layers as source/sink terms in the balance of **gas exchange between atmosphere and biosphere**. After more than one year performance of the exposure system with spruce saplings it has been shown that:

- the controlled climatic/edaphic environment (air turbulence, radiation, temperature, moisture, soil nutrients, soil water) allows the normal growth of saplings for at least one year;
- the controlled atmospheric environment (SO_2, O_3, NO_x, VOC, CO_2, H_2O) allows direct monitoring of the total gas exchange of the whole tree canopies without any disturbance: mass fluxes of gaseous pollutants, of VOC-emissions, of photosynthetic gas exchange, of chemical transformations.

Mass fluxes of pollutants to the canopy and emissions of terpenes are dominated in day conditions by stomatal conductance. Low level pollutant (<50 ppb) exposure did not affect photosynthesis.Terpenes emitted from the canopy promote deposition and/or transformation of SO_2 in the presence of O_3.

In the wake of the previous studies on **kinetics and mechanisms of nighttime tropospheric reactions** the transformation of atmospheric trace gases of biogenic origin by reaction with nitrate radical, NO_3, has been further investigated in the laboratory.

- In the reaction of NO_3 with 1,3 butadiene and with isoprene in air, the formation of nitroxy-substituted carbonyl compounds has been demonstrated. A mechanism is proposed for the reaction of 1,3 butadiene which should be qualitatively valid also for isoprene.

- Values for the equilibrium constant of the reactions $NO_3 + NO_2 + M \rightleftharpoons N_2O_5 + M$ and for the unimolecular thermal decay of the NO_3 radical, $NO_3 \rightarrow NO + O_2$, both of importance for the modelling of the NO_3 chemistry in air, have been determined.

Further studies on the mechanism of the reactions between NO_3 and organosulphur compounds (CH_3SH, CH_3SCH_3, $SSCH_3$) have provided information on the yield of the oxidized sulphur products: SO_2 and methanesulphonic acid (MSA, CH_3SO_3H). The results are applied in the study of gas to particle conversion of dimethylsulphide by NO_3 oxidation in air.

Several technological problems concerning the components of the **Ispra Mark 13A flue gas desulphurisation** pilot plant at SARAS refinery in Sarroch (Sardinia) have delayed the schedule of the experimental testing programme. The bench scale plant at JRC Environment Institute has been of great help in tackling specific problems in support to the pilot plant.

As far as it concerns the combined desulphurisation-denoxing process, a detailed study of the poisoning mechanisms of the noble metal catalyst in the catalytic reduction process with hydrogen showed that an industrial process based on these principles is not feasible, while promises are offered by an electrolytic process involving NO absorption in aqueous Fe (EDTA) complex.

EUROPEAN MONITORING NETWORK

Aerosol parameters and trace gas concentrations have been evaluated simultaneously with a commercially available differential absorption spectrometer, the achieved results - for hazy weather conditions - being in fairly good agreement with those of more specific instruments.
Photochemical processes both at local scale and for long-range transport as well as other processes responsible of ozone build-up and distribution, have been investigated through the measurement of meteorological and chemical parameters at stations located at various altitudes.

Perfluorocarbon tracer techniques have been successfully applied in the framework of the **TRANSALP** programme aimed at elucidating the dynamics of atmospheric transport processes of pollutants over the Alps. Several national laboratories participated in a campaign devoted to the study of the overflow of the first alpine barrier and of the dispersion at the leeside of the mountains.

Meteorological parameters, needed for the development of wind field models and for the interpretation of migration processes, were measured by means of different sensors located at three different places. A very strong thermally induced local effect coupled to tracer detection at high altitude (probable transalpine transport) were among the major issues of the experiments.

As far as it concerns the **aerosol science and technology**, a special apparatus has been set up and tested for the production and the characterization of aersol particles.

WATER QUALITY

The metal concentration in various compartments (water, sediment and their interface) has been assessed in view of its use in **metal dispersion studies** entailing a predictive mathematical model for total metal concentration evolution in lake water. It has been shown the dependence of the water-sediment system on the water properties with a fairly good interpretation of the short term effects of the liming experiment performed on the Lake Orta.

CHEMICAL WASTE

Within the framework of the **pollutant/soil interaction studies** long term release of vanadate from fly ash and the retention by soils has been verified. Retention of trace metals in specific chemical forms has been determined by means of radioactive labelling of toxic trace elements in fly ash samples.
Realistic environmental conditions have been approached by setting a 32 column lysimeter test site.
Soil sorption of PCBs, likely to migrate to underground water, has been investigated with special emphasis on physico-chemical parameters, Empirical QSAR models predicting the PCBs behaviour in a variety of soils could be established.
Interferences on the determination of PCB-138 were ascertained which could lead to modify the present legislation in some EEC countries.

For the study of the Lake Garda, organochlorine pesticides, PCBs and chemical waste residues have been determined in lake sediments.
Time-resolved Laser-induced fluorescence revealed to be a powerful technique to investigate the complexation capability of humic substances in natural waters, thus opening the way to the development of chemical sensors for the remote control of the aquatic environment.
The absorption mechanisms of Tl and Cr in selected mineral oxides has been investigated by means of X-ray absorption spectrometry (XANES/EXAFS) using synchrotron radiation, showing

the depression of Cr mobility due to reductive processes and sink capability in respect of Tl of MnO (s) inclusions in sediments.

Within the framework of the **environmental informatic studies**, the FEMSUN model and a code based on a stochastic approach have been tested for better assessing the impact of pollutants on soils, groundwater and food chain. The approach involves repeated simulations using variable input parameters on the basis of Monte Carlo or Latin Hyper Cube techniques. Laboratory and field experiments were needed for the chemical and hydrodynamic characterization of the soils.

As far as it concerns the **waste immobilization in cement**, efforts have been focused on the leaching behaviour of matrices prepared and tested under different experimental conditions. It has been shown that leachability is related to the water-to-cement ratio employed in the preparation.

The **OIL-PCB Manager (OPM)** decision support system has been completed and adapted to fulfill the requirements of the EEC directive on PCB. The system has been specially developed for the management of PCB-containing electrical devices.

ENVIRONMENTAL STUDIES OF THE MEDITERRANEAN BASIN

The joint european **MITO** Project - to be developed in cooperation with Portuguese, Spanish, French, Greek and Italian research bodies - is focussed on :

- Analytical cytology of phytoplankton
- Aquatic biotoxins
- Algal taxonomy and physiology
- Prediction of toxins occurrence.

Test sites selected in first priority are located in Northern Adriatic sea, the Ebro delta and the coastal areas of the Saronikos gulf.

A second project is aimed at :

- ascertaining the present quality of analytical measurements referred to water pollution and pollutant dispersion from point and non-point sources
- identifying the measurement errors and eliminating them
- progressively introducing elements of **analytical quality assurance**.

A first collaborative field study - which has been agreed upon by the cooperating laboratories - will deal with sampling procedures and associated errors for determining selected trace metals or organic compounds in sea water,fish sediment and fresh water samples.

FOOD AND DRUG ANALYSIS

The activity of the laboratory has been specially devoted to the **detection of wine sugaring by means of a Nuclear Magnetic Resonance methodology**, with special emphasis on accuracy and repeatability of the mesurements. In parallel, the developments of a European data bank of NMR fingerprints of European wines has been pursued.
As far as **dairy products** are concerned, several procedures have been tested and applied to reveal fraudes in the trade of dairy as well as of other products (as an example: vegetable oils added to milk fats; soya proteins in meat preparations, common wheat in durum wheat flours).

1.2. Radioactive Waste Management

Theoretical and experimental activities have been focussed on the assessment of long term safety of nuclear waste disposal in geological formations.

Risk assessment studies have dealt with the development of probabilitic codes and their application to specific cases. The achieved results, which consist of the LISA package, represent the conclusion of the activity. The package has been circulated among some 20 national institutes and/or organizations and tested through a bench mark campaign.
A project has been developed jointly with the Japan Atomic Energy Research Institute of Tokai on the performance of non-parametric tests to be employed for sensitivity analysis of model output, leading to a new version of an already available non-parametric test.

Laboratory studies have concerned on one hand Pu and Np migration experiments in soil columns in view of clarifying the nature of the mobile species. On the other hand the absorption of Am (III), Th (IV) and Pu in systems containing γ Al_2Oa_3 or amorphous SiO_2 and polidispersed humic acid, has been investigated. In multicomponent systems - such as the natural waters - trace metals and major cations compete for the binding sites available on humic compounds. In addition the dynamic rather than equilibrium characteristics of these systems have been sorted out.

Time-resolved Laser-induced Fluorescence has been applied to the study of Tb-humic acid-EDTA-Ca multicomponent system. The investigations on **transport processes** in fissured media have been continued in collaboration with CIEMAT (Spain) within the framework of field experiments of JRC-Ispra and El Berrocal test sites.
A combined laboratory-field experiment, in collaboration with CEN Cadarache, has concerned the determination of the Sr-85 diffusion coefficient in water-saturated clay, the field test involving a careful control, by laboratory tests, of a multiplicity of experimental parameters.

2. S/T Support to Community Policies

The Environment Institute is providing technical support and assistance for the largest part to the Directorate General for Environment, Nuclear Safety and Civil Protection (DG XI) in the areas of Chemicals, Waste, Water Quality, Atmospheric Pollution and Radioactive Environmental Monitoring (REM), for the implementation of EEC directives. In addition, support is also provided to the following Directorates General and associated areas :

DG I : Support to PACT programme
DG II : Data bank on pharmaceutical products
DG V : Biological data in occupational health
DG VI : Databank on NMR fingerprints of European wines
DG XIII : Mark 13A flue gas desulphurisation pilot plant
DG XXI : Chemical characterization of imported goods.

2.1 Chemicals

The **EINECS** inventory has been published in all the Comunity languages in the EC Official Journal. The Annex 1 to the Directive listing the substances subject to classification, labelling and packaging rules, has been updated.
Various models for estimating physicochemical properties, the diffusion in the environment and acute toxicity of a large number of EINECS' inventoried compounds have been evaluated in the framework of QSAR applicability studies.

Six European reference soils have been tested with selected harmful herbicides to establish the sorption capacity in view of the implementation of the EEC 79/831 Directive on "testing requirements and testing guidelines for chemicals".

2.2 Waste

Analytical methodologies for the fast determination of PCBs in waste oils have been investigated as a part of the scientific support given to DG XI on the subject. A method has been proposed which might become reference for EEC directives, and has been succesfully employed in a BCR (DG XII) interlaboratory certification analytical campaign.

2.3 Water Quality

EEC standards for drinking water quality have been assessed and a critical review has been made of frequency monitoring and surveillance for updating the Appendices II and III of EEC Directive 80/778. In addition a draft directive concerning the ecological quality of water in EEC member countries has been prepared.

A PC data bank on 132 substances and/or group of substances listed in the Annex to EEC Directive 76/464 has been developed. Studies on pollution from non-point sources were completed for the elements Cu, Zn, Ni, Cr, As, B and Mo leading to the evaluation of the yearly release to the aquatic environment. Domestic sewage and run off turned out to be the major sources.
As far as it concerns the point sources, quantification could be completed for Cu, Zn and Ni.

2.4 Atmospheric Pollution

In the framework of the activity of the Central Laboratory for Air Pollution, the harmonization programme for implementing EEC Directive 80/79 has led to the preparation of a manual for the network stations, giving guidelines and standardized procedures for determining SO_2 and black smoke.
A joint measurement programme has been launched, in the frame of EEC Directive 85/205, for the intercomparison of calibration standards for the elaboration of a test procedure for NO_2 and for a quality assurance programme for both calibration and routine NO_2 measurements.

Three analytical campaigns have been performed using passive diffusion tube technique in view of the re-assessment of urban monitoring networks. A mobile laboratory has been used for mapping the pollution distribution at ground level and aloft in industrial, commercial, pedestrian and recreational areas in Madrid.

The EMEP station at JRC Ispra has pursued with the measurement of a series of parameters in air atmospheric particulate and precipitation samples,the obtained data being distributed at regional, national and international level.

Lastly, support has been provided for the implementation of EEC directive 87/217 concerning the prevention and reduction of asbestos pollution. For the purpose, the analytical methods presently employed in EEC member countries are being evaluated.

2.5 Radioactivity Environmental Monitoring (REM)

More than 380.000 data have been stored in REM data bank covering all the EEC member countries as well as other european countries, for environmental samples and foodstuffs. Significant improvements have been introduced such as the addition of new fields, improved coding and extended user interface. A PC-based data bank on REF (Radioactive Effluents) from nuclear installations in the period of time 1976-86 has been implemented.

Further, a REX (Radioactive Exposure) data bank on exposure records of staff employed in nuclear installation and a RIS (Radiological Inspection) data bank related to the monitoring of radioactivity in the environment around nuclear installations are being developed. The four data banks will be eventually merged into one.

In the field of the models of atmospheric transport of radionuclides, fractal analysis has been applied to C-137 deposition in FRG and to the evaluation of monitoring capabilities of the european real-time monitoring network for airborne radioactivity.

A model for long-range transport has been updated resulting in the improvement of the location of the radioactive cloud from Chernobyl accident up to 500 km, and of the absolute concentration up to 10 fold.

The construction of the aerosol laboratory, specially designed for intercomparison and air monitoring within the frame of the quality assurance of the techniques for radioactivity monitoring is proceeding. Completion is scheduled for end 1991.

3. Exploratory Research

Four projects have been tackled in the course of the year, namely :

Laser Spectroscopy for Medical Diagnosis
Innovative Laser Technologies for Chemical Analysis
DNA Adducts
Laboratory for Separation Science.

The first project has dealt with the investigation of the feasibility of real-time determination, for diagnostic purposes, of trace gases in human breath by means of optical spectral methods based on tunable diode lasers. The determination of the $^{13}CO_2/^{12}CO_2$ isotopic ratio with a precision of 1% has been considered and preliminary tests have been performed.

Approaching analytical sensitivities in the range of sub-femtograms (10^{-15}g) to attograms (10^{-18}g) for metals by laser-induced fluorescence in a graphite crucible and the study and the characterization of an "ionization detector" are the goals to be achieved by the second project. A computer programme based on a ray-tracing algorithm evaluate the light collection efficiency of the optical system, thus allowing to minimize spurious signals. The detection limit of 0.1 femtogram obtained for Tl looks very promising.

The applicability of a photon "ionization detector" has been demonstrated for Raman emission from CCl_4, Mg being used as ionized species.

The detection and characterization of adducts in microsamples of DNA is aimed at by the third project which considers the development of suitable biochemical and physicochemical methods for the purpose. Efforts have been focused on mass spectrometry and ^{32}P post-labelling methods. The study has considered both in vitro and in vivo systems.

The laboratory for separation science has concerned in particular Microliquid Chromatography and Capillary Electrophoresis as separation techniques in tandem with Mass Spectrometry for determining ultratrace amounts of chemical compounds in different matrices. Detection limits in the subpicomole ($< 10^{12}$ Mol) can be anticipated.

4. Third Parties Work

This item includes a variety of activities from which a total income of approximately 580,000 ECUs was obtained in 1990. Worth of mentioning, among the others, are the activities performed in the areas of air pollution, water quality, long range atmospheric transport (ATMES) and radionuclide migration in geochemical bodies.

The control of the operation of air pollution monitoring stations, the calibration of the instrumentation, the data validation and the definition of air quality in sites not provided with measuring stations are the subjects of a contract with Lombardy Region. The Italian Ministry of Environment has entrusted the Environment Institute with relevant tasks within the framework of the MAPO Project aimed at the recovery and management of the Po river as well as with the study of the main components of the ecosystem of the Lake Garda. In addition the recovery of shallow lakes in the district of Varese is the aim of a contract signed with the Administration of the district.

The comparison of the models for long range atmospheric transport (ATMES) has been concluded, the achieved results being addressed to weather forecast services and to bodies charged with model predictions in emergencies. ATMES provides several measures of skill for each model as well as of the reliability of the calculated results. A special data bank including the output from the participants to the study to be used in future researches on the subject has been implemented.

Within the framework of the contract with ENRESA (Spanish Agency for Radioactive Waste Management), laboratory studies at JRC and in-situ experiment at El Berrocal (Spain) have been performed in view of clarifying and quantifying the process and the dynamics of radionuclide migration in granite formation.The investigation has concerned Uranium, Neptunium and Selenium. The role played by humic substances in governing radionuclide mobility has been once more stressed.

Main Achievements

1. Specific Research Programmes

1.1 Environmental Protection

The main achievements in the following research areas are presented :

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

The above areas were included in the JRC Environmental Protection programme adopted by the EEC Minister Council on October 1988 to cover the activities until December 31st 1991.

As the consequence the results which are reviewed do represent the follow up and the development of activities the aims and targets of which have been already presented in the Annual Report 89.
In respect to the adopted program, no activity has been launched in the area of Genetically Engineered Substances as the feasibility study has shown that - at the time being - the Environment Institute is not prepared to enter this field with reasonable chances of successful results.

ENVIRONMENTAL CHEMICALS

This item includes three different activities, i. e. : the ECDIN data bank, the Indoor Air Pollution and the Trace Metal Health Effects.

ECDIN

ECDIN (Environmental Chemicals Data and Information Network) is a factual Data Bank on Chemicals which actually or potentially are affecting the Environment, or Human Health. All relevant information suitable to forecast and/or to control any undersirable environmental effect of chemicals is stored in ECDIN, and can be retrieved by a sequence of menu-type searches. The adopted Data Base Management System is ADABAS, and the loading/searching programmes are written in Natural language. The European Inventory of existing Chemicals (EINECS) is also stored in ECDIN.

Several data files have been improved and/or updated in 1990. Suitable data summaries are being produced for toxicity records covered with analytical data. Similar work is in progress for carcinogenicity, mutagenicity and aquatic toxicity files.

Data files on environmental fate of chemicals have been improved and extended in the frame of a collaboration contract with the "Umweltbundesamt", Berlin. A pilot study was initiated to evaluate the present overall data content and distribution in ECDIN by multivariate analysis in order to identify unbalances in data availability with a view to guide future data collection and input strategies. At the same time, work for the production of an ECDIN-data subset on CD-ROM is far advanced with the aim to make selected ECDIN data files available for use in personal computers and a first version will be ready early in 1991.

Also, arrangements for the on-line distribution of ECDIN-data have been changed substantially. The contract with the previous hosting institute (Datacentralen) was terminated on October 1st., 1990 and in the future, ECDIN data will be distributed through "Deutsches Institut für Medizinische Dokumentation und Information" (DIMDI, Ministry of Health, FRG). The agreement foresees transfer of licence fees to the Commission after an initial trial period, ending June 30 ,1991. Also an agreement, which has been negotiated with the Environment Ministry of the FRG for cooperation in the field of factual chemical data banks, and which foresees a joint effort in data collection and validation for specific data files, has been approved.

An exchange of data was initiated between ECDIN and AQUIRE, an aquatic toxicity databank developed by the Natural Resources Research Institute, Univ. of Minnesota and EPA Research Laboratory.

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 with sealed structures and typically equipped with air conditioning systems is of increasing concern to public and private administrations.

The JRC's effort in this field consists in the management and scientific coordination of the COST-Concerted Action "Indoor Air Quality & Its Impact on Man" (COST Action 613) and in research activity aimed at an assessment of organic indoor pollutants and their sources and is based on its European commitment on one side and on specific competence developed in the past decades on the other. The following major results have been obtained in the reporting period:-

COST Action 613 - Indoor Air Quality & Its Impact on Man

COST project 613 has continued its successful effort to promote consensus among European workers about the more important issues and research needs in the field of indoor air quality and to pool efforts of experts in the 14 participating countries to develop and harmonize methods and tools for investigations and control of indoor air quality and its impact on man. The Community-COST Concertation Committee (CCCC) has continued the effort to summarize essential information on key indoor pollutants by publishing Report Nr. 7 "Indoor Air Pollution by Formaldehyde in European Countries" (see section 5.2 for more details). .

Studies on Volatile Organic Compounds (VOC)

VOC are indoor pollutants of particular concern since many of them are known or suspected to cause carcinogenic, neurotoxic, allergenic, immunotoxic, irritating or sensory effects. They 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 during 1990 regarded three topics: emission studies, VOC measurements in buildings of the European Parliament, quality assurance of VOC sampling.

Emission studies of VOC. In the Annual Report 1989 emission studies of building/furnishing materials performed in small environmental chambers (250-450 l volumes) were described. In 1990 the method developed for these studies was adapted to the study of VOC emitted from household products and applied to a liquid floor detergent, a floor wax paste, a spray cleanser for carpets, a spray polish for furniture and a liquid cleanser/disinfectant. In contrast to the solid building materials the household products emit VOC after being applied to a surface. Because of the thin layer of material applied, these products represent sources with strongly time dependent emissions. After application and introduction into the environmental chamber the concentration of the emitted VOC reaches a maximum value after a few seconds up to about one hour, depending on the volatility of the emitted compounds, and then decreases within about 4-12 hours to 10% of the maximum value. The complexity of the emitted VOC patterns varies considerably between the products: for one product a single emitted compound accounted for more than 95% of the maximum total VOC concentration, whereas for the other products the five most abundant compounds accounted for 50-85% of the maximum total concentration.

The measured concentration-time curves could be well described by the same empirical model used for the characterization of VOC emitted from building/furnishing products. The model allows to describe the total emission or the emission of single compounds as a function of time with four parameters.

In addition to the chamber experiments the emission of the household products has also been analyzed by a simple headspace assay of the bulk material without application to a surface. Headspace analysis has been proposed and applied as a simple means to determine the qualitative composition of VOC emissions. The comparison of the chamber and headspace analysis yielded, however, significant qualitative differences for several products. In chamber experiments polar compounds tend to be more abundant and unpolar compounds less abundant than in headspace experiments and these differences are most significant for water emulsions. As an example, in Figure 1 the relative abundances of twelve compounds emitted from a liquid cleanser/desinfectant as determined by the chamber and the headspace experiment are compared. The example shows that headspace analysis of a bulk product may lead to large errors when used to predict the qualitative composition of the emission after application of the product to a surface.

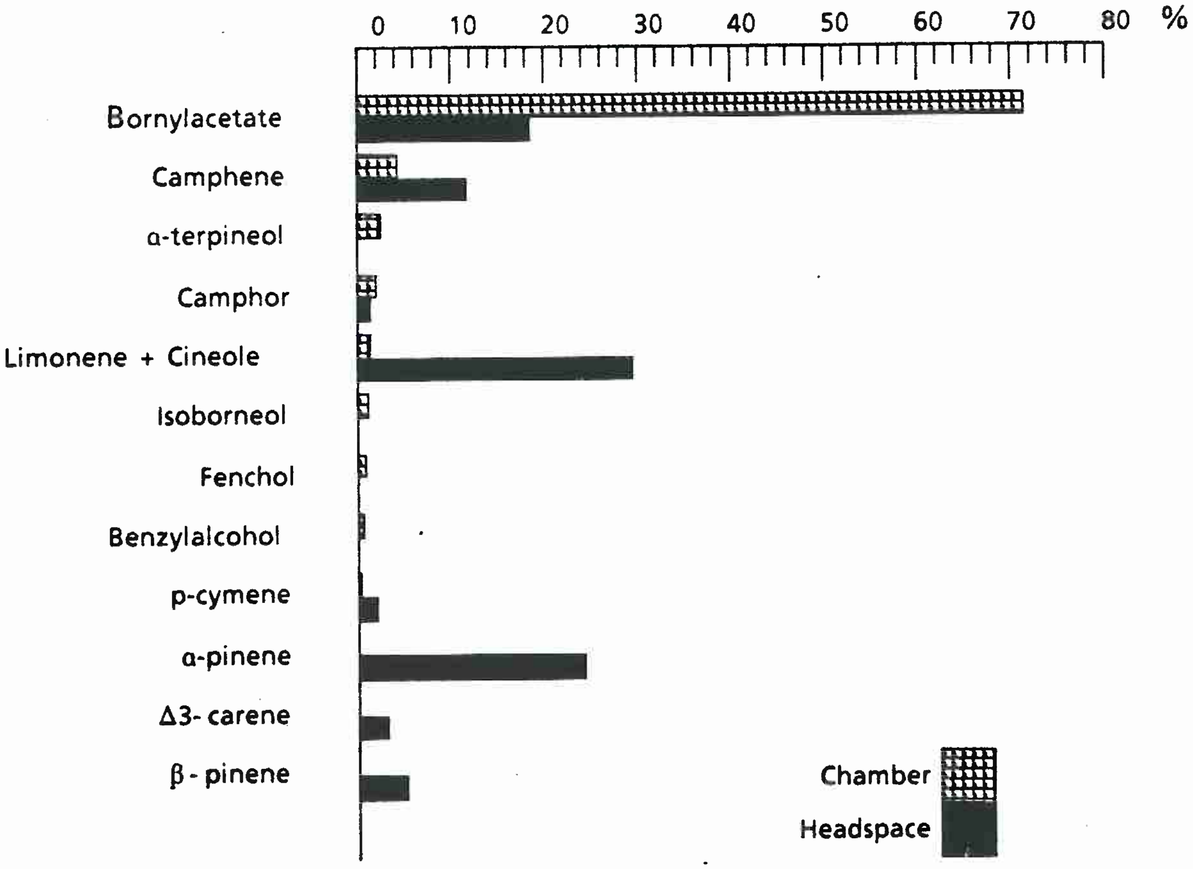

Fig. 1 Comparison of the relative abundance of twelve compounds emitted from a liquid cleanser as determined by chamber and headspace experiments

VOC measurements in buildings of the European Parliament. The work, sketched in the previous report, has been completed: on the basis of a questionnaire compiled by the employees (787 answers) two room samples of 10 offices each were selected for measurements, one with no complaints and one with maximum complaints. Measurements of formaldehyde, of total VOC and of selected compounds resulted in concentrations not significantly different between the two groups of offices, leading to the conclusion that VOC and formaldehyde, at the levels concerned (<1 mg/m^3 and <0.05 mg/m^3, respectively) do not contribute appreciably to complaints unless complainers are more sensitive than non-complainers.

The VOC pollution in a new building in Brussels has been measured by means of diffusion (passive) samplers, exposed for up to 240 hours, during working time only and continuously. The concentrations were not high, but some indications are appearing that occupation and/or cleaning of the rooms contribute remarkably to the indoor air pollution by VOC. Further work is needed to identify and quantify the different contributions.

Quality assurance of VOC sampling. Few papers in the scientific literature questioned the reliability of the solid adsorbent Tenax for VOC sampling, particularly claiming erratic results and poor retention of polar compounds. Experiments have been undertaken sampling different volumes of test chamber air, loaded with known concentrations (at levels normally observed indoors) of 9 compounds with zero to moderate polarity. The first results, obtained withTenax and Carbotrap, show a good reproducibility (% standard deviation of replicate samples between 1 and 10), no significant differences due to the sampled volume (between 0.5 and 5 liters) and good agreement between observed and expected concentrations. The work is continuing, in particular to check retention of more polar compounds.

Trace Metal Exposure and Health Effects

The activity aims to establish scientifically sound dose-effect relationships to prevent potential health risks of trace metal (TM) exposure. In particular, there is a fundamental need to relate the pathological processes that arise from the exposure to environmental and occupational agents to the specific characteristics of the tissues and the cells from which they originate and finally to extrapolate these events, investigated in different experimental systems, to the human situation.

This calls for a continuous integration between the quantitative estimation of trace metal concentrations in tissues and body fluids from differently exposed humans and the data from in vivo studies by experimental animal models and newer in vitro approaches to provide data on metabolism and toxicological effects resulting from TM exposure.

TM exposure in humans

The aim is to establish TM concentrations in body fluids and tissues of general population, professionally exposed workers and pathological cases in biomedical research on TM-related diseases(in collaboration with the DG V, Employment, Industrial and Social Affairs, Health and Safety Directorate, Luxembourg).

Major achievements were :

- the determination of 46, 35 and 26 elements in urine, blood and serum, respectively, of unexposed Italian subjects living in the same region (Lombardy). The results allowed the proposal of reference values for various elements determined in more than 350 healthy subjects, these being Ag, Al, As, Be, Bi, Cd, Co, Cr, Cu, Hg, Mn, Ni Pb, Sb, Se, Tl, V, Zn in urine; Ag, As, Bi, Cd, Cr, Co, Cu, Hg, Pb, Se, Tl, Zn in blood; and Ag, Al, Be, Cd, Co, Cu, Hg, Mn, Ni, Pb, Se, Tl, V, Zn in serum. For all other elements indicative values were suggested
- determination of cobalt, tantalum and tungsten in BAL, urine, blood, toenails and pubic hair from ten hard metal workers engaged in the production of hard metal tools or in grinding hard metal components of tools by diamond-cobalt discs. No relation exists between internal dose of metals and symptoms of disease. These findings further support the theory of an individual susceptibility towards to the hard metal pneumoconiosis based on immunological response. Since it is not possible at present to propose sensitive and specific tests for the early identification of hypersusceptible individuals, in the medical surveillance of hard metal workers the aim should be to detect early respiratory alterations. Lung function tests and BAL in selected cases should be at present the methods of choice.

- examination of two cases of thallotoxicosis resulting from resorption of a thin wire of metallic thallium (6 - 7 g) mistakenly implanted in a facial haengioma instead of magnesium wire as part of a surgical "magnesium-seed" method for the treatment of this condition. After 10 months one of the patient still presented polyneuropathy and serious mental abnormalities. In the second patient, the health status rapidly deteriorated. He died two months later. The clinical data suggest that adverse effects of the continuous thallium resorption from the implantation site in tissues was as severe as after ingestion of a single large thallium dose.

TM metabolism and toxic effects

In order to reduce the number of animal tests, the activity was focussed on the development and use of *in vitro* bioassays which involved the use of:

- subcellular preparations, to study the distribution of cadmium among sperma components. The largest cadmium content in the germ cells was localized in the tail region in agreement with the hypothesis that the toxic effects of the metal on male gonads would be related to competitive interactions with zinc which is essential for the sperm motility;
- isolated cellular components, to investigate the effect of vanadium on the activity of antioxidant enzymes such as superoxide dismutase, glutathione peroxidase and catalase;
- cell culture systems, to study the concurrent uptake, intracellular fate, biotransformation, cytotoxicity and morphological transformation in the BALB/3T3 cells by monomethylarsonic and dimethylarsinic acid as well as trimethylarsine oxide; to develop a metabolic model for vanadate and vanadyl compounds in relation to the cytotoxicity and the carcinogenic potential of vanadate and the absence of these effects of vanadyl compounds (Fig. 2); to carry out a screening study on the effects of 14 metal compounds on the proliferation and differentiation of B16 mouse melanoma cells; to investigate the effects of 16 metal compounds on the cellular toxic stress by the test system involving the use of human 70 Kd heat-shock promotor to establish mouse fibroplast lines capable of producing and secreting human growth hormon at high level following exposure to environmental toxic substances.

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

- the simultaneous distribution of barium, calcium and strontium was investigated in rats and rabbits by multitracer experiments using ^{133}Ba, ^{47}Ca and ^{85}Sr radiotracers. An effect of calcium on the barium behaviour in rats 2 hrs post injection was mainly seen in its liver concentration. It was about ten times higher than after injection of barium alone. Injections with barium and strontium showed no effect whereas when all the three elements were applied, the liver showed nearly the double amount of barium. In femur and rib no differences were observed. Since this tissue has a high affinity for barium, it seemed that calcium and strontium, which are both metabolized by the rat skeleton in the same way, are not able to alter in any way the bone barium concentration.
- distribution of low doses of cobalt in rat tissues including testicles and its subfractions. At 16 hrs post injection the amount of the element incorporated in the testicles was 0.056% of the dose, 0.038% in the epididymis and 0.018% in the deferens. In parallel, *in vitro* studies on the distribution of cobalt in testicles homogenate showed that about 50% of the element was associated with the nuclear fraction while the 39% with the soluble fraction. In this latter fractions it was proved that most of the cobalt was protein bound or associated with low molecular weight components.

These findings are of particular interest to assess the potential effects of the abnormal amounts of cobalt found in the sperma of hard metal workers (see Annual Report 1989, section TM exposure in humans).

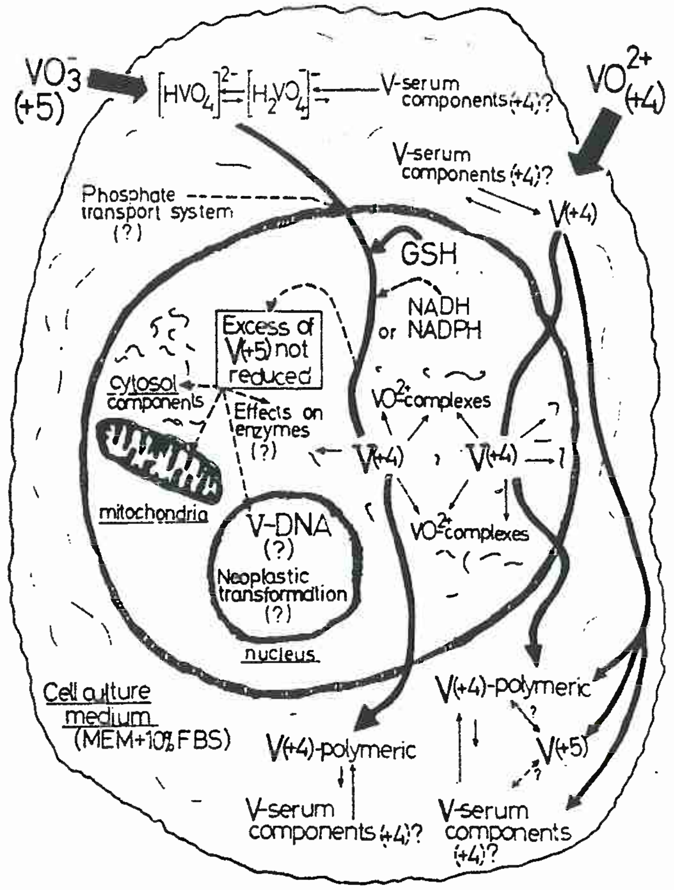

Fig. 2 A schematic representation of the metabolic patterns of vanadate (+5) and vanadyl (+4) ions in the BALB/3T3 cells. Dotted lines: hypothetic pathways

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:

- simulated atmospheric conditions (teflon bag experiments), their contribution to transformation processes leading to acidic compounds;
- exposure chambers, the atmosphere/biosphere interactions;
- laboratory studies, the kinetics and mechanisms of their chemical and photochemical reactions;
- field campaigns, the evaluation and distribution of their sources.

As far as the first item is concerned, the activity is focussed on the tropospheric reactions of natural emissions (monoterpenes) with emphasis on product identification and quantification and gas-to-particle conversion.

Carbonyls, especially formadehyde, acetaldehyde and acetone are to be expected as the final products of the monoterpene/ozone reaction. Their occurence in the air over remote areas, e.g. within forests, far from any extended anthropogenic activities could be explained in terms of this reaction.

In order to assess the contribution of monoterpenes as a source of carbonyls, which are one of the key species in photochemical processes, teflon bag experiments were carried out in the dark to study the gas phase reaction of selected monoterpens (ß-pinene, α-pinene) with ozone.

Formation of carbonyls is significantly influenced by the presence of H_2O vapour.

At 5 % RH, depending on the initial conditions, e.g. O_3/terpene ratio and SO_2 concentration, 3.6 to 6.8 % and 11 to 54 % of the reacted ß-pinene are converted to formaldehyde and total carbonyl respectively.

At 50-60 % RH, the yield of formaldehyde varies between 12 to 15 % and that of total carbonyls between 28 to 65 %.

Aerosol formation is also strongly influenced by RH and SO_2 additions (Fig. 3).

Without SO_2 addition, aerosol yields vary between 2.10^5 particles/cm^3 and 5.10^5 particles/cm^3.

SO_2 additions lead to aerosol yields up to $2.5\ 10^6$ particles/cm^3 under our experimental conditions (O_3, = 600 ppb, terpene = 300 ppb).

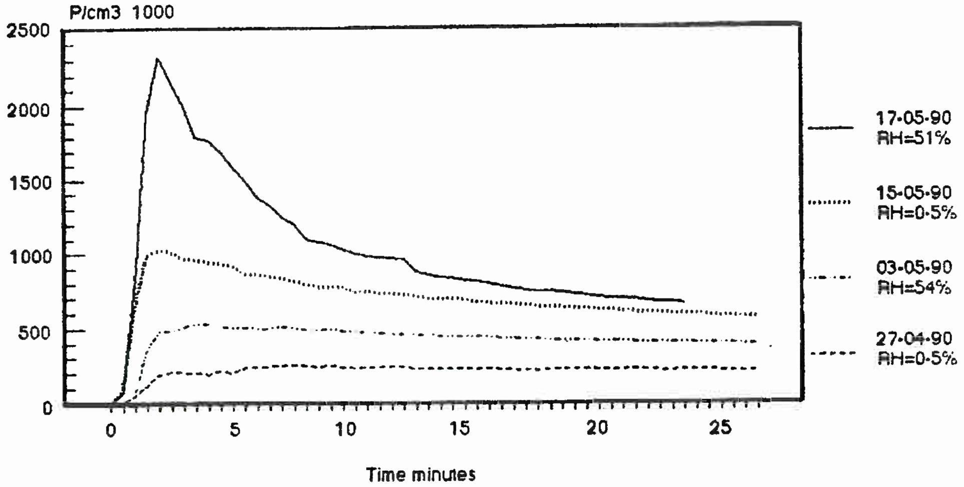

Fig. 3 Particle formation by the reaction of ß-pinene with ozone in the dark (with and without SO_2-additions) at different humidity (RH) levels.
27.04.1990 and 03.05.1990: ß-pinene + O_3
05.05.1990 and 17.05.1990: ß-pinene + O_3 + SO_2

As far as the second item is concerned, a new laboratory experimental activity has been started aiming at studying the contribution of plant canopy layers as source/sink terms in the balance of gas exchange between atmosphere and biosphere.

At plant surface/atmosphere interfaces different processes of emission, deposition and physical/chemical transformation are involved simultaneously which cannot be clearly separated and quantified under ambient conditions. However, the quantitative determination of elemental input to ecosystems has to be ascertained before risks due to changed atmospheric chemistry can be assessed.

Atmospheric contents of radiatively (H_2O, CO_2) and chemical (VOC) active gases are influenced by plant canopies and hence the interactions between air constituents of natural and anthropogenic origin in the plant surface/atmosphere boundary layer play a key role with respect to ecological effects as well as to eventual climatic change.

As a first step, the study focussed on low level, continuous exposure of spruce (Picea abies) canopies in dry conditions to the gases SO_2 and O_3, either alone or in combination, to monitor simultaneously the mass balance of the pollutants, of the photosynthetic gas exchange and of the biogenic hydrocarbon emissions.

A Continuous Stirred Tank Reactor (CSTR), as developed by Henck and co-workers (Raleigh, USA) for gas uptake studies with crops, has been modified to be used with tree canopies in a continuously monitored linear airflow. The CSTR-system has been designed to give ideal and instantaneous mixing of components entering and present in the chamber.

Controlled turbulence as generated by an impeller at the chamber top was adjusted to set atmospheric and leaf boundary resistances to zero. A shared-time gas distribution unit supplies sample air to the gas analysers (O_3, SO_2, NO, NO_2, CO_2, H_2O). Samples for GC-analysis of biogenic hydrocarbons are taken discontinuously.

The mass balance of the canopy gas exchange is calculated as $qc = f\ (C_{in}\text{-}C_{out})$ - qw, where flux density (qc) to or from the canopy is balanced by the product of flowrate (f) and concentration difference (C_{in}-C_{out}) between inlet and exhaust duct, minus flux density to and from the walls (qw).The system performance test indicates gas concentrations at the outlet representing any point within the reactor. Mass flux to and from the walls, as observed in a chamber without plants, is near zero.

Results on gas exchange per canopy surface area show close relation between climatic/edaphic parameters, photosynthetic gas exchange, pollutant deposition and VOCs emission. Photosynthetic gas exchange (CO_2, H_2O) representing stomatal conductance is strongly related to radiation, air temperature, humidity and soil moisture. The deposition velocity of SO_2 and O_3 in dry conditions is dominated by stomatal conductance with respect to diurnal changes as well as to the absolute values in different seasons.

Pollutant exposure did not affect VOC-emissions and photosynthetic activity. An additional SO_2-sink of 5 to 15 ng/sec was observed in the system $SO_2 + O_3$ + trees. This could be attributed to enhanced chemical transformation of SO_2 when biogenic emissions are present.
Work is in progress to balance the products of chemical transformation.Laboratory studies of kinetics and mechanisms of atmospheric reactions have maintained their focus on that part of the atmospheric chemistry occurring at night and bound to the role of the nitrate radical NO_3.

NO_3 + *Isoprene*

As for the past studies, main attention was given to the reactions of NO_3 with biogenic hydrocarbons in the frame of a project aiming to clarify the involvement of nitrogen oxides and volatile organic compounds in oxidant formation in the perturbed troposphere. Following the previous research on terpenes and alkenes, the studies have addressed the reaction between NO_3 and dienes, with particular attention to the environmentally important species isoprene. The optical analytical facilities, FTIR and UV-VIS spectrometers, have been supplemented by gas chromatographic analysis (GC-FID at the reaction chamber and GC-MS after sampling on absorbers) for identification and measurement of products and intermediates. Contrary to the case of the daytime reaction with the OH radical, unsaturated nitroxy-substituted carbonyl compounds were observed as main products with only small yields of CH_2O and unsaturated unsubstituted carbonyl compounds. Products have been identified in the case of 1,3 butadiene and a reaction mechanism is proposed for this compound (Figs. 4 and 5). The results on isoprene seem to indicate that this diene follows a similar reaction scheme as 1.3 butadiene; however, further work is needed to clarify the relative importance of alternative reaction pathways and for a definitive identification of products.

NO_3 + *Aromatics*

In order to achieve further information on the reaction mechanism, the kinetic isotope effect (kH/kD) was investigated by deuterated o- and p-xylenes. Values equal to 1.5 - 1.9 were found by full deuteration of the methyl groups. The results are not conclusive and further experiments are in progress using GC-MS and FT-IR as analytical techniques, in collaboration with the University of Milan.

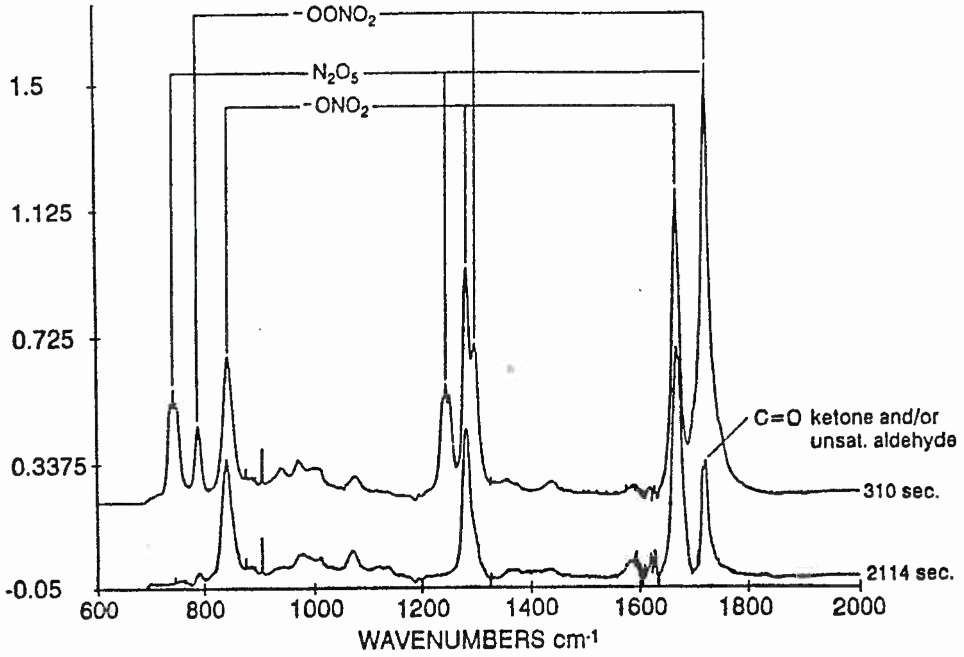

Fig. 4 Infrared absorption spectrum of the products of the reaction between NO3 and 1,3 butadiene. The two spectra recorded at different time show the decay of the reactant N2O5 (used as source of the NO3 radicals) and of the nitroxy-nitroperoxy - intermediate to nitroxy-carbonyl compounds.

Equilibrium $NO_3 + NO_2 + M \leftrightarrows N_2O_5 + M$ and Kinetics of the $O_3/NO_2/NO_3/N_2O_5$/air System

The kinetics of the system has been investigated by simultaneous direct spectroscopic measurements in the IR and in the UV-VIS of the species involved, using a geometry of the optics in the reaction chamber which permits to probe nearly the same gas volume by the two spectrometers. Two aspects have been in particular investigated: the debated value of the equilibrium constant of the reaction

$$NO_3 + NO_2 + M \leftrightarrows N_2O_5 + M$$

and the rate constant of the thermal unimolecular decomposition reaction $NO_3 \rightarrow NO + O_2$.
Both these kinetic parameters are important in modelling the concentration of the nitrate radical in air.
The equilibrium constant has been determined over a restricted temperature range obtaining a value at 298K of 3.73 (± 0.41) x10^{-11} cm^3 molecule^{-1} (Table I).
The unimolecular thermal decomposition of NO_3 was previously considered as relevant for the description of the $O_3/NO_2/NO_3/N_2O_5$ system in the atmosphere by one group only; computer simulations of the kinetics of this system, applying different schemes of chemical reactions, show best agreement between the experimental results of this study and simulations, when this reaction was included in the model. The rate constant was evaluated as 1.6 (± 0.7) x10^{-3}s^{-1} at 295±2 K; a value lower but still within the error limits with respect to that previously determined.

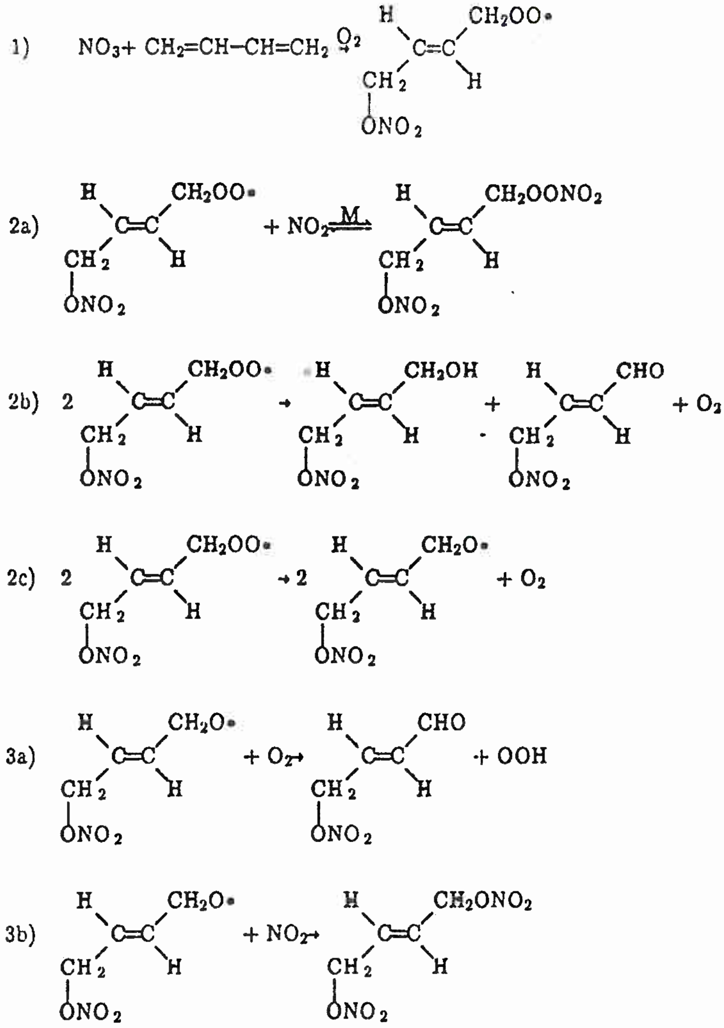

Fig.5 Mechanism proposed according to the experimental study for the reaction between NO_3 and 1,3 butadiene in air for the case of an initial 1,4 addition. The 1,2 addition, estimated to occur with the same probability, leads to analogous products. Reaction 3A, which seems to be the main reaction pathway, leads to the formation of nitroxy unsatured aldehydes and hydroperoxy radicals. The reaction of NO_3 with alkenes is a significant source of hydroperoxy radicals HO_2, precursors of hydroxyl radicals OH, capable to trigger chemical reactions supposed to occur only at daytime.

Table 1

Comparison of measured K_{eq} values referred to 298 K

Reference	$K_{eq} \times 10^{11}$ $cm^3 molecule^{1}$	
Schott and Davidson [1]	0.98	
Graham and Johnston [2]	2.34	
Tuazon et al. [3]	3.44*	3.99**
Kircher, Margitan and Sander]4]	3.25	
Smith, Ravishankara and Wine [5] a)	4.00	
Smith, Ravishankara and Wine [5] b)	2.06	
Perner et al. [6]	2.12*	1.27**
Burrows, Tyndall and Moortgat [7]	2.50*	2.82**
Cantrell et al. [8]	4.44*	5.14**
Orlando et al. [9]		
(preliminary data)	3.35	
This work	3.73*	3.67**

Measurements of K_{eq} at 298 K and atmospheric pressure reported in literature:
a) using k_2 from Connel and Johnston [10];
b) using k_2 from Viggiano et al. [11].
*: direct. determination of K_{eq}
**: the value of K_{eq} has been recalculated using common spectral parameters for all of the determinations as discussed by Wayne et al. [12].

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[7] J.P. Burrows, G.S. Tyndall and G.K. Moortgat, "A study of the N2O5 equilibrium between 275 and 315 K and determination of the heat of formation of NO_2", Chem. Phys. Lett., 119, 193 (1985).

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NO_3 + Organosulphur Compounds

A detailed study of the reaction of dimethylsulphide, methyl mercaptane and dimethyldisulphide with NO_3 was performed in the reaction chamber to identify products and to evaluate reaction mechanisms. The reaction, limited to dimethylsulphide, was studied also in large Teflon bags, to evaluate the aerosol (clouds) forming properties of the oxidation products of this species. The evolution of the size distribution of the particles formed in the system was followed by a differential mobility particle sizer and a condensation nuclei counter.
Significative differences have been found in the gas to particle conversion of the two oxidized sulphur end products, mathanesulphonic acid and sulphuric acid, with the first species mostly present in the gas phase and not in the particle phase. These findings are tentatively explained with an aerosol dynamic model (see item "Aerosol Science and Technology").

NO_3 + Halogenated Alkanes

This study addresses the atmospheric compatibility of some halogenated alkanes, proposed as alternative to Freons (chlorofluorocarbons, CFC) and characterized by the presence of hydrogen atoms in the molecule (hydrochlorofluorocarbons, HCFC; hydrofluorocarbons, HFC) and then by a definitively shorter tropospheric lifetime. This limits the transport of HFCs and HCFCs to the stratosphere and their danger for the stratospheric ozone layer. However, the increased reactivity of these compounds may pose problems in the troposphere and the formation of stable halogenated degradation products may renew the danger to the stratopheric ozone.
Five of these compounds (HCFCs and HFCs) were reacted with NO_3 in air in a smog chamber study: all of them exhibited a very weak reactivity towards this radical and upper limits for the rate constants $<10^{-21}$ cm^3 molecule^{-1}s^{-1} at 296 K were evaluated. The attention was then addressed to the night-time chemistry of aldehydes, which are supposed to be formed from the day-time attack of HCFCs and HFCs by the OH radical (that is known to be much faster). CCl_3CHO and CF_2ClCHO were synthesized as case study reacted with NO_3 and the products analysed by infrared spectroscopy. Evidence was obtained that $COCl_2$ in the first case and COF_2 in the second case are main reaction products.

As far as the in-field measuring campaigns are concerned, these have been undertaken within the EUREKA/EUROTRAC sub-project BIATEX (Biosphere/Atmosphere Exchange) to:

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

Emission rates of the main emitted monoterpenes (α- and ß-pinene, camphene) range between 0.9 to 21.8 ng/m^2·sec.

Generally, emission rates are higher during springtime than in autumn.

The monoterpenes concentration has been estimated at different heights: ground level, 21, 31 and 51 meter. Concentrations of α- and ß-pinene range between 0.04 to 1 ppbv (ground level); 0.02 to .,7 ppbv (21 m) and 0.04 to 0,16 ppbv (31, 51 m).

Concentrations of formaldehyde and acetaldehyde in the forest air ranged between 7.5 to 12.5 µg/m^3, those of acetone between 4.1 to 14.6 µg/m^3.

For 1991 two new experiments have been planned at the experimental tower in the Bavarian Forest in order to follow the emission behaviour and the seasonal variation of the terpene emission and to measure the carbonyl concentration at the different heights. Assuming the monoterpenes, upon reaction with ozone, as the main source of carbonyls, the above measurements should give information on the atmospheric reactivity of a forest area.

The Ispra Mark 13A Process for Flue Gas Desulphurization

The Commission is strongly supporting the final stage of the project invented at the JRC Ispra in 1980 i.e. the design, construction and operation of pilot plant to desulphurise a flue gas throughput of 32 000 Nm^3/h at the SARAS Refinery at Sarroch in Sardinia (Italy). JRC Ispra bears the responsability for the technical supervision of this pilot plant project which is administratively under the responsability of DG XIII Luxembourg.

The pilot plant in Sarroch was completed during the year 1988 and the start-up and operation phase started in the first months of 1989. The first year of operation was mainly dedicated to the testing of components (flowmeters, pumps, piping...) where the plant was in full operation for more than 2000 hours. Several problems with components were encountered during this phase. The most serious one was the untightness of the reactor piping circuit due to a supplier's error in the manufacture of the GRP flanges. It proved to be necessary to replace all flanges and a large part of the piping of this plant section. Also maintenance problems with the liquid circulation pumps and with liquid flowmeters occurred. Both problems were satisfactorily solved during the year 1990. It has to be stressed that the main troubles occurred in classical equipment items, utilised in many similar industrial plants, and were not associated with the intrinsic properties of the Ispra Mark 13A process. The solving of the aforementioned problems caused considerable delays in the scheduled experimental programme. The delays caused, on their turn, financial and organizational problems to the main contractor, Ferlini Technology. Consequently, work on the pilot plant project was temporarily suspended and new organization forms for the project are now under study.

A bench scale plant of the Ispra Mark 13A process is in operation at the Environment Institute. This plant is mainly used to study specific problems for support of the pilot plant project, for example the testing of candidate electrolytic cells, the study of the effects of specific impurites in the flue gas etc..

A main problem emerged during 1990 was the fact that during the pilot plant operation an excessive HBr emission in the purified flue gas was observed (approximately 150 mg/m^3). The problem is most probably caused by the formation of a stable aerosol of aqueous HBr during the condensation of saturated water vapour in the scrubber.

The possible formation, prevention and abatement of aqueous hydrogen bromide aerosols was studied in the bench-scale unit. During these experiments, it proved to be possible to reduce the HBr concentration in the purified flue gas to approximately 15 mg/m^3 by prevention measures (increasing the efficiency of the reactor) without the application of special abatement equipment. The study will be completed during 1991 and suitable modifications of the pilot plant will be proposed.

Removal of nitrogen oxides from flue gases

Besides the abatement of sulphur dioxide, the JRC conducts a research for the extension of the Ispra Mark 13A process to a combined desulphurisation-denoxing process. Two possibilities are under study:

- catalytic reduction with hydrogen
- cathodic electrolytic reduction.

During 1990 it appeared that the poisoning of the noble metal catalysts by remnants of sulphur dioxide was a decisive obstacle for the direct catalytic reduction. The mechanism of the poisoning was studied in detail. The conclusion was that adsorption and chemisorption of sulphur compounds on the active sites of the catalyst cause an irreversible deterioration of the catalytic activity. Consequently, the development of an industrial denoxing process based on the direct reduction of nitrogen oxides with hydrogen at low temperatures, is not feasible.

The main step for the alternative electrolytic process is the absorption of NO in an aqueous Fe(EDTA) complex. The chemical equilibrium of this absorption was studied including the effect of remnant SO_2 on this process step. Subsequently, work was concentrated on the possible preparation of a stream of concentrated NO by desorption at higher temperatures, for instance by steam stripping. The production of gaseous NO in concentrations of more than 15 vol% could open the way to the development of attractive regenerative denoxing process alternatives.

EUROPEAN MONITORING NETWORK

The long-range transport of pollutants is presently a major issue of atmospheric reseach , not only for practical implications such as trans-boundary transport of pollutants but also in relation to global environmental issues, which are becoming a general concern of human society. Problems like deposition of acidifying substances and the formation of tropospheric ozone in remote rural areas are stricly linked to the combination of air chemistry and meteorological processes. The classical air pollution monitoring networks were however designed for urban and industrial areas with high pollution level so that the need for more sensitive instruments and new measuring strategies arose. With this in mind the Environment Institute at Ispra tests and develops advanced tropospheric air monitoring systems which could become an integrated part of a European Monitoring Network, participates with its own staff and instrumentation in regional, national and international field campaigns and finally takes the lead in organising field campaigns and field measuring programmes with more general scientific objectives.

Monitoring of Pollutants and Gas-Particle Interaction Processes

The possibilities of a commercial differential absorption spectrometer to measure aerosol parameters and trace gas concentrations simultaneously over the same air volume have been investigated. The instrument, operated over 729 meter beampath provided information on the number concentration of particles and the mean particle diameter. The results, obtained for hazy weather situations, were compared with those of a differential mobility particle sizer and a low pressure impactor and showed reasonable agreement.

This characteristics would be extremely helpful in investigations of gas-liquid particle interactions; the technique has been applied in a preliminary study of the formation of HONO in polluted air in the presence of fog, in Ispra. The observations showed a rapid formation of gaseous HONO during fog and haze episodes, confirming the importance of the contribution of reactions on wet aerosols to the transformation of NOx into HONO. (Fig. 6)

Ozone Distribution in the Prealpine Region

In the frame of an informal collaboration with the Italian Electricity Board (ENEL/CRTN Milano) and with the Swiss Department of Environment (Bellinzona), meteorological and chemical parameters measured at stations located at different altitudes (from 209 m of Ispra to 2550 m of Sestriere) in the south-alpine region have been collected and analysed. This situation made possible to investigate the different mechanisms responsible for ozone build-up and distribution; i.e. photochemical processes at local scale or from long-range transport, transport of natural ozone from the free troposphere (foehn episodes) or from the stratosphere (jet streams and/or tropopause folding). During July and August of this year severe photochemical pollution episodes in the area were observed and increasing daily ozone concentrations along well defined trajectories have been recorded (Figs.7, 8).

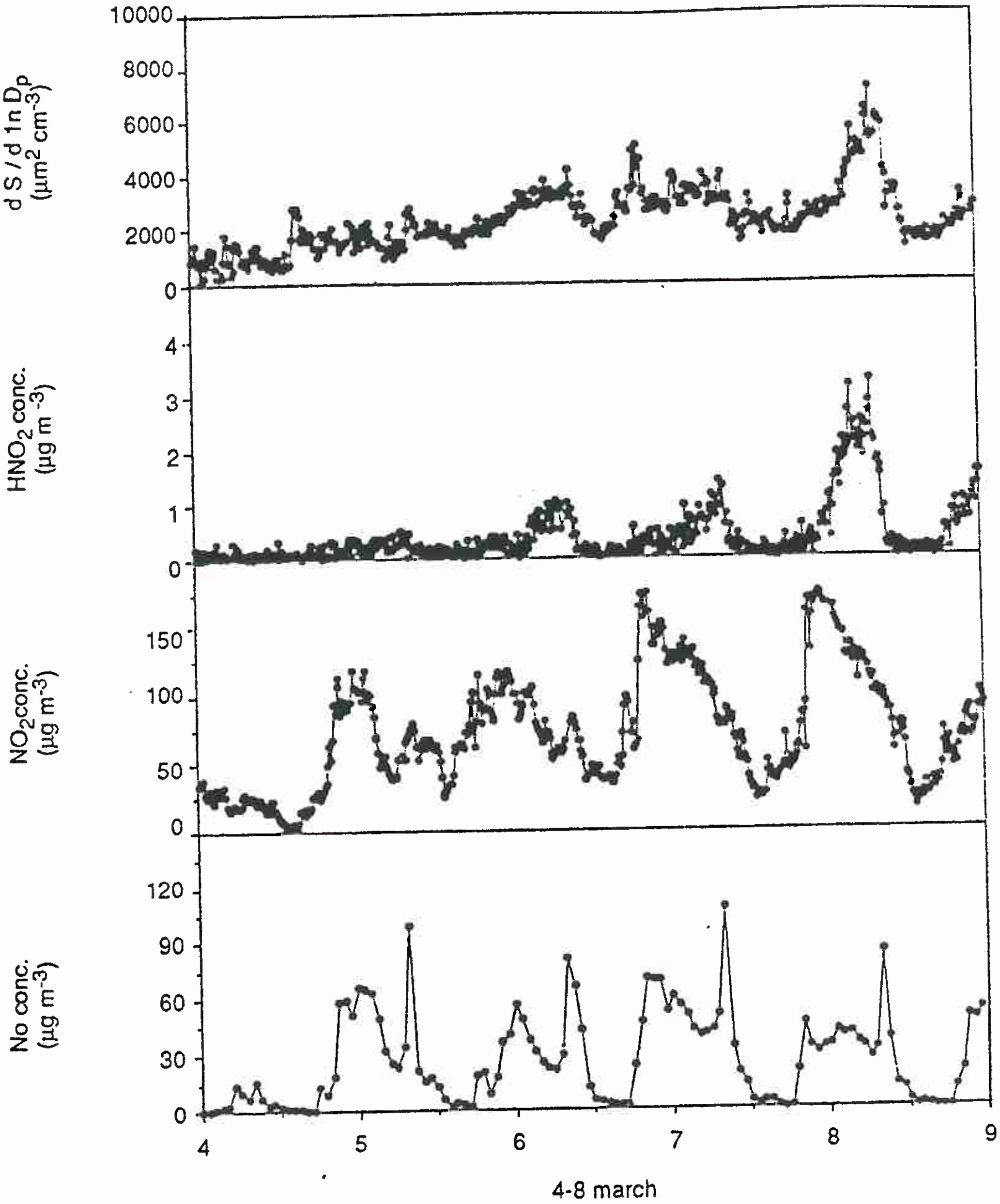


Fig. 6 Observation of total surface of particles, HONO and NO_2 concentrations measured by long path differential optical absorption spectroscopy. Semirural area, Ispra, Opsis system operated over a 729 m beam path. The NO concentration was measured by a conventional point sampling monitor.
The series of measurements seem to indicate that HONO formation is correlated with the simultaneous occurrence in air of liquid aerosol partilces, NO_2 and NO.

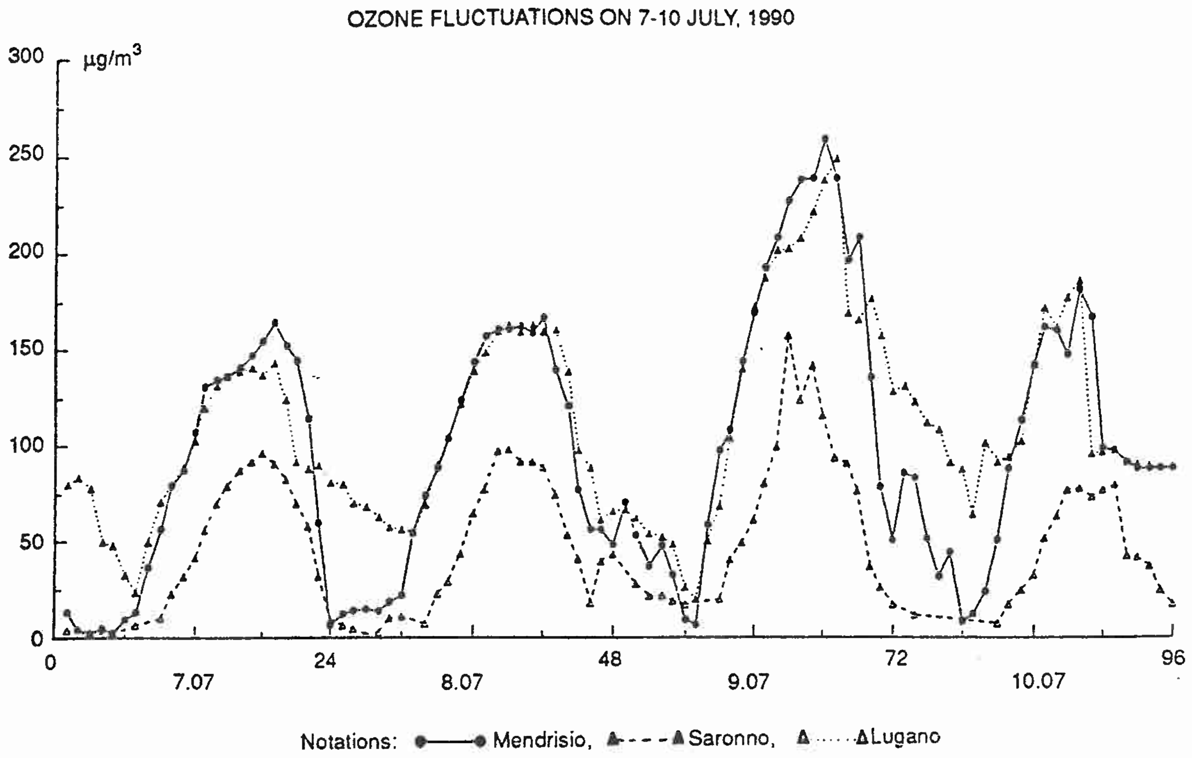


Fig. 7 Build-up of ground level ozone along the Olona river basin, till the arrival (on July 10th) of a front.

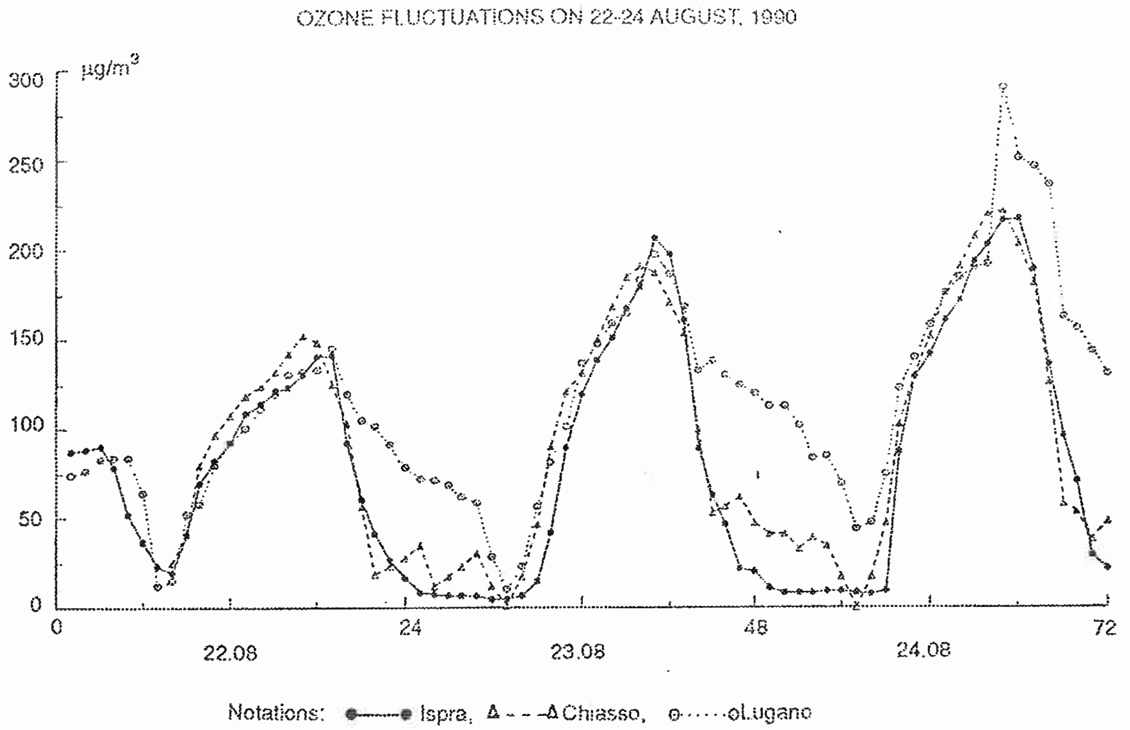


Fig. 8 Build-up of ground level ozone, recorded during a severe photochemical pollution episode, in the prealpine region.

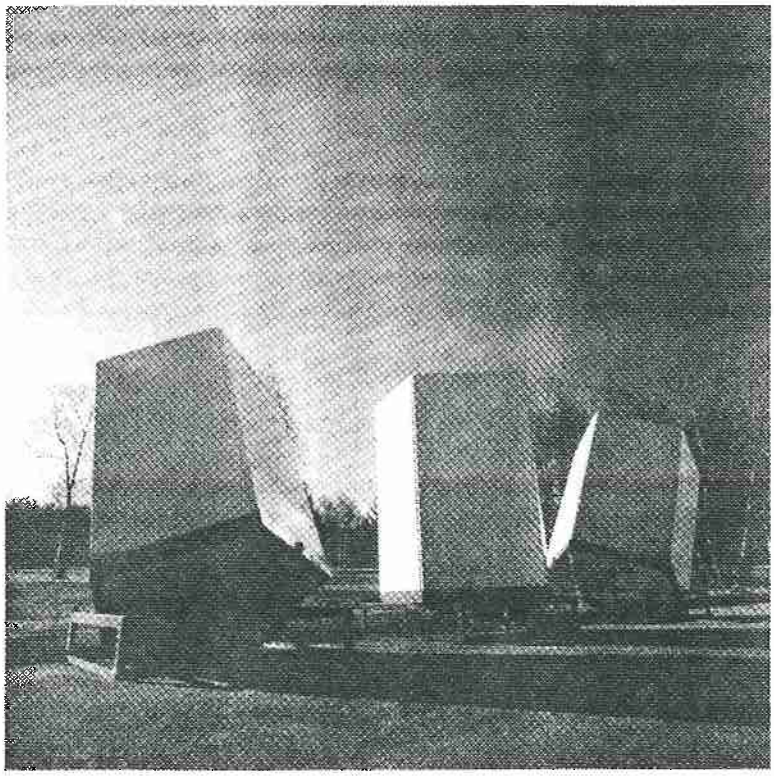


Fig. 9 View of the Doppler sounder for wind measurements (Sodar)

Development and Application of the Atmospheric Tracer Technology

Tracing the atmosphere with minute amounts of inert gases which can be detected with high sensitivity at long distances from the release point is a unique technique to study the transport of air masses, making it possible the validation of air transport models and the relationship between atmospheric pollutant concentration and transport phenomena.

Ispra has successfully developed the perfluorocarbon (PFC) tracers technology. PFCs are inert and non toxic, they cannot be deposited by rain and they do not interact with atmospheric trace gases, ozone included. The technique has been applied in 1990 in the TRANSALP programme, which has the following objectives:

- to gain knowledge on the dynamics of atmospheric transport processes governing the transfer of atmospheric trace constitutents over the Alpine barrier from the Western Po Valley to the Swiss Plateau and vice versa,
- to identify the main transport channels in the Alpine region (including an estimate of flow rates), their relative importance and the diffusion properties of the PBL over the Central Alps,
- to improve knowledge of trans-Alpine exchange of anthropogenic pollutants.

A TRANSALP experiment was successfully conducted in September 1990 with the participation of several laboratories: PSI, Villingen (CH); Metair, Zürich (CH); ENEL, Milano (I); AERODATA, Braunschweig (D)).

Whilst the 1989 campaign was limited to study the transport of air masses through the valleys Leventina and Blenio, for the 1990 campaign the study of the overflow of the first alpine barrier (Lucomagno, Gothard, Nufenen) and the dispersion at the leeside of the mountains was planned. The experimental layout was based on a series of releases from the upper Leventina valley, with ground and aircraft sampling in the appropriate sampling network. Meteorological parameters were measured during the release periode, in order to provide input data for a wind field model that will be run for the interpretation of the tracer migration. The meteorological instrumentation was installed at three different places along the Ticino river valley, as described below.

A three-dimensional Doppler sounder (Sodar, see Fig. 9) was in operation at an altitude of 2000 a.s.l., near the alpine passes, in order to observe the complex patterns of wind circulation that are due to the many valleys ending in the same area. The Nufenen Pass is located at a distance of five km from the Sodar, at an altitude of 2500 m. Since the Sodar's range is of about 1000 m a.g.l., the observation also beyond the boundary layer and the access to the synoptically induced winds. were achieved as expected This was actually the case. Generally, the boundary layer had a depth of 200-300 m., with moderate breeze circulation winds. Fig. 10 gives an example of these observations.

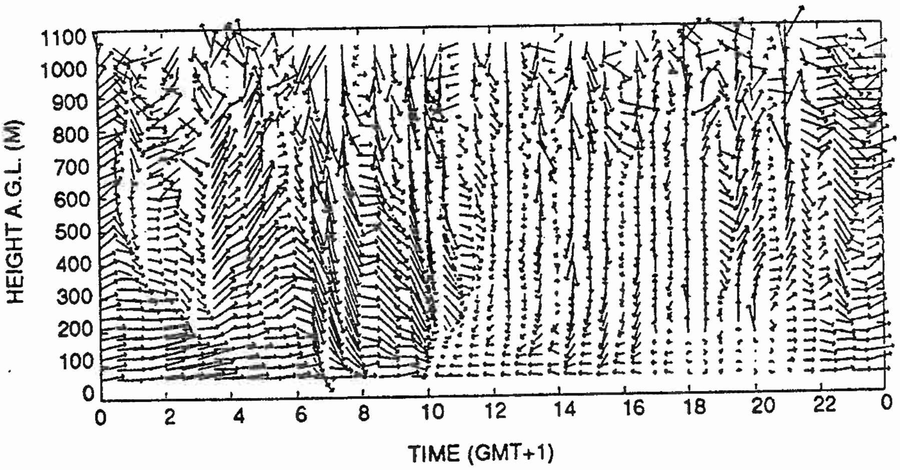


Fig. 10 **Wind speeds and directions, as observed by the Sodar on September 21, 1990 at Alpe Cruina.**

A conventional meteorological station was observing at mid-distance between the tracer release point and the end of the valley (Varenzo). The parameters measured were air temperature and moisture, wind speed and direction, net radiation and ground temperature.
Near the release point (Giornico), a series of parameters were recorded by means of two Kaijo-Denki sonic anemometers. One of them was put in the middle of the valley where the sunny period of the day is the longest; the other was placed near the edge of the valley where that period is shorter due to the shadow of the neighbouring mountain. The main parameters observed were the turbulent heat fluxes, friction velocities, wind speed and direction, vertical wind and the standard deviations for these variables, due to the turbulent fluctuations.
An example of the sonic anemometer measurements is given on Fig. 11.

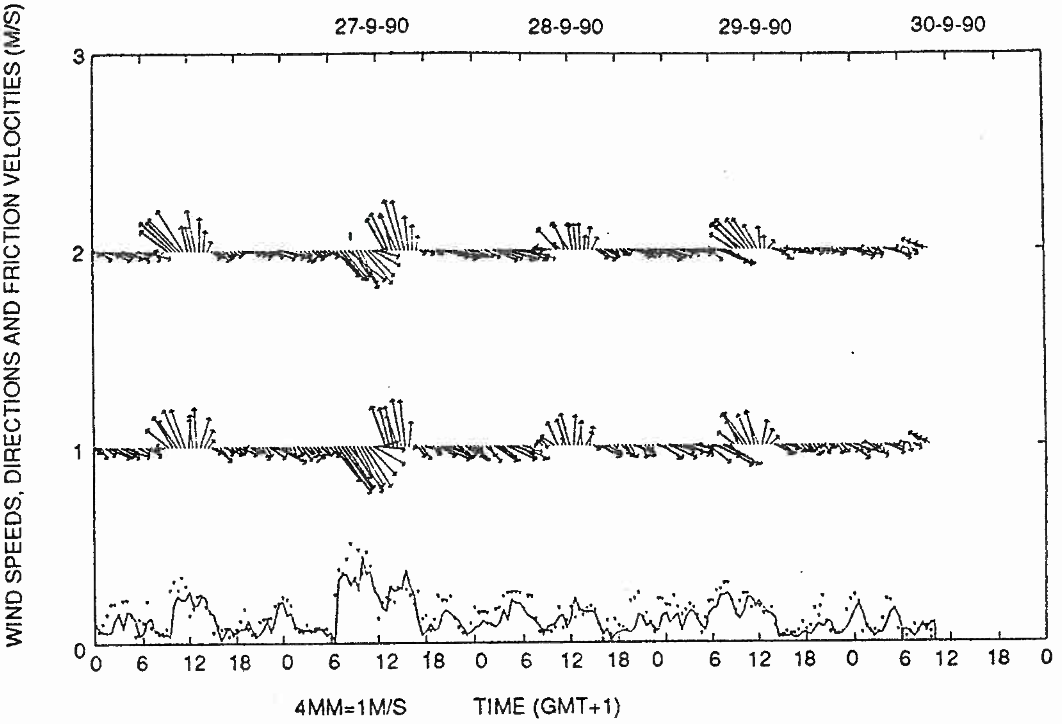


Fig. 11 Sonic anemometer measurements carried out at Varenzo from September 26 to 30, 1990. The lower arrows are the wind speeds and directions given by the anemometer placed in the middle of the valley; the upper arrows correspond to the other anemometers. The curve and the points are the friction velocities recorded by the two instruments.

The major findings of the 1990 TRANSALP campaign were :

- The tracer was detected on the other side of the passes: Nufenen, Gothard and Lucomagno;
- a large quantity of tracer climbed across the North ridge of the Levantina valley (10 km distant from release point) with a height difference of 1700 m. (Such a strong thermally induced local effect was already found in the 1988 "Campo dei Fiori" Experiment.);
- tracer was found as high as 3700 m which makes a coupling of the air mass to the free troposphere, and thus a transalpine transport probable;
- at the bottom of the valley the tracer may remain for several days, a finding which may create "background"problems in repeating tracer experiments on a short time distance;
- during rain the tracer concentration remains constant, an expected but now experimentally confirmed effect;
- 24 duplicate samples (2 automatic samplers put side by side) confirmed the good quality of our data.

Aerosol Science and Technology

An equipment for generation and physical and chemical characterization of aerosol particles has been set up. Test measurements were performed in the open atmosphere, in an industrial process system (Ispra/Mark 13A) and in the laboratory.

Laboratory experiments were performed on the formation of acid aerosol particles from reactions with DMS, using teflon bags (see Fig.12) (see "Air Chemistry, NO_3 + Organosulphur Compounds").

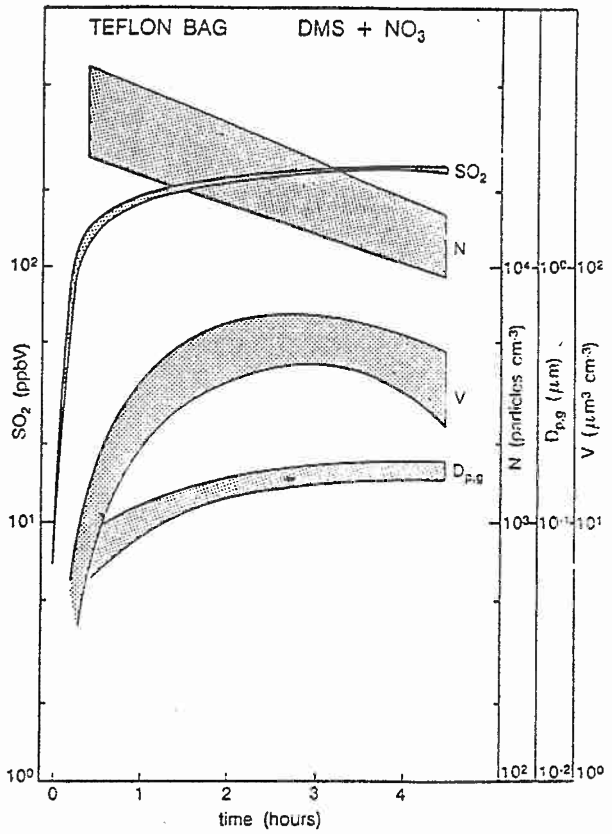


Fig.12 The reaction between DMS and NO_3 leads to the formation of SO_2, MSA and traces of H_2SO_4. MSA and H_2SO_4 rapidly nucleate and form an aerosol. This Figure shows the evolution in time of the SO_2 concentration and of the total number, mean diameter and total volume of the aerosol. Calculations with IMAD3 try to simulate these experimental results in order to obtain information on the formation and growth properties of MSA-H_2SO_4 aerosols.

A theoretical investigation on the thermodynamic properties of sulphuric acid and methane sulphonic acid (MSA) particles has been performed, giving preliminary insight in the nucleation and growth properties of such particles. Using this information the model IMAD3 (Integral Model for Aerosol Dynamics) has been written for interpreting the experiments. The model tentatively explains the excess of MSA in the gas phase by a condensation and deposition rate of MSA which is much lower than that of H_2SO_4.

Our sectional aerosol model AERO2 has been further refined especially with respect to nucleation, condensation and deposition. AERO2 now serves as a reference for investigating the effect of the simplifications made in IMAD3.

The construction of the aerosol laboratory is proceeding. A 70 m^3 environmental room and an aerosol flow reactor have been designed and will be installed during 1992.

WATER QUALITY

Lake Orta

The metal dispersion study as described earlier (Annual Report 1989) had to be completed by the assessment of lake-internal metal remobilization rates, from which the last missing input component was to be derived for use in the model runs.
Dialysis chambers (sediment "peepers") implanted into the sediment by divers have been used for the *in situ* assessment of metal concentration in the open pores of the sediment, the sediment water interface and the first 20 cm next to the sediment.

Three series of experiments were carried out at the south and center of lake Orta near to the external metal sources and at the north of the lake near to its outlet river Nigoglia.

Results, expressed as net copper diffusive fluxes vary much with test site and test period. Yearly positive net fluxes measured four times during the year range from 7.4 to 163.4 µg Cu/m^2.d near to the outlet and between - 6.0 and 87.7 µg Cu/m^2.d in the southern basin.

Having completed the experimental work, the results of the different sampling campaigns, described in previous Annual Reports, have been analysed and discussed in the framework of a mathematical (trace metal distribution) model. This is conceived as a predictive tool concerning the evolution of the total metal (Cu) in lake-concentration, and flexible enough to treat the ecosystem either as a lake-sediment system, or as a epilimnion-hypolimnion system.

System characteristic times and asymptotic Cu concentrations have been referred to the properties of the lake water as ascertained before the "liming" experiment (water neutralization by addition of $CaCO_3$), which began in spring 1989. Nevertheless, a first evaluation of the short term effect of this experiment on the Cu concentration is included in the project.

The predictive calculations rely upon the assessment of the following parameters:

- mean residence time of water,
- meanresidence time of copper in the lake (involving the evaluation of the characteristic time of the sedimentation process),
- average total metal load after implementation of diversion measures (t Cu yr^{-1}).

The evaluation of these parameters includes discussion of the uncertainty due to the mean deviations of the basic measured quantities.

For the sake of completeness of the requested information, predictive calculations have been performed for a total metal load, a fraction of which, properly determined, was assumed to be supplied by internal loading (release from sediments).

The obtained results indicate that the lake-sediment system evolution is essentially determined by the lake properties as the external loading is predominant; and that, on an annual basis, the evolution of the epilimnion-hypolimnion system is essentially determined by the hypolimnion properties.

In both cases the characteristic time of the dominant transient is approximately equal to the mean residence time of Cu in the lake (about 5.5 yr). The metal in-lake concentration in equilibrium with the assessed "residual" Cu load results to be slightly above 30 mg m^{-3}.

A numerical model, solving the balance equations with time depedent coefficients, has been used to analyse the seasonal evolution of the epilimnetic Cu concentration, which shows oscillations with minima during summer stagnation. Finally, the anaytical model has allowed to interprete, to a satisfactory extent, the first experimental indications concerning short term effects of the liming experiment (i.e. a decrease of epilimnetic Cu concentration down to 10 mg m^{-3}).

Pollutant/Soil Interaction Studies

Water transport of pollutants in surface soil horizons is characterized by unsaturated water flow conditions. Effective simulation of unsaturated flow in column laboratory experiments has been realized applying negative pressures on the outlet of the columns using either vacuum chambers or peristaltic pumps.

Using unsaturated flow the long term release of vanadate from coal fly ash column and its retention by an underlying soil column has been demonstrated and followed in time by ion chromatographic analysis using UV detection at 254 nm.

Reactor neutron irradiation of coal fly ash allowed radioactive labelling of some of the toxic trace metals contained in the ash. A series of column leaching experiments with underlying soil columns of different length has been performed in order to determine the retention of these trace metals released from the waste material in the specific chemical form.

Fig.13 shows the grade of retention and partial breakthrough of some of these metals applying on underlying soil column. Employing ion chromatographic speciation analysis (conductivity or/and UV detector) it has been proven that As, Se, Cr, Mo, W contained in the aqueous phase are present as anionic forms.

A field site has been established consisting of 32 column lysimeters for large undisturbed soil core samples. This facilitates the study under realistic environmental conditions of soil chemical and physical parameters such as water contents pressure head, sorption/desorption of inorganic and organic chemical waste compounds. Small cup-lysimeters of porous teflon or ceramic materials are inserted at different depths allowing for periodic subsampling of leachate. Tensiometers are continuously measuring the pressure-head at different depths in order to monitor the water movement at unsaturated conditions.

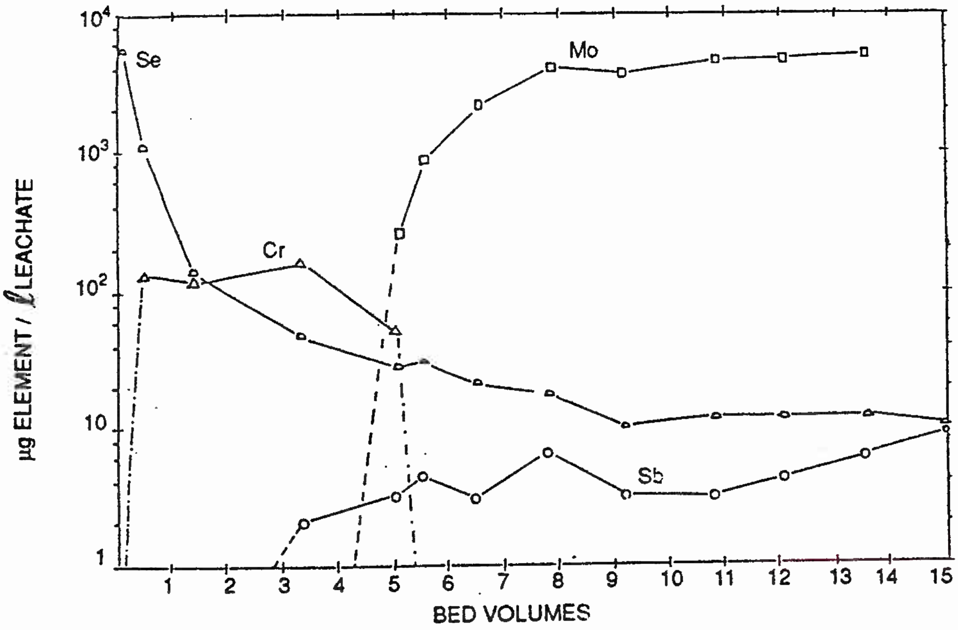


Fig. 13 Leaching and breakthrough of different elements from a coal fly ash column (6 g, d = 1 cm, 1 = 8 cm) superposed to a soil column (6 g, d = 1 cm, 1 = 5.4 cm)

The cup-lysimeters have been tested for inertness towards PCBs, atrazine and various trace metals. Teflon proved to be performing well with the most water soluble species but less well with PCBs.

The soil sorption of atrazine was studied in 110 different soil horizons from 24 different soil profiles all deriving from granodioritic materials . The soil 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 was speculated that coating of the clay by organic matter may mask sorption sites in the clay.

The soil sorption of PCBs is of major importance for their possible migration to ground-water. A series of experiments for the study of parameters determining soil sorption of PCBs was concluded. This resulted in empiric and QSAR models for the predictors of the behaviour of all 209 PCBs in a broad range of alluvional soils, a group of sandy soils specially vulnerable to chemical waste leaching to the ground water. Fig.14 shows the soil-water distribution coefficients predicted from GC-retention data (a) and molecular descriptors (b), versus the observed values.

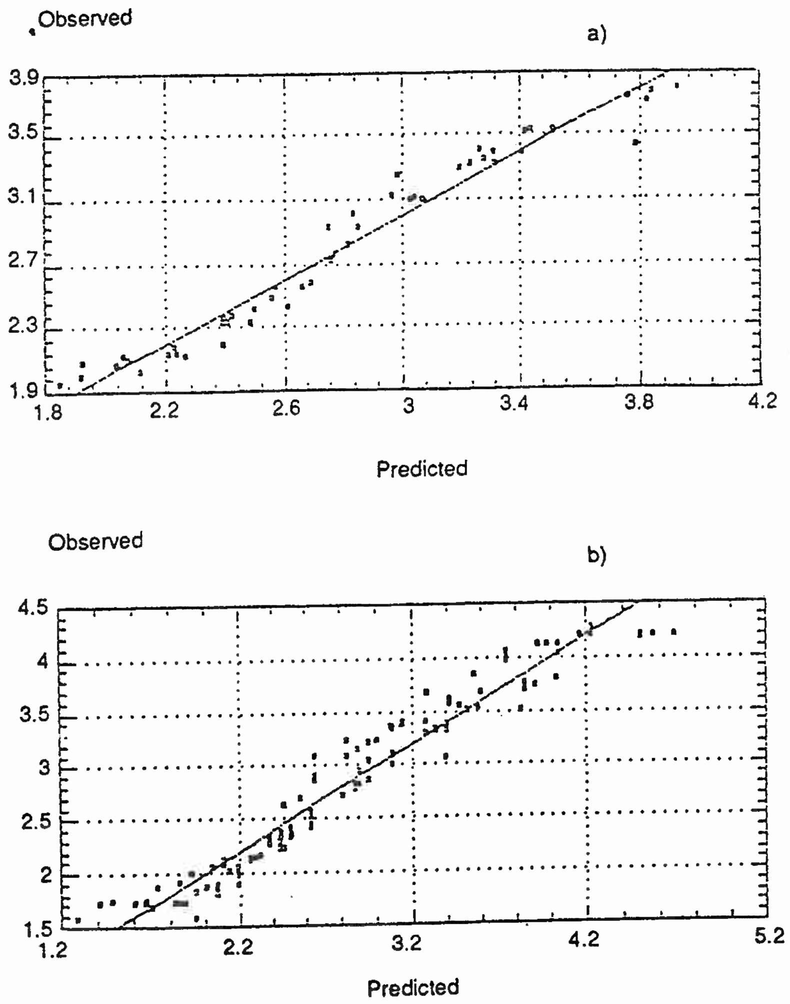


Fig. 14 **Prediction of the soil-water distribution coefficients for PCBs from: a) GC retention data end b) molecular describtions**

PCBs as chemical waste is one of todays' major environmental problems. It is estimated that 1.5 mio tons of PCBs have been produced in the past, of which one third is believed to be distributed throughout the environment and two thirds are still in circulation mainly in old electrical installations.

The congener and isomer specific analysis of PCBs by high resolution GC-ECD or GC-MS was studied. Methods were developed for the precise and accurate analysis of selected prevalent and/or toxic PCBs in environmental and technical samples. An important pre-normative result was the revealing of an interference for the detection of 2, 3, 4-2', 4', 5' hexachloro-biphenyl (PCB-138) existing in all examinated technical and environmental samples . A consequence of this finding is likely to be a modification of existing PCB legislation in some EC-member states.

A method for the interference-free determination of PCB congeners and isomers in waste soil was developed based on the selective extraction of aromatic species from an aliphatic matrix by dimethylsulphoxide (DMSO).

A method for the isomer specific analysis of persistent organochlorine compounds in top soils was developed for the quality control of six European Standard Soils .

A method for the organochlorine trace analysis by cyclic steam distillation and capillary GC was investigated for the analysis of non lipid matrices .

A sensitive analytical procedure was introduced for the trace-analysis of organochloride pesticides, PCBs and chemical waste products in lake sediments. This method was applied in the study of sediment cores from Lake Garda, as a part of a major investigation of the environmental conditions of the lake .

Concerning the basic mechanisms of interaction of inorganic pollutants in natural environments, time resolved Laser Induced Fluorescence was applied for studying metal complexation with humic substances (HS) in natural waters. This activity is carried out in the framework of the development of chemical sensors for remote control of aquatic environments.

Europium and Terbium have been used as probe elements due to their pronounced luminescence properties, and therefore low detection limit (10^{-8} M), also in the presence of high concentration of humic substances.

Spectrofluorimetric titration of lanthanides in the presence of metallic contaminants allowed the determination of loading capacities and complexation constants of HS with diamagnetic non luminescent elements like Cr (III) and Al, for which direct detection methods at typical natural concentration are not available. Values of $\log \beta = 6.40$ and 5.95 respectively have been measured at $pH = 5.5$ and 0.1M ionic strenght.This result corroborates the hypothesis that in the presence of HS the formation of chelates can alter substantially the environmental behaviour of Al and Cr (III) promoting their geochemical mobility.

These studies clearly indicate that fluorescent species of lanthanides with humic substances can be used for in-situ determination of complexing ability of natural groundwaters.

A second study concerns the examination of the absorption mechanism of Tl and Cr on selected mineral oxides by X-ray absorption spectroscopy (XANES/EXAFS) using synchrotron radiation. Some oxidation states of Tl and Cr are expected to be highly mobile in soils, nevertheless changes of oxidation state may occur at a mineral-water interface and alter significantly their geochemistry.Surface precipitation of TlO(s) was found to take place on MnO(s) as a result of surface oxidation of Tl(I) followed by precipitation of Tl(III) oxide at the mineral surface. Absorption of chromates on Iron oxides was at the contrary observed to be followed by partial surface reduction to Cr (III) induced by Fe (II) species generated by irradiation with light.

Sunlight-induced photoreduction may therefore favourably contribute to the lowering of the environmental mobility of Cr species, as well as MnO(s) inclusions in sediments may act as a sink for Tl species..

Environmental Informatics Studies

Environmental informatic techniques and applied modelling studies were performed in order to better assess pollutant impact on agricultural soil, groundwater quality and human food chain. A model and code based on a stochastic approach have been studied and developed. The approach focuses on the coupling of a sensitivity and uncertainty methodology with the previously implemented 2-dimensions deterministic water flow and contaminant transport. In the stochastic method simulations are repeated using the same deterministic model but employing a different set of input parameter values for each simulation. These values are generated at random from their respective probability functions employing Monte Carlo or Latin Hyper Cube techniques. The result of the research effort was the model designated as FEMSUN: Finite Element Model coupled with Sensitivity and UNcertainty analysis. Finally two programmes have been developed for plotting of the outputs in 2- and 3-dimensions produced by the model . The function of these programmes, named Plot-2D and Surf respectively, consists in the following:

- automatic generation of the finite element mesh able to represent site specific formations of a soil-ground water site system;
- water flow plottings including pressure heads, total heads, water contents and Darcy velocities;
- drawings of the iso-concentration contour levels which represent the contaminant distribution in time (2D);
- three dimensional graphs of concentration values at each point of the finite element grid.

The parameter estimate required in the implementation of the stochastic concept by the FEMSUN code, along with its ranges of variability, are determined through laboratory and field investigations, including:

- soil chemical characterization, in particular the study of Kd values by batch and column experiments,
- soil hydrodynamic characterization. The three most important parameters for characterizing the dynamic water flux through the unsaturated-saturated soil porous media are: the conductivity, the pressure head and the moisture content. Only by a good estimation of these parameters it will be possible to obtain a realistic evaluation of the dispersion movement of water and transported contaminants through the soil porous media.

For the hydrodynamic characterization of soils in cooperation with the Hydraulic Institute of the University of Grenoble a specific apparatus employing gamma-ray attenuation measurements in soil column experiments is under construction. Two gamma sources (241Am, 137Cs) of different gamma energy and a NaI-detector in the vertical direction are employed. The moisture content can be adjustable determined directly from the absorption of energy.Simultaneously the hydraulic pressure head is measured by a series of fixed ceramic cup pressure gauges at different points on the vertical axis of the column specimen.Finally, the hydraulic conductivity can be derived from the vertical moisture gradient and water flux. A data aquisition system with scanning measurement permits fully automatic measuring sequences. All the data are treated by a personal computer the construction of the mechanical components, lead shieldings and of the collimators have been already completed.

Waste Immobilization

The physico-chemical characteristics of cement and new matrix forms containing waste have been investigated.
The leaching behaviour of matrices, in which nuclear Medium Level Waste (MLW) or industrial hazardous waste are immobilized, represents one of the most important properties which characterize the retention capacity of the host material.

The influence of different conditions (curing for 11 days at 60°C, 98 % relative humidity or 28 days at 30°C and 60% relative humidity) and of leach test procedures (static water condition or water renewal) have been investigated.

The leaching of Cs and NO_3 immobilized in cement, indicates a release which is governed by a diffusion mechanism, irrespective of the different adopted procedures.

In all cases, a diffusion coefficient, De, of 1.5×10^{-7} and 2.5×10^{-8} (50°C) has been calculated for Cs and NO_3 respectively. The effect of the preparation procedure (variable amount of hydrating water, water-to-cement ratio W/C) on the leachibility of a soluble contaminant ($CsNO_3$) from cement specimens immersed in water, as well as the physical characteristics of the cement specimens,were also considered .

From the values of the fraction release (Fr) in water, the results of the investigation put in evidence the dependence of the leachibility on the porosity of the material, which in turn depends on the water-to-cement ratio, W/C, employed in the preparation procedure.

A granulation procedure has been implemented in order to improve the characteristics of the matrix immobilizing wastes . The granulation technology seems to meet the requirement of easily handling, transport by pneumatic conveyor and heating treatment in view of improving the leaching resistance and to decompose organic hazardous waste.

The feasibility of improving the retention capacity of chromium compounds immobilized in cement or clay matrices is being investigated.

Other Contribution

As a part of the studies on PCBs in oils of electrical installations, the OIL-PCB Manager (OPM), a support system for user decisions related to the management of PCB containing electrical devices, has been completed (version 1.0 Mac). It has been designed to:

- satisfy the needs connected with the entire information operating cycle, i.e.: collection, management, distribution analysis according to the present legislation;
- contribute to the standardization process in a natural, flexible and evolving mode in the context of telematic integration;
- coordinate planned actions for the prevention and/or mitigation of risk at installations, sites, containers, oils/fluids containing and/or contaminated by PCB above the allowed threshold limit (EEC Directive 89/677 = 50 ppm).

OPM has been adapted to meet the requirements laid down by the EEC Directive of PCB and its enforcement in Italy. Its distribution and application support is guaranteed by SEA Marconi Technologies S.A.S. - 10093 Collegno (TO), Italy - Tel. 011/7731477 - Fax 011/77311384.

ENVIRONMENTAL STUDIES IN THE MEDITERRANEAN BASIN

MITO Project

Within the frame of its environmental studies relevant to the Mediterranean Basin, the JRC has promoted, in close collaboration with Institutions of five Member States (Portugal, Spain, France, Italy, Greece) the development of a Joint European Project on algal blooms, i.e. the MITO Project.

The project mainly addresses the characterization, identification and quantification of algal blooms with particular emphasis to the phytoplanktonic species producing toxins. Algal genera considered in the proposed project are *Alexandrium*, *Gymnodinium*, *Prorocentrum* (for marine waters); *Prymnesium* (for brackish waters) and *Microcystis* (for freshwaters). More specifically, the MITO Project focuses on:

- *Analkytical Cytology of Phytoplankton*: to develop fast and easy-to-use systems for the detection, enumeration and characterization of phytoplanktonic populations at the cellular level and to detect changes in populations structure associated with environmental factors.

- *Aquatic Biotoxins*: to develop alternative , sensitive and adequate methods for toxin detection, to study biotoxin production mechanisms and to develop monoclonal antibody against principal toxins.

- *Algal Taxonomy and Physiology*: to recognize the exact taxonomic position of toxic or potentially toxic bloom agents, to study the biological cycle of selected species, to ascertain the effect of environmental factors on growth and toxin production of selected strains and to explore the application of biochemical indices for the evolution of the physiological state of algae.

- *Prediction of toxin occurrence:* application and/or development of hydrodynamic, transport and biological process models to provide a tool for the prediction of toxin occurrence, distribution and ecosystem effects.

These studies should lead to a better understanding of the role of the cell cycle in toxin production and of its interaction with the aquatic environment. Interactions between Flow Cytometry (FCM) and image analysis techniques, ecophysiological laboratory studies, remote sensing and image analysis of large areas, where algal bloomings occur, could contribute to partially remove the problems and guide Authorities to undertake a substantial programme of environmental restoration. Field experiments, coupled with modelling studies, serve to provide adequate data to construct an useful tool for the prediction of toxic blooms and to develop a decision support instrument for water quality management in relation to toxic blooms. Possible test sites which have been firstly selected are in the Northern Adriatic Sea, in the Ebre Delta and in the coastal area of Saronikos Gulf. Field surveys will be performed in connection with local environmental agencies.

Analytical Quality Control and Error Assessment Studies

There is an urgent need for objective, reliable and comparable information at Community level on the contamination status and the present trends in contaminant dispersion from point and non-point sources and subsequent accumulation in the foodwebb.

The quality of such information depends upon the reliability of data,derived from complex measurement processes, which need to be interrelated for use in decision processes at Community level.

Observed measurement uncertainties, assessed on the basis of collaborative studies, demonstrate, that the results of the majority of laboratories participating in such studies are influenced by remarkable systematic and random errors and the conclusion is that environmental analytical data are hardly comparable unless specific proof from well designed and consistently implemented measurement quality control and assurance programmes is offered.

Objectives of the project are:

- to explore the present status of measurement quality for selected and critical analyses and matrices;
- to identify, quantify, and eliminate measurements errors;
- to introduce stepwise elements of analytical quality assurance.

The JRC organized on 14-15 March 1990 a meeting with experts in the field of environmental analytical chemistry from Italy, Greece, Spain, Portugal and France.
To identify specific needs and requirements and on the basis of information collected, a joint programme has been established for the next years and discussed on the second meeting 13-14 December 1990.

Agreement was reached on the need to harmonize measurement methods amongst the EC-member country calls, besides the laboratory-based part of the mesurement process for the organization of field-related collaborative studies. Sampling procedures have been shown to constitute major error sources in environmental trace analysis and deserve critical examination and refinement by laboratory collectives.

Most critical in this respect are the sampling procedures for both trace metals and organic micropollutants in water.

The extended and qualitatively very inhomogeneous group of laboratories running environmental analyses, for a number of different reasons, requests, first of all, an assessment of measurement quality, advice and practical help on the way towards measurement improvement.
The problem areas, with respect to analytes and matrices have been identified by the national delegates and, not surprisingly, there is a consistent agreement with the requirements of the EC Directive development (List I and II substances).

The first collaborative field study project will deal with sampling error quantification, spatial variability assessment and offer sampling and analysis under quality control conditions to the participants.

The following subprojects have been designed:

Subproject 1: Collaborative sampling error assessment study "Trace metals in seawater"
Subproject 2: Interlaboratory comparison: "Total mercury and organic mercury species in fish"
Subproject 3: Interlaboratory comparison "Trace metals in sediments"
Subproject 4: Interlaboratory comparison "Persistent organochlorine compounds in sediment"
Subproject 5: Collaborative sampling and analysis field study "Organic compounds in water".

A number of further subprojects, both collaborative field and laboratory studies, are under discussion and will be defined in the first half of 1991.

The test materials for the subproject 2 (tuna fish muscle), subproject 3 (high-metal sediment) and subproject 4 (high-organic contaminant sediment) have been prepared and are ready for mailing.

FOOD AND DRUG ANALYSIS

The aim of this activity, so far limited to foods, is the development of a European Laboratory to support, where necessary, EC sectorial policies on agriculture, consumer protection, custom tariffs etc.The laboratory, the implementation of which started in 1988 and is now definitively installed in two renewed buildings, has been equipped with analytical techniques, such as : NMR, IR, HPLC, GC, IC, Capillary Electrophoresys, Polarimetry, Refractometry, Elemental Analysis, Microscopy, Enzymatic and Immunological methods, classical food analytical methods, and

Microbiology. Moreover, other existing analytical facilities of the Environment Institute will support this activity when needed.

The activity of the laboratory in 1990 has been focused on the detection of "sugaring" of wines (chaptalization) by Nuclear Magnetic Resonance (NMR), (Martin's method); about 500 samples on Franconian wines have been investigated.

The influence of different yeast varieties on the D/H ratios in the corresponding ethanols have been studied in collaboration with Prof. Scholten at the Landesuntersuchungsamt Trier (Germany).

A particular effort has been devolved on the accuracy and repeatability of the Martin SNIF method, taking into account the purity of the wine distillates (ethanol) and the stability of the tetramethylurea (TMU) employed as NMR internal standard. It has been shown that the distillates can contain up to 0.5% volatile compounds other than ethanol and the water content of TMU is rising in use, thus a weight correction in both cases is necessary to obtain more accurate reuslts. The identification of oxidative degradation products in TMU is under investigation.

As far as it concerns the development of the databank for the NMR fingerprints of the European wines, the new 1990 samples are being analyzed by the different laboratories of the Member States producers of wine.

The determination of inexpensive sweeteners (beet medium invert sugar, beet invert sugar, high fructose corn syrup, white grape concentrate) in citrus juice fruits has been performed using the new Low's method; about 50 different samples originating in the EC market have been analysed.

Dr. Low, from the University of Saskatchewan (Canada) has spent seven months in the Environment Institute as visiting scientist; this method is in the process of being published in AOAC Journal and is currently in use on a routine basis by the Florida Department of Citrus and the Food and Drug Administration (USA).The extension of this method to the detection of "sugaring" of wine, which he started in Ispra, is still in its infancy and will require further experimentation.

Worth mentioning, in the field of dairy products, the determination of phytosterols in butter oil by capillary gas chromatography; the separation and determination of cholesterol, β-sitosterols, stigmaterols, campesterols and lanosterols allowing the detection of vegetable oils added to milk fats;the preliminary test of fatty acids and triglycerides profile in pure milk fats by capillary gas chromatography;the separation of λ, β and γ caseins in goot's milk and cow's milk by capillary gas chromatography and gel isolectric focusing.

Further, the detection of soya proteins in meat preparations using PAGE-SDS electrophoresis, optical microscopy and enzyme-linked immuno assay and some determination of common wheat in durum wheat flours by gel isoelectric focusing (by the request of the Consumer Protection Service) have been carried out.

A microbiological laboratory for the control of foods has been set up and a suitable programme proposal established.

In collaboration with the Commission's Department of Agriculture, Consumer Protection, Industrial Affairs and Internal Market detailed programmes for the future period 1992-1994 have been established.

Analytical Work

On 1990 ca 9000 samples (34.000 parameters) originating for the most part (ca 90%) by Environment Institute research activities have been analysed. The wide ranging nature of the analysed samples included waters (lake, fluvial, marine, meteorological precipitations etc.) sediments, soils, air and water particulate, leachings, alloys, gases, liquid wastes, superconductors etc.

The most employed analytical techniques have been :IC, UV-vis Spectrophotometry X-Ray Fluorescence and Diffraction, GF-AAS, AAS, Elemental Analysis (C, H, N, O), TOC, A.S.V., Potentiometry, other electrochemical methods, classical wet chemistry etc.

1.2 Radioactive Waste Management

The contribution of the Environment Institute to this programme concerns the assessment of the long term safety of waste disposal in geological formations under conditions presently studied in the European Communities. Both theoretical and experimental activities contribute to the objective.

RISK ASSESSMENT

The activity deals essentially with the development of probabilistic codes for safety assessment and their application to specific projects.
The year 1990 saw the closure of this activity. An attempt was made to finalize the on-going works, especially as far as code development is concerned. The LISA package represents the main realisation of the JRC in the field of computer studies for nuclear waste disposal. The package, which consists of a pre-processor (PREP) a main code (LISA) and a post-processor (SPOP) has been distributed through the OECD-NEA data bank of Saclay to about twenty international institutes or organizations. It has been tested through a benchmark campaign held within the PSAC (Probabilistic System Assessment Codes) user group. During 1990 the manual of the last release of the SPOP utility has been finalised . The manuals of the last releases of PREP and LISA are being finalised. The geosphere transport module has been upgraded .

In the same year the participation to the activities of the PSAC came to an end. A revision was made of the report documenting the benchmark "Level 1A", a code intercomparison exercise which is the last of a series conducted within the PSAC user group. This body is coordinated by the Nuclear Energy Agency (NEA) of the OECD. The JRC has been one of the promoter of the group in 1985, participating with LISA to the benchmark campaign.

A cooperative research was undertaken in 1990 with the Japan Atomic Energy Research Institute of Tokai to conduct an investigation on the performance of nonparametric tests to be used for sensitivity analysis of model output. The conclusion of this study can be summarized as follows:

- a new (in house) version of the "Importance Measure", a nonparametric test for sensitivity analysis, was devised in order to make the calculation more computer efficient.
- in its original version the "Importance Measure" seemed indeed resistant to model non-monotonicity, as pointed out in a comparative analysis of the performances of this technique against other nonparametric estimators. On the other hand the method appeared to be affected by poor reproducibility.
- a simple manipulation of the method, involving rank transformation of its input, was found to produce an estimator whose accuracy was in average better than that of the other investigated nonparametric tests, while retaining its favourable characteristics of indipendence from model non-monotonicity.

Laboratory Studies

Long term migration experiments, at different residence time, of Pu and Np into soil columns are still underway in order to clarify the nature of mobile species. In parallel systematic studies on actinide behaviour in solution containing suspended particles were carried out.

Although the significance of humic (HA) anf fulvic (FA) acids to bio-geochemical processes in water environments has long been recognized, knowledge of their interactions with radionuclides in multicomponent systems, in the presence of solid adsorbents, is relatively limited. The radionuclide potentially released from nuclear waste matrices may sorb on particulate matter coming from the degradation of the waste packages and on natural colloids present in the leaching groundwater.

The adsorption behaviour of Am(III), Th(IV), Np(V) and Pu was investigated in multicomponent systems containing gamma-alumina or amorphous silica as model inorganic particles, and polydispersed HA colloids isolated from an organic-rich clay formation.

Surface coordination of tri-, tetra- and pentavalent actinides with hydrous mineral oxides follows the same tendency observed for complex formation with hydroxide ions in aqueous solutions. The sorption selectivity of the actinide ions on bare mineral oxide particles can thus be explained on the basis of the hard-soft Lewis acid-base behaviour. The geochemical pattern of actinides in mixed HA-mineral oxide systems is likely determined by the HA affinity toward the surface. An enhancement of actinide uptake onto the solid phase occurs in the presence of adsorbable HA which strongly compete with unadsorbed organic ligands for metal complexation.

Competition experiments using HA indicated that the extent of actinide adsorption depends on the coordinating strengths of HA on the surface and in the solution.

Nevertheless, natural waters are multicomponent systems where trace metals and major cations compete for binding sites available on humic compounds. Various dissolved contaminants of anthropogenic origin can also act as chelating ligands and alter the bio-geochemical pathway of metals. Moreover, because of the existence of chemical and physical gradients, these multicomponent systems are dynamic rather than in condition of equilibrium. Kinetic methods of speciation then provide a better approximation of the kinetic behaviour of metal species in natural waters.

The kinetics of ligand displacement reactions in the multicomponent system Tb-Humic Acid-EDTA-Ca at pH 8.5 was studied by Time Resolved Laser Induced Fluorescence. Two kinetically distinguishable components of HA were identified. The rate of Tb mobilization with EDTA from the TbHA chelate was found to decrease considerably in the presence of Ca and with decreasing Tb concentrations. The rate determining steps of the reactions are the transformation of the mixed ligand complex intermediate Tb-EDTA-Ca and the Tb dissociation from the slower reacting component of HA.

Field Investigations

The geochemical and hydrogeological characterisation of shallow geological formation was pursued in both porous and fractured media (JRC-Ispra and El Berrocal-Spain). The work on the JRC experimental site aimed at optimizing the hydrodynamic conditions necessary to set up tracer tests. To this end pumping tests have been performed changing both the abstraction rate and depth. Due to the high content of silty-sandy component in the groundwater, submersible pumps of different power and efficiency have been used. The most appropriate conditions for the experiment have been defined applying a flow rate of 3.3 cubic metres-hour at a depth of about 40 metres. This allows a conservative tracer test to be carried out at a mean rate of 10^{-5} m/sec. Taking into account all the parameters involved (well's geometry, dispersivity, etc.) the tracer peak would be expected about 80 hours after the injection.

Concerning the field investigation at "El Berrocal" site, a second campaign has been performed to verify the preliminary work in the boreholes, in particular hydraulic connections based on the initial geochemical and geophysical data. Some peculiar aspects observed during the previous campaign have been confirmed: negative values of redox potential measured below 40 m depth in borehole n07 appear constant in time; the water geochemistry in the same well shows the presence of Fe(II) and sulphide ions. However, iron bearing minerals are uniformly distributed along the granite core, so that the sudden decrease of Eh in correspondence with a breccia zone at about 40 m depth indicates a ground water seapage from permeable fractures. Whether this water is in equilibrium with the granite still has to be clarified. This well shows discernable sensitivity to the level fluctuations imposed in borehole n01, seven metres away, which would indicate the existence of hydraulic connections between the two. Their different solution phase geochemistries, however, do not seem to corroborate this hypothesis.

A further activity, focussed on the measurement of Sr-85 diffusion coefficient in water-saturated clay, involves combined lab-field experiments. Clay samples of different length will be immersed in groundwater spiked with Sr-85 contained within a sealed probe. The system will be placed 30 m. depth within a borehole.

The operating principle is the following: the probe is placed inside the well and the porous material is equilibrated with the water at the selected experimental level. The reaction vessel is equiped with openings toward the outside which can be opened or closed utilizing the hydrostatic pressure inside the well or an external gas pressure. In the open position the geological material is at first allowed to equilibrate with the groundwater then, after closure, the radionuclide is released by remote control by breaking of a glass bulb containing it.

This experiment, which will be performed in collaboration with the CEN-Cadarache, is required to be carefully planned by laboratory tests. Tracer concentration, expected diffusion times, sample preparation and characterization as well as safe recovery procedures, have been controlled in the laboratory before launching the field experiment.

2. S/T Support to Community Policies

2.1 Chemicals

The work in support of the Commssion's activities in the sector of chemicals evaluation and control focussed on certain aspects of risk assessment, testing methods (soils) and on the publication of the EINECS (European Inventory of Existing Chemicals Substances) inventory.

The official version of the EINECS-inventory has been published in the Official Journal of the EC in June 1990 in all Community languages. The Ispra team has also contributed significantly to the correction and updating of Annex 1 of the Directive which lists substances which are subject to classification, labelling and packaging rules with a view of publishing an updated version of Annex 1 (including more than 1500 substances) in the Official Journal in 1991. In order to stimulate the development and application of general criteria and principles for the environmental hazard and risk assesssment of chemicals in the context of Directive 79/831/EEC, a workshop has been organised with DG XI at Ispra in October 1990 with the participation of industry representatives, research institutions and the competent authorities for the Directive in the member States. Development work and validation efforts for promoting the application of quantitative structure-activity- relationships in screening chemical risks was stepped up significantly. In this context, models for the estimation of physicochemical properties, environmental distributions and acute toxicity have been evaluated. A study for grouping about 10.000 existing chemicals from the EINECS inventory according to structural similarities is in progress. In the frame of the JRC "Eurocourse" programme, a five-day course was organized in June 1990 entitled "Practical Applications of QSAR in Environmental Chemistry and Toxicology". The lectures were published as volume 1 in the "Chemical and Environmental Science Series" in May 1990 (Kluwer Academ. Publ.).

In the area of testing methods, testing of the six European reference soils with the test chemicals atrazine, lindane and 2,4-D was continued with special emphasis on absorption kinetics. Sorption coefficients reference points for the long-term storage stability of the EURO-soils were determined.

Finally, a workshop was held in December 1990 at Ispra to evaluate the European ring-test concerning adsorption/desorption of chemicals on soils.

In the frame of the EC programme "Europe against Cancer" and in support of DG V a second review volume under the title "The toxicology of chemicals- carcinogenicity. Summary reviews of the scientific evidence" has been published under the supervision of the Environment Institute.

For various other services of the Commission, assistance and scientific advice was provided in planning and establishing new data bases. For instance, a feasibility study was completed for the development of a specific data bank for pharmaceutical products which are on the market in the EEC. Another project concerns the development of a PC data base for hazardous substances in water in the context of directive 76/464/EEC.

2.2 Waste

A major investigation was completed for DG XI on analytical procedures for the rapid determination of PCBs in waste oil. It was demonstrated that existing official procedures in EC member states use frequently old and non-effective techniques. An analytical method was described that may serve in an official EC protocol in context of the PCB chemical waste directive.

The proposed method was successfully used in an interlaboratory certification exercise arranged by DG XII, BCR.

A further development is carried on, and it takes into consideration a new instrumental method. The study will be completed by the end of 1991.

2.3 Water Quality

JRC scientific expertise is made available to DG XI to support the implementation of existing EEC Directives and to contribute to the development of the new ones. The main achievements are the following:

- scientific assessment of EC Standards for Drinking Water Quality: monitoring, frequency and reference methods of analysis;
  This work considers and compares, how Member States have transferred in their own national legislation the procedures regarding surveillance and analytical monitoring, included in Annexes II and III of EEC Directive 80/778. Furthermore, a critical review has been conducted about many parameters to update the Annex III (reference analytical methods).
- draft directive related to the ecological quality of the Community waters;
  Classification matrices for lakes have been proposed for decisions of the Commission and comunication to the national experts.
- identification of suitable water quality objectives for phosphorus in running and lacustrine waters;
- environmental compatibility of possible non-phosphate detergent builders.

A further study concerns the 132 substances (and/or groups of substances) contained in the List 1 of the Annex to the Directive 76/464/EEC.
In 1990 the development of a PC data bank containing the information on these substances was started. Such a bank should enable the users to receive rapid information concerning the physico-chemical and toxicologic characteristics, production data, etc.

For the major part of the 132 substances (and/or groups of substances), written scientific reports are available. When the report received a scientific opinion, a data sheet was developed, subdivided into two sections:

- The first one should contain basic information, building-point, toxicity for rats. (Data sheet of "De Bruin").
- The second one contains additional information, eg. effects on human health.

This data sheet was prepared on a PC data bank (SUPERBASE for WINDOWS) but the records are still empty.
Afterwards the substances on List 1, which are in the files of ECDIN, were identified. Most substances are present but it is necessary to complete the information, for example, by using the reports.

Studies on the impact of trace elements (list I and II substances) from non-point and point sources on the aquatic environment have also been continued.

Major non-point sources considered in the studies were atmospheric dry and wet deposition, surface runoff, sewage work effluents, spreading of sewage sludge on agriculturally used land, leaching from waste deposits and remobilization from sediments.

Studies on the non-point sources of Cu, Zn, Ni, Cr, As, B and Mo have been completed, while Be, Tl and Sb are actually in progress.

Typical results are total discharge rates calculated for the Community as 360-740 t/y of Cr, 3380-4460 t/y of Cu and 5840/10260 t/y of Zn released to the aquatic environment from non-point sources. Domestic sewage and runoff can be regarded as the major sources.
With regard to point sources, input quantification is much hampered by the extremely scattered information concerning the specific industrial production and correlated release.

Up to now studies on point source quantification of Cu, Zn and Ni have been completed and reports on Cr, As, B and Mo are expected to be ready in 1991. For the elements Cu, Zn and Ni the input from point sources is estimated to 924 t/y, 2560 t/y and 738 t/y, respectively.

2.4 Atmospheric Pollution

Central Laboratory of Air Pollution

Harmonization programmes for current directives

In the frame of the Directive 80/779/EEC on sulphur dioxide and suspended particulates, two expert groups have been set-up for the elaboration of instruction manuals at the use of network stations.

As a practical outcome of the 1st Joint Measurement Programme (JMP) organized in previous years, the manuals will give guidelines and describe the harmonized procedures for SO_2 and Black Smoke monitoring. The Central Laboratory is responsible for the coordination of the work carried out by the experts and for the editing of the manuals.

In the frame of the Directive 85/205/EEC on limit and guide values for NO_2, a second JMP has been worked-out in collaboration with the Member States. The programme foresees the following actions:

- elaboration of a test procedure for NO_2 monitors;
- intercomparison of different NO_2 primary calibration standards;
- a quality assurance programme (QAP/1) for calibration procedures implemented in the Member States;
- a quality assurance programme (QAP/2) for routine NO_2 measurements in EC networks.

Discussions have been initiated for the selection of a test procedure for NO_2 analysers.

A new technique for the preparation of primary calibration gas mixtures by static volumetric dilution has been set-up. A bench designed to control the reliability of the different NO_2 permeation sources used in national laboratories for calibration of network instrumentation, has also beeen developed.

Station and Network Design

As a result of the second Quality Assurance Programme for SO_2, a Test Atmosphere Generator (TAG), able to generate multicomponent gas mixtures at the inlet of the sampling lines of network stations, has been designed and manufactured; it will be implemented in the next JMP.

For the reassessment of urban monitoring networks in European cities, three campaigns have been performed using the passive diffusion tube technique. This technique, making use of relatively inexpensive and easy to handle devices, allows to map the NO_2 distribution over large areas. In the case of the new design of the Paris network, managed by AIRPARIF, a survey of the NO_2 concentration in the city area has been accomplished following a 6 month campaign performed in the second half of 1989. This study has been pursued by a 3 month campaign performed in spring 1990 in the Rouen-Le Havre area, in collaboration with ALPA-REMAPPA (Laboratoire de Pollution Atmospherique en Basse Seine). In summer 1990 a monitoring campaign has been initiated in the Greater Madrid Area. In this last case, during two weeks in November, in situation of thermal inversion, a mobile unit of the Environment Institute has mapped the pollution distribution at ground level (SO_2, NO_2 , NO, CO, suspended particulate) and aloft (as vertical burden of NO_2 and SO_2) in industrial, commercial, pedestrian and recreational areas. The survey, including also the calibration of two monitoring stations in the centre of Madrid, intends to add information to those available from the urban network recently put into operation.

EMEP Monitoring Programme

The evaluation and Monitoring European Pollution (EMEP) Programme is a Cooperative Programme for Monitoring and evaluation of the Long Range Transmission of Air Pollutant in Europe. It is carried out under the auspices of the Economic Commission of Europe (ECE) and the Unit Nations Environment Programme (UNEP). Its main objective is to provide Member States with information on the concentration and deposition of air pollutants and on the quantity and significance of pollutant fluxes across national boundaries.

By the end of 1990 EMEP data were being collected about 100 measurement sites in 24 European countries. Following the Council Resolution No. 81/462/EEC, article 9, DG. XI, proposed an active participation in this programme by establishing an EMEP monitoring Station at Ispra. Since November 1985 this Station has operated on a regular basis in the extended measurement programme and data are transmitted monthly to the Norwegian Institute for Air Research (NILU) for the statistical evaluation and to DG. XI for information.

The following parameters are measured:

- *in air*: O_2, NO, NO_2, O_3 and CO, continuously; HCl and NHO_3, NH_3 non- methane hydrocarbons, methane peroxyacetylnitrate (PAN) and organic acids occasionally ;
- *in atmospheric particulate*: SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, TSP and acidity on daily acidly basis. Heavy metals are measured with 7 days sampling periods;
- *in precipitation samples* (wet only): SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, pH, electrical conductivity and strong acidity on daily basis, organic acids and heavy metals occasionally;
- *meteorological parameters*:direction and speed of wind, temperature and relative humidity of air, atmospheric pressure, rainfall and solar radiations solar radiation continuously.

The detailed results of all collected data for each year are reported in the corresponding Annual Report.

Various collaborations at different levels have been undertaken:

At regional level: all the data are sent on a monthly basis, to the Municipality of Varese (in order to have informations on the monitoring of a semirural region);

At national level: as participants of the Italian network atmospheric deposition (RIDEP) data of atmospheric precipitations, based on weekly sampling as requested, are transmitted to the Italian Ministry for the Environment through the Istituto Idrobiologico di Pallanza;

At international level: participation to the intercalibration programme on PAN measurement organised by NILU and sponsored by EEC. In this activity eleven European laboratories are involved. Preliminary work concerning the preparation of PAN standard (in organic liquid medium) has been undertaken. Concentrations between 700-100 mg/l. have been obtained and their control by I.C. and IR seem to give valuable results.

Collaboration with EMEP Station not yet equipped with on line NO_2 monitors to extend the use of inexpensive diffusion tubes for NO_2 monitoring The concentrations of the most important pollutants in air (SO_2, NO_2 and O_3) measured at the JRC EMEP Station during the last five years as monthly averages are reported in Fig. 15.

We can observe (Fig. 16 and 17) the SO_2 decreasing concentrations and the NO_2 increasing concentrations starting from 1986 till now.

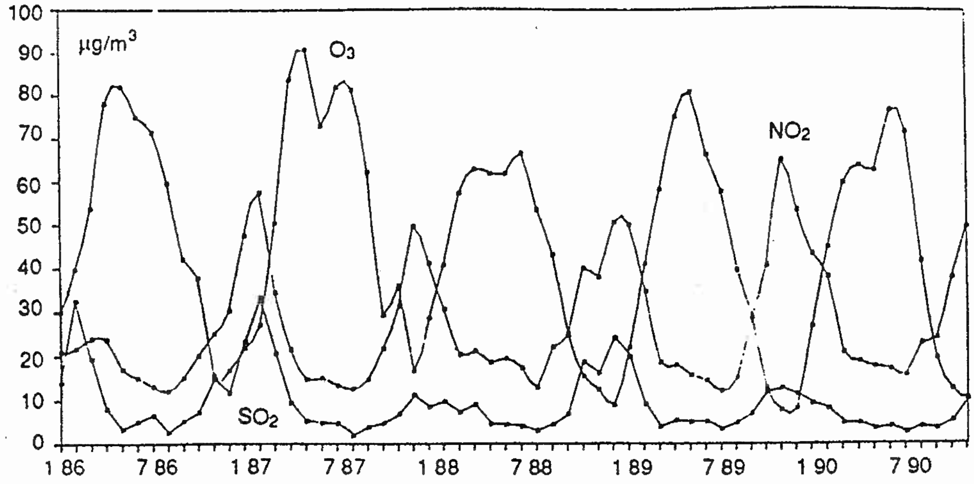


Fig. 15 Monthly average concentrations of pollutants in air January 1986 - December 1990

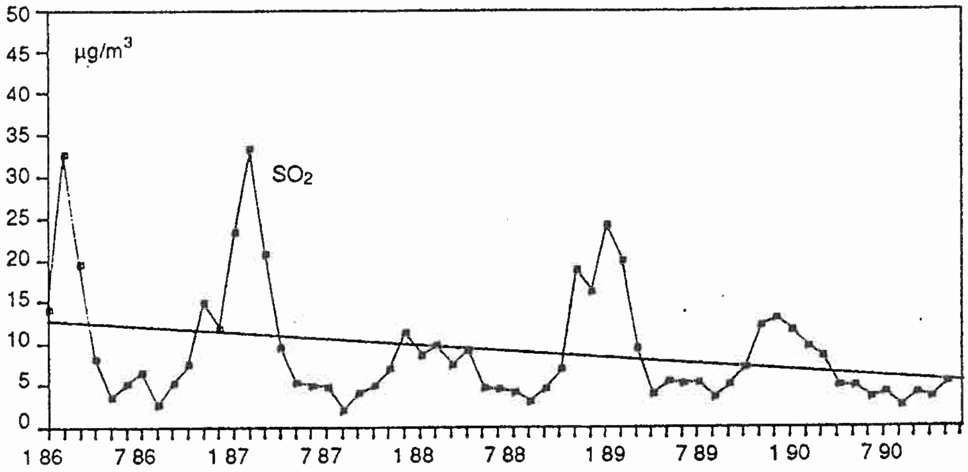


Fig. 16 Monthly average concentrations and trend of SO$_2$ January 1986 - December 1990

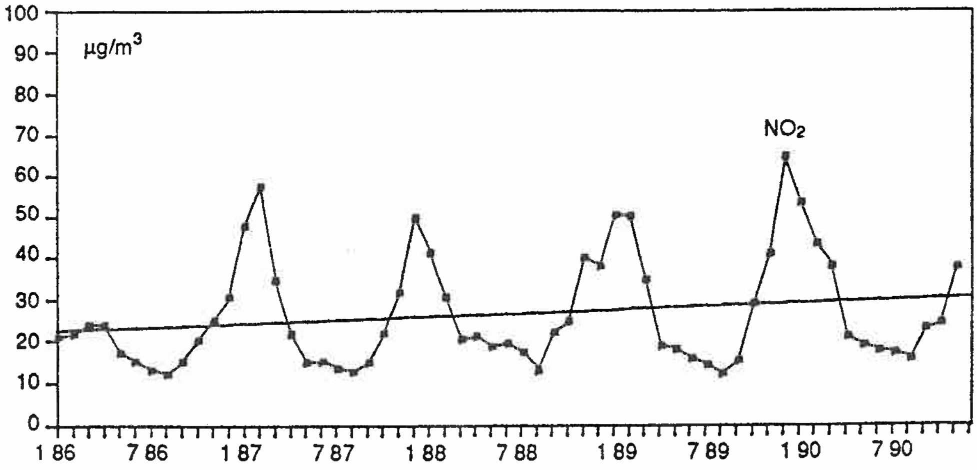


Fig. 17 Monthly average concentrations and trend of NO$_2$ in air January 1986 - December 1990

Support for the Implementation of Directive 87/217/EEC Prevention and Reduction of Environmental Pollution from Asbestos.

Participation in developing a standard method by ISO for the determination of fibre emissions from asbestos plants. The revised draft ISO DF 10397, concerning a standard for the determination of asbestos plant emissions by a fibre count method has been made and recently submitted to ISO for dissemination as a draft international standard (DIS).

All the necessary equipment, including sampling apparatus for the determination of the number concentration of airborne inorganic fibres by phase contrast optical microscopy using the membrane filter method has been set up. The acetone vaporiser using the acetone-triacetin method for clearing and mounting slides for asbestos determinations has been experimented.

Collecting informations about the procedures and the methods applied in the various Member States for the determination of asbestos in air has been started. During this considered period contacts have been taken with UK and FRG experts.

2.5 Radioactivity Environmental Monitoring (REM)

Following the Chernobyl accident, the Task Force created by the Commission in may 1986 evidenced the opportunity of storing in an easily accessible form the large number of radioactivity measurements performed in Member Countries as well as elsewhere. The task of collecting the data in form of a data bank was given to the JRC. The task evolved into a more general activity dealing with environmental radioactivity monitoring and assessment of occupational radiation exposure.

REM consists of 3 main lines of research, which are closely linked together, with the basic goal to improve the overall preparedness of CEC in case of a nuclear accident :

- data bank development,
- modelisation of the atmospheric transport and dispersion of the radioactive nuclides,
- quality assurance of the radioactivity monitoring techniques, and experimental studies to improve input data of the models.

Data Bank Development

REM data bank

The actual total number of data records stored in REM exceeds 380,000; of these about 280,000 are currently available to external users via the network connection to REM (X.25). Information held by the bank covers data from the 12 E.C. member states, as well as other European Countries for both environmental samples and foodstuffs. 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 will be released at the beginning of 1991. Significant changes have been made to REM for this new version including the addition of new fields, improved codings, an extended user interface, as well as the inclusion of new data.

REF data bank (Radioactive effluents)

The radioactive effluent releases from nuclear installations have been collected on a PC-based data bank for the period 1977-1986

The information is used to prepare summarising periodical information documents by D.G.XI-A1.

REX data bank (Radioactive exposure)

The bank stores information on the radiological exposure records of personnel working in nuclear installations, classified according to a set of jointly established parameters. The bank, which was originally made on LOTUS spread sheets has been converted to UNIX-ORACLE.
Procedures for data input were prepared in 1990, including conversion of old data in the new format. The bank can presently be interrogated using the standard SQL language. Simplified procedures based on menus and presentation of results in tabular and graphical form will be prepared in 1991.

RIS data bank (Radiological inspections)

The Commission decided in 1989 to implement the right of inspecting the facilities for monitoring radioactivity in the environment around nuclear installations foreseen by the CEEA Treaty. Results will be stored in an appropriate data bank. Only preliminary investigation of the bank structure were made in 1990, pending a final decision on the implementation of the inspection.

The four data banks will eventually be merged into one, when a final set up of the informatic structure linking JRC to DGXI-A1 in Luxemburg will be reached.

Models of the Atmospheric Transport

In the field of modelling the atmospheric transport of radionuclides following a major nuclear accident, most of the effort was devoted to the conduction of the ATMES (Atmospheric Transport Model Evaluation Study) project. The study, which is carried out in cooperation with WMO and IAEA with a financial participation of both Agencies, is reported in section ASTMES.

In addition, the following studies were conducted :

- Fractal geometry has been applied to the Chernobyl deposition of Cs-137 in W-Germany. It was proven to be a very useful tool for characterising the observed patchiness and hot spots. The deposition was shown to be multi-fractal, leading to the conclusion that hot-spots with concentrations higher than the intervention levels might not have slipped through the monitoring net undetected.
- Fractal analysis has further been applied, together with more classical techniques for evaluation the monitoring capability of the European (=sum of national) real-time monitoring network of airborne radioactivity. This resulted in a rough delineation of the conditions under which the data from the network can be interfaced with predictive long range transport models (see below).
- A study on the use of real-time monitoring data of airborne radioactivity for updating long-range transport models came to an end. The result is a procedure to interface monitoring data with model calculations that could be implemented in the Commission's rapid information system ECURIE. The procedure has been tested and illustrated using the REM Chernobyl data base. In this case it resulted in an improvement of the location of the radioactive cloud with up to 500 km and with an improvement of the absolute concentrations up to a factor of 10 (after a travel distance of 3000 km) (see Fig.18)

Quality Assurance of the Radioactivity Monitoring Techniques and Aerosol Research

Data Quality Objectives have been developed for the monitoring of radioactivity in the environment, leading to a number of CEC proposals for harmonizing environmental radioactivity monitoring in the EC Member States. This work was presented and discussed at the meeting of the national experts of EURATOM Articles 35-36, resulting in the creation of two working groups on the matter.

The construction of the aerosol laboratory came to an end. A 70 m^3 environmental room and an aerosol flow reactor have been designed and will be installed during 1991.

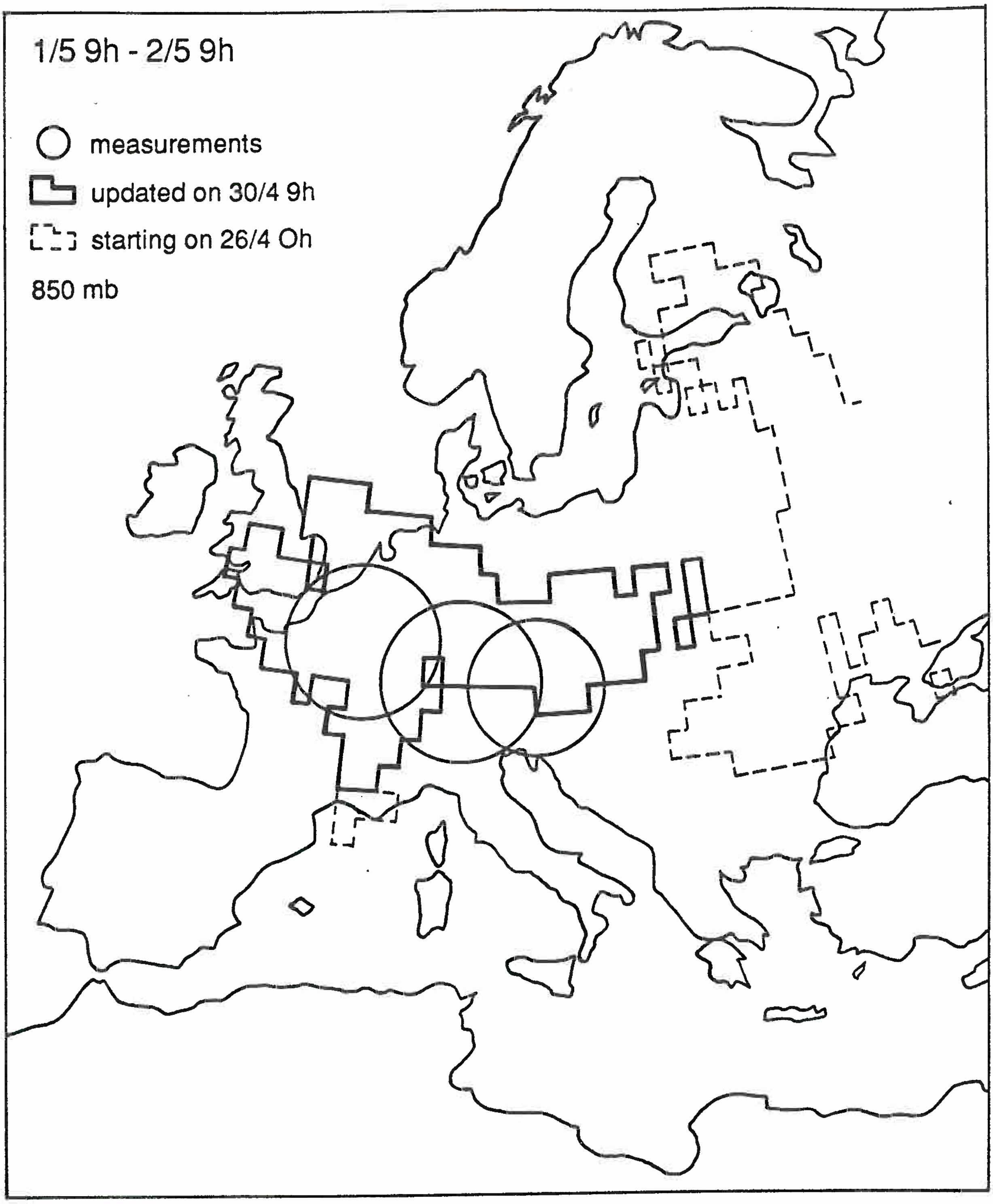


Fig. 18 Comparison of the concentration field of C-137 in air measured between 1 May 1986, 9am, and 2 May 1986, 9am, with the results of 1) the calculation starting at Chernobyl on 26 April 1986 00h and 2) the update of the former calculation taking into account the measurements available on 1 May 1986, 9am. It can be seen that including measurements in the model calculations imrpoves both the location and the concentration levels of the predicted cloud.

A prototype system has been built for measuring in real time the size and activity of alpha and beta emitting aerosols, by impacting the aerosol on a nuclear detector. First laboratory tests with an alpha emitting aerosol have shown that the design objectives have been met : i.e. a nearly maximal resolution and efficiency.

The termination of the aerosol laboratoy in 1991 will make it possible to utilize the 70 m^3 environmental room for intercomparison of air monitoring system.

2.6 Other Miscellaneous Contributions

DG I	In support to the agreement between DG I and the International Atomic Energy Agency (IAEA), technical assistance to the Agency' PACT program (Technical Assistance to Developing Countries) through the training of scientific staff at JRC in analytical chemistry with special emphasis on X-ray techniques.
DG III	Set up and implementation of a prototype data bank on pharmaceutical products.
DG V	Assessment of the potential health effect of trace metals (TM) on uricemic patients under regular dialytic treatment (RDT) including source of TM contamination and patient exposure, TM in body fluids and tissues, mechanism of toxicity.
DG VI	Development of a databank of NMR fingerprints of european wines (see section 1.1.7).
DG XI	Consultancy for the evaluation of progress and final reports issuing from the research contracts with national laboratories in the field of measuring and monitoring the natural environment.
DG XIII	Technical assistance and supervision of the Mark 13A pilot plant at SARAS refinery for flue gas desulphurisation. Experimental demonstration (pilot scale) of the JRC patent on "Antioxydants for Plastics".
DG XXI	Chemical characterisation of goods for custom classification; consultancy for chemical and biological compounds imported duty-free in the EEC countries for research applications.

3. Exploratory Research

3.1 Laser Spectroscopy for Medical Diagnosis

The possibility of real time measurements of the content of some trace gases (CO_2, CO, NH_3, CH_4) in human breath is of great interest as diagnostic technique in medical analysis. Optical spectroscopic techniques using tunable diode lasers appear adequate to this scope, when applied in conjunction with laser frequency modulation and derivative detection.

In this context the most interesting goal is the determination of the $^{13}CO_2/^{12}CO_2$ isotopic ratio following the ingestion of isotopically ^{13}C tagged compounds. The precision required for this parameter is of the order of 0.1%.The achievement of this target appears however difficult particularly due to the large difference in the temperature dependence of the line strengths of close lying pairs of $^{13}CO_2$, $^{12}CO_2$ absorption lines, as needed by the tunable diode laser technique.

An accurate search for pair of transitions of the two isotopes having wavenumber within 0.1 cm^{-1} to be detected into the same laser mode and energy of the lower state nearly identical to have the same strength dependence on temperature, has been made. A suitable couple of lines has been found around 2314 cm^{-1}, but the intensity of the $^{13}CO_2$ transition is about fifty times lower than that of the other isotope. This would imply the design of a multipass cell system to detect with good accuracy the weaker isotope together with precise calibration procedures to normalize the ratio of the two lines detected with different optical paths.

A spectroscopic system using tunable diode lasers operated at liquid nitrogen temperature has been assembled and preliminary tests performed on the instrumentation with exclusion of the multiple reflection cell.

3.2 Innovative Laser Technologies for Chemical Analysis

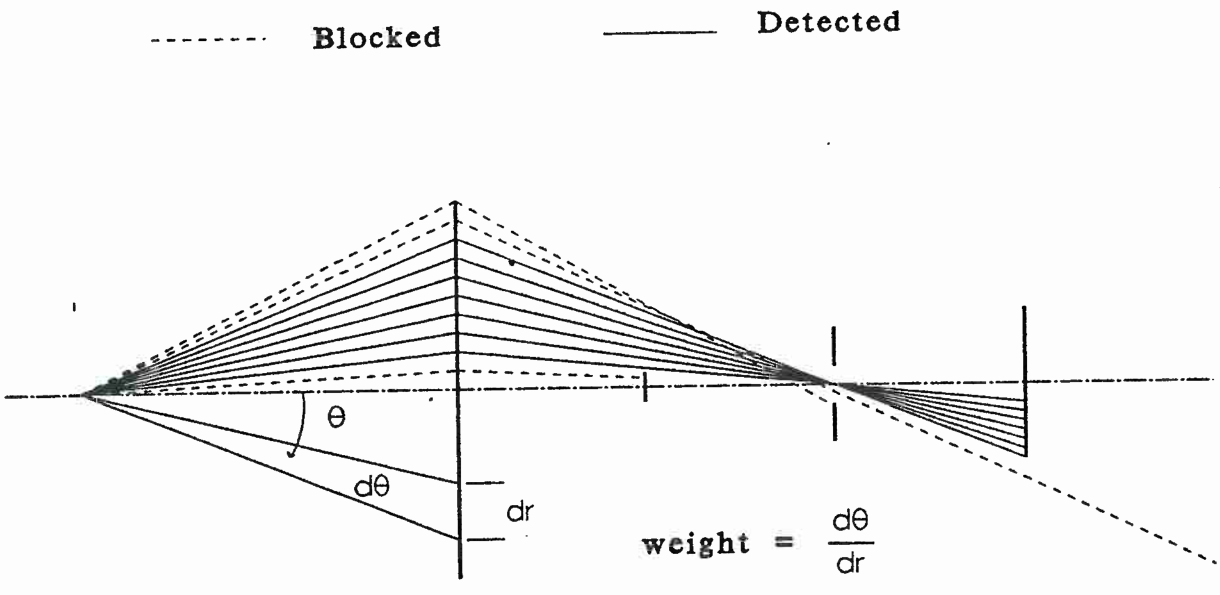
The aim of this research was twofold:

1. the development of the technique of laser induced fluorescence, coupled with a graphite furnace as atom reservoir, capable of approaching analytical sensitivities in the range of sub-femtograms to attograms (i.e. from 10^{-15} to 10^{-18} g); and
2. the study and validation of the concept of an "ionization detector", based upon a conventional air-acetylene flame and the laser-assited ionization technique.

Both topics have been successfully tested and critically evaluated.

In the Laser Induced Fluorescence approach, a complete set-up, consisting of a commercially available excimer laser-pumped dye laser and a graphite tube atomizer, has been assembled. In order to evaluate how well one could predict theoretically the analytical performances of such a system, a computer program was developed with which it was possible to calculate the collection efficiency of an arbitrary combination of lenses and stops as a function of position in cartesi space. The program is based upon a rigorous ray-tracing algorithm, accounting for optical aberration effects. As shown in Figure 19, a reference aperture of the system (e.g., a lens), usually selected to match the limiting aperture of the optical train, is uniformly filled with a cone of rays emanating from a selected point. Each of the generated rays is traced through the optical train until it strikes a stop, misses a lens or reaches the detector. The efficiency at the point is then proportional to the fraction of rays that reach the detector. Calculated efficiencies differ considerably (because of aberration effects) from those which would be expected based on ideal solid angle considerations. The attractiveness of the ray-tracing approach is that it allows to follow geometrically the path of light due to spurious sources, such as for example fluorescence from the windows and other scattering effects. As a consequence, these spurious effects can be minimized by placing suitable masks and filters in the optical train. This advantage was clearly borne out experimentally, as shown in Fig. 20, where the level of the overall noise in the measurement is plotted as function of time for three cases, as indicated. The noise reduction obtained with the mask and filter is very significant. With this system, a calibration graph could be obtained for thallium at concentration levels of tens of picograms per milliliter (see Fig. 21) The calculated detection limit for thallium, in absolute amount of material deposited in the furnace, was found to be 0.1 femtogram.

The idea behind the development of an ionization detector stems from the fact that the flame system as a simple atom reservoir and the laser Enhanced Ionization technique can be combined together to form what can be classified as a "photon detector based upon ionization". The practical implementation of such detector, whose principle is illustrated in Fig. 22, is the following: a metal atom, M, emits resonance photons $h\nu_M$ as a consequence of some excitation process (thermal, electrical or radiative excitation). These photons are collected and transferred to the flame containing pure metal vapour M, mainly in the ground state. The absorbed photons will then create M^* excited atoms. If the flame is simultaneously illuminated with one or two lasers which ionize M^*, the flame will act as an ionization detector for the primary photons at $h\nu_M$. This principle was demonstrated in our case with Raman photons generated by illuminating a quartz cuvette, filled with CCl_4, with a frequency-doubled, tunable dye laser. Magnesium was chosen as atomic vapour in the ionization detector,which was a conventional air-acetylene flame. As shown in Fig. 23, two well-known Raman peaks of CCl_4, are clearly visible above the background level. These results, obtained with a non-optimized arrangement, are encouraging evidence that the use of a photon detector based upon ionization is indeed worthly of furhter experimental investigation.



$$\text{Efficiency} = \frac{\Sigma\ (\text{Detected Weights})}{\Sigma\ (\text{Detected Weights}) + \Sigma\ (\text{Blocked Weights})}$$

Fig. 19 Simplified scheme of the ray-tracing procedure used in the calculation of the optical collection efficiency of the fluorescence set-up. From left to right, the optical train is composed of a point source, a lens, an aperture, the entrance slit of the monochromator and the collimating mirror. Since rays near the edge of the cone have a smaller angular separation from their nearest neighbors than do those at the center, a weight factor ($d\sigma/dr$) is assigned to each ray.

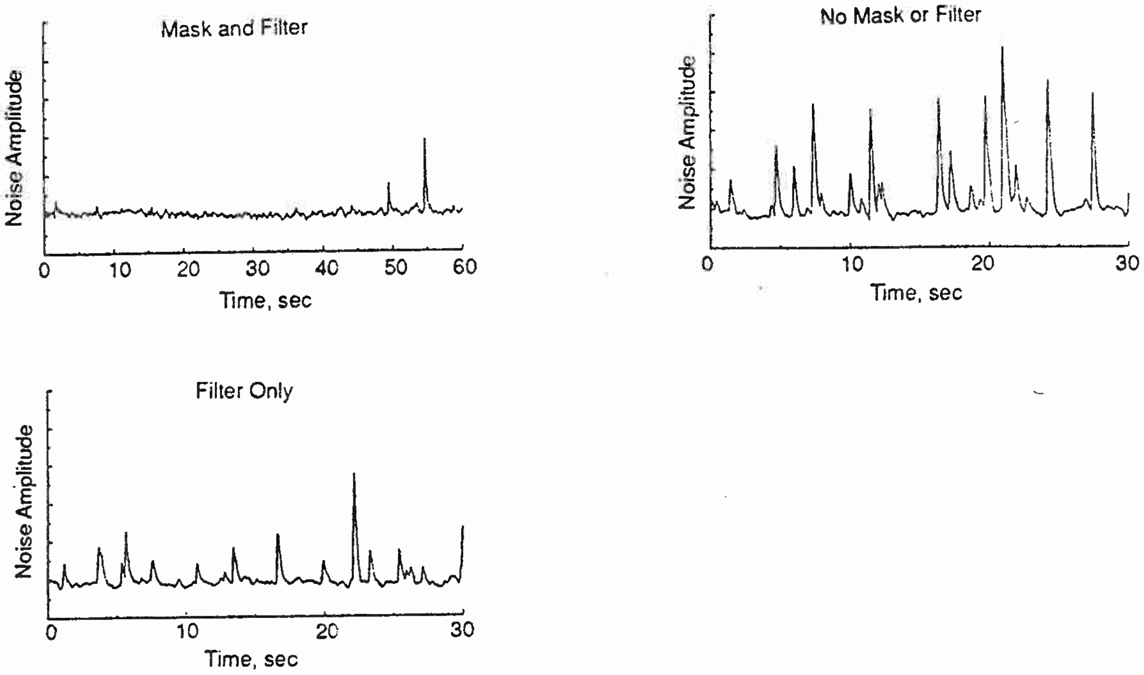


Fig. 20 Effect of the mask and filter on the experimentally measured noise level for the laser induced fluorescence set-up. The geometrical dimensions of the mask and its position in the optical train were calculated from the optical collection efficiency maps generated by the ray-tracing program.

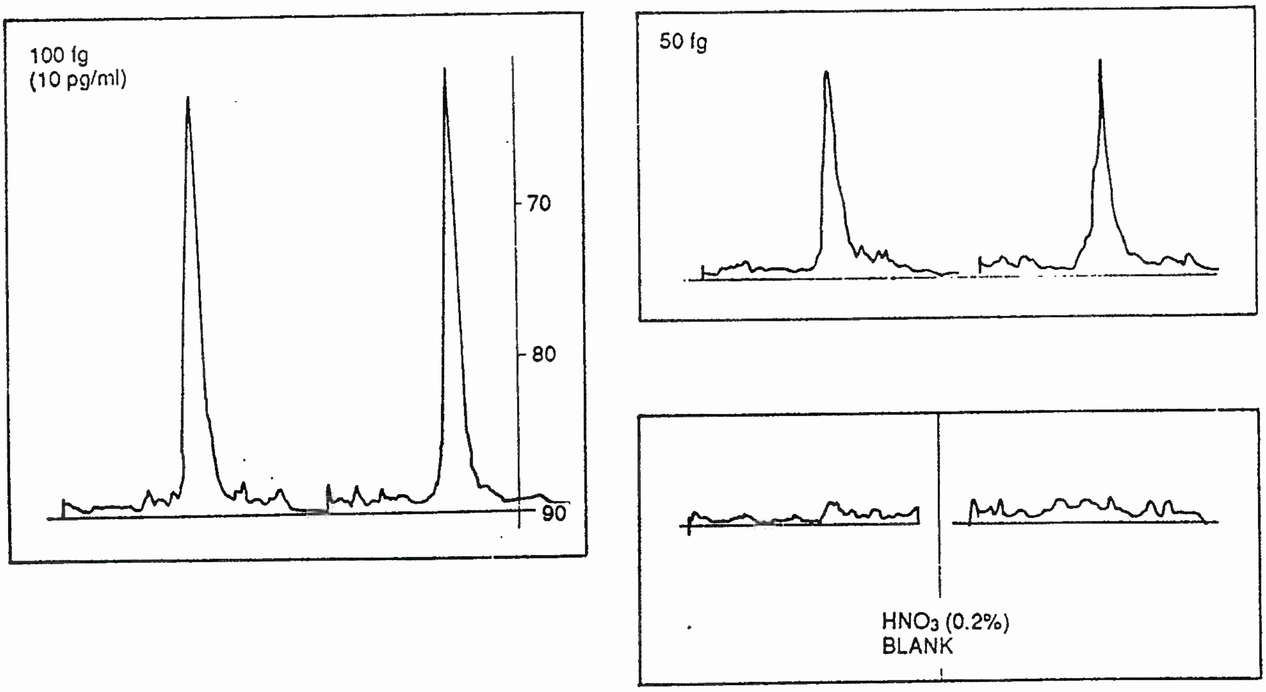


Fig. 21 Representative tracings of the signals obtained for the blank level and for two solutions of thallium. 10 μl of each solution was injected in the furnace.

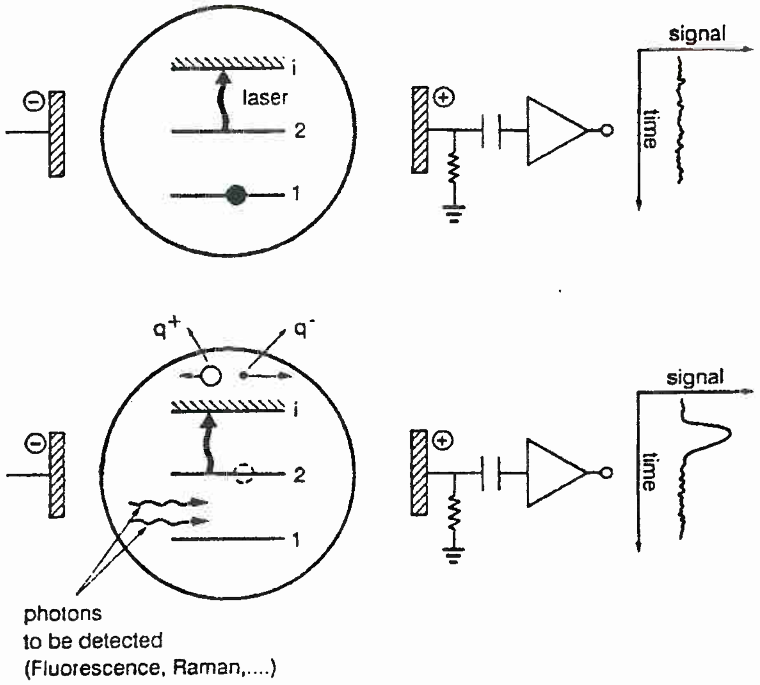


Fig. 22 Oversimplified scheme of the operating principle of the ionization detector

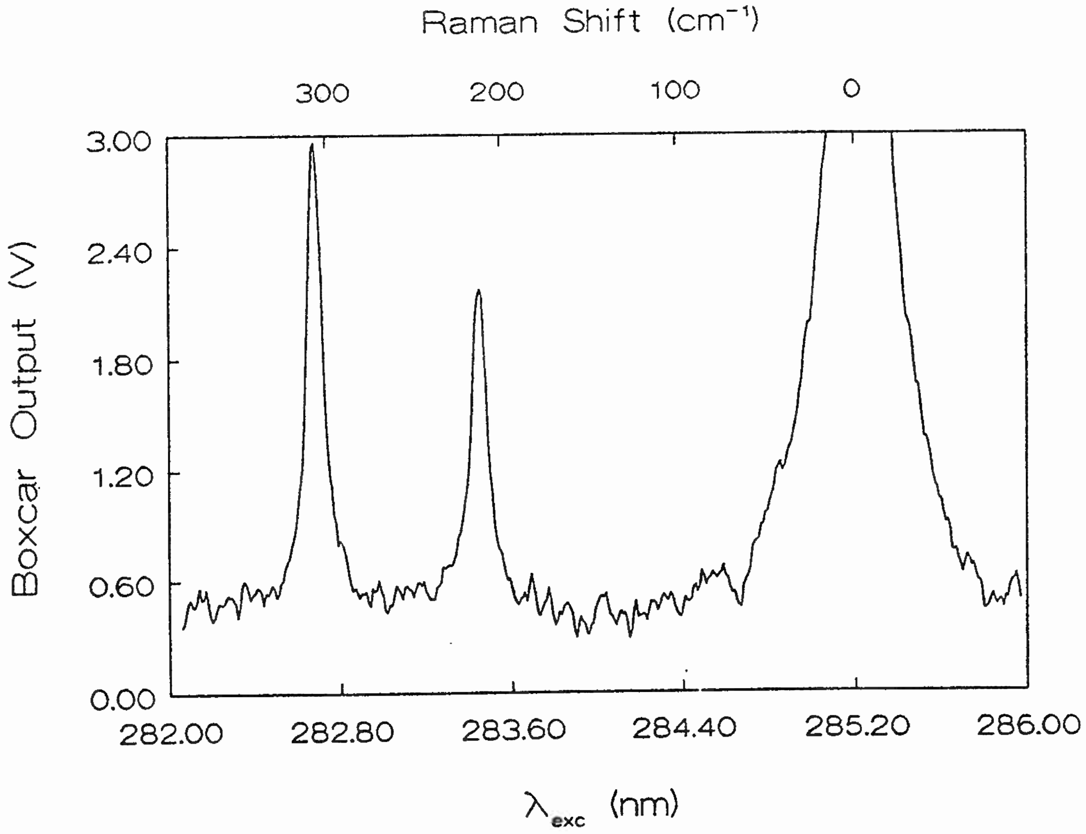


Fig. 23 Partial Stokes Raman spectrum obtained with the flame ionization detector. Magnesium concentration in the flame: 50 μg/ml. The two peaks correspond to $\Delta\nu$ shifts of 314 and 218 cm^{-1}

3.3 DNA Adducts

The objective of this study is the development and optimization of biochemical and physico-chemical methods for the detection and characterization of adducts in microsamples of DNA.

The formation of Dna adducts is a primary event in chemical carcinogenesis; thus the detection of DNA adducts in human lymphocytes provides direct evidence of exposure to environmetal genotoxic chemicals and makes possible individual risk estimation. In wildlife animals the detection of DNA adducts in the tissues of sentinel species constitutes a useful dosimeter of exposure to environmental chemicals.

Major efforts were devoted to the development of mass spectrometry and ^{32} P-Post-Labelling methods for the characterisation of DNA adducts formed by Epoxybutene (MOX) and by Diepoxybutene (DOX), both metabolic intermediates of 1, 3 - Butadiene. According to EPA (,), 1,3-Butadiene is the second most important air pollutant. Since MOX and DOX are mono and bifunctional agents suspected to produce different types of adducts in DNA and are potent mutagenic agents inducing multiple organ tumors, they have been choosen in these studies as model compounds.

The formation of DNA adducts was examined in the following systems:

- reactions with isolated DNA bases and nucleotides for the development of the characterization and measurement methods.
- *in vitro* studies on calf-thymus DNA and polynucleotides;
- *in vitro* studies on human blood and blood lymphocytes for the individuation of specific DNA adducts;
- *in vivo* studies on mice exposed to MOX and DOX for the validation of methodologies already developed;
- *in vivo* studies of cat-fish exposed to PAH and herbicides for the development of specifie methods for the detection of bile metabolites and DNA adducts in the liver.

The most significant results achieved so far can be summarized as it follows.

The reaction products of MOX and DOX with Guanosine were purified by HPLC and characterized by Mass Spectrometry. With dGMP they reacted in different experimental conditions giving rise to compounds which were also found in exposed polynucleotides.

After reaction with DNA, two Guanine derivatives induced by MOX and a specific DOX adducts were isolated and characterized.

In human blood and lymphocytes exposed to MOX and DOX, major adducts having chromatographic properties similar to those isolated from calf-thymus DNA were observed. The formation of these adducts is dose related (Fig.24).

For the identification of DNA adducts, a novel separation method by Capillary Electrophoresis confirmed the presence of specific adducts similar to those identified by HPLC and MS.

^{32}P Post-Labelling, a novel approach, based on RP-HPLC after enzymatic DNA hydrolysis is in progress. ^{32}P-adducts specific for MOX and DOX have been identified. These results support the set up of specific methodologies for the assessment of exposure to MOX and DOX.

A modified ^{32}P Post-Labelling method was lastly set up and successfully applied in laboratory studies on the exposure of aquatic sentinel species (cat-fish) to PAH and toxic herbicides (Fig.25).

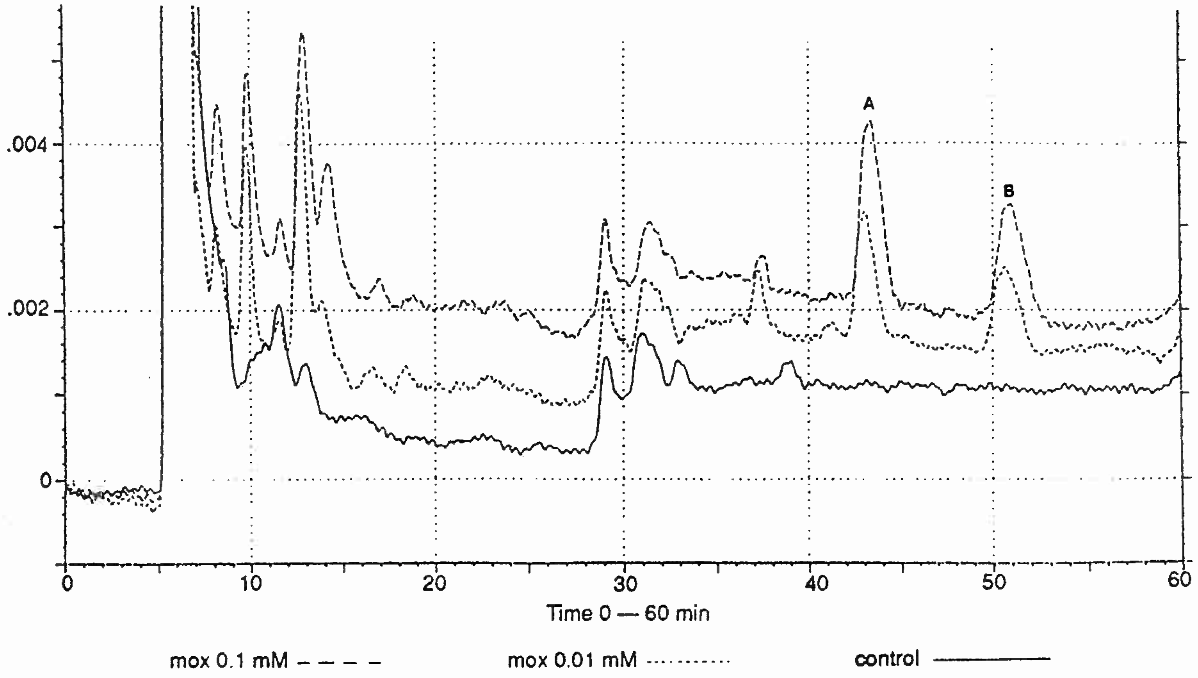


Fig. 24 Formation of DNA adducts in human lymphocytes exposed to epoxybutene. Peaks A and B of the chromatogramme correspond to 7-N (2-hydroxy-3-buten-1-yl) guanine and 7-N (1-hydroxy-3-buten-2-yl) guanine respectively.

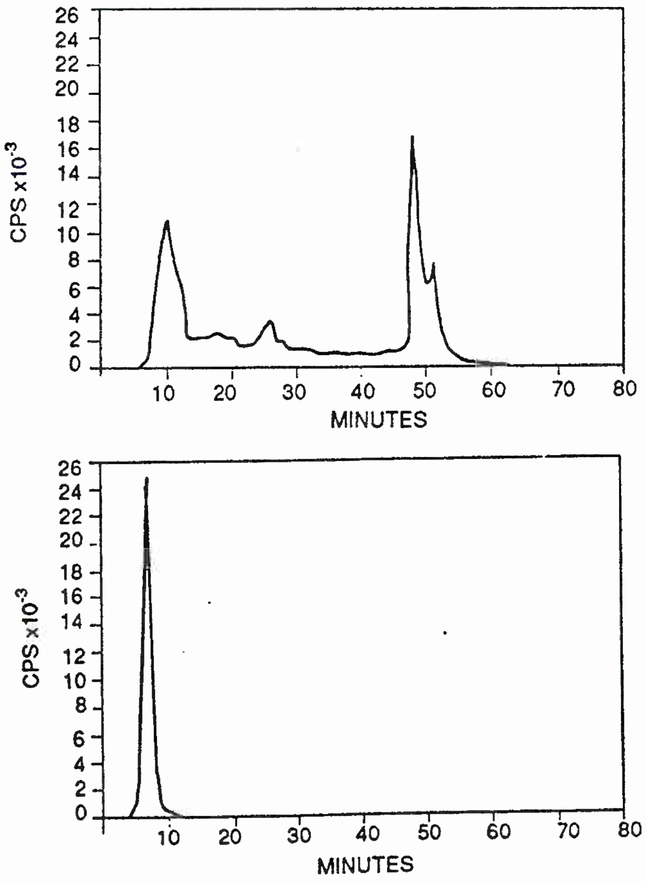


Fig. 25 Radiochromatogrammes of 32 PPL DNA adducts in the liver of cat-fish exposed to Benzo(a) pyrene. A: exposed; B: control

3.4 Laboratory for Separation Sciences

The research project is aimed at investigating some special separation techniques of particular significance for the decisive improvement of the detection limits and the specificity of instrumental analysis in respect of both organic and inorganic traces in complex matrices.

So far the studies have been focused on the evaluation and the optimization of **Microliquid Chromatography** (µLC) and of **Capillary Electrophoresis** (CE) in combination with Mass Spectrometry (MS) for determining trace and ultratrace amounts of chemicals in various matrices.

Direct interfacing with Mass Spectrometry is possible by the use of high yield soft ionization techniques such as fast atom bombardement (FAB). This required the development of specific interfaces based on a co-axial approach which has been adopted (Fig.26).

In the **Liquid Chromatography - Mass Spectrometry** approach the separations are carried out in classical reverse phase manner. The principal advantage of the µLC system is that it allows the direct interfacing of well established LC separations with MS detection. However, the small sample loading (typically up to 60 nl) capacity is problematic and limits the sensitivity of the overall methodology. Furthermore, commercially available, µLC pumps operate only in isocratic mode. A chromatographic system, based on a classic HPLC combined with different valves and splitting system was developed (Fig.27). to be directly compared with standard HPLC-columns and detectors.The system allows for narrowbore columns to be used, i.e. the introduction of higher volume of sample (200 µl).

In the MS interface, the column effluent is mixed with the FAB matrix only at the target, thus the separation remain unaffected by the matrix. The introduction of the matrix is regulated by a microsyringe pump.

Both MS and MS-MS modes of a VG-70-SEQ systems are under evaluation. It is anticipated that monitoring of ions derived from collision activated decomposition (CAD) in the MS-MS mode will result in the enhancement of sensitivity and specificity leading to detection limits in the subpicomole range.

CE is emerging as a highly efficient separation technique; e.g., plate numbers as high as 600.000 to 700.000 have been obtained in microcapillaries of 50-75 µm (i.d.). The potential of CE in analytical biochemistry, food analysis and genetic engineering is well established. The technique should readily lend itself to the detection of other classes of chemicals. The overall approach, to interfacing CE with MS-MS system, is analogous to the one developed for µLC-MS. However tests using this approach are still at their very beginning.

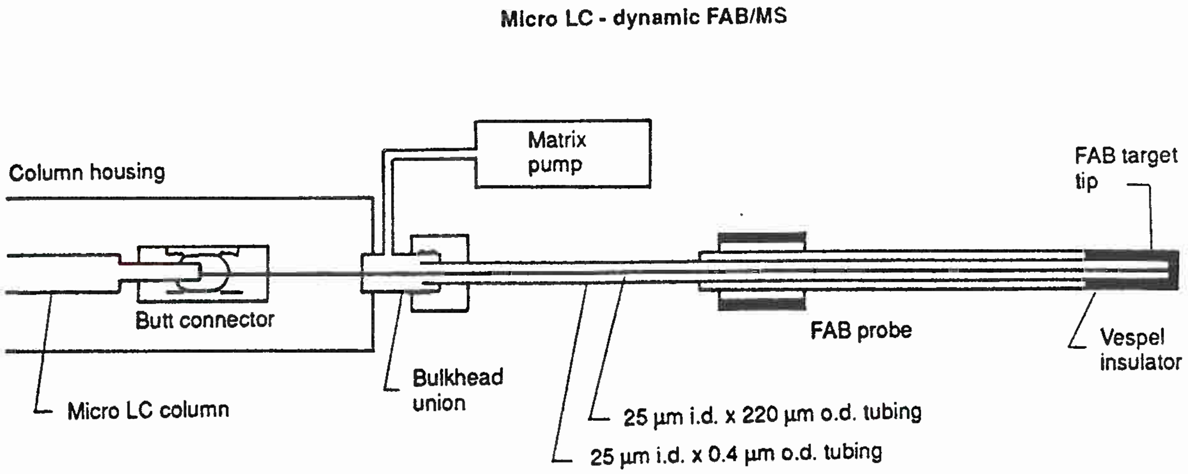


Fig. 26 Schematic of the co-axial interface developed for HPLC-tandem mass spectrometry

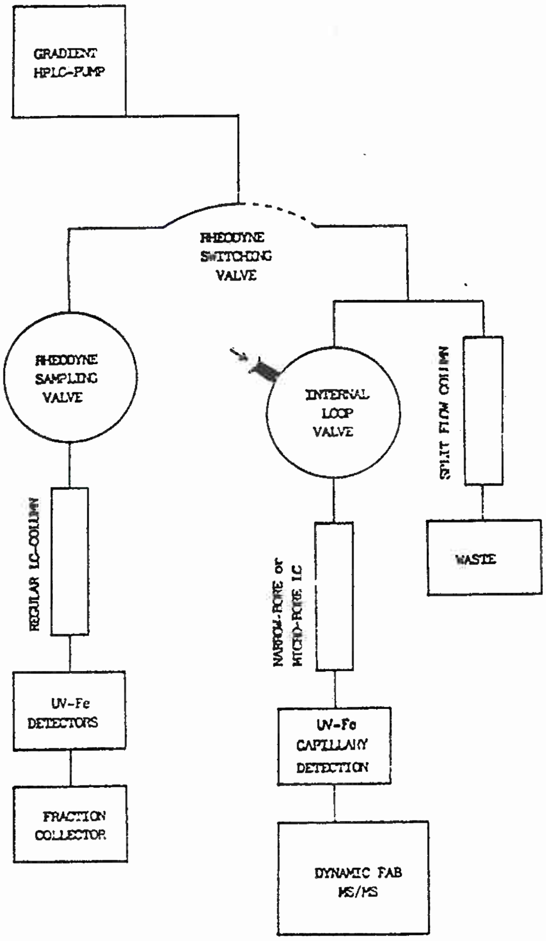


Fig. 27 Schematic of the chromatographic system developed for the interfacing of μ HPLC to MS-MS

4. Third Parties Work

4.1 Air Pollution

A three years contract with the Regione Lombardia has been signed; the contract foresees:

1) consulting and help in the set-up of a manual of procedures for operation and calibration of air pollution monitoring stations and sub-networks (data acquisition and analysis)
2) in-situ parallel measurements at selected network stations to validate the acquired data (15 stations per year).

The programme for the first year, as at point 2., has been completed (6 stations controlled) and a draft manual has been prepared and submitted to regional authorities for comments.

A second contract with the Regione Lombardia is in preparation. It foresees the use of the Environment Institute mobile laboratory to define air quality levels at sites unprovided with monitoring stations. The study should be addressed to polluted sites, urban or industrial, observed in situations of unfavourable meteorological conditions.

A three years study contract has been signed in the frame of an agreement ENEL/CNR. The contract concerns exchange of information on the studies of the Environment Institute in matter of the physical-chemistry of photo-oxidants and their precursors (O_3, VOC, NO_x).

4.2 Water Quality

A contract has been signed witht he Italian Mnistry of the Environment on the recovery and management of the Po river basin (MAPO Project).

The project aims at:
1) supplying the different decisors with a synthetic, easily comprehensible picture of the basin situation, using available data and models;
2) elaborating predictive scenarios for programming different action plans and for the evaluation of their impact;
3) supplying a decision support system through the use of a multiobjective decision model taking into account cost-efficiency analysis of the action plans and the priority of the actions.

The work on needed background information, choice of necessary parameters and functional specifications of the Expert System for the Decision Support (ESDS) has started jointly with JRC's Institute for Systems Engineering and Informatics.

A cooperation agreement with the **Italian Ministry of the Environment** has behaved the assessment of trophic conditions of Lake Garda, the largest lake of the European Communities.
The research concerned the principal ecosystem components, i.e.:
- physical, chemical and biological characteristics of lake waters,
- structure of the phytoplanktonic and zooplanktonic populations,
- fish populations with particular reference to the presence of any pesticide bioaccumulation phenomena in more prized fish species (PCB, HCB, DDT),
- lake sediments with reference to the content of eutrophicating substances (P,N), heavy metals (Cd, Cr, Cu, Hg, Pb, Zn), organochlorinated compounds (PCB, HCB, DDT) and radionuclides (137 Cs).

This study represented a reference point for setting up a correct safeguarding plan and pollution prevention scheme, and the rational management of the waterbody.

A contract has been signed with the **Amministrazione Provinciale di Varese** on the recovery of shallow lakes (i.e. Comabbio, Varese) aiming at:

- assessing present trophic level of waterbodies,
- evaluating epilimnetic P deficit due to algal biomass,
- predicting the effect of internal measures in restoration programmes,
- quantifying internal nutrient loadings,
- evaluating daily oxygen supply necessary to prevent nutrient release from sediments and
- predicting lake recovery times.

4.3 ATMES

The ongoing ATMES activity on the long range atmospheric transport model comparison has been completed with the preparation of a Draft report and a 2 volume appendix in which the main findings of the study are presented.

Seldom a model comparison has been performed over such a large set of data. It is not only the number of Participants (21) but also the number of data sets examined (6) which is large.

A special data bank had to be created to include all the Participants' output.Such a data bank can be an excellent tool for future research in the area. In fact ATMES has only dealt with a limited number of analyses, accurately selected to cover the various aspects of the study.

The results of the study will be analysed in detail during a Workshop (Varese, 12-14 March, 1991), in which the presence is expected not only of the laboratories participating, but also of a considerable number of Observers.

The results of the study can be used by two broad categories of organisations: weather services, which are interested in the determination of the general skill of the models or in the improvements of their meteorological inputs, and organisations involved in model predictions during emergency situations.

Therefore, the conclusions of this study can be addressed separately to those two categories.

The Meteorological Data and the Models

The calculations of arrival times of a radioactive cloud on a location depend on both winds, usually supplied to a modeler by weather services, and the treatment of the winds which transport the pollutants.

With a given set of winds, ATMES provides several measures of skill for each of the models.

In most cases, the forecast winds are of poorer quality than the measured winds. The study shows the model's skill in calculating the time of arrival and in the determination of the concentration level, by means of spatial and temporal figures of merit, FM. These are the best indicators of the goodness of the wind information. Both of these indicators generally show less skill when forecast winds replace measured winds.

The Emergency Situations

The benefits for emergency situations of the statistical analysis performed are based on the results produced by the models which perform best. However even if a ranking of model performances is difficult to establish, a net separation exists between the statistics pertaining to the radionuclide concentration in the air (relevant for immediate action) and that of deposition, which has to be considered only for later actions (milk and foodstuffs contamination).

Furthermore, ATMES describes the uncertainty and hence the reliability of any of the results calculated by the models. In many ways these statistics may be optimistic for future accidents, since greater uncertainties are likely to enter under the stress of a real emergency. On the other hand, there may be many real time measurements which can guide both the models and the users of the products which can significantly reduce uncertainties of the model outputs.

4.4 ENRESA/JRC Cooperation

In the framework of the Contract Nr.3384-88-03 TG ISP E with ENRESA (Empresa Nacional de Residuos Radioactivos S.A.) geochemical investigations have been carried out in-situ at El Berrocal uranium mine as well as with laboratory radionuclide migration experiments.
The laboratory experiments were conducted at the JRC-Ispra with a contribution of spanish CIEMAT staff.

Most data concerning El Berrocal's geochemical conditions have been collected during various survey campaigns. For this purpose two JRC probes were used inside ten existing boreholes: a multiple electrode geochemical probe allowing simultaneous acqisition of six physico-chemical parameters, and a color TV inspection probe.

Many aspects due both to the groundwater chemical equilibria and his channelling must still be clarified in order to quantify the processes and dynamics of Uranium migration in the granite formation.

Laboratory migration experiments, under controlled conditions, must provide a better understanding of transport phenomena. These are mainly governed by the presence of colloids and-or complexes with Humic Substances (HS). Column migration experiments with granite cores taken from the El Berrocal site are going-on under oxic and anoxic conditions, in conformity with a fixed planning. Several redox sensitive elements (Uranium, Neptunium and Selenium) were investigated.
As expected on the basis of ionic charge-radius consideration, Selenate ions behaved as conservative tracers while Selenium species in more reduced state exibited a stronger interaction with the geomatrix resulting in an effective retardation.
Sequential flow-through tests of Uranium and Neptunium at increasing HS concentration showed indeed a progressively corresponding enhancement of metal ion mobility.

4.5 Miscellaneous

Within the frame of its research programme on amino acids as nourishment and protein metabolism in patients suffering from certain types of cancer, the Besta Institute in Milan has requested the measurement of labelled and unlabelled amino acids in samples of plasma. In fact in the above studies amino acids labelled with stable isotopes are employed.

In order to perform these analyses it was necessary to select and to validate appropriate sample clean-up and derivatisation procedures. The final method uses ion-exchange micro-column clean-up followed by lyophilisation and derivatisation of the amino acids to their N-pentafluoropropionyl methyl esters. The derivatives are analysed by gas chromatography-mass spectrometry using electron impact ionisation and selected ion recording.

The first two sets of samples from control experiments with healthy subjects have been succesfully analysed and the results reported.Further samples from patients under treatment are expected in the course of 1991 and 1992.

5. Participation to EUREKA and COST Concerted Ations

5.1 EUREKA

The Environment Institute has pursued in 1990 activities undertaken in the framework of its participation to EUREKA projects in the field of environmental studies, namely Eurotrac and Euroenviron.

EUROTRAC

As it has been already mentioned in the Annual Report 1989 of the Environment Institute, this European joint effort is aimed at investigating the impact of human activities on the continental (Europe) tropospheric chemistry. For the purpose several sub-projects are developed - each one specially addressed to the study of one aspect of the very comprehensive problem - the Environment Institute being active participant in the following :

TRACT

This sub-project has been specifically designed to clarify the transport of pollutants from industrial areas over complex orographic areas, and it involves repetitive in-field analytical campaigns.. The tracer technique (see section 1.1.3.) has been successfully employed in the course of a TRANSALP experiment to which several laboratories took part.

BIATEX

The activities covered by this subproject are addressed to the quantification of bioshere-atmosphere fluxes of compounds likely to enhance photooxidant reactivity (see section 1.1.2.). For the purpose in-field measuring campaigns have been performed which allowed good estimates for a series of compounds to be made (Eg. monoterpenes, α and β pinene, formaldehyde).

JETDLAG

The major objective of this subproject is to promote the technological development of absorption spectroscopy with tunable diode laser for environmental research and monitoring.
The Environment Institute contribution mainly addresses the objective of the subproject which consists in providing spectral data which are presently missing or disputed. During 1990 two studies have been concluded, concerning spectral parameters (absolute line/band intensities, pressure broadening coefficients) of formic acid and of methyl cloride. This second study has been conducted in collaboration with the Laboratoire Infrarouge-Orsay, France.

LACTOZ

This project is coordinated within the framwework of COST 611 and aims to provide a proper description of the complex chemical processes which lead to ozone formation and destruction in the troposphere. The main objective is to provide kinetic and mechanistic data for input in mathematical models for a quantitative description of the tropospheric ozone budget.

As described in another part of this report, the contribution of the Environment Institute has been focused on the nighttime chemistry of biogenic and anthropogenic hydrocarbons. In this framework the reactions of the nitrate radical with dienes (isoprene and 1,3 butadiene) and with aromatics (xylenes) and the kinetics of the $NO_2/NO_3/N_2O_5/O_3$/air system have been investigated.

EUROENVIRON

The general scope of the Euroenviron project is the development of processes, systems, services and technologies all in support to the protection of the environment. In a similar way to Eurotract, this project is intended to cover a series of specific sub-projects addressed to a variety of areas.
The Environment Institute has finalzed a proposal for a twin mobile unit which should provide sampling, in-field sample treatment and analysis capabilities with special reference to toxic wastes soils and waters. The proposal has been introduced to EUREKA's secretariat.

5.2 COST Concerted Actions

The Environment Institute is deeply involved since several years now in the following COST actions:

COST 611	**Physico-Chemical Behaviour of Atmospheric Pollutants**
COST 613	**Indoor air Quality and its Impact on Man.**

More than 50 European laboratories participate in the first action, subdivided into three working parties (WPs) to deal with:

- development of analytical methods,
- atmospheric chemical and physical processes,
- field measurements and meaningfulness of the obtained data.

The study on the application of DOAS technique to trace gas and aerosol particle monitoring desribed in another part of this report, fits into the activities coordinated in the WP (i) and the research on the nighttime chemistry of organosulphur compounds in the OCEANO-NOX project of the WP (ii).

The Proceedings of the Fifth European Symposium on Physico-Chemical Behavior of Atmospheric Pollutants have been published, co-edited by the JRC-Environment Institute and the Directorate General XII/E, Science Research and Development, Brussels.

As far as COST Action 613 is concerned, for the time being 6 working groups (WG4 - WG9) are active and the start of a seventh working group has been decided by the CCCC. The final draft of a summary report on health effects of indoor air pollution prepared by WG4 has been discussed at the CCCC and will be published in Spring 1991. WG6 has prepared draft guidelines for ventilation requirements in buildings which introduce the concept of perceived air quality. The building, in addition to man, is considered as a source of pollutants and odours which need to b e ventilated. the guidelines will be firther developed.

The final draft of a guideline for the characterization of volatile organic compounds emissions from indoor materials and products using small test chambers has been prepared by WG8 and will be published in 1991. Meanwhile an interlaboratory comparison exercise including European and American laboratories is being prepared in order to validate the guideline.

Draft reports on procedures for sampling biological particles in indoor air of homes and non-industrial workplaces, on how to perform longitudinal or intervention studies in "sick" buildings, and on guidelines for VOC measurements of indoor air are currently in preparation.

6. Associated Laboratories

The JRC Environment Institute has very close collaboration with a number of European laboratories within the framework of Cost Concerted Actions and EUREKA projects.

Further, the Third Parties Activity has naturally brought several national laboratories to establish new links with the Institute. Apart from the above the following collaborations are worth of mentioning :

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

- **Aeronautica Militare Italiana, Rome, Italy**
  in connection with the delivery and analysis of wind-fields data over Europe, needed for the investigations in the area of pollution mass balance and transport;

- **Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Madrid, Spain**
  in the field of environmental research and industrial risk;

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

- **Centro Informazioni Studi Esperienze (CISE), Milan, (Italy)**
  as far as it concerns measurement strategies and technologies for environmental studies;

- Within the framework of **REM** a large number of national laboratories and international organisations are providing data on the basis of a timely and tigth collaboration. Among the others:
  - **The European Center for Medium Weather Forecast (ECMWF), Reading, United Kingdom**
  - **The Royal Meteorerological Institute of the Netherlands (KNMI), The Netherlands**
  - **The International Atomic Energy Agency (IAEA), Vienna, Austria**
  - **The World Meteorological Organization (WMO), Geneva, Switzerland.**

7. Large Installations

7.1 Operation of Large Installations

As it was already mentioned in the preceeding Annual Report the facilities of the Environment Institute do not comprise large installations but some facilities which in the past could be considered as less conventional and which have been and are even more employed for special measurements.

It is referred here in particular to a series of mobile laboratories which are being extensively employed for atmospheric pollution studies such as :

- measurement of a variety of gaseous species, of their mass flow and total vertical burden;
- physics and chemistry of the atmosphere involving conventional meteorological and micrometeorological data measurements;
- pollutant diffusion studies in complex orographic areas as the basis for the validation of mathematical models at both local and regional scale;
- calibration of ground based measuring stations all over the EEC area in view of the standardisation of the procedures for determining atmospheric pollutants. Nowadays these mobile laboratories cannot be considered any more less conventional facilities as they should form the basis of any well equipped research body deeply involved in large scale pollution measurement strategies.

On the contrary worth of mentioning is the fumigation chamber system which allows trees to be submitted to selected air pollutants under controlled environmental conditions.

Experiments with this facility have been started in 1990 and the results achieved are described in the section "Air Chemistry" of this report.

7.2 Construction of New Installations

As already mentioned in the 89 Annual Report, the high volume (30 m^3) **Indoortron** - which is worth of being classified among the large installations - is ready to be installed.

The construction of a dedicated building to accomodate it has been started and is expected to be available, in operational conditions, by the end of 1991 so that first experiments can be reasonably planned for early 1991.

The Indoortron will allow for the study of emission rates of volatile compounds from materials utilized "indoor", the test of building and furniture materials for their sorption properties and the investigation of humans and animal exposure to selected pollutants under controlled environmental conditions.

In a similar way the construction of the **15 m high tower** to accomodate the experimental assembly for precipitation scavenging studies has been started and will be concluded in 1991.

This large facility - which comprises also a 70 m^3 stianless-steel chamber - has been conceived for takling pollution problems related to airborne aerosols and particular matters, in realistic conditions, but completely isolated from the outdoor ones.

Also in that case the beginning of the experiments can be foreseen for early 1992.

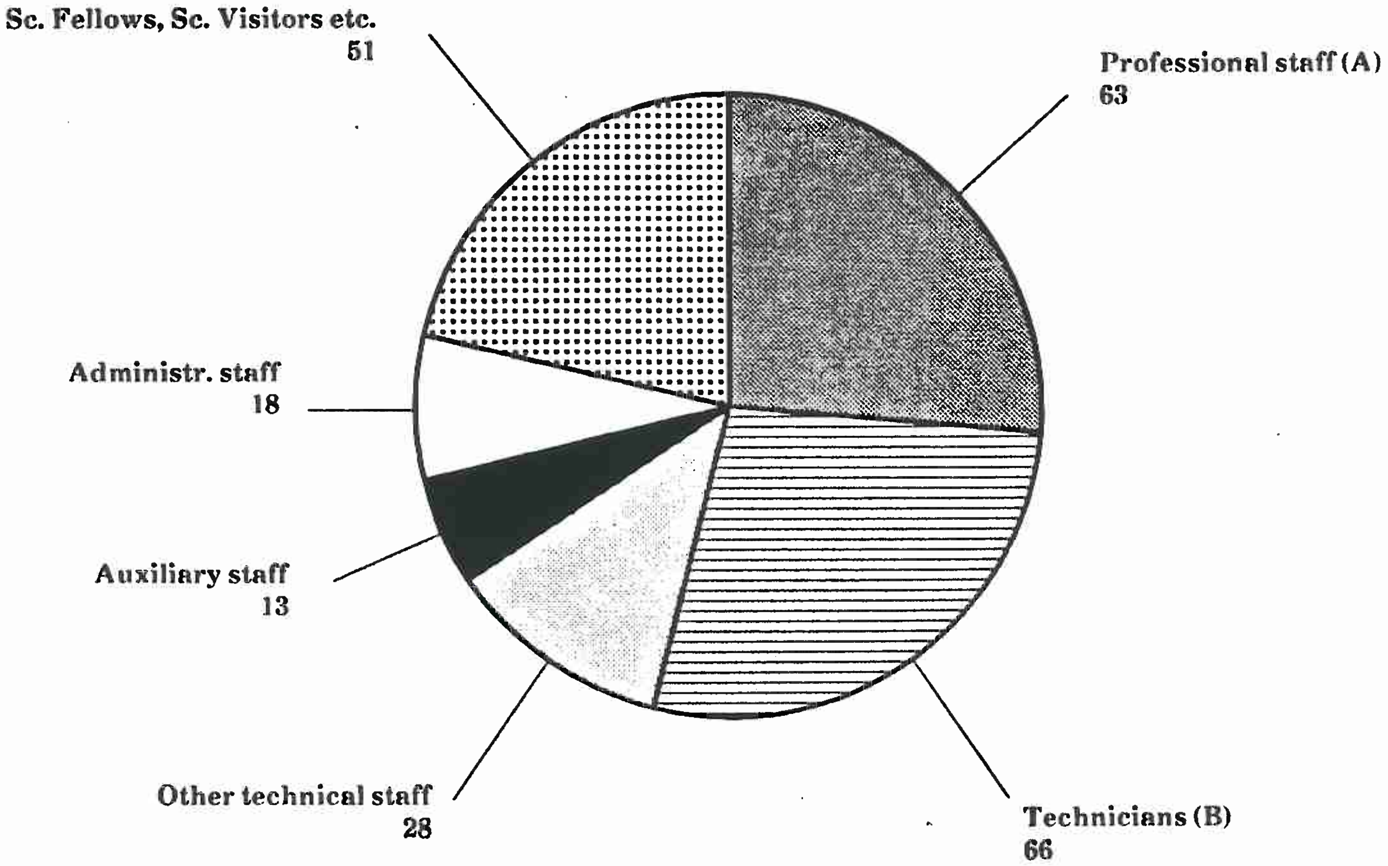
Human Resources

Total Staff present : 239

ENVIRONMENT INSTITUTE

Staff statistics

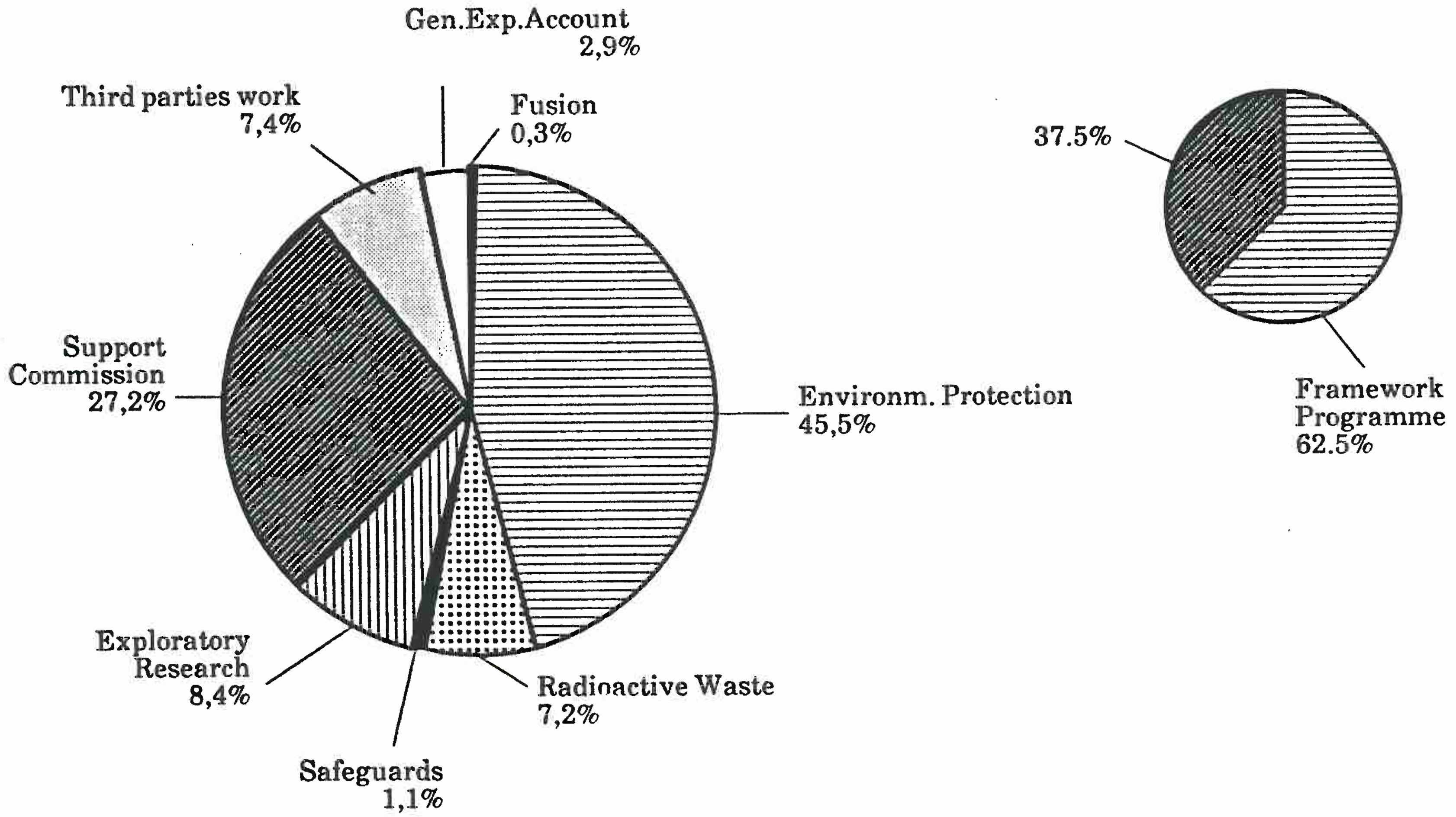
12.02.1991



Finances

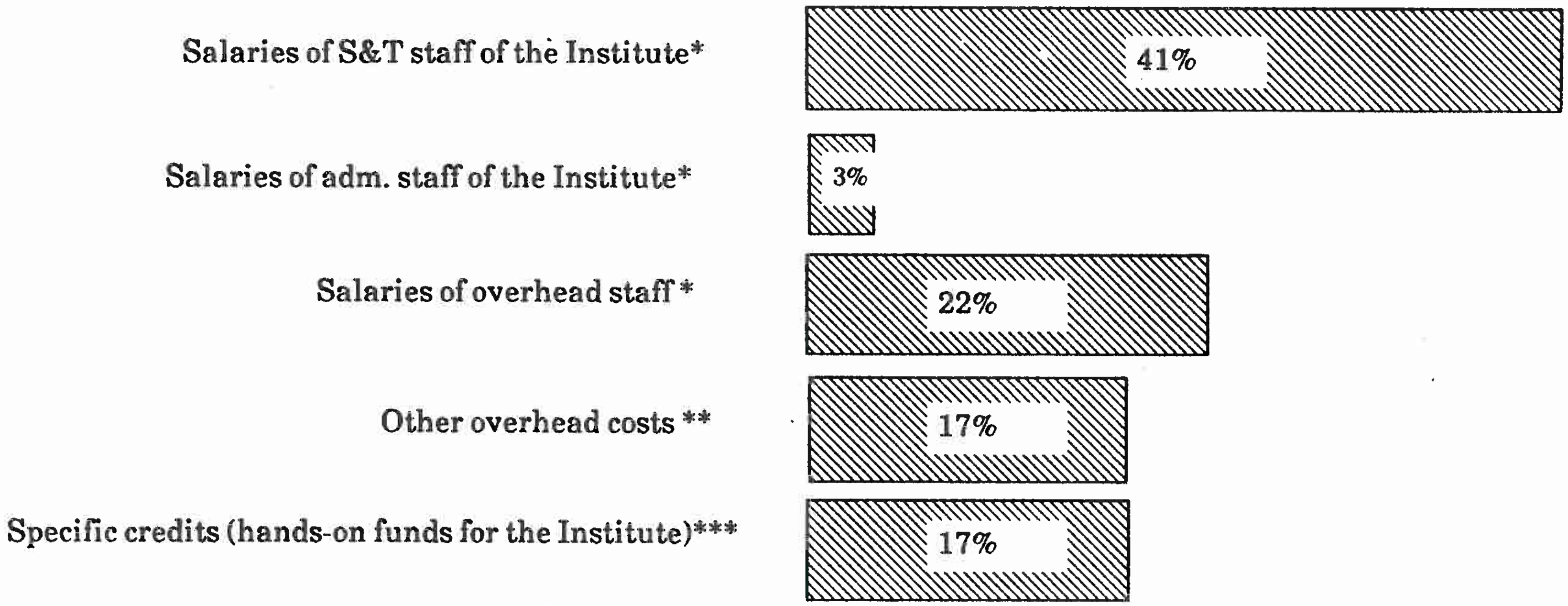
27.3.91

Environment Institute
Specific credits (hands-on funds) 1990



Expenditures of the Environment Institute1990

27.3.91



* Includes travel costs, social costs
** All infrastructure costs, energy, telephone, buildings, computer centre, workshop etc.
*** Instruments, chemicals, small expenditures, contracts

Appendices

A: Publications, Conferences
B: Organisation Chart
C: Glossary of Acronymes and Abbreviations

1. Specific Research Programmes

1.1 Environmental Protection

ENVIRONMENTAL CHEMICALS

Indoor Air Pollution

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Appendix B

Organisation Chart

JRC Environment Institute

Institute Director
Friedrich Geiss

Deputy Director
Bruno Versino

Administration and Technical Services
Guglielmo Rossi

Atmospheric Physics
Francesco Girardi

Atmospheric Chemistry
Giambattista Restelli

Atmosphere/Biosphere Interactions
Bruno Versino

Environmental Informatics
N.N.

Environment Chemicals: Soil, Water, Waste
Sergio Facchetti

Environment Chemicals: Life Sciences
Helmut Knöppel f.f.

Environment Chemicals: Indoor Pollution
Helmut Knöppel

Food and Drug Analysis, Consumer Protection
Giorgio Serrini

Glossary of Acronyms and Abbreviations

ATMES	Atmospheric Transport Models Evaluation Study
BIATEX	Biosphere Atmosphere Exchange of Pollutants
CCCC	Community COST Concertation Committee
CD-ROM	Compact Disk Read-Only-Memory
CFC	Chlorofluorcarbons
COST	Scientific Technical Cooperation
CRTN	Centro di Ricerca Termica e Nucleare Milano
CSTR	Continuous Stirred Tank Reactor
DIS	Draft International Standard
DMSO	Dimethylsulphoxide
DOAS	Differential Optical Absorption Spectrometry
ECDIN	Environmental Chemicals Data Information Network
ECURIE	European Communities Urgent Radiological Information Exchange system
EDTA	Ethylen Diamino Tetracetic Acid
EINECS	European Inventory on Existing Chemical Substances
EMEP	Evaluation Monitoring European Pollution
ENRESA	Spanish Agency for radioactive Waste Management
ESDS	Expert System for the Decision Support
EUROTRAC	European Experiment on Transport and Transformation of Environmentally relevant Trance Constituents
FA	Fulvic Acid
FCM	Flow Cytometry
FEMSUN	Finite Element Model coupled with Sensitivity and Uncertainty Analysis
FT-IR	Fourier Transform Infrared Spectrometry
GC	Gas Chromatigraphy
GC-ECD	Gas Chromatography-Electron Capture Detector
GC-FID	Gas Chromatography-Field Ionization Detector
GC-MS	Gas Chromatography-Mass Spectrometry
HA	Humic Acid
HCFC	Hydrochlorofluorocarbons
HCB	Hesa Chloro Benzene
HFC	Hydrofluorocarbons
HPLC	High Performance Liquid Chromatography
HS	Humic Substances
IC	Ion Chromatography

IR	Infra Red
ISO	International Standard Organisation
JETDLAG	Joint European Development of Tunable Diode Laser Absorption Spectroscopy for Measurement of Atmospheric Trace Gases
JMP	Joint Measurement Programme
LACTOZ	Laboratory Studies of Chemistry related to Tropospheric Ozone
LISA	Long Term Isolation Safety Assessment
MAPO	Management of the Po-river basin
MITO	Microphyte Toxins
MLW	Medium Level Waste
NEA	Nuclear Energy Agency
NILU	Norsk Institut Luftorskning
NMR	Nuclear Magnetic Resonance
OPM	Oil-PCB Manager
PAGE-SDS	Polyaxilamide Gel Electrophoresis-Sodium Dodecyl Sulphate
PAN	Peroxy Acetyl Nitrate
PBL	Planetary Boundary Layer
PCB	Polychlorinated Biphenyl
PFC	Perfluoro-Carbons
PPT	Parts per Trillion
PREP	Pre-Processor
PSAC	Probabilistic Safety Assessment Code
QAP	Quality Assurance Programme
QSAR	Quantitative Structure Activity Relationship
RDT	Regular Dialytic Treatment
REF	Radioactive Effluents
REM	Radioactivity Environmental Monitoring
REX	Radioactive Exposure
RIDEP	Italian network of atmospheric deposition
RIS	Radiological Inspections
STOP	Post-Processor
TAG	Test Atmosphere Generator.
TM	Trace Metal (exposure)
TMU	Tetramethylurea
TRANSALP	Transalpine Transport of Air Pollutants
UNEP	United Nations Environment Programme
UV-VIS	Ultraviolet-Visible
VOC	Volatile Organic Compounds
XANES	X-ray Absorption Spectroscopy Near Edge Spectrometry
EXAFS	Extended X-ray Absorption Fine Structure

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This is the second 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 1990 in the various projects included in the multiannual (1988-91) Specific Research Programmes tackled by the Institute i.e. **Environment Protection** and **Radioactive Waste Management,** the former being focussed on environmental chemicals, air pollution and pollutant transport, water pollution, chemical waste, food & drug analysis, the latter on safety assessment for waste disposal in geological formations.

The scientific support given to the Commission Services for the implementation of EC directives dealing with chemicals, air pollution, water pollution, chemical waste and radioactive environmental monitoring (REM) is also described.

Lastly the outcome of various activities related to work for third parties and to the participation of the Institute in EUREKA and COST projects is shortly outlined.

The report includes data on the Institute Structure, human and budget resources and large installations operated by the Institute.