ANNUAL·REPORT·92

Environment Institute

JOINT RESEARCH CENTRE

COMMISSION OF THE EUROPEAN COMMUNITIES

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Contents

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

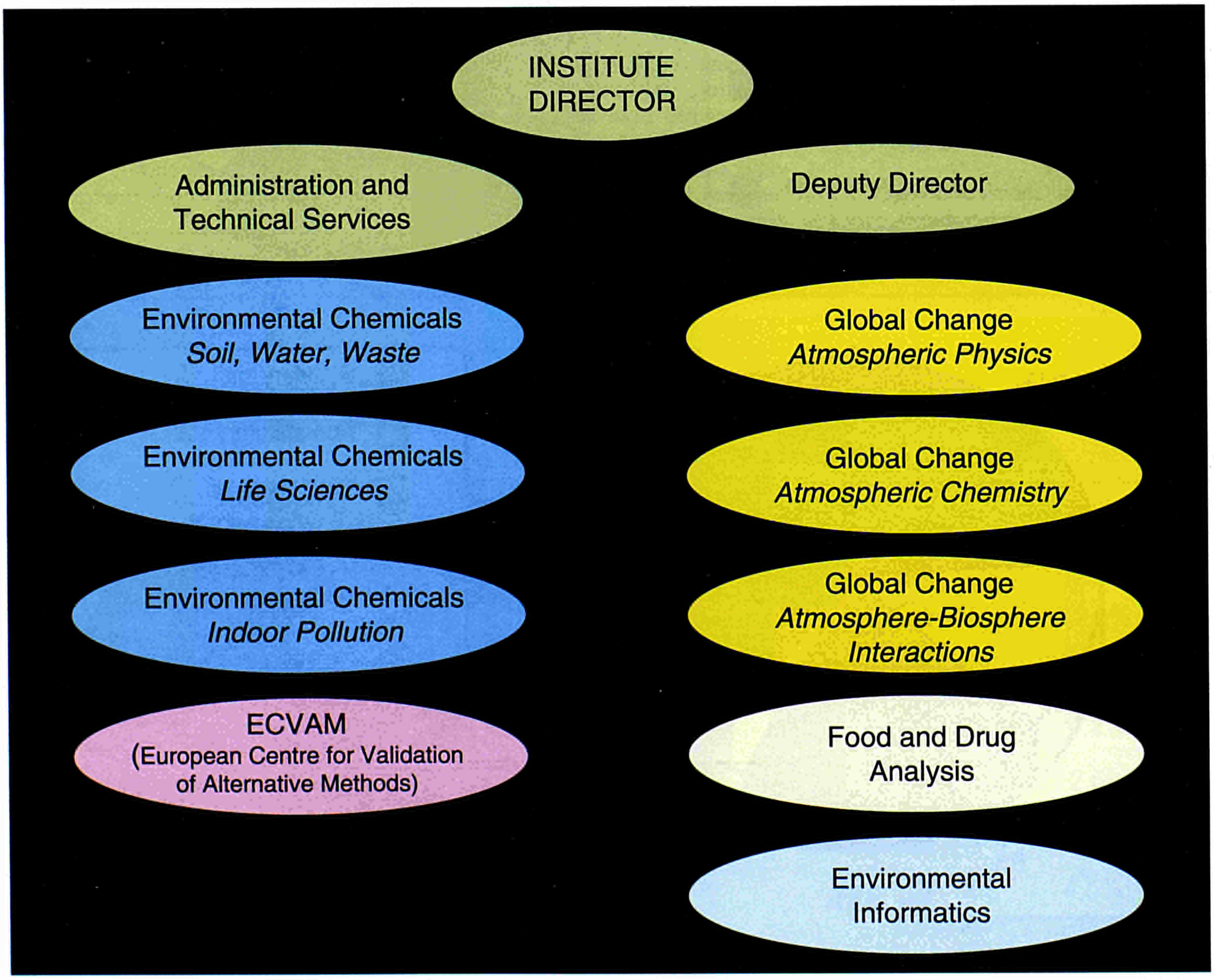
THE ENVIRONMENT INSTITUTE

Executive Summary
1. Specific Research Programme
2. Scientific-Technical Support to Community Policies
3. Exploratory Research
4. Third Parties Work
5. Participation to EUREKA Actions
6. Appendices

THE ENVIRONMENT INSTITUTE

The staff of the Environment Institute.

From left to right: seated Francesco Girardi, Head, Atmospheric Physics Unit ; Fiederich Geiss, Institute Director; Bruno Versino, Deputy Director, Head, Atmosphere-Biosphere Interections Unit; standing up Flavio Argentesi, Head, Environmental Informatics Unit; Sergio Facchetti, Head, Environmental Chemicals: Soil, Water, Waste Unit ; Giambattista Restelli, Head, Atmospheric Chemistry Unit; Helmut Knöppel, Head, Environmental Chemicals: Indoor Pollution Unit; Sergio Serrini, Head, Food & Drug Analysis Unit; Guglielmo Rossi, Head, Administration and Technical Services Unit.



The growth of the Institute has continued in the course of 1992 and is reflected in the greater incidence of the Environmental Protection Programme within the new 1992-1994 JRC's research programme.
The number of people working in the Institute has reached a total of 280, 198 out of them on a regular position; 80 have a university degree.
The extremely wide ranging spectrum of disciplines represented - from chemistry to mathematics and informatics, from physics to biology and toxicology, from chemical engineering to ecology, geology and soil sciences - testify the multi-disciplinary character of the approach to the environmental issues.
The enlargement of the tasks of the Institute is reflected also in the modification of its internal organisational structure which encompasses, in addition to the previous eight scientific unit, i.e.:

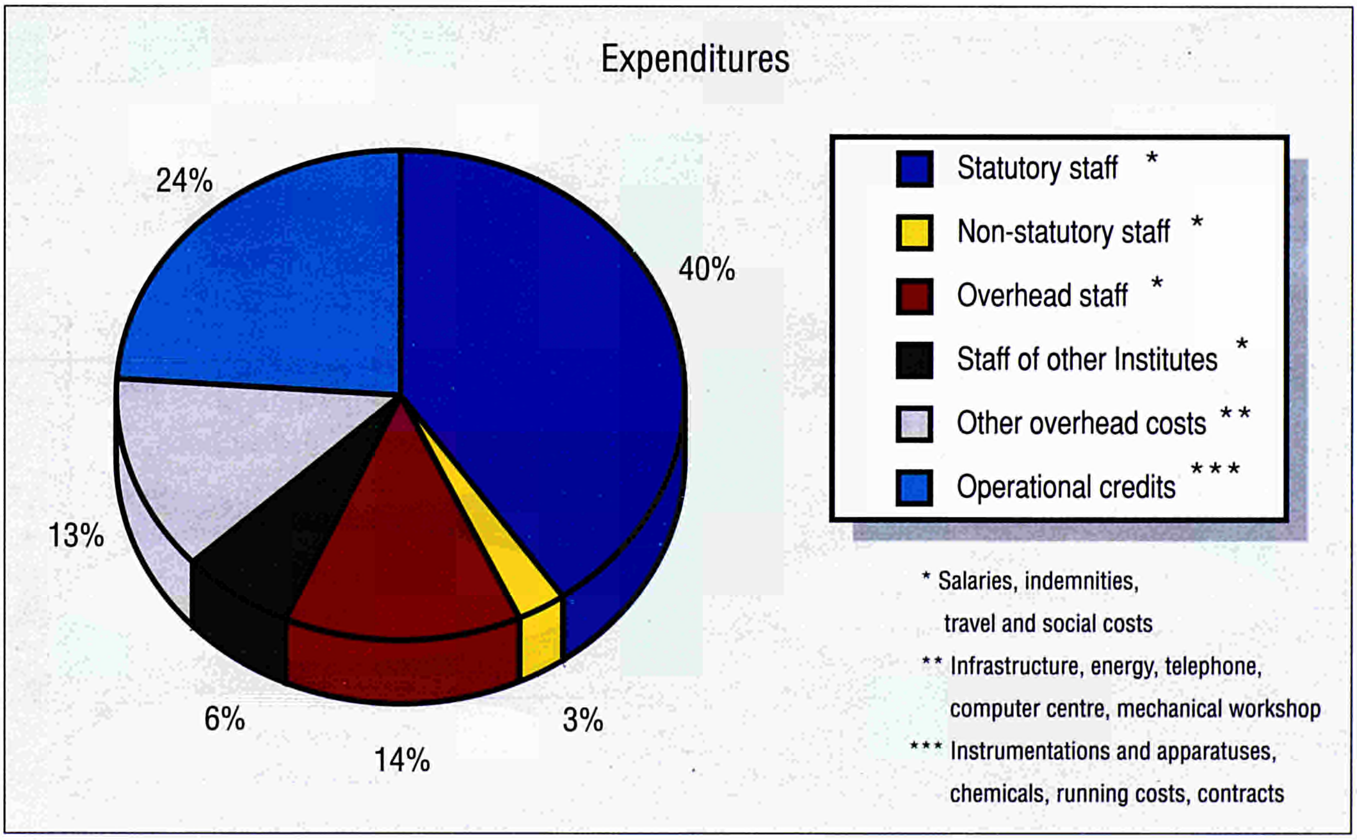
- Atmospheric Physics
- Atmospheric Chemistry
- Atmosphere-Biosphere Interactions
- Environmental Chemicals: Soil, Water, Waste
- Environmental Chemicals: Indoor Pollution
- Environmental Chemicals:Life Science
- Environmental Informatics
- Food and Drug Analysis, Consumer Protection,

the new European Centre for the Validation of Alternative testing Methods (ECVAM).
During 1992 the Environmental Informatics Unit was made operational with the task of developing the informatic infrastructure and services required by the Environment Institute to achieve an adequate information technology level.
As for the past, administration and technical services are managed by a dedicated Unit.

As shown in the map of the JRC Ispra site, the facilities of the Institutes are scattered in premises located in a dozen of different buildings. New premises are being built and a re-organization of the space allocation is being implemented so as to concentrate both the staff and the facilities within two "core" areas in view of facilitating the interaction between the research teams and of improving the management.

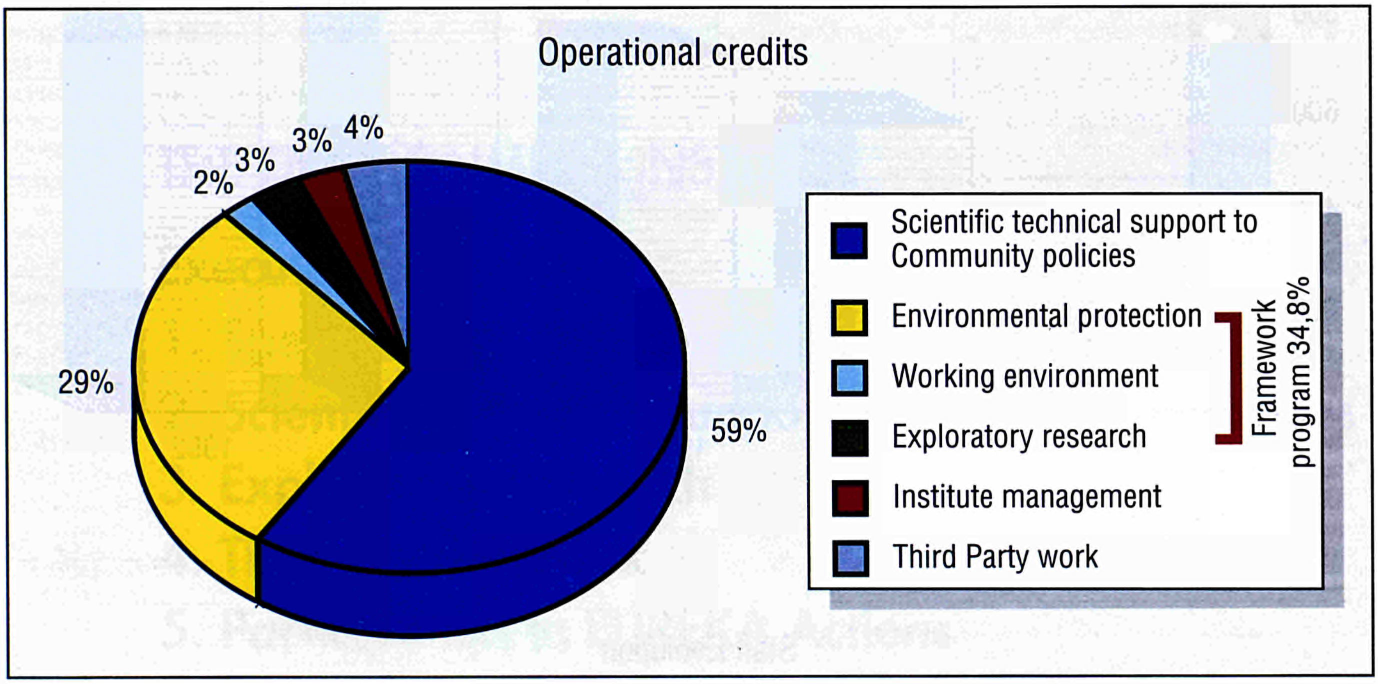
The Environment Institute contributes essentially to the "Environmental Protection" Programme and to the "Working Environment" Subprogramme.
The research activities, while at most being the continuation of those of the preceeding programme, have been more markedly focused on the" Global Change" issue which has adsorbed some 10% of the resources.
Of equal relevance, however, are to be considered the projects developed within the framework of the "Environmental Chemicals" and of the "Food & Drug Analysis".

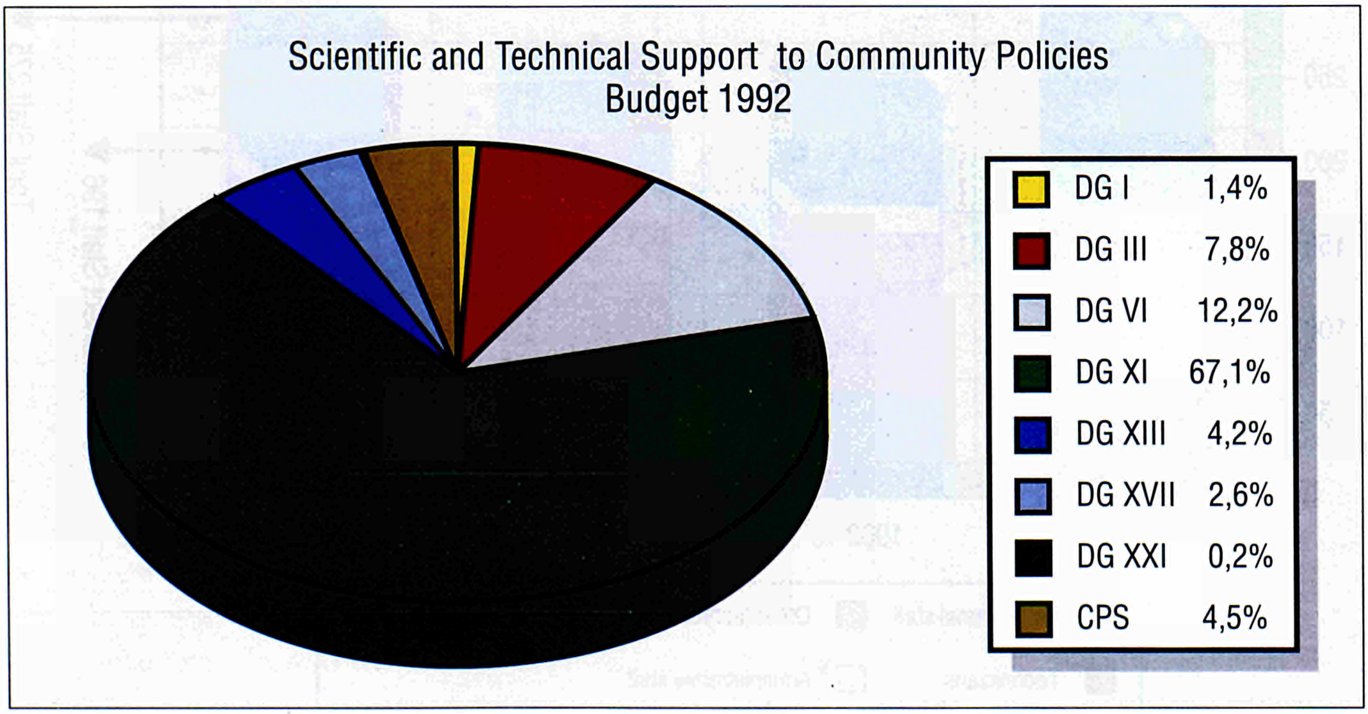
The Scientific and Technical support provided to the Commission Services in Brussels has been furtherly strenghtened, some 40% of the whole Institute's activity having been geared to that, with particular emphasis on the support provided to the General Directorate XI (Environment, Nuclear Safety and Civil Protection) which has to be considered the preferential customer of EI's expertise.
The statistics, which are given in

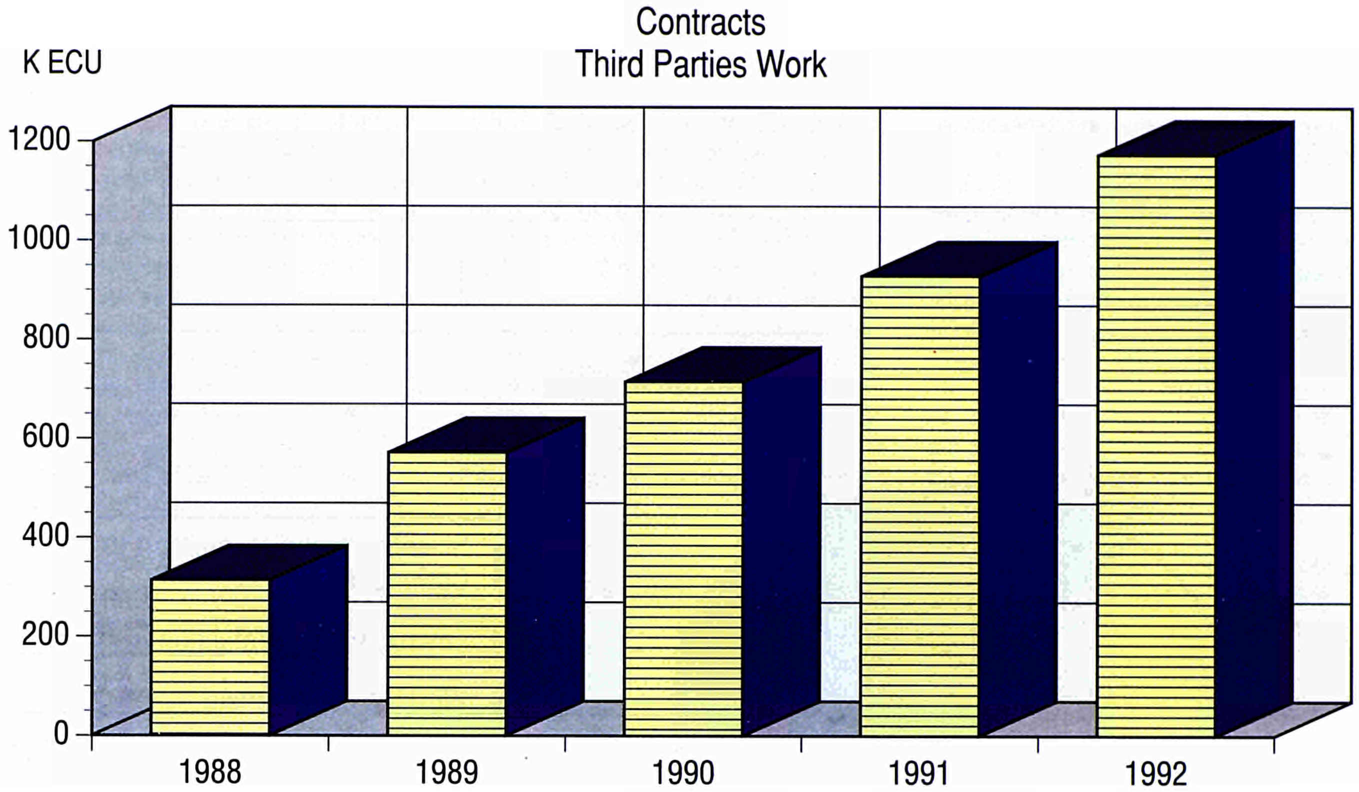


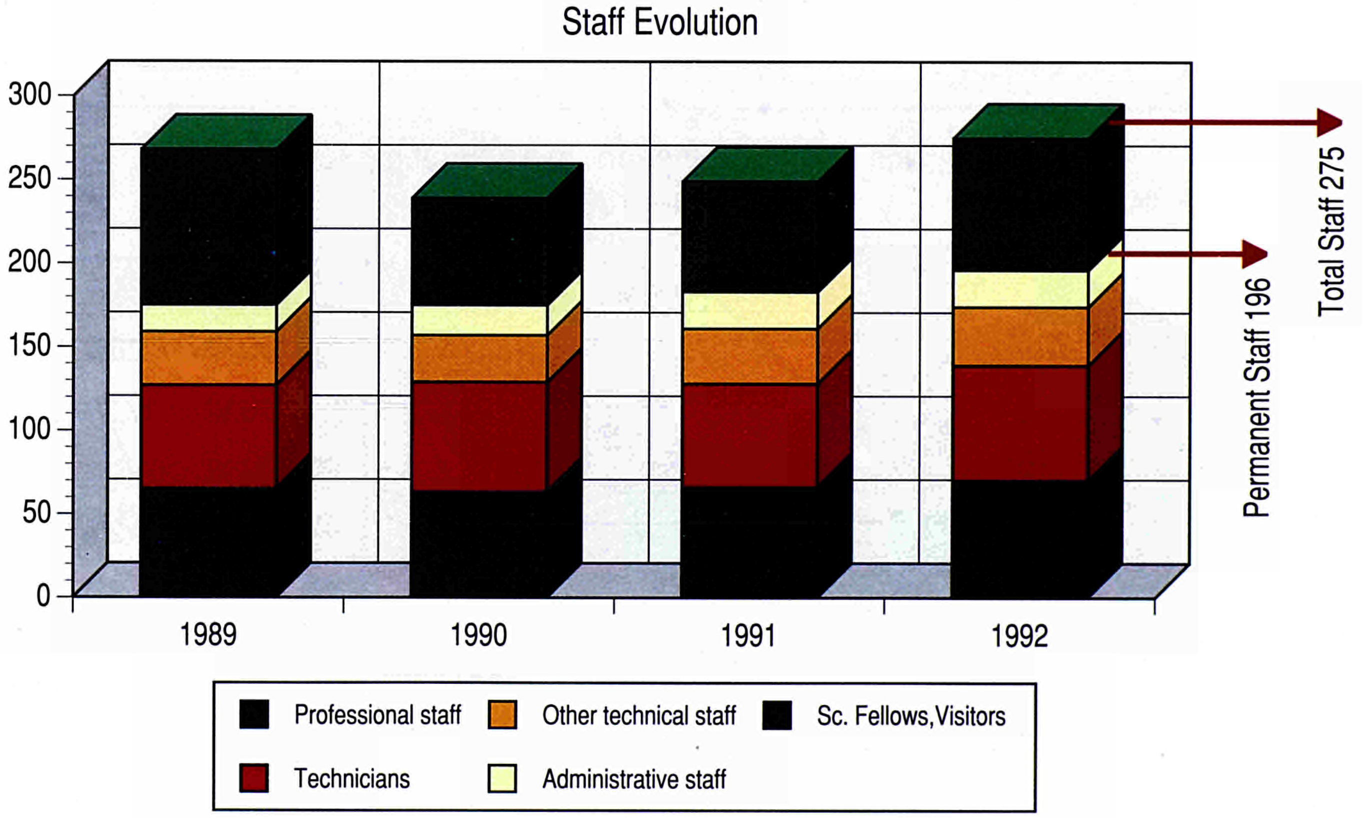
graphical form, are felt to be of assistance in assessing the value of the Institute effort in its contribution to both the Framework Programme and the establishment and implementation of EC Directives.

The achievements of 1992 are presented according to the research areas which they are referred to, rather than to the scientific units where they have been obtained.
Thus section 1 summarizes the progress for the projects of the areas "Global Change" and "Environmental Chemicals" included in the Specific Research Programme.
Relevant information concerning the Scientific and Technical Support provided to the Commission services are presented in Section 2.
Section 3 and 4 are dedicated to the results of the "Exploratory Research" and of the contract work for Third Parties, respectively.
In addition to the Annual Report the Institute is editing the half-yearly publication "Environmental Research Newsletter" which provides information on research and legislative action of the European Communities. The "Newsletter" is distributed freee-of-charge to those interested.






Contracts
Third Parties Work
K ECU
1200
1000
800
600
400
200
0
1988
1989
1990
1991
1992


Staff Evolution
300
250
200
150
100
50
0
1989
1990
1991
1992
Total Staff 275
Permanent Staff 196
Professional staff
Other technical staff
Sc. Fellows, Visitors
Technicians
Administrative staff

THE ENVIRONMENT INSTITUTE

Executive Summary

Executive Summary

1. SPECIFIC RESEARCH PROGRAMME

This report summarizes the main achievements of the research carried-out in 1992 by the Environment Institute.
The new multiannual research programme (1992-94) does represent at large extent the continuation of the preceeding one. However the presentation of the results is made by grouping them according to the main topic which they are referred to.
Section 1 presents the results of the Specific Research Programme according to the following research areas which the Institute has contributed to, i.e. :
- Global Change
- Environmental Chemicals

both included in the Environment Protection Programme.
Further, a minor contribution is provided to the Working Environment Programme in the form of scientific and technical information on issues related to chemical agents.

Global Change

This research areas encompasses five activies, i.e.:
- Tropospheric Chemistry;
- Environmental Monitoring;
- Atmospheric Sulphur and Climate;
- Atmosphere/Biosphere Interaction;
- Pollution Abatement.

As far as it concerns the first activity, laboratory studies of kinetics and mechanisms of atmospheric chemical reactions have continued to be addressed to the degradation processes of biogenic species having potential consequences on the oxidizing capacity of the troposphere and on the planetary radiation transfer. In this context, the reactions of the nitrate radical at night have maintained the main focus.
Further insight into the nighttime degradation of isoprene by the reaction with NO_3 radicals, have excluded that oxiranes, observed in the reaction at low pressure, can be an important reaction product in air at ambient pressure. Tetramethyloxirane has however been observed as a main product in the reaction of 2,3-dimethyl-2-butene.
In the oxidation of dimethylsulphide DMS) by the nitrate radical or by the OH radical in the presence of NO_x, a peroxynitrate (PAN-like) intermediate of still undetermined structure $(CH_3S(O)_xO_2NO_2$, is formed. Its thermal stability has been investigated. The formation of this compound, favoured in polluted coastal air, appears of potential importance for the transport of NO_x and sulphur over long distances in cold marine air masses.

In the gas phase reaction of the nitrate radical with methylsubstituted benzenes, nitro-derivatives appear to be formed as minor products. The formation of these toxic species may be relevant for the pollution of urban air.

The results obtained in studies performed at ambient pressure of the reactions,
alkenes + NO_3 —> products,
and
HO_2 + NO_3 — > products,
show a pronounced difference with respect to results in literature of studies performed at low pressure (< 20 Torr). This fact emphasizes the problem of the application of kinetic data for tropospheric reactions, measured by techniques requiring a low pressure of the reacting mixture. The case of reactions with occurrence of competitive pathways seems to be most sensitive to this problem and underlines the importance of testing reaction schemes in smog chamber studies at tropospheric pressures.

The activities for Environmental Monitoring of atmospheric pollutants have been continued. The extension of the re-evaluation of historical data of tropospheric ozone levels, show that one century ago, the surface ozone levels at mid latitudes of the southern hemisphere (SH) were comparable to those observed in the northern one (NH). At the present time, the ozone levels at mid latitudes of the SH are lower than those observed in the NH. Moving to tropical latitudes, the re-evaluated historical data are lower than those observed at mid latitudes of both NH and SH. The same difference, with ozone levels at tropical latitudes lower than at mid latitudes, holds for the present situation.
During the 1991-1992 European Arctic Stratospheric Ozone Experiment (EASOE), the Environment Institute acted as a network station (Ispra: 45.803° Latitude, -8.627° Longitude) of the ground based observing system, set-up to provide, on a daily basis, maps of the total ozone fields over Europe and the Arctic.
A decrease of the total ozone column has been observed at Ispra in winter months, when compared to the monthly means recorded at Arosa (CH) over the 1957-1988 period.

For what it concerns Atmospheric Sulphur and Climate, within the framework of modelling studies have concerned the formation of aerosols from the gaseous precursors dimethyl sulphide (DMS) and sulphur dioxide and their role in cloud formation.
Two new modules of the model were developed for DMS kinetics and for aerosol to cloud transition respectively. At each stage of the development the model results are compared with literature data by assessing in particular the impact of system uncertainties on model prediction.
The sulphur version of the global tracer model MOGUNTIA has been successfully installed on the main institute workstation.
MOGUNTIA has been extended to study the feasibility of modelling aerosol dynamics within a 3-D global transport model. A short study was also undertaken using the model to assess the contribution of European sulphur emissions to global atmospheric sulphate concentrations.
Two scenarios for the production of cloud condensation nuclei (CCN) from DMS have been compared. The first assumes that DMS emission, chemical reaction and subsequent aerosol formation and growth all take place within the marine boundary layer (MBL).
The second assumes that DMS is transported to the free troposphere, where it is transformed into aerosol

particles that eventually subside back to the boundary layer. Only the second scenario predicts aerosol concentrations, cloud condensation nuclei in particular, that correspond with the observations.Laboratory studies have been focused on the oxidation path-ways of DMS and on aerosol formation from the products of DMS and SO_2 oxidation. These studies, performed as part of the LABVOC/CEC-DGXII joint European project, have concerned in particular the role of a relatively stable PAN-like intermediate formed by the degradation of DMS in the presence of NO_x.
For the laboratory studies on the interactions between sulphur containing gases (DMS, SO_2, H_2SO_4 (gas) and aerosol particles (soot, sea-salt) an experimental facility is being set up, of which two major components have been completed, i.e. the photochemical flow reactor and the OH generator. HO radicals are produced within a continuous generator of HONO by UV light-induced HONO dissociation.
Field measurements on the North Atlantic, were aimed at evaluating the relative importance of natural and anthropogenic sources to the sulphur budget of the marine atmosphere in this area, the gathered data being eventually used to improve the description of sulphur aerosol in global circulation models, and assess its effect on climate; this latter step is done within the framework of international collaborations (GLOMAC/EUROTRAC, SINDICATE / CEC-DGXII and IGAC /IGBP).
Global models have been used to assess the transport of European (aerosol) pollution on a global scale.

Work on atmosphere-biosphere interactions continued the previous year's activities contributing to the understanding of the impact of natural and anthropogenic emissions on the processes that determine the chemical composition of the atmosphere. Within the framework of the global change issue, the work has been further re-oriented from the acid deposition problem to the study of biogenic emissions from Mediterranean ecosystems and their potential role in tropospheric chemistry. To this aim, a project on Biogenic Emissions in the Mediter-ranean Area, the BEMA project, has been developed in collaboration with some European laboratories.
The core of BEMA is a series of intensive field campaigns conducted at representative sites in Italy, France and Spain. The operational plan for the first campaign in June 1993 at the Castelporziano site near Rome has been completed. Besides by upscaling activities, the field campaigns are prepared and complemented by laboratory experiments to: (i) identify, under defined environmental conditions in teflon-cuvettes, at selected Mediterra-nean plant species in the green-house, the compounds emitted and the factors controlling trace gas exchange, and (ii) study, in teflon bags, the chemical transformation of emitted compounds in the NO_x photochemical system.

The first topic has been investigated in the Continuous Stirred Tank Reactor (SCTR)-systems already described in the Environment Institute Annual Report 1991. Permanently installed chambers in the large greenhouse are used to study trace gas exchange at tree canopies, whereas mobile cuvettes have been developed for screening studies at shrubs and tree branches and will be used during the field campaigns.

Studies on emission rates and on the environmental/physiological factors controlling them have been continued, with spruce *(Picea abies)* being more and more replaced by the common Mediterranean tree species *Pinus pinea* and *Quercus ilex*. It has been shown that this evergreen Mediterranean oak is emitting large amounts of monoterpenes, besides isoprene, though having no detectable content of monoterpenes in leaf or bark.
Another experimental work with plants was the screening of 15 Mediterranean shrub species cultivated in the greenhouse for their pools and emissions of volatile organics.
The second activity has dealt with the role of biogenic emissions (monoterpenes and isoprene) in the chemistry of the clean and perturbed atmosphere, including product identification, ozone forming potential and gas-to-particle conversion. In 1992 the experimental work was focussed on studies with selected terpenes (α-, β-pinene), isoprene and, for comparison, with an anthropogenic compound (toluene), with regard to their ability to form ozone in the NO_x-photochemical system. Compared to isoprene/ NO_x and toluene/NO_x mixtures, α- and β-pinene/NO_x-mixtures were found to be less reactive (ca. 30 %) in terms of ozone production rates with the reactivity being in the order isoprene >toluene>> α-, β-pinene. Moreover, comparing the data obtained for the pinenes with the data obtained for isoprene and toluene under similar experimental conditions (UV-intensity, temperatures, humidity) it can be seen that the compounds with the highest reactivity towards ozone (α-, β-pinene) are the most effective in suppressing ozone formation.

Lastly, within the framework of the pollution abatement the activity has been focused on the removal of nitrogen oxides from waste gases Gas absorption experiments in a 4 cm diameter laboratory column have been continued to study the absorption of NO in a Fe(II)NTA complex. A suitable reaction model was developed. The equilibrium constant for the system NO/Fe(II) NTA was determined for a temperature range from 22 to 80°C.

Work for the electrolytic removal of nitrates from waste waters was continued. It was proven that the electrolytic reduction is a mass transfer controlled process This implies that the application of electrodes with an enlarged surface area is necessary.

Environmental Chemicals

This research area includes a multiplicity of activities grouped under the following headings:
- Evaluation of chemicals, comprising the ECDIN databank and the Trace

Metals Exposure and Health Effects;
- Indoor Air Pollution;
- Soil, Water, Waste.

While a public version of ECDIN is accessible through DIDMI (Deutsches Institut für Medizinische Dokumentation und Information, Köln) and through a host in USA, a new version of ECDIN CD-ROM has been made available, the number of chemical compounds included in it having been raised to about 7,500.

As far as it concerns Trace Metals exposure and Health Effects the activities are aimed at establishing dose-effect relationships to prevent health hazard from exposure to trace metals. For the purpose three projects -EURO TERVIHT, TRACY and HAMBIHT - are being developed.

Reference values for trace elements in tissue from EC inhabitants are established within the framework of the EURO TERVIHT project as the baseline values for clinical /toxicological assessment studies.

For the purpose, criteria for approaching background value measurements have been established. In cooperation with the Institute of Occupational Health of Copenhagen an assessment has been done for a wide ranging number of trace elements in body fluids of danish population.

As a further development of the studies on the general population in northern Italy, the influence of parameters affecting the experimental ranges of values for trace elements has been investigated. The study has highlitgthed the environmental factors and the biological variations including dietary intake as well as individual metabolism.

As a further development of the HAMBIT (Hard Metal Biomonitoring in Human Tissues) project the biological monitoring of 252 hard metal workers has been performed by determining Co in air and in different human body compartments (urine, blood, pubic hair, toenail, bronchoalvedar lavage). The study has showed that immunological mechanisms causes pathological alterations, the development of the disease being more related to individual factor then to environmental conditions.

The AMAMMET (Animal Testing Methods vs. Alternative Testing Methods in Metal Toxicology) is being developed within the framework of Trace Metals Metabolism and Biochemical Effects studies. Focus has been placed on risk to Co exposure. ^{57}Co, ^{58}Co and ^{60}Co labelled compounds have been used for the study of the interaction of Co as well as of its biotransformation in urine. Speciation of Co in urine of hard metal workers suggests that inorganic Co inhaled can undergo biotransformation in vivo. Experiments of exposure to Co performed on rats have been utilized to elucidate the mechanism of Co transfer in specific body tissues.

Eight cell lines have been developed for *in vitro* environmental and occupational metallotoxicological studies, for screening tests to establish metal toxicity rankings, for setting up uptake effect relationship and for clarifying molecular mechanisms of metal toxicity.

In the framework of genotoxicological studies on environmental chemical compounds a new line of transgenic mice has been constituted offering the advantage to perform a semplified analysis of chemically-induced damages. The methodology for deriving primary cell cultures from liver, kidney and lung of mouse has been established. The above organs deserve top priority investigation as they are target of many genotoxic compounds.

Lastly, techniques allowing the selective inactivation of any gene in the mouse genome have been set up. This makes feasible animal models in which human hereditary pathologies originated by mutations in well known genes are reproduced.

Within the framework of the "indoor" pollution activity, research was focused on the development and validation of methods for the characterization of organic indoor pollution, its sources and sinks. An international interlaboratory comparison experiment aimed at validating a small chamber method for the determination of organic emissions from indoor materials and products was completed. The development of a method for the determination of semivolatile organic compounds (SVOC) in home dust and indoor air has been continued and a study of the deposition of organic vapours on indoor surface materials has been started, partially supported by the CNR-ENEL project 'Interactions of energy systems with human health and environment', Rome, Italy (see also Section 5 of this report). In addition a walk-in type environmental chamber of 30 m^3 has been installed and tested.

The Concerted Action "Indoor Air Quality and its Impact on Man" has been included as European Collaborative Action in the JRC Environment Programme. Scope and purpose of the action have been reviewed, guidelines for ventilation requirements in buildings have been published which introduce new rationales for the assessment of ventilation requirements, the final draft of a report on biological particles in indoor environments has been reviewed and accepted by the Steering Committee and a Working Group has been charged to develop criteria and protocols for the evaluation of organic emissions from indoor materials.

In the field of Chemical Waste, soil pollutant interaction studies have been addressed to evaluate the mobility in different soils of organic pollutants having wide ranging water solubility. This has included both organic compounds (pesticides, tanning agents, polychlorinated byphenils) and trace metals (Cr, As, Se). The studies are performed by means of open air lysimeters and field experiments. In view of determining the complexation constant the study of the competition between Rare-Earth (RE) elements, humic acid and Cr (III) has been continued using continuous, synchronous and time-resolved fluorescence spectroscopy. Contrary to the fast complexation of Tb and Eu, a slow kinetic for Cr (III) has been found the equilibrium being reached after at least 24 hours.

Further studies have concerned the adsorption of Co and Hg on γAl_2O_3

in the presence of different concentration of humic acid and the Cr (VI) interaction with a mixture of clay minerals. In the latter case the reduction of Cr (VI) to Cr (III) seems to occurr the hypothesis being supported by separate sorption tests in the presence of phosphate to displace anionic Cr (VI).
In a similar way an experimental program has been launched using tracer techniques aimed at investigating mobilizing and scavenging processes for Co in aquatic system, focus being placed on the role played by MnO_2 and by humic acids.

Within the framework of the analytical development, systematic studies have been carried out on the application of supercritical fluid extraction (SFE) in trace organic analysis and on novel extraction techniques for determining semivolatile compounds in drinking water. The technique, which is based on PTFE membranes with C8 or C18 bonded silica particles, has been successfully applied to PBCs, chlorinated pesticides and PAHs at ppb levels from spiked drinking waters.
An Ion Trap Mass Spectometer coupled to a Purge-and-Trap and to gas chromatography in a completely automated system has been set up and applied to the analysis of volatile organic compounds in drinking water.
The study for the set up of a method for the analysis of PCB congeners has been concluded allowing for isomer-specific determination at ppt-ppb levels of PCB in samples of wide ranging nature.

As far as it concerns the Waste Management, research on the cement matrix solidification of hazardous waste has been continued. Leaching experiments both in static and dynamic water conditions have been run to evaluate the technique; further work is planned to investigate the release mechanism taking into account the matrix composition.

In the field of Water Quality further progress has been achieved in the development of the MITO project focused on the analytical cytology of phytoplankton, on aquatic biotoxins, on algal taxonomy and physiology and on modelling. The results from a first experi-mental cruise in Greece have been circulated and have shown that flow cytometry (FCM) can be used for fast and accurate measurement of total living cells and for evaluation of the phytoplankton biomass.
As regards algal toxines, the use of murine parenchymal cells from the perfusion of the liver of CD-1 male mice has been investigated for accurate measurement of the toxicity of algal extract, the 50% lethal dose (DL 50) of the Okadaic Acid being used for calibration. The approach appears to be 10,000 and 15 times more sensitive than the mouse and the Aune tests respectively.

The development of a new hydrodynamics code (ISPRAMIX), to be applied in the Northern Adriatic area, has been started for the numerical modeling of the biological activity. Preliminary verification studies have shown a satisfactory agreement with the results of earlier studies.

Within the framework of the studies of point and non-point sources of trace metals in a fish water system, Cr has been evaluated in terms of imput/output balance in Lake Orta. Cr has been found to show a strong tendency to particularization.
Analytical data from the monitored tributaries to the lake, from the sediments and from the outlets indicates that the internal Cr loading is negligible and that Cr concentration in the lake can be decreased in a rather short time by reducing the external loading.
In the context of the AQUACON project - which is aimed at identifying, quantifying and eliminating / reducing systematic and random measurement errors associated with the analysis of environmental samples - collaborative studies have been organized to deal with diffferent steps of an analytical procedure.
These have included :
- sampling errors in the determination of trace metals in sea water;
- errors associated with the sample treatment in the determination of Hg in fish;
- systematic and random errors in the procedure for the analysis of acid rain;

allowing to identify critical steps to be further investigated.

2. SCIENTIFIC-TECHNICAL SUPPORT TO COMMUNITY POLICIES

As the follow up of the activities carried-out in the preceeding year, expertise and technical assistance has been provided to the following Directorates General or Services of the Commission:
- **Directorate General I** (External Relations) for the implementation of the support to IAEA's PACT program;
- **Directorate General III** (Internal Market and Industrial Affairs) for the development of a data bank on pharmaceutical products;
- **Directorate General VI** (Agriculture) for the analysis of wines and dairy products as well as well as the set-up of a data-bank of NMR fingerprints of european wines;
- **Directorate General XI** (Environment, Nuclear Safety and Civil Protection) in the field of the Environment, of the Radioactive Environmental Monitoring (REM) and of the European Centre for the Validation of Alternative Testing Methods (ECVAM);
- **Directorate General XIII** (Telecommunication, Information Industry and Innovation) in the field of innovative technologies for flue gas desulphurisation (Ispra Mark 13 pilot plant);
- **Directorate General XVII** (Energy) for the control of fissile materials;
- **Directorate General XXI** (Customs and Indirect Taxation) for the characterization of imported goods;
- **Consumer Policy Service** for the control of cosmetics, food products and water.

As the major effort has been spent for the support to DG XI, in the following only the essential achievements related to the activities devoted to DG XI are summarized, while a short description of all the activities in support to Community Policies is given in the section "Main Achievements".

Scientific-Technical Support to Directorate General XI

In the field of Environment the support provided to DG XI has concerned the following issues:
- Chemicals
- Atmospheric Pollution
- Chemical Waste
- Water Quality
- Radioactivity Environmental Monitoring (REM)
- European Centre for the Validation of Alternative Testing Methods (ECVAM)

As far as it concerns the chemicals, the support for the implementation of EC Dangerous Substances directive (67/548/EEC and subsequent amendments) has been continued. This has entailed full responsability for the collection, processing and storage of all data supplied by industry and commerce to the Commission as well as for the development, management and updating of the European Chemicals Inventory Database (EUCLID).
In addition, expertise has been provided in the preparation of priority lists and in the development and application of risk assessment procedures for existing chemicals. Within the framework of the Quantitative Structure - Activity Relationship (QSAR), methodologies have been developed for comparing statistical models and a computer program has been tested for the clustering of a large number of structures.
As far as it concerns the Testing Methods work has been continued for the preparation of 200 kg EURO-soil samples and for the definition of adsorption/desorption testing of chemicals on soils.

In the area of atmospheric pollution the problem of equivalence of methods for the measurement of fine suspended particulate matters has been tackled for the implementation of the directive 80/779 EEC amended by 89/427 EEC. The EC reference equivalence procedure will be based on ambient field testing, JRC Ispra being one of the 4 sites selected for field campaigns.
Actions have been continued for the quality assurance of NO_2 calibration procedures implemented in the Member States in the framework of the directive 85/205/EEC. For the purpose, ten laboratories from seven Member States took part in an intercomparison exercise, 90% of the measurements being within 10% confidence limit.
The results of the intercomparison exercise on VOC measurement - as recommanded by the directive 92/72/EEC - have been evaluated. The lack of sufficient accuracy (acceptable target: 15%) coupled with the observed good precision within each participating laboratory suggest that gas phase mixtures in cylinders might not be appropriate as calibration standard.
The JRC took part (NO_2) to an intercomparison campaign for NO_2, SO_2 and O_3 passive samplers, carried out within the framework of a collaboration with the Bavarian Lander and the GSF Institute, to evaluate the transport of pollutants in the alpine region. The EMEP station of the JRC has been selected as one of the measuring sites. The statistical evaluation of the data will be completed early in 1993.
A survey of NO_2 pollution in Toulouse (France) by means of passive samplers has been designed in collaboration with the Observatoire Régional de l'Air en Midi-Pyrénées (ORAMIP) in view of identifying the sites sensitives to emission from traffic, to emission from industrial plant and to mixed pollution, respectively.
In addition to the chemical parameters regularly monitored in air, atmospheric particulate and precipitation samples, and to meteorological parameters, discontinuous measurements of VOCs in air samples collected in ten different sampling sites over EC have been started as a part of the EMEP monitoring programme.
Further progress has been achieved in the intercalibration programme on PAN measurement, a good correlation between PAN and Ozone values having been experienced.
Lastly, a contribution has been given to the development of a ISO standard method for determining fibers in emissions from asbestos plants, in view of implementing the EC directive EEC 87/217.

Within the framework of the Chemical Waste work has been started for the informatisation of the European Waste Catalogue which is being elaborated by a specialized working group. For the purpose a detailed work programme has been designed.

As far as it concerns the Water Quality, emphasis has been given to the evaluation of non-point sources and discharges to the aquatic environment of As, Pb, Hg, Ni, B, Mo and Sn.
Expertise has been made available for the development a new EC Directive concerning the ecological quality of surface waters. In this connection a first study on quality assessment schemes for lakes within the EC area has been completed. A simplified classification scheme for assessing the ecological status of freshwater lakes based on widely-accepted physico-chemical and biological features has been elaborated.
In a parallel way, a study on the methodologies adopted for surveying and monitoring the marine environment has been completed. The study has considered the fundamental processes of the marine environment, the parameters describing the environmental behaviour and the related analytical methods, the automatic monitoring systems, the numerical simulation models, the relating criteria of calibration and their utilization with territorial /environmental information system and the water quality standards for different uses.

In the field of the Radioactive Environmental Monitoring (REM) major focus has been placed on :
- the REM data bank;
- the Occupational Exposure data bank;
- the Atmospheric Transport Models

both for long range and mesoscale distances;

- ETEX (European Tracer Experiment);
- ECURIE (European Community Urgent Radiological Information Exchange).

As far as it concerns the REM data bank the data have been transferred to the UNIX server URANO entailing the adaptation of the existing ADABAS software. Tables and figures referred to the monitoring report (1987-1990) were prepared from the data gathered from the Member States and stored in the data bank.

The development of Easy Proteo package for digitising monitoring data has been completed, this tool being also useful for Member States for entering their monitoring data in their respective national data bank.

The complete database system for occupational exposure has been upgraded from Oracle-5 to Oracle-6. Exposure data for 1991, supplied by 114 reactor units, have been introduced into the database and a set of procedures has been developed to extract information from the database according to specific formats. Further, the definitive version of the Electronic Questionnaire has been developed the software package, under MS-DOS operating system, having been deliverd in seven versions, i.e.: English, German, Spanish, Dutch, Italian versions plus French version for EDF and non-EDF plants, respectively.

Within the framework of atmospheric transport models an automated procedure has been developed based on a fitting of a function describing the observation field which thus becames a new area source for updating the predictions.

As far as it concerns mesoscale distances two circulation models have been applied to different localities, i.e. near Marseille, where sea-breeze develops over a complex but rather flat area and the Athens region where the local circulation driven by the sea-land breeze is strongly influenced by a montainous ridge. The results of the comparison of the simulation with the two models showed a good agreement for daytime data while considerable differences were experienced for the night data. A new code (MONTE-CARLO) has been developed - based on further improvement of routines of an existing codes - for the description of transport and dispersion of pollutants.

A Technical Specification Document has been prepared for the ETEX experiment; the document is only valid for the first dry-run. According to this document, during the dry-run, the participants to the experiments have to send to JRC concentration contours every 24 hours, as a real accident would occur, to anticipate the kind of results that they are going to load on floppy disk. A system for the conversion of points and polygons in different projections to the same map had to be created.

Lastly, as far as it concerns ECURIE, the encoding-decoding software has been developed by IAEA and by JRC (encoding part). This will be made available in the nine official EC languages.

Two working groups have been set up to deal with the proposal of the Environment Institute for the harmonization of the measurements and the reporting of environmental radioactivity in EC Member States. The working group will tackle the following issues :

- data transfer between Member States and CEC;
- establishment of a dense monitoring network;
- establishment of a sparse network of sensitive monitoring stations;

Lastly, as far as it concerns the European Centre for the Validation of Alternative testing Methods (ECVAM) efforts have been focused on the preparation of premises and facilities for in vitro toxicology studies.

On the other hand, several meetings have been convened for the organization and the evaluation of activities aimed at the development and the validation of in vitro alternative methods for acute system toxicity, the use of cultured hepatocytes and the establishment of a data base on in vitro alternative tests.

3. EXPLORATORY RESEARCH

Four projects were included in this area, i.e. :

- **Absolute Chemical Analysis by Laser Methods;**
- **Laboratory for Separation Sciences;**
- **DNA Adducts;**
- **Aerosol Tracer Technique for Long Range Applications;**

the first three out of them being the evolution or the continuation of activities related to topics already dealt with in the preceeding year.

The first project is aimed at the theoretical evaluation of an absolute methodology of analysis of both atomic and molecular species, based on laser excited fluorescence and ionization. To achieve this goal, the theoretical modeling of the interaction with the laser radiation is needed, a three energy level scheme for Tl and a four energy level scheme for Au having been used for temporally resolved measurements. This has given access to the quantification of fundamental parameters required for the characterization of the analytical signal.

Within the framework of the laboratory for Separation Sciences, further progress has been achieved in the evaluation of crossflow membrane techniques in the treatment of waste water using a dedicated pilot plant.

Both tubular and spiral membranes have been characterized as far as their fluxes and separation capabilities are concerned.

A Capillary Electrophoresis (CE) method has been developed and evaluated for its use ofr the separation, quantification and further identification of modified nucleosides 3' monofosphates.

Capillary Zone Electrophoresis (CZE) has been investigated for micro-preparative applications, the collected fractions having been characterized and identified in many cases by FAB mass spectrometry.

The separation of the same compounds in Free Zone Electrophoresis has been studied, good resolution for nucleotides and for most nucleosides having been obtained. This allows mass spectrometry analysis to be performed avoiding the limitations associated with the presence of Na dodecylsulphate in the collected fractions as it was the case with CZE.

Research on DNA Adducts have been focused on DNA alkylation following exposure to 1, 2, 3, 4 diepoxybutane (BUT) especially in relation to the development of a method for human biomonitoring.
A major adenine adduct has been identified and a HPLC/^{32}P-post labeling method for its detection in DNA samples has been developed.
Studies on DNA damage and repair following exposure of rodents' cells and their mutants dejective in DNA excision repair are being performed to ascertain whether damage is lasting so long as to be used as biomarker of BUT exposure.
Studies on the identication of biomarkers in fish have been carried out both on in vivo eat fish and on in vitro primary culture of hepatic cells.

The problem of producing tagged particles in the submicron size range has been afforded as the perequisite condition in the development of an Aerosol Tracer.
In fact the siumltaneous release of an inert tracer with a tracer which reacts and deposits would allow to get information on these processes along the tracer trajectory.
A number of substances have been screened for the purpose, luminal or an equivalent chemiluminescent compound representing the best approach in view of its excellent detectability at very low concentrations level.
A 70 m^3 environmental room has been prepared where the aerosol can be generated and kept for several days in view of performing the necessary detectability and stability tests.

THE ENVIRONMENT INSTITUTE

1. Specific Research Programme

GLOBAL CHANGE

This topic encompasses three main research areas, closely linked each other, i.e., atmospheric chemistry, atmospheric physics and atmosphere / biosphere interaction.

The projects developed within these areas are aimed at studying transport, diffusion and chemical fate of biogenic and anthropogenic emissions in perturbed atmospheres, at establishing the trends of trace atmospheric species relevant to the photochemistry and the planetary radiation budget with emphasis on sulphur-containing gases, at the theoretical modeling and experimental validation of mesoscale and long range atmospheric physico-chemical transformation and transport processes, and at laboratory and in-situ studying biosphere /atmosphere interaction with emphasis on the Mediterranean area.
The progress accomplished in the course of 1992 is shortly described in the following.

Tropospheric Chemistry: laboratory studies of reaction mechanisms and kinetics.

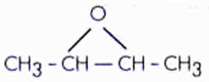
Oxidation at night by the nitrate radical, NO_3, is more and more felt as an important sink for biogenic and anthropogenic compounds in the troposphere, affected by increasing levels of NO_x.
The nitrate radical, which is rapidly photolized in daylight, builds-up at night, formed by the reaction between NO_x and O_3. Its reaction with atmospheric trace gases , in addition to providing relevant scavenging pathways, alternative to those photochemically driven at daytime, may have other consequences. On one side it may lead to the formation of noxious compounds, on the other side it may change the budget and the equilibrium distribution of NO_x, with an impact at the regional/global scale on the tropospheric ozone budget and on the atmospheric oxidation capacity.
The research in progress in the previous years on the chemistry of this radical has been extended to get further insights into the mechanisms of the nighttime oxidation of alkenes, dialkenes and of aromatics.
The results of the studies on the mechanism of oxidation of organo-sulphur compounds, with special attention to dimethylsulphide, are part of the joint effort in the "Environmental Sulphur Project" and presented in another part of the Report.

Reaction of NO_3 with alkenes and isoprene

A study was carried out in collaboration with the University of Kiel on the formation of oxiranes in the reaction of the nitrate radical with alkenes and with isoprene. The main goal was to solve some discrepancies observed in the results of experiments previously conducted in Ispra and Kiel. REMPI studies performed at Kiel reacting the species at low pressure showed oxiranes to be the main product of the reaction between NO_3 and the alkenes under investigation. On the contrary, FTIR studies performed at Ispra and in other laboratories reacting the same species at ambient pressure showed nitroxy- and carbonyl-compounds to be main reaction products. In the joint study the Ispra chamber facility was used to react cis- and trans-2-butene, 2,3-dimethyl-2-butene and isoprene with NO_3 radicals in N_2/O_2 mixtures or in Argon at pressures ranging from 740 to 20 Torr.
Oxirane derivatives were found as most abundant products in the reaction in argon at 20 Torr; but were below their detection limit when the reaction was performed in air at 740 Torr. An interesting observation was that both cis- and trans2-butene gave a mixture of cis- and trans-1,2-dimethyloxirane. This demonstrates the formation of a reaction intermediate that allows rotation around the C2-C3 bond, i.e.

$$CH_3-CH=CH-CH_3+NO_3 \xrightarrow{M}$$

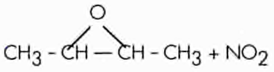
$$CH_3-CH(ONO_2)-CH-CH_3 \to$$



$$CH_3-\overset{O}{\widehat{CH-CH}}-CH_3$$

and not

$$CH_3-CH=CH-CH_3+NO_3 \to$$



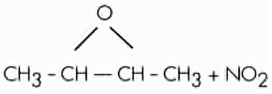
$$CH_3-\overset{O}{\widehat{CH-CH}}-CH_3+NO_2$$

The yield of oxirane observed to be as high as 20% in the reaction of isoprene with NO_3 in argon at 20 Torr, was reduced to a negligible value in the reaction in air at ambient pressure. This information adds and supports the results of the previous studies on the nighttime oxidation of isoprene.
The reaction of 2,3-dimethyl-2-butene with NO_3, which has the oxirane as main product (16.2% yield) also at ambient pressure in air, was studied in the range 20-740 Torr using either argon or air as diluent gas and in a N_2/O_2 mixture varying the oxygen concentration. The oxirane yield shows a strong negative dependence upon the O_2 concentration. In general this relation can be explained by a competition between reactions (the example refers to the 2-butene), controlled by the different amount of oxygen present:

$$CH_3-CH=CH-CH_3+NO_3 \xrightarrow{M}$$

$$CH_3-CH(ONO_2)-\dot{C}H-CH_3$$

$$CH_3-CH(ONO_2)-\dot{C}H-CH_3 \to$$



$$CH_3-\overset{O}{\widehat{CH-CH}}-CH_3+NO_2$$

$$CH_3-CH(ONO_2)-\dot{C}H-CH_3+O_2 \rightleftarrows$$

$$[CH_3-CH(ONO_2)-CH(O^{\cdot}{}_2)-CH_3]^*$$

$$[CH_3-CH(ONO_2)-CH(O^{\cdot}{}_2)-CH_3]^*+M \to$$

$$CH_3-CH(ONO_2)-CH(O^{\cdot}{}_2)-CH_3+M$$

$$CH_3-CH(ONO_2)-CH(O^{\cdot}{}_2)-CH_3 \to \text{products}$$

Reaction of NO_3 with aromatics.

A result of the previous studies performed on the nighttime oxidation of methylsubstituted benzenes, was the observation of nitroderivative compounds in the reaction products. The possible occurrence of artifacts, caused by reaction of the products on the sampling columns, was evaluated in a series of experiments performed in collaboration with the University of Milano, Italy. The conclusion of these investigations is that nitro-derivatives appear to be formed as minor product in the gas-phase reaction between NO_3 radicals and methyl-substituted benzenes.
The formation of these toxic compounds is especially worth of attention in polluted urban air, where the presence of aromatics shows a tendency towards an increase.

NO_Y interconversion processes: the reaction between NO_3 and HO_2.

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

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

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

and in particular to the second branching reaction which may be under some conditions an important source of OH radical at night. The study conducted in 1991 at atmospheric pressure resulted in a rate constant for the second branching reaction slower by one order of magnitute than the values measured under low pressure conditions, thus reducing the impact of this potential nighttime source of OH radicals. In the experiments performed at 750 Torr only one measurement could be done at the end of each run, by reducing to 50 Torr the total pressure in the chamber.The study was then repeated, using the same experimental approach, with the radicals reacting at 50 Torr total pressure. The pressure applied was still higher than that used in the above mentioned flow tube experiments (<2Torr). The important advantage of this experimental condition was however the possibility to follow, by frequent measurements, the build-up of the reaction product $^{16}O^{13}C^{18}O$ (see Annual Report 1991), resulting from the reaction between the OH radicals formed by the reaction b) and the isotopic tracer $^{13}C^{18}O$ added to the reaction mixture:

$$^{13}C^{18}O + {}^{16}OH \rightarrow {}^{16}O^{13}C^{18}O + H$$

The chemical system was modelled using the FACSIMILE computer program to evaluate the rate constant K_b by a best fit to the experimental data.
Again only an upper limit could be measured since oxidation of $^{13}C^{18}O$ in the camber was observed in some cases even when the tacer was mixed with purified air only. The average of the best fit values for K_b (in parenteses one standard deviation) was $0.17 \cdot (\pm 0.26) \cdot 10^{-12}$ $cm^3 \cdot molec^{-1} \cdot s^{-1}$ at 296 K. The upper bound of the 95% confidence interval for the mean of the upper limit calculated for the different runs was $0.80 \cdot 10^{-12}$ $cm^3 \cdot molec^{-1} \cdot s^{-1}$ at 296 K. This conservative estimate of the upper limit of K_b at 50 Torr is significantly below the values measured at low pressures (0.5 - 2 Torr) : $(3.6 \pm 0.9 \cdot 10^{-12}$ $cm^3 \cdot molec^{-1} \cdot s^{-1}$ at 0.5 Torr and $(2.5 \pm 0.7) \cdot 10^{-12}$ $cm^3 \cdot molec^{-1} \cdot s^{-1}$ at 2 Torr.

Application of spectroscopic techniques

The set-up of a general purpose fluorescence system with multispectral detection capabilities has been completed. The set-up includes two tunable dye lasers: a nitrogen laser-pumped dye laser, with a pulse width of approximately half nanosecond, tunable from the uv through the near infrared and an excimer laser-pumped dye laser, also tunable throughout the entire uv - visible - near infrared range, but characterized by a pulse width of several nanoseconds. The fluorescence ligth is dispersed with a 1 m monochromator, equipped with three interchangeable gratings, and detected with an intensified, gateable diode array, with extended uv response. Time resolved fluorescence spectra from solid, liquid and gaseous samples can be taken with a nominal time resolution of 5 nanoseconds, and with a spectral coverage which ranges from about 4 nm to 140 nm, depending upon the grating selected.

The system has been tested with atmospheric pressure flames for the detection of the fluorescence spectrum of OH radicals. The two-photon fluorescence of atomic radicals, such as hydrogen and oxygen, is planned by using a low uv wavelength obtained by Raman shifting the uv output of the dye laser. Other schemes for chlorine and nitrogen are also possible.

The design of a new cell allowing photoacoustic measurements with laser excitation in the liquid phase has been planned. The cell should also permit simultaneous measurements of the fluorescence of the liquid sample as well as fluorescence from the gaseous atmosphere above the liquid surface. Both excitation and detection will be accomplished by means of fiber optics.

Environmental Monitoring

Tropospheric ozone in the pre-alpine and alpine regions.

As follow-up of previous studies on the mechanisms responsible of influencing the tropospheric ozone distribution in the preAlpine region, ozone measurements available in the pre-Alpine and Alpine regions since 1987 have been collected. The 5-year database has been analysed in terms of relations between measured ozone concentration, synoptic meteorological evolution and air masses circulation on regional scale *(Fig. 1.1)*. A study on the characterization of the meteo-rological conditions leading to photochemical pollution episodes on regional scale is in progress.

Historical ozone data.

The large concern on the positive

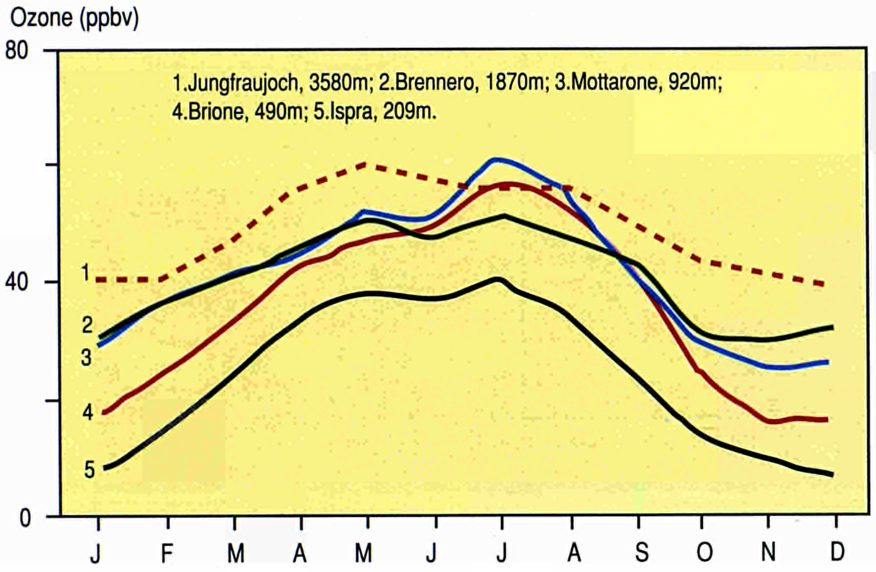


Fig.1.1 Seasonal course of tropospheric ozone levels recorded at different altitudes in monitoring stations of the alpine/prealpine region. The values have been calculated averaging data measured over the period 1987-1991 (for most, but not all the stations): the photochemical contribution at lower altitudes is apparent.

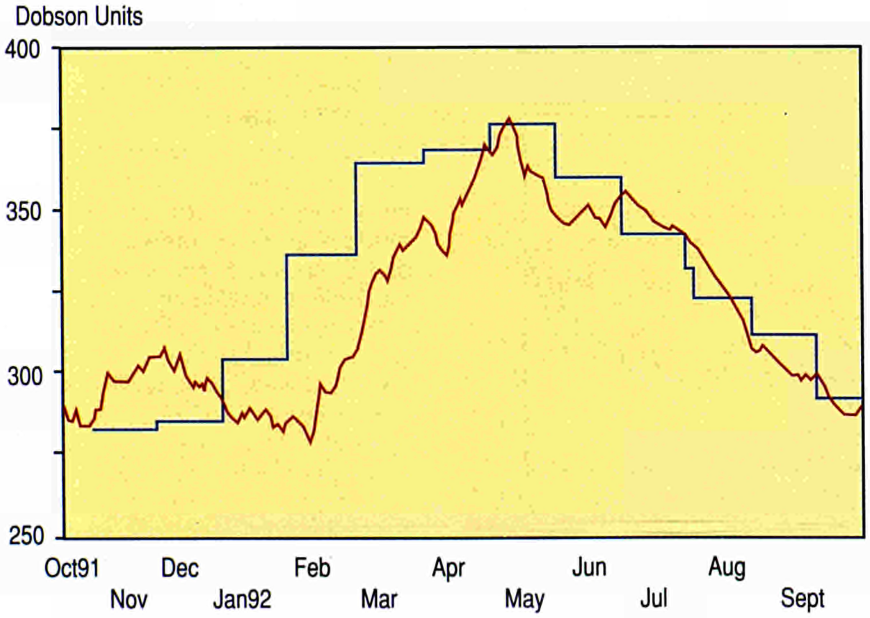


Fig.1.2 Total ozone column measured at Ispra compared with the monthly means data of Arosa (CH) averaged over 30 years (1957 - 88)

trend of tropospheric ozone at mid-latitudes of the northern hemisphere (NH) has focused attention on historical ozone obervations made by the Schonbein technique one century ago. An ad-hoc procedure to convert the original readings into present-day concentrations (in ppbv) has been set up and validated. The same procedure has been applied to observations made around 1880-1890 in South America and at tropical latitudes. Meteorological observations (including ozone readings) were made by the same instrumentation and following the same procedures from scientists trained in Europe. The re-evaluated historical data show that one century ago the surface ozone levels at midlatitudes of the southern hemisphere (SH) were comparable to those observed in the NH. Moving to tropical latitudes, the converted historical data are lower than those observed at mid-latitudes of both NH and SH. At present-time, the ozone levels at mid-latitudes of the SH are lower than those of the NH, indicating a change with respect to the past century, while in both hemispheres, the levels at tropical latitudes are lower than those observed at mid latitudes, showing a situation qualitatively similar to that of the preindustrial period.

Measurement of total column atmospheric pollutants by UV-VIS spectroscopy.

The Brewer ozone spectrophotometer, on loan from the Italian Ministry of the Environment,has been operated continuously along the year. The instrument has participated to the 1991-1992 European Arctic Stratospheric Ozone Experiment (EASOE) as a network station of the ground based ozone observing system, thus providing, on a daily basis, measurements of the ozone field at the Ispra site (45.803° latitude, -8.627 longitude). The instrument is now participating to the 1992-1993 exercise in preparation of the next EASOE campaign.

The 1991-92 campaign that completed its main measurement phase at the end of March 1992 has confirmed at this site the anomalously

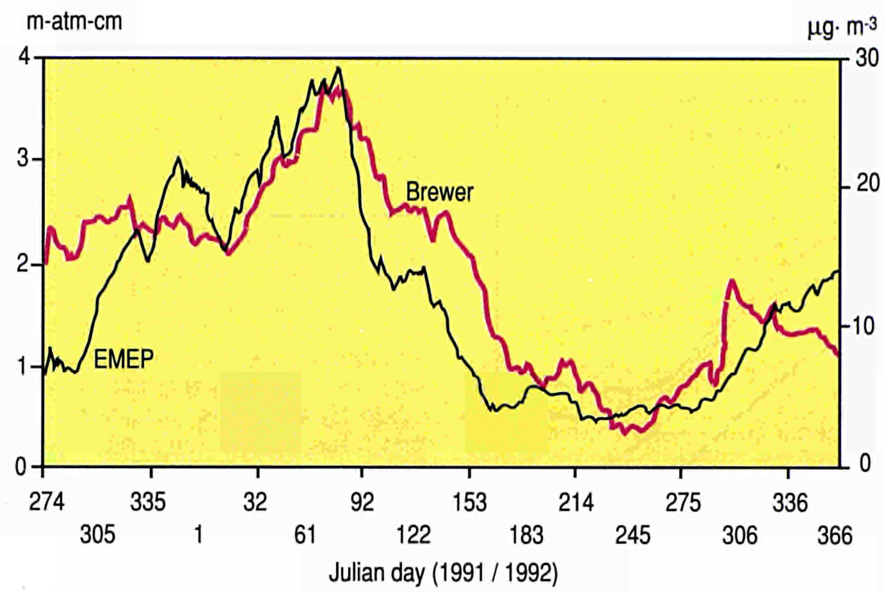


Fig. 1.3 Variation of SO_2 at Ispra from Oct. 1991 to Dec. 1992 as measured by the Brewer (right scale) and the EMEP station averaged using a 30 days filter.

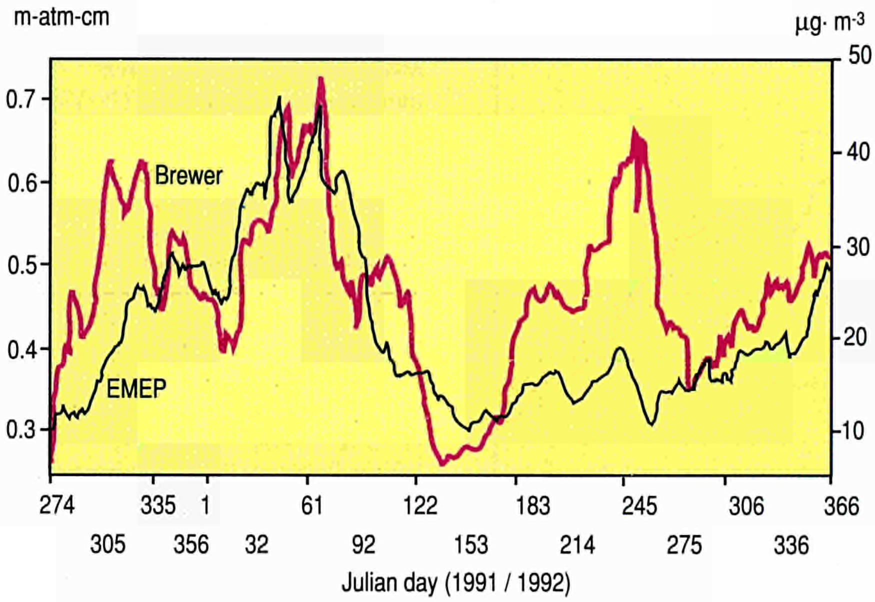


Fig. 1.4 Variation of NO_2 at Ispra from Oct. 1991 to Dec. 1992 as measured by the Brewer (tropospheric monitoring NO_2, right scale) and the EMEP station averaged using a 30 days filter.

low ozone column values as measured from other ground stations and from satellite determinations by the NASA Total Ozone Mapping Spectrometer. *Fig. 1.2* shows the total ozone column (smoothed with a 30 days filter) measured at Ispra from October 1991 to October 1992 and the monthly means of Arosa (CH) data averaged over thirty years measurements (1957-1988): the decrease of the ozone content in the winter months is evident.

The Brewer spectrophotometer allows to perform measurements, in addition to O_3, of NO_2 (separating tropospheric and stratospheric components) and SO_2 total column, however with an accuracy by far lower than that obtainable for O_3. Due to the emission at surface level, these pollutants are mainly concentrated below the inversion layer, which permits a comparison with values measured at ground, provided suitable meteorological data are available. The variation of the total SO_2 column in the period Oct. 1991-December 1992 is reported in *Fig. 1.3* together with the in situ measurements of SO_2 density made at the same location and daytime by the Ispra EMEP station. The agreement is satisfactory taking into account that measurements of pollutants at the ground may be influenced by local effects while integrated amounts of pollutants in the mixed layer and above are determined by influences over a much larger horizontal scale. The similarity of the two curves suggests that nearly the whole SO_2 amount in the vertical column is found in the lower troposphere. The differences may be due to the effect of the varying mixing layer depth and to a lesser extent, to variations of the SO_2 mixing ratio vertical profile Analogously to *Fig. 1.3*, *Fig. 1.4* shows the variation of the total tropospheric NO_2 amount determined by the Brewer at sunrise and the NO_2 point measurements made at the EMEP station at the same day hours. Here again a certain agreement between the two curves is present; the differences could be accounted by influence of the mixing layer depth

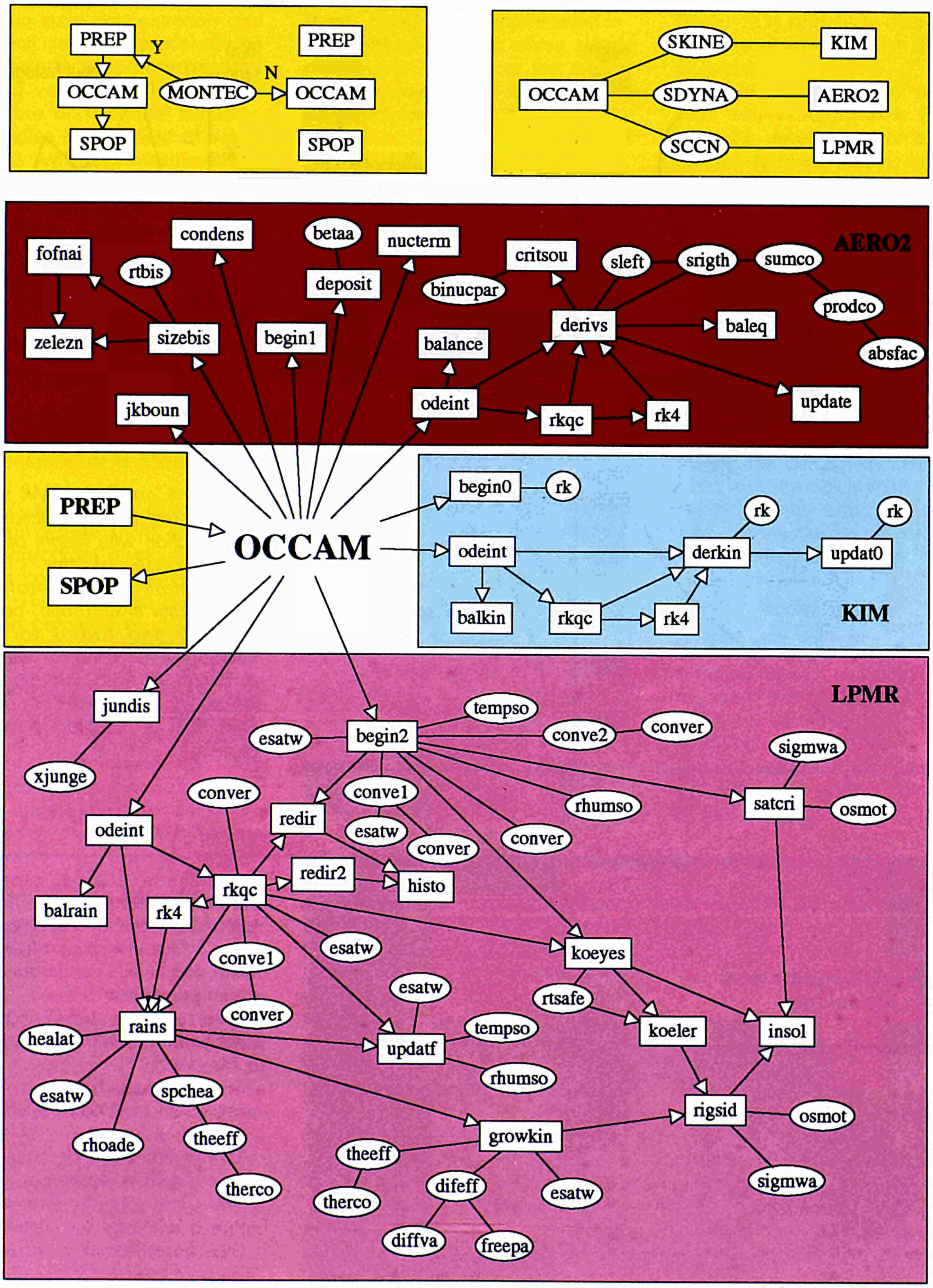


Fig. 15 OCCAM. Above: main switches (ellipsoids); for MONTEC='Y' a Monte Carlo simulation is performed, PREP generates data overriding OCCAM standard input. SKINE, SDYNA and SCCN control the execution of three submodules, each of which can be run indipendently from the others. Below: flow diagram of the three modules. The integration subroutines (odeint, rkqc and rk4 are the same for all the modules.

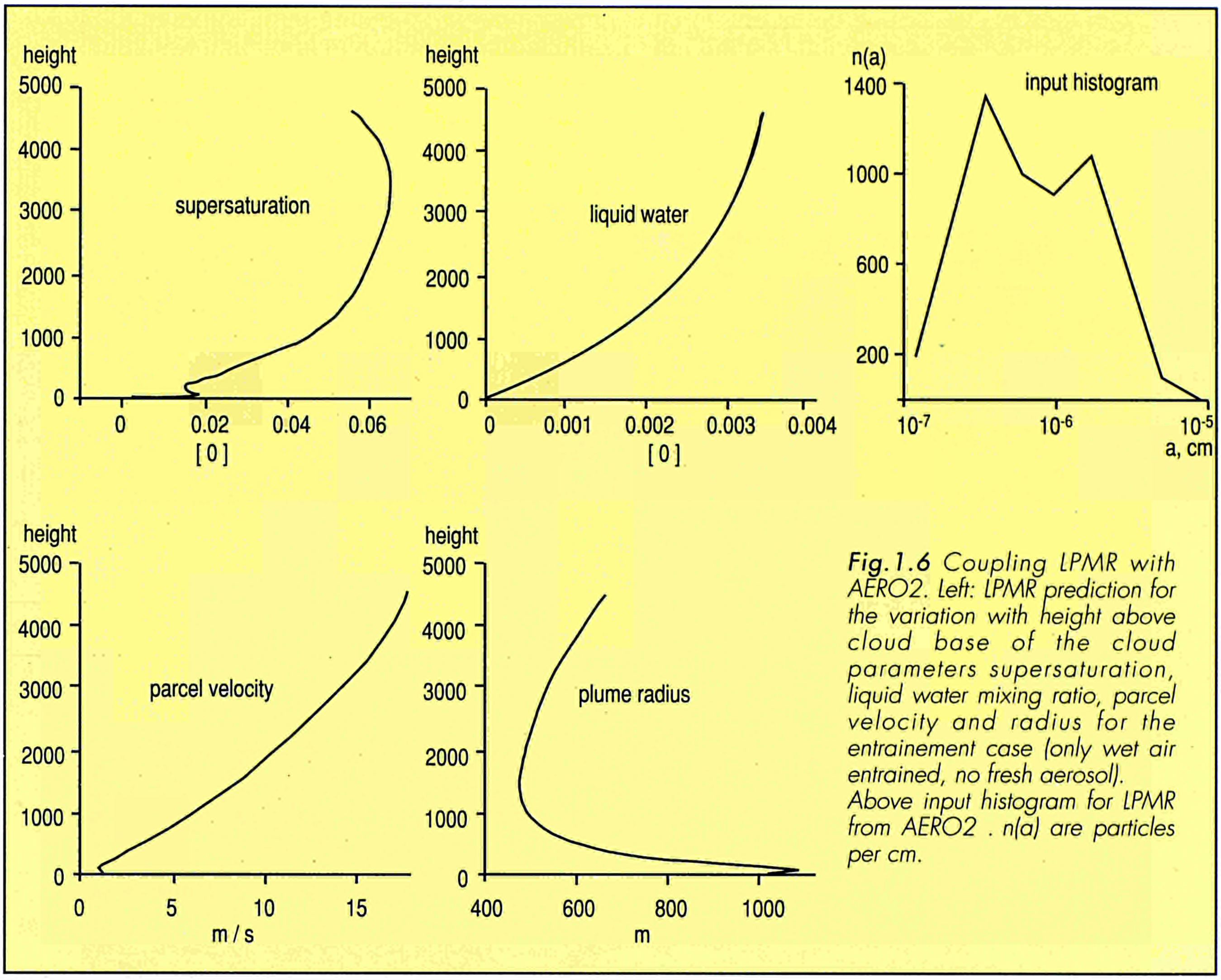


Fig. 1.6 Coupling LPMR with AERO2. Left: LPMR prediction for the variation with height above cloud base of the cloud parameters supersaturation, liquid water mixing ratio, parcel velocity and radius for the entrainement case (only wet air entrained, no fresh aerosol). Above input histogram for LPMR from AERO2 . n(a) are particles per cm.

and by variations in the NO_2 concentration profiles into the mixing height.

Atmospheric Sulphur and Climate : *Modelling*

Stochastic modelling of the natural sulphur cycle

Model and code development were initiated in 1991 starting up from an existing module for aerosol dynamics (OCCAM).
OCCAM *(Fig. 1.5)* presently consists of a module for DMS kinetics (KIM), a module for aerosol dynamics (AERO2) and simple cloud model (LPMR). All three modules are embedded into a statistical driver which allows parameters to be input in the form of distribution, thus enabling uncertainty analysis on the model predictions. This also implies that the impact of any given input parameter on the predicted output can be immediately quantified by simply acting on the appropriate execution switches, once the uncertainty in that parameter is known. The three modules are described more extensively below.

KIM is a simple chemical kinetics model for DMS. The simplified flow diagram of the KIM section of OCCAM is given in *Fig. 5.1.*

AERO2 is the aerosol dynamics module which includes the following processes:
- Spatially averaged (constant or time dependent) DMS source term from the ocean;
- Simplified DMS to SO_2, H_2SO_4 reaction kinetics;
- Aerosol particle nucleation;
- Aerosol growth by particle coagulation and H_2SO_4 condensation on existing particles;
- Heterogeneous SO_2 to H_2SO_4 oxidation (by SO_2 diffusion in existing particles);
-Aerosol deposition and - for the smog chamber version - dilution.

AERO2 has been described in the previous Institute Report.

LPMR is a model for cumulus cloud water droplet formation, a schematic view being given in *Fig. 1.6.*

LPMR is a Lagrangian plume (or ascending thermal) model, where the velocity and the radius of the rising parcel as well as the water drop spectra (in size, concentration and salt content) inside the parcel can be predicted. It uses interpolated sounding values for the external temperature and relative humidity, and handles entrainment of water vapor as well as entrainment of external aerosol particles.

LPMR uses to a large extent the system equations of the original model of Lee and Pruppacher (Pure and Applied Geophysics, 115;523;1977). The results obtained by these Authors are used for the verification part of the study.

The PREP and SPOP programmes are FORTRAN utilities to assist in the implementation of a Monte Carlo analysis.
Fig. 1.6 shows the results of a simulation where LPMR input (the aerosol histogram distribution, radii and salt content) is generated by AERO2. The input size distribution has been obtained by assuming a three days aerosol generation phase, at an average temperature of 10°C, with a DMS flux at the ocean surface assumed constant at the value $5 \cdot 10^{18}$ molec $\cdot m^{-2} \cdot day^{-1}$ and a mixing height of 1,000 m for the DMS concentration in the gas phase. Taking constant values is rather unrealistic, but is due to the preliminary nature of these simulations; both modules could easily process time dependent flux and temperature. The test case of *Fig. 1.6.* includes entrainment of wet air.

Worth of stressing that in spite of the rather high DMS emissions allowed for a three days period the resulting particle histogram is positioned at much lower particle sizes than those normally assumed for ocean conditions. LPMR computations show that only about 50 particles are activated to cloud drops in these conditions. The three modules of the model developed so far, describe some of the processes which link the DMS flux at the ocean floor to the cloud droplets in the atmosphere. It is evident that the analysis and the quantification of the uncertainty will play an important role in the study.
At a later stage a simplified model for stratus cloud will be implemented in OCCAM in order to allow simple parametric studies of the marine boundary layer cloud formation with uncertainty and sensitivity analyses.

3-D Modelling of the global atmospheric sulphur cycle

The sulphur version of the global tracer model MOGUNTIA , acquired from Stockholm University Institute of Meteorology, has been installed on the institute's principal IBM RISC 6000 workstation. MOGUNTIA is a three-dimensional Eulerian transport model of the lower atmosphere with a horizontal resolution of 10° latitude by 10° longitude, and ten vertical layers between 1000 hPa and 100 hPa.

The sulphur version of MOGUNTIA considers the principal gaseous emissions of sulphur compounds, namely DMS, SO_2, and SO_4, their atmospheric transport and removal, and a simplified representation of their chemistry. DMS is oxidised to SO_2 in the presence of OH; both in-cloud and gas phase oxidation of SO_2 to SO_4 are included in the model, and both SO_2 and SO_4, but not DMS, are subject to dry and wet removal. Thus MOGUNTIA can simulate the global atmospheric DMS, SO_2 and SO_4 distributions, and the distributions of deposited SO_2 and SO_4.
The objective of the major part of the work with MOGUNTIA in 1992 has been the development of a sulphate aerosol dynamics model, that can be implemented in such a global tracer model.
A straightforward implementation of AERO 2 in MOGUNTIA would involve repeating the calculations in each of the 36 x 18 x 10 elements of the model domain, for each time interval,leading unreasonably long computation times. In view of overcoming the problem, AERO2 is being adapted to run within MOGUNTIA, and more efficient algorithms for solving the aerosol dynamics equations are being investigated. In parallel to this effort, a feasiblility study of. the the whole problem of implementing an aerosol dynamics model, in MOGUNTIA has been undertaken.
A simple aerosol dynamics model IMAD,which considers a monodisperse aerosol has been modified and implemented in MOGUNTIA using the same algorithm of the sulphur chemistry model.
This first version of IMAD/MOGUNTIA takes as a starting point the gas phase production of H_2SO_4 from

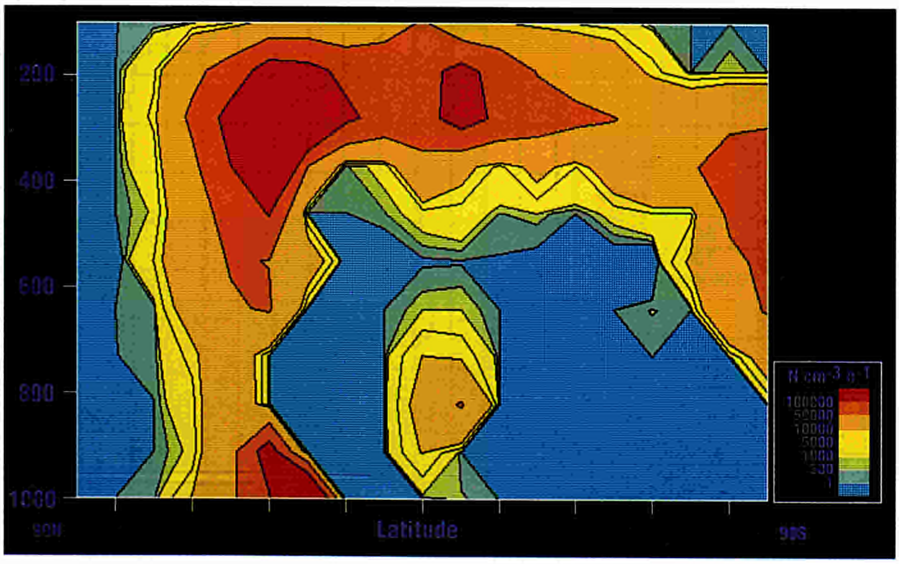


Fig.1.7 Zonal average nucleation rates averaged over January, as calculated by MOGUNTIA/ IMAD. The nucleation occurring at the surface is over continental regions.

MOGUNTIA. With this approach, nucleation can be simulated within MOGUNTIA.(*Fig 1.7.*) Nucleation occurs predomi-nantly within the upper troposphere rather than at the surface, the latter does occur in regions with large anthropogenic sources, rather than in the remote MBL.

Contribution of European sulphur emissions to global sulphate levels in air

In a separate study, the sulphur version of MOGUNTIA has been used to model the global annual average SO_4 concentration distribution and calculate the fraction that can be attributed to anthropogenic sulphur emissions from Europe. The annual average SO_4 concentration at the surface and the fraction that is attributable to anthropogenic emissions of sulphur from Europe are shown in *Fig. 1.8* and *Fig 1.9*.

Initial results from the implementation of the IMAD aerosol dynamics model in MOGUNTIA have shown that it is possible to model sulphate aerosol nucleation within a global 3-D model.

However, although not inconsistent with the results of the 0-D model simulations of the Hadley Cell circulations, they should not be used as support for them, due to the deliberate favouring of nucleation adopted in MOGUNTIA.

A project has been started on the dynamics of the carbon component of aerosol, including its sources and sinks, as the first stage in replacing the currently used static aerosol climatology with a dynamic one based on the sources, sinks and dynamics of the principal aerosol components.

Formation of cloud condensation nuclei from DMS: development and testing of hypotheses

The aerosol dynamics model AERO2, has been expanded to include simple DMS > SO_2 > H_2SO_4 photochemistry and a simple parametrization for in-cloud SO_2 oxidation and wet deposition.

In a first scenario (*Fig. 1.10*),it is assumed that CCN for Marine Boundary Layer (MBL) St clouds are formed 'in-situ', i.e. all processes (DMS emission, chemical transformation, nucleation,..) happen within the subtropical MBL.

The maximum available time time for

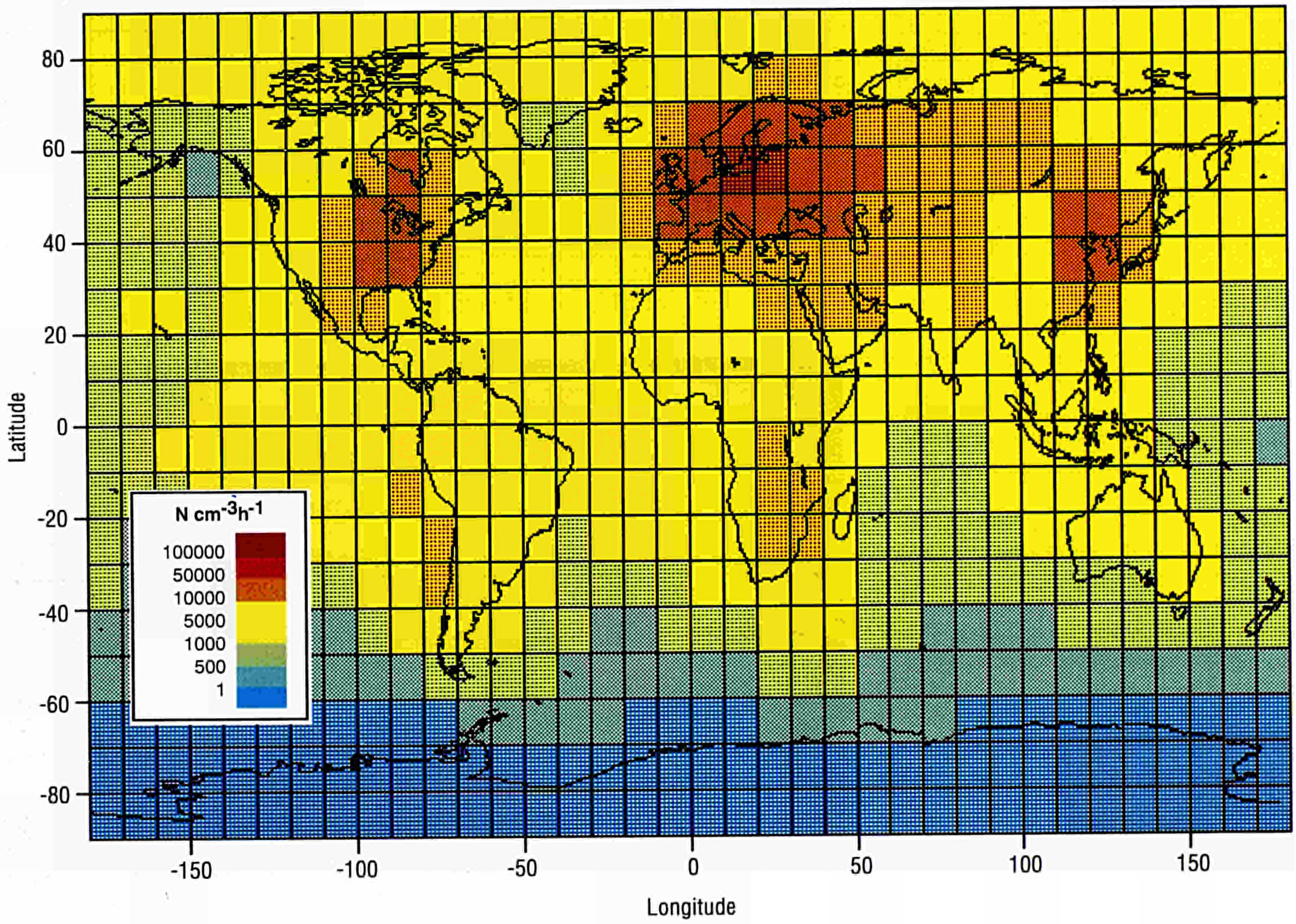


Fig.1.8 Annual average sulphate concentrations at the surface (1,000 mbar) expressed as volume mixing ratios, as calculated by MOGUNTIA.

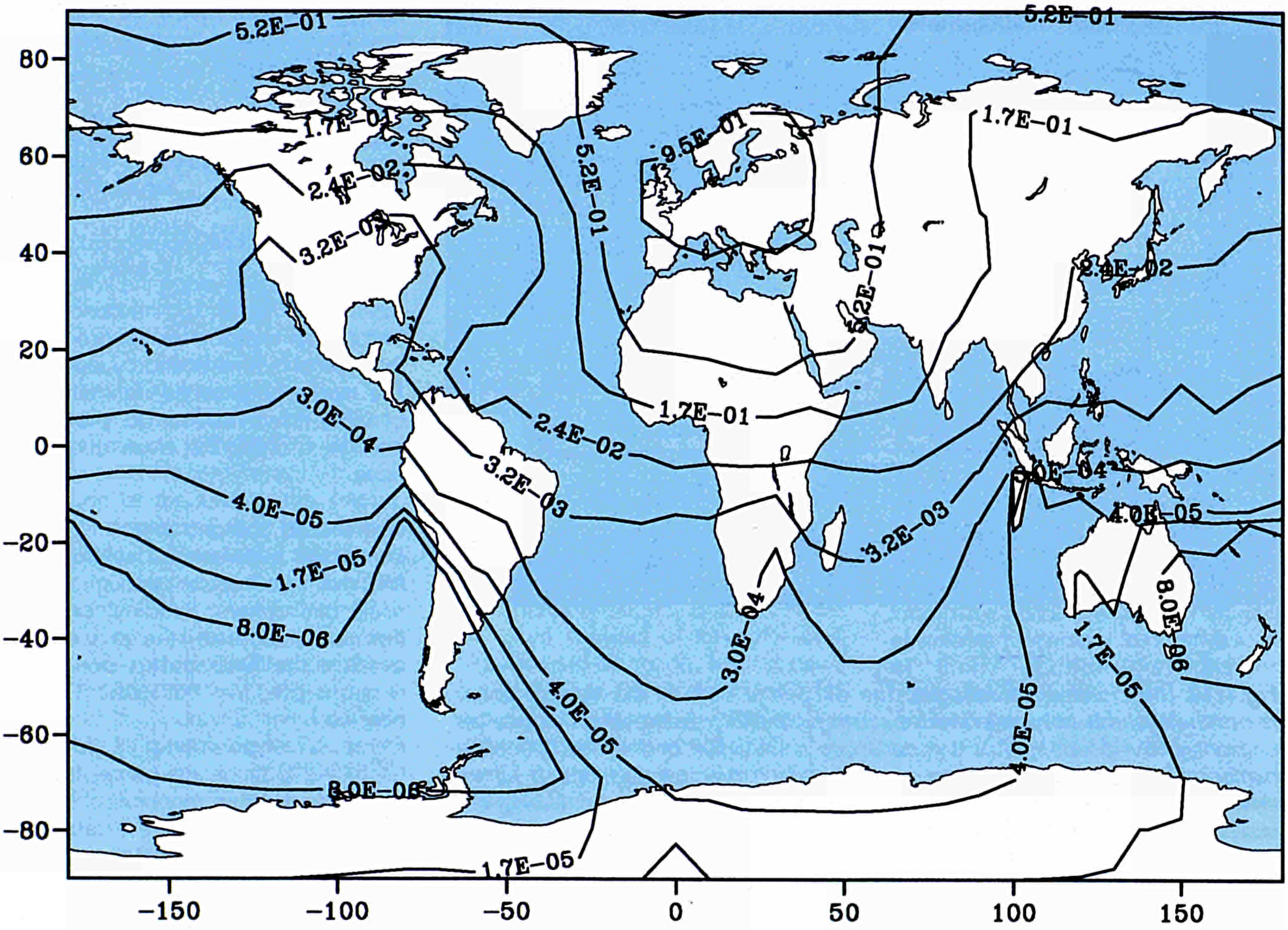
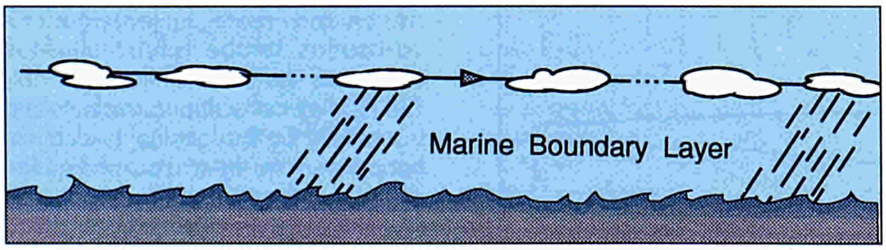


Fig.1.9 *The fraction of the annual average sulphate concentration field in Fig. 1.8 that is attributable to anthropogenic sulphur emissions from Europe West of 50° East.*



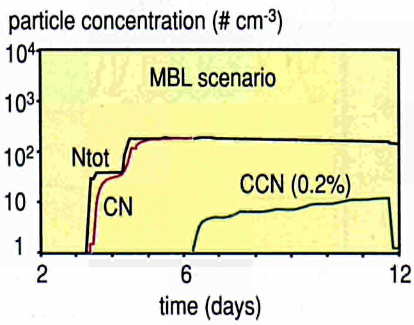


Fig.1.10 *Schematic of the MBL scenario. The air parcel starts free of particles. Outside clouds the parcel experiences a DMS flux and sulphate aerosol forms by photochemical reactions followed by nucleation and growth. Inside clouds, a supersaturation of 0.2% is assumed, and the activated particles aquire more sulphate by in-cloud SO_2 oxidation and scavenging of the interstitial aerosol. The air parcel goes through a number of such cloud cycles before it encounters a precipitating cloud.*

Fig.1.11 *Concentrations of N_{tot}, CN and CCN (0.2%) in an air parcel travelling through the marine boundary layer, and experiencing a flux of DMS of $2 \cdot 10^9$ molec$\cdot$cm$^{-2}\cdot$ s^{-1}.*

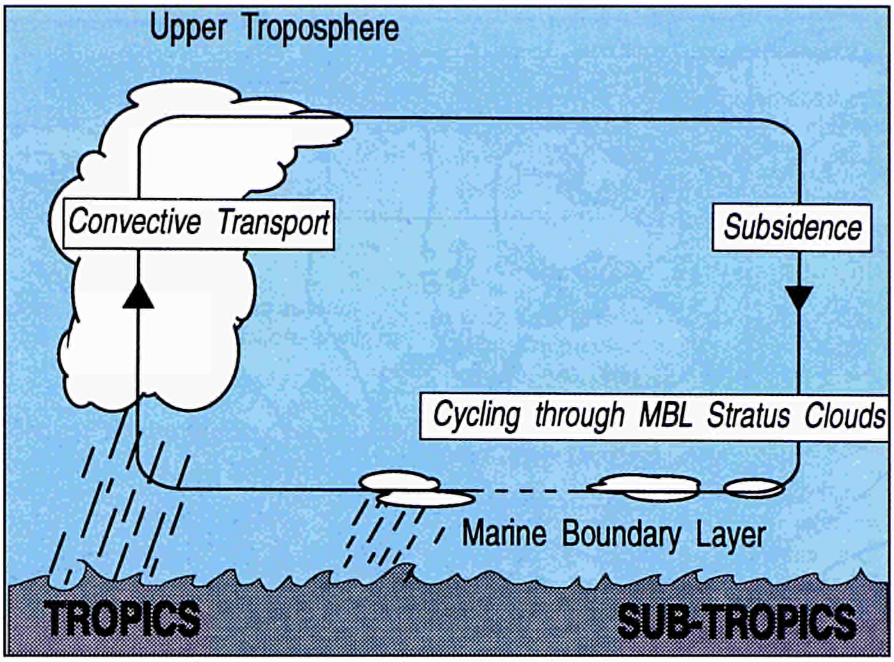


Fig.1.12 The Hadley cell scenario. The air parcel starts in the tropical upper troposphere and is transported to the sub-tropical MBL, during which it does not encounter any cloud. In MBL it experiences a DMS flux and cycles through a number of stratus clouds, before it encounters a precipitating one. It further travels to the tropics where it is pumped up by a convective cloud. During this convective transport, DMS will remain undisturbed, but a fraction of the SO_2 and the particles will be rained out.

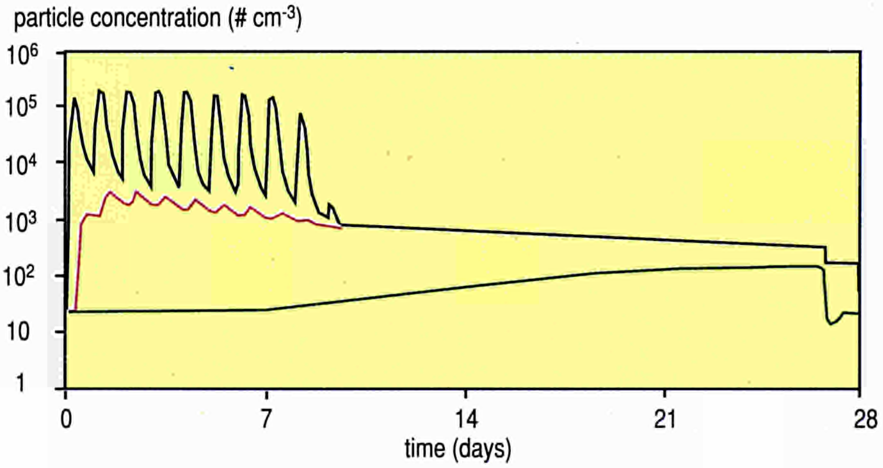


Fig.1.13 Concentrations of N_{tot}, CN and CCN (0.2%) in an air parcel that is moved through a Hadley cell. At time zero, the parcel starts in the free troposphere. In the MBL, it experiences a DMS flux of $2 \cdot 10^9$ molec·cm^{-2}· s^{-1}.

their production equals the transport time through the subtropics, which is at most 12 days.

Fig.1.11 shows the total number concentration of particles (Ntot), the concentration of those particles detectable with a regular particle counter (CN) and the concentration of those particles active at 0.2 % supersaturation CCN (0.2%) in an air parcel that moves along the trajectory sketched in *Fig. 1.10*; the conditions are those typical for the remote subtropical marine boundary layer.

The model predicts the right number of CN, however fails to produce enough CCN(0,2%) even after 12 days.

In a second scenario *(Fig 1.12)*, the connection between the subtropical MBL with the tropics , through large scale atmospheric (Hadley) circulation is considered, the processes outside the MBL being possibly responsible for the MBL CCN observed.

Fig.1.13 shows Ntot, CN and CCN(0.2%) in an air parcel travelling along the trajectory of *Fig. 1.12*. The model predicts new aerosol production in the upper troposphere, favoured by both the low temperature, and the low concentration of background aerosol that remains after cleansing by the convective cloud.

Despite the high relative humidity and the source of DMS, the model does not predict nucleation within the MBL. A sensitivity analysis shows that the CN and CCN (0.2%) concentrations are much more insensitive to variations in the environmental conditions than in the first scenario. The Hadley cell scenario explains this insensitivity by the fact that nucleation happens in the free troposphere, far away from the MBL, so that its critical dependence on the enviromental parameters is 'forgotten' in the coagulation process by the time the particles subsided back to the MBL.

The aerosol dynamics model developed and tested over the years turns out to be essential to make the link between the gas phase (DMS, SO_2) and the aerosol phase, hence to advance hypothesis about cloud condensation and nuclei production. These hypothesis will be further tested, performing thourough sensitivity analyses with PREP and SPOP.

Atmospheric Sulphur and Climate : *Laboratory Experiments*

The oxidation of DMS in the Troposphere

The oxidation of dimethylsulphide (DMS) in air is initiated by reaction with the OH radical at daytime and with the NO_3 radical at night. It is generally accepted that the reaction of OH radicals with DMS is initiated by two different mechanisms: addition of the OH to the sulphur atom or abstraction of H atom from a methyl group. The second mechanism seems to be predominant at ambient temperature.The oxidation of DMS initiated by OH radicals is believed to be the most important tropospheric sink. The reaction with NO_3 is known to be of importance in some polluted sites but its global importance is not known. Even more uncertain is the importance of other possible loss processes such as reactions with halogen atoms and heterogeneous reactions.

Previous studies in this laboratory have aimed at understanding the initial steps in the mechanism of the reaction of DMS with NO_3. It has now been clearly demonstrated that this reaction proceeds via hydrogen abstraction:

$$CH_3SCH_3+NO_3^{\bullet}\text{->}CH_3SCH_2^{\bullet}+NO_3$$

Probably the reaction involves the formation of an adduct, formed by addition of the radical to DMS, which decays with practically 100% yield by H-atom abstraction from a methyl group. After this step, the mechanism is the same as in the H-atom abstraction channel of the OH initiated DMS reaction. The results of studies performed on the mechanism of the reaction between DMS and NO_3 are thus applicable also to the most important channel of the reaction between DMS and OH.

The chemical laboratory experiments are mainly carried out using a 480 l teflon-coated evacuable chamber equipped with two White-type multiple reflection mirror systems. One of these is connected to either a Bruker 113V FTIR spectrometer or a tunable diode laser spectrometer while the other is connected to a UV/VIS spectrometer set-up.

Chemical kinetics of DMS oxidation: modeling and laboratory experiments

Based on literature data and some laboratory results, a simplified kinetic model of the OH-initiated oxidation of DMS has been set up to be used as a submodule (KIM) in the OCCAM model, as previously discussed in this report. However, some important aspects of this process are not understood, e.g. the route to formation of SO_2, which, in the laboratory studies, appears to be the main product of the OH- and NO_3-initiated oxidation, has not been clarified. Thus the model cannot be expected to accurately reproduce the experimental observations, but it is useful for testing the sensitivity to changes in various parameters and thus to evaluate which of the elementary reactions involved in the oxidation process that need to be studied further. Eventually such an analysis should also allow to evaluate how the environmental conditions (e.g. temperature and concentrations of reactive trace gases) influence the oxidation pathways of DMS. One of the important questions that have been raised recently, is to which extent sulfuric acid is formed from DMS via the oxidation of SO_2

DMS (+OH or NO_3) –>SO_2
SO_2 (+oxidant) -> H_2SO_4
or via a reaction not involving SO_2 as an intermediate:

DMS (+oxidant) -> H_2SO_4.

The impact of the two types of reactions on the formation of new particles in the atmosphere is likely to be rather different.

Another relevant question concerns the ratio between MSA and H_2SO_4; this ratio is often used as an indicator of the relative contribution of DMS emissions to the sulphur budget in a certain area because MSA is believed to be formed only by the oxidation of DMS, but the parameters governing the yield of MSA are not understood.

A flow diagrammme of the proposed reaction scheme is shown in *Fig. 1.14*.

While the model can give a clue to understanding which reactions in the various possible reaction pathways that may be the most important, laboratory work is compulsory to improve our understanding of these reactions.

The relevant radical reactions are mainly the reactions of the CH_3S, CH_3SO, CH_3SOO, CH_3SO_2 and CH_3SO_3 radicals. An effort was initiated to find suitable methods to produce such radicals under laboratory conditions (e.g. photolysis of suitable precursors) in order to look at their reactions with other tropospheric species.

Another experimental study aims at understanding the role of photolytic reactions in the OH-initiated oxidation of DMS. For the purpose OH radicals are produced by a non-photochemical method (the reaction between O_3 and NH_2NH_2 in air) and then let to react with DMS.

The non-photochemical method for generating OH has been tested by studies of the decay rates of hydrocarbons in this system and the observed relative decay rates have been found to be in excellent agreement with those calculated on the basis of the known rate constants for the reaction with OH of these species.

During the previous studies of the DMS-NO_3 reaction, the formation of a peroxynitrate intermediate has been shown. Its structure, has not yet been clarified

$CH_3S(O)O_2NO_2$ or

$CH_3S(O)_2O_2NO_2$

Analogously to PAN, the stability of the intermediate has been found to exibit a strong temperature dependence and its lifetime with respect to

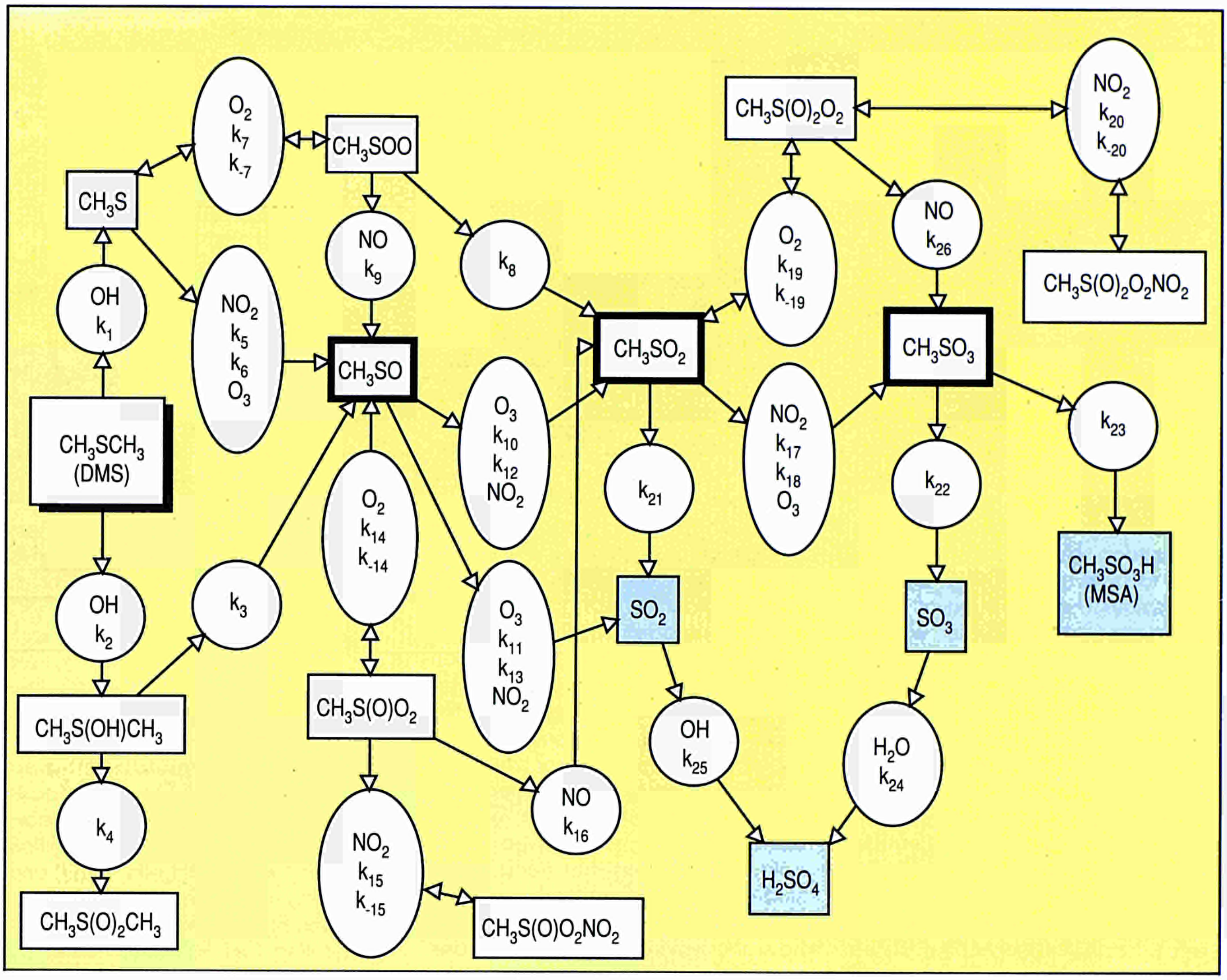


Fig. 1.14 Scheme of chemical kinetics of DMS-oxidation by OH (flow diagram)

thermal decomposition is comparable at low temperatures to that of PAN. This means that the formation of this intermediate in the oxidation of DMS in air, may play a role in the transport of sulphur and nitrogen over long distances in cold marine air masses. The highest leves of this species must be expected at low temperatures and high NO_x with a predominance of NO_2 over NO; conditions which are best fulfilled in polluted coastal zones at night. Spectroscopic evidence has been reached that peroxynitrate intermediates are formed by the oxidation by NO_3 of other reduced organic sulphur species (mercaptanes, sulphides and disulphides).

Gas/particle interaction studies

A continuous generator of HONO was built, HO radicals being produced within the reactor by the UV light-induced HONO dissociation.

The reactor is shown in *Fig. 1.15*. The flow reactor consists of two concentric 5m long borosilicate tubes. At two positions sampling probes are provided; the upper one (1m from the entrance) removable, the other (4 m from the entrance) fixed. At the inlet of the reactor a perforated teflon disk serves to establish a flat flow profile, which subsequently develops into a laminar profile in the first 1m. Around the reactor, between the twosampling probes, UV-lamps are mounted. The inner wall of the reactor is kept at constant temperature by water circultating between the two tubes. The laminar flow profile between the two sampling probes has been checked by means of two parameters,i.e.:

- the time needed by an air parcel to travel from probe1 to probe 2 and
- the shape of the concentration time profile, when a small cloud of aerosol is injected in the reactor.

The set-up used to investigate those parameters is shown in *Fig. 1.15*: Salt particles (NaCl) were generated

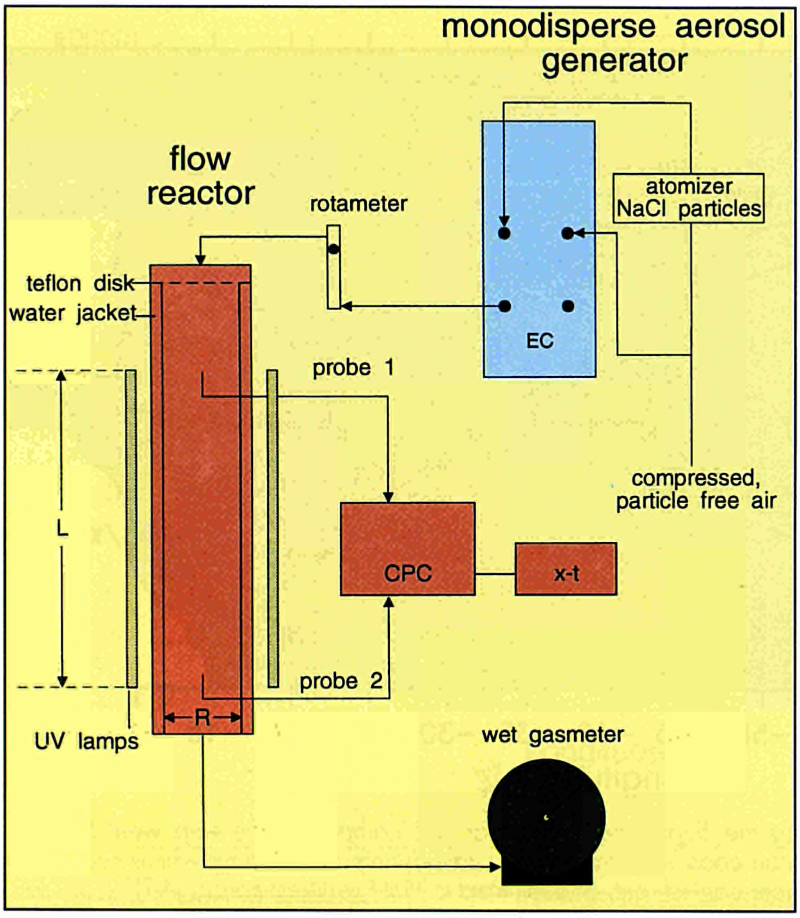


Fig. 1.15 *Set up for testing the laminarity of the flow reactor. EC= electrostatic classifier; CPC= condensation particle counter; x-t= x-t recorder.*

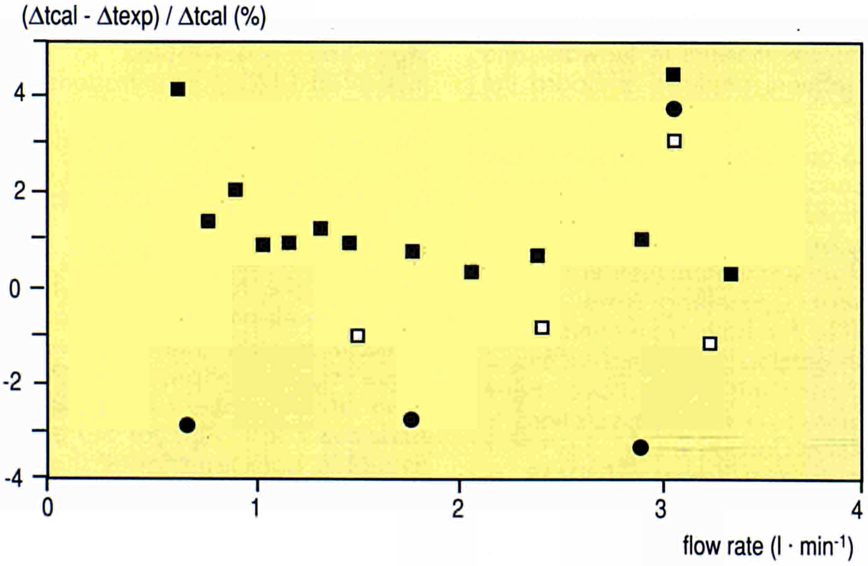


Fig. 1.16 *Difference between the measured and the theoretical residence time of two sampling probes, as a funcion of the flow rate.*

by a constant output atomizer, and subsequently led through a electrostatic classifier (EC). The latter instrument allows to introduce a small cloud of NaCl aerosol in the reactor flow stream, without disturbing this flow. The flow rate of the air entering the reactor is monitored by a rotameter upstream and measured by a wet gas meter downstream the, reactor.

The arrival of the particles at the two probes is detected with a Condensation Particle Counter (CPC).

The deviation between calculated and measured values is -1 % (±2 %) for flow rates between 1 and 3.5 $l{\cdot}min^{-1}$ *(Fig. 1.16).*

HONO in the gas phase has been obtained by leading gaseous HCl over a fluidized bed of solid $NaNO_2$ ($HCl + NaNO_2$ $HONO + NaCl$).
Gaseous HCl is obtained from a permeation system; i.e. a teflon tube immersed in a HCl solution, through which humidified nitrogen is flown as a carrier gas.
Assuming a complete conversion of HCl, the HONO concentration is determined by the concentration of the HCl, which in itself is determined by the concentration of the HCl solution, the length of the teflon tube (2m), the temperature of the HCl solution, the flow rate through the tube, and the humidity of the carrier gas.

The HONO output of the generator is being tested in three different ways:
- with a chemiluminescence NOx-monitor, in which HONO is detected (as 'an interference') in the NO_2 channel;
- by ion-chromatographic analysis of the denuder for NO_2,
- by bubbling air through a alkaline eluent in which HONO and HCl are caught.

It was shown that stable HONO concentrations (within 5 % over 1 day) are obtained.
Quantitative agreement between the 3 methods has not been obtained yet.

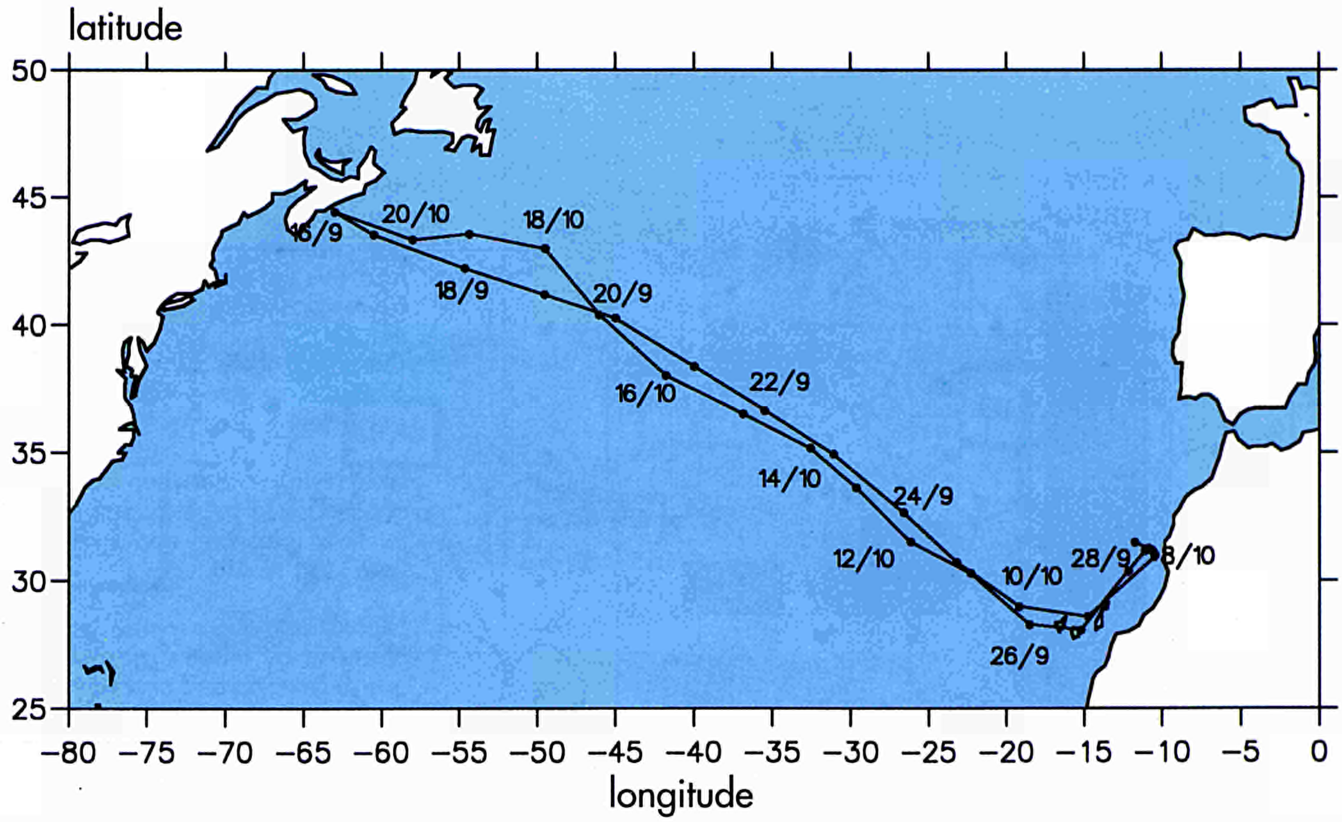


Fig.1.17 The CSS Hudson cruise track during the September - October '92 campaign: the ship went from Halifax (Canada) to the upwelling area off the Maroccan coast (East transit, ET), stayed there for 10 days where two drift station studies (DS) and a hydrographic section (HS) were carried out, and returned to Halifax (West transit, WT).

Atmospheric Sulphur and Climate : *Field Experiments : The Hudson 92 Cruise*

Trace gas measurements over the North Atlantic

The aim of the cruise, the track of which is shown in *Fig. 1.17*, was threefold, i.e.:

- to study the hydrogeochemical cycling of C, N and S in the upper ocean;
- to better understanding the bearing of DMS and its oxidation products on the formation of aerosol particles in marine environment;
- to study the anthropogenic influence in remote Atlantic.

Equipment for trace gas analysis consisted of:

- an automated sampling - analyzing system for DMS concentrations in sea water and in air,
- on-line gas monitor for CO (Environment),O_3 (Dasibi model 1108) and NO_x (Scintrex LMA-3).

DMS in air and seawater samples were measured on board of the research vessel. Additional samples for the determination of the precursor of DMS, dimethylsulphoniopropionate (DMSP) were prepared by filtration of particulate material in seawater and subsequent analysis off-board the ship.

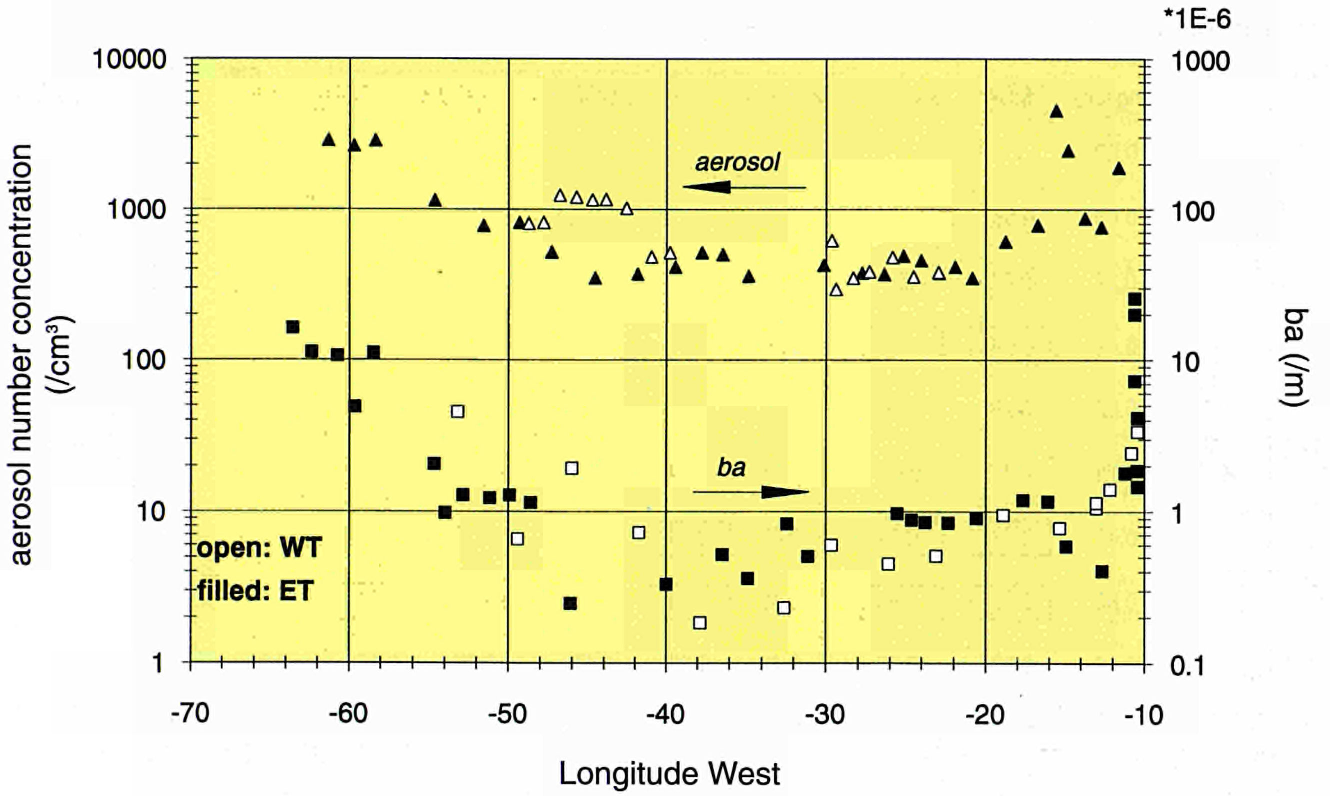
DMS and DMSP concentrations have been obtained for the two cross-sections of the Atlantic and more detailled measurements have been performed within the Northwest African Upwelling Area. Depth profiles for both compounds have been obtained at several locations. Air concentrations have been measured on both cross-sections to and from Canada.
The measurements of DMS in seawater, together with measured data on sea-surface temperature and windspeed, have allowed to calculate DMS flux rates to the atmosphere.

The measurements of DMS and DMSP in sea water, combined with data obtained by the biological oceanographers during the cruise will also allow to assess biological processes in the water column which may have contributed to the measured DMS concentrations in seawater.
The available data allow to perform more detailed analyses, taking into account the trajectory of the air-mass.

The lowest concentrations of SO_2 are found at the MidAtlantic while elevated levels are found close to the Westafrican coast (prevailing winds come from Europe) and (less pronounced) close to the North American coast. Also for SO_2, the available back-trajectories should allow to make a detailled analysis of some of the data.

Aerosol measurements over the North Atlantic

The aerosol equipment on board of



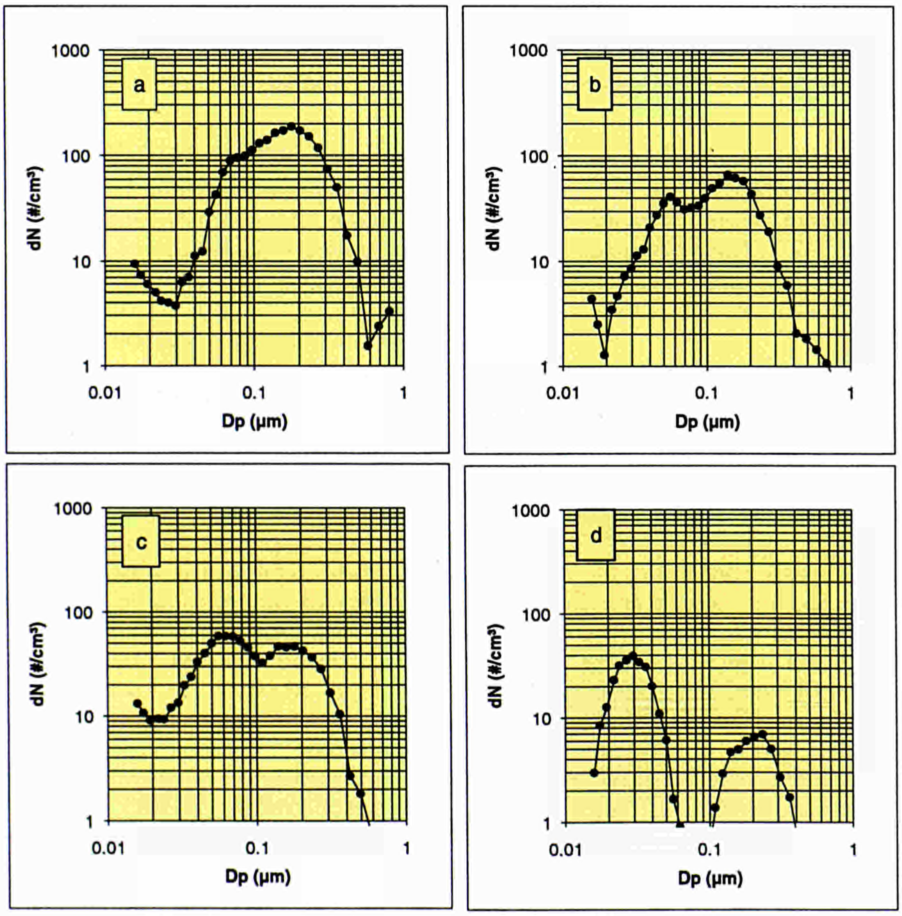


Fig.1.18 *Total sub-micron aerosol concentration as inferred from the size distribution measurements (tiangles) light absorption coefficient (squares) measured along the cruise track, as a function of longitude. Values are averaged over 3 - 6 hours periods.*

Fig.1.19 *Examples of sub-micron aerosol size distributions measured over the North Atlantic.*
(a): 36 hr after departure (43°N, 56°W); lower air masses have passed over coastal region off Maritime Canada, higher air masses over Great Lakes region. Total concentration 2,000 cm^{-3}, first features of bimodal distribution start to appear.
(b): 48 hr after departure (42°N, 54°W); last 72 hr air masses advected from over the ocean, coming from East coast of USA. Total concentration 750 cm^{3}. Gap between 2 modes appears at Dp = 0.07 mm.
(c): 24 hr after (b) (41°N, -48°W), air masses have travelled mainly over ocean, away from coast. Total concentration 885 cm^{3}.First mode clearly higher than second one, gap appearing at 0.1 mm.

	Longitude	MSA	nss-SO_4=	MSA/nss	NO_3-	HCOOH	CH_3COOH	$(COOH)_2$	NH_4+	PO_4(3-)	particles
MSA	0.32										
nss-SO_4=	0.46	0.56									
MSA/nss-SO_4=	-0.32	-0.01	-0.57								
NO_3-	0.49	$\boxed{0.69}$	$\boxed{0.77}$	-0.32							
HCOOH (formic acid)	0.02	-0.28	0.28	-0.35	0.16						
CH_3COOH (acetic acid)	-0.21	-0.47	-0.03	-0.13	-0.14	0.52					
$(COOH)_2$ (oxalic acid)	0.41	$\boxed{0.72}$	$\boxed{0.94}$	-0.45	$\boxed{0.89}$	0.16	-0.15				
NH_4+	0.60	$\boxed{0.72}$	$\boxed{0.88}$	-0.46	$\boxed{0.93}$	0.05	-0.23	$\boxed{0.94}$			
PO_4(3-)	0.46	0.22	0.28	-0.46	0.23	0.10	-0.07	0.17	0.31		
particles	0.08	0.46	$\boxed{0.80}$	-0.36	$\boxed{0.77}$	0.38	0.15	$\boxed{0.83}$	$\boxed{0.72}$	0.38	
absorption coefficient	0.32	$\boxed{0.65}$	$\boxed{0.74}$	-0.46	$\boxed{0.84}$	0.29	-0.06	$\boxed{0.85}$	$\boxed{0.82}$	0.39	$\boxed{0.92}$

Table1.1 Mutual correlation coefficients between several quantities measured during the CSS Hudson research cruise. Correlation coefficients larger than 0.65 are underlined. One values out of the 23 was suspect for stack contamination and was rejected.

the CSS Hudson consisted of:
- a high volume sampler (30 $m^3.hr^{-1}$) for total aerosol load;
- a medium volume sampler ($3m^3.hr^{-1}$) with 3 stacked filters for size separation between coarse (stage 1) and fine (stage 2) aerosol and for SO_2 measurements (stage 3);
- an aethalometer for on-line measurement of the light absorption coefficient of the airborne black carbon particles;
- a "Differential Mobility Particle Sizer" system for aerosol number size distribution measurements in the range 0.01 - 1 mm.

So far only part of the data has been processed and their interpretation is in the early stage.
Fig.1.18 shows the measurements of aerosol and black carbon performed under the assumption that the latter is the dominant light absorber.
The measured values for the absorption coefficient ba range between $20.10^{-6}m^{-1}$ in air masses advected recently from the continents and $0.2.10^{-6}m^{-1}$ halfway the Atlantic, the latter value being about the instrument detection limit.

As far as the aerosol size distributions are concerned *(Fig 1.19)* they show the remarkable but typical transition from single-peaked distribution in continentally influenced air to bimodal one in more remote regions.

The results concerning the chemical composition which are presented below do refer to 23 filter samples collected with high volume samplers during ET and WT, (sampling period between 12 and 72 hours). The filters were analysed by ion-chromatography, for methane sulphonate (MSA), nss sulphate, nitrate, oxalic, acetic and formic acid, ammonium and phosphate.
Correlation coefficients between those quantities and longitude, aerosol concentration and ba, are presented in *Table 1.1*.
The strong correlation between anthropogenic tracers on the one hand, and nss-sulphate on the other hand, suggests that the bulk of the latter is of anthropogenic origin. This follows also from *Fig.1.20* where nss sulphate are plotted against oxalic acid.
MSA shows much less fluctuations than nss sulphate, although a slight positive correlation is observed with tracers of anthropogenic activities (e.g. with oxalic acid, *Fig.1.20*).
This can be explained by a higher yield of MSA in the oxidation of DMS under NO_x rich (hence polluted) conditions.
Although sulphate is known to be an oxidation product of DMS, the relatively high correlation between MSA and nss sulphate in *Table1.1* is rather a consequence of anthropogenic

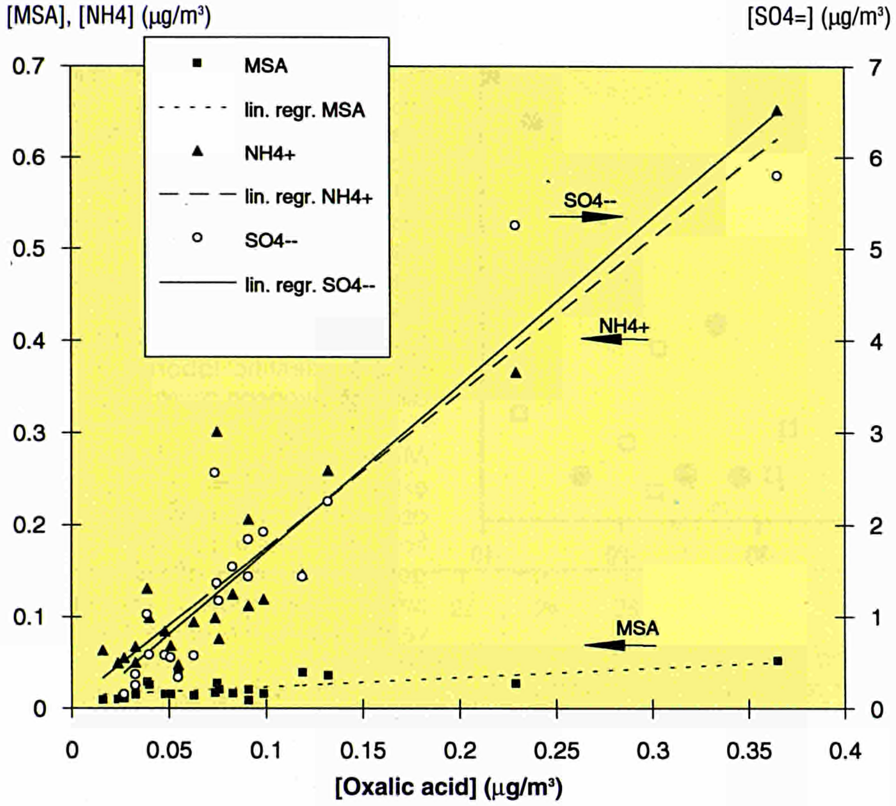


Fig. 1.20 Scatter plot and linear regression for nns sulphate, ammonium and MSA versus oxalic acid.

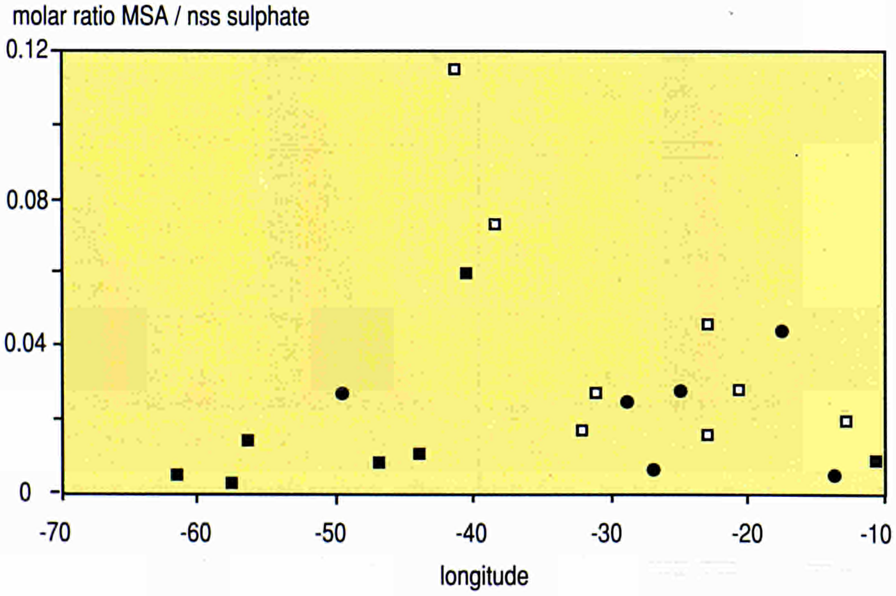


Fig. 1.21 MSA/nss sulphate ratio as a function of longitude ad classified according to the origin of the 72 hr old air masses advected

- ■ *air masses with mainly continental influences;*
- ● *air masses of continental origin which have travelled over the ocean;*
- ☐ *air masses which have travelled solely over the ocean during the past 72 hr.*

influence, advecting sulphate and simultaneously increasing MSA yields from biogenic DMS oxidation, than resulting from a common precursor (DMS). For formic and acetic acid wich are products from both anthropogenic and biogenic precursors, there is a complete lack of correlation with any of the other measured quantities.

The anthropogenic impact on most of the North Atlantic appears also from the MSA/nss sulphate ratios which range between 0.03 and 0.12 with a distinct maximum halfway the cruise track *(Fig. 1.21)*. The latter value compares well to remote values obtained at similar latitudes and temperatures.

Fig. 1.22 shows nss sulphate values measured along the cruise track, and roughly classified according to the origin of the airmasses obtained from 72 hrs. backtrajectory calculations by the German Weather Service. The measured concentrations are significantly higher than those obtained at remote marine stations (0.15 ± 0.10 mg m^{-3} , Cape Grim). The lower values we measured over the Atlantic are comparable with those of the Ispra EMEP station under clean air conditions (0.2 - 1 mg m^{-3}).

Table 1.2 compares our measured values for MSA and nss sulphate with those from similar studies in the same region.

The data indicate that the North Atlantic is not a suited region to study the fate of biogenic DMS in the atmosphere, but rather to investigate the perturbation of the natural atmospheric sulphur cycle by anthropogenic activities, and its effect on the production of condensation and cloud condensation nuclei.

Atmosphere-Biosphere Interactions

Work on atmosphere-biosphere interactions has been mostly focussed on the study of vegetation emissions and their transformations in the Mediterranean basin in order to contribute to the understanding of the chemical composition of the atmosphere in that area and, hence, its potential contribution to the

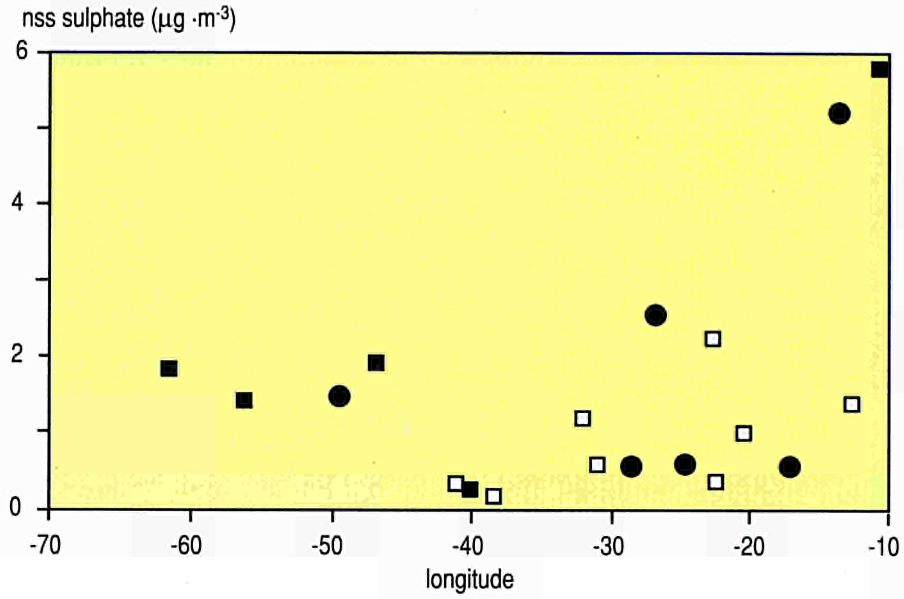


Fig.1.22 nss sulphate concentration measured over the Atlantic, classified according to the origin of 72 hr old air masses reaching the ship. (Symbols as in Fig. 1.21)

SHC	period	nss-SO_4= (μg m^{-3})	MSA (μg m^{-3})	MSA/nss-SO_4-	ref.
Coastal SHC Brittany	June	4.2 - 35	0.06 - 1.2	0.06	(a)
North Atlantic (30° - 45°N)	Sep.- Oct.	0.7 - 5	0.02 - 0.03	0.045 - 0.33	(b)
North Sea	Sep. average	2	0.08		(c)
North Atlantic	Oct. average	4	0.02		
North Atlantic	April - May	0.9 - 4.5	0.02 - 0.1	0.013 - 0.057	(d)
North Atlantic	Sep.- Oct.	0.25 - 19	0.009 - 0.056	0.03 - 0.012	(e)

(a) Mihalopoulos,N., et al.:J. Atm. Chem. 14; 459-477; 1992
(b) Bürgmeister,S and Georgii, H.W.: Atm. Envir. 25A; 587-595; 1991
(c) Watts, S.F., et al.: J. Geophys. Res. 96; 18705-18725; 1991
(e) This work

Table1.2 nss sulphate and MSA values obtained in the described as well as other comparable campaigns.

tropospheric ozone formation and to the global change. To this aim, a European project has been launched on Biogenic Emissions in the Mediterranean Area, i.e. the BEMA project. The project has been already outlined in the Environment Institute Annual Report 1991 and is now in the operational stage. The first measuring campaign is scheduled for June 1993 at the Castelporziano test site near Rome and it will be joined by 14 scientific laboratories from different European countries.

Main goal of BEMA is the extrapolation of the emission fluxes obtained from Castelporziano and from other sites in Europe in order to get an estimation of the type and amount of compounds emitted from vegetation in the entire Mediterranean basin. Comparison will be made with anthropogenic concentrations. The data will be of value for the parametrisation of tropospheric chemistry models and in particular for the assessment of the role of these compounds in the ozone formation processes. Without these data, the effects of proposed EC emission control strategies on ozone formation for the photochemically active Mediterranean region could hardly be predicted.

The uncertainties of the best estimates of mean emission rates from a single plant can be as large as a factor of five. This factor may easily increase up to 50 by extrapolating and upscaling data to large areas of inhomogeneous terrain. Thus, an essential prerequisite to provide realistic figures on biogenic emissions at the regional or global scale, as needed for atmospheric chemistry models, is improving our understanding of the factors controlling biogenic emissions at the leaf-level, the canopy-level, and the ecosystem-level.

During the 1993 two weeks measuring campaign at Castelporziano, both emission fluxes and ambient concentrations of the primary compounds and their reaction products will be determined. Fluxes will be assessed for selected

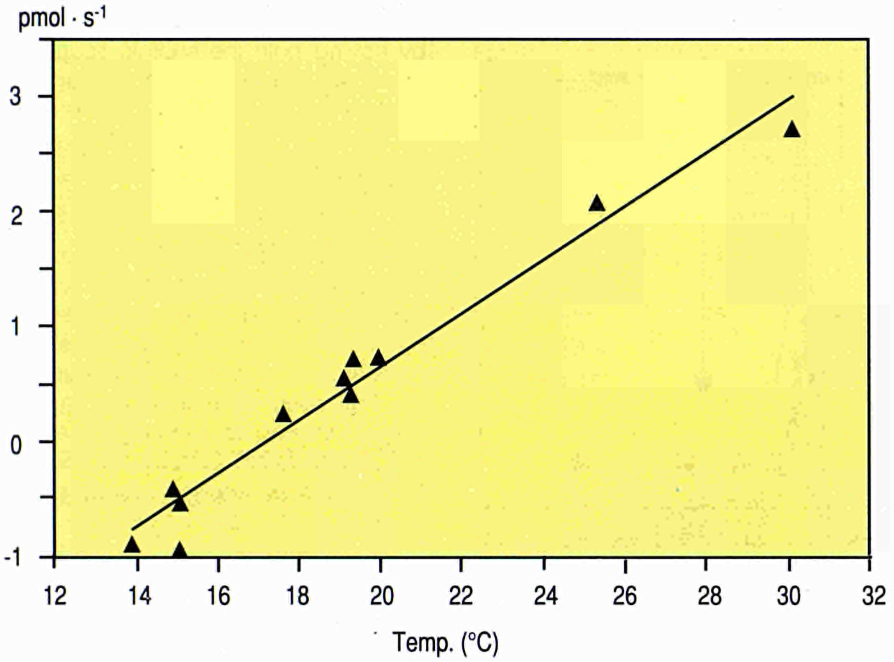


Fig. 1.23 Monoterpene emissions from Pinus Pinea (as from Picea abies, not shown) are controlled by air temperature, indipendent of day or night.

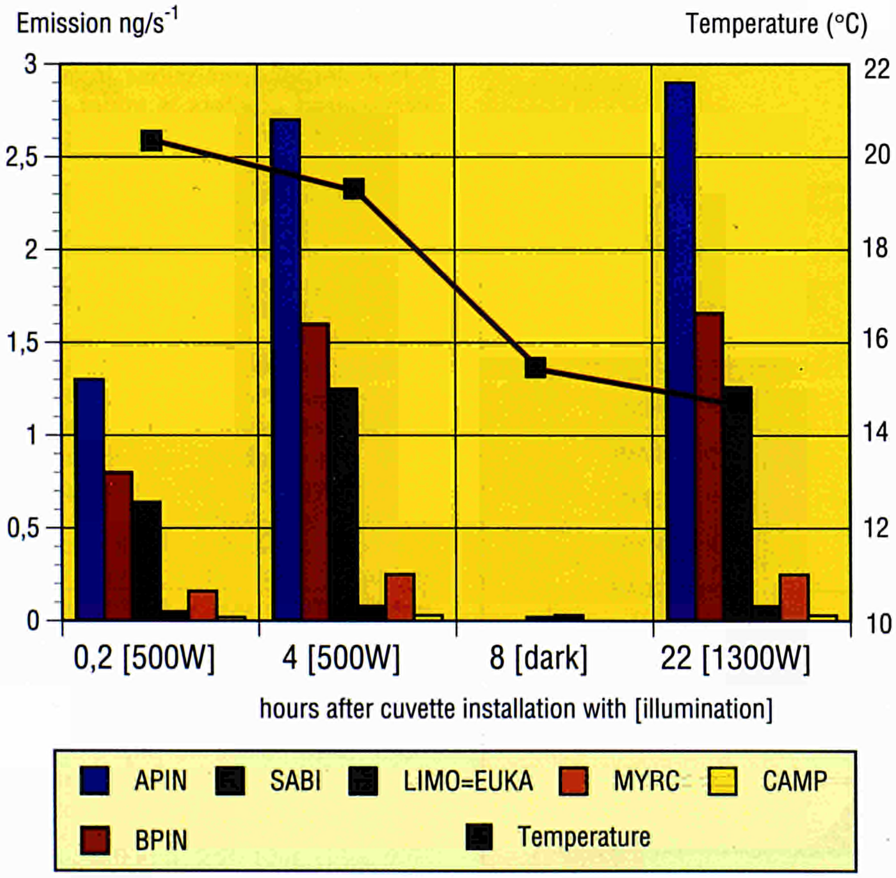


Fig. 1.24 Monoterpene emissions from Quercus ilex are controlled by physiological activity / illumination; at comparable temperatures, there is no emission at night. cuvette installation does not increase emission rates, in contrast to conifers.

ecosystems: a *Pinus pinea Quercu silex* forest with underbrush formed by typical Mediterranean shrubs and a semi-natural grassland. Enclosure based measurements of emission fluxes and of trace gas exchanges will be done in order to obtain species specific and reproducible fluxes under controlled conditions. Nevertheless, possible chamber effects should be checked carefully as results obtained for single plants or plant organs could be difficult to be transferred to a canopy. This is why the BEMA project is methodically based on a balanced combination of enclosure methods with micrometeorological -, tracer- and modelling-techniques. Longer term, less intensive measurements are already carried out at Castelporziano by the home institutes (Rome and Ispra) to characterize seasonal and spatial variabilities in concentrations of biogenic and anthropogenic compounds, emission rates and some environmental / physiological parameters controlling them.

The field measurements campaigns are further complemented by a series of other activities, including the identification of the major vegetation types in the Mediterranean basin; intercomparison exercises to ensure the compatibility of the sampling, analytical and enclosure methods used; laboratory experiments in chemical reaction chambers and in greenhouse systems under controlled environmental conditions, in order to identify hydrocarbon reaction products, vegetation emissions and the emission controlling parameters.

The latter activity has been performed in the Continuous Stirred Tank Reactors (CSTR) in the greenhouse. As described in the previous report, six 1200 l teflon-covered chambers are used to study simultaneously the mass balance of trace gas exchange on long term installed small trees. In addition, a system with six 100-400 l mobile, size adjustable, cuvettes is used for trace gas exchange measurements at shrubs in the greenhouse and will be used during the campaign to study shrubs and/or branches of old trees. The greenhouse and field measurements are closely related to each other by

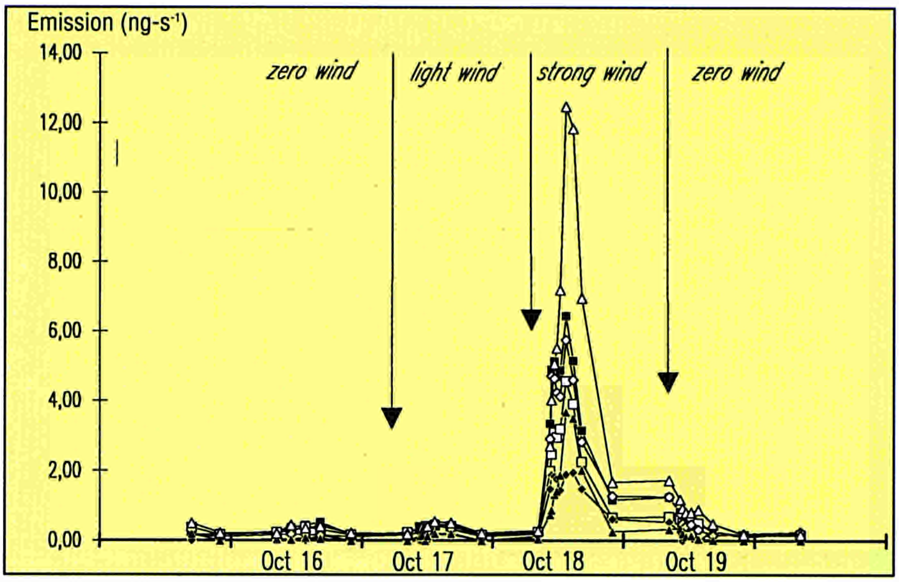


Fig. 1.25 Strong winds may enhance monoterpene emission from Picea abies; there is no effect, if the twigs and needles do not contact each other as is the case with a light wind of < 3 m s^{-1}.

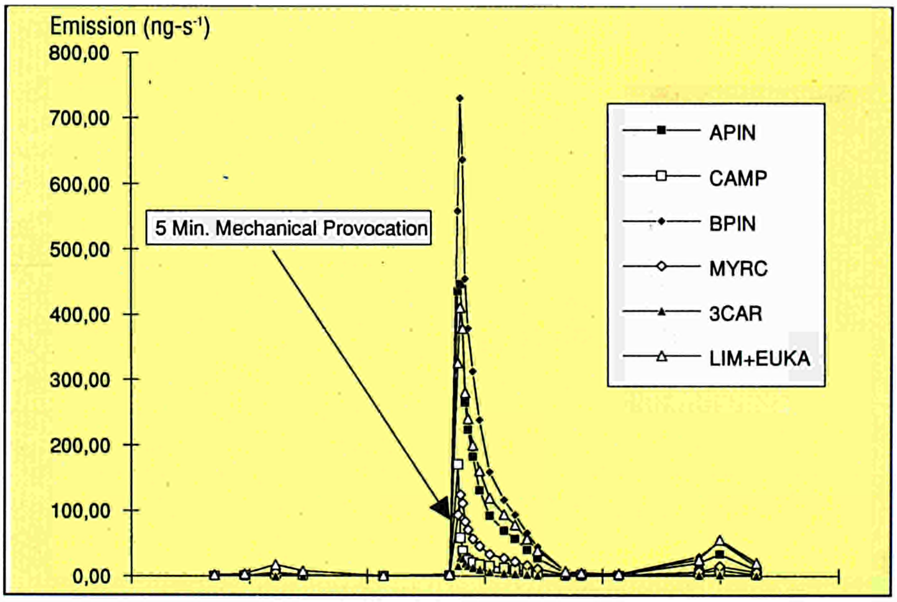


Fig. 1.26 Increase of monoterpene emissions from Picea abies due to mechanical provocation by shaking of the canopy with a manipulator from outside the chamber.

studying the same plant species and by having both the twofold scope (i) to screen the type and amount of compounds emitted and (ii) to search for the environmental and physiological key factors controlling the emissions. This research required improvement of the methods of VOC-sampling and analysis: a device consisting of cooling traps for water, bypass fitting and remote solenoid switching of the Tenax tubes in combination with mass flow controllers has been developed for simultaneous sampling at up to eight measuring points. Internal standards and an artificial tracer terpene are supplied in the cuvettes by a dynamic, gas phase calibration device based on terpene diffusion tubes.

The study of the emission rates and of the factors controlling them has been continued, with spruce (*Picea abies*) being more and more replaced by the common Mediterranean tree species *Pinus pinea* and *Quercus ilex*. It has been shown that:

- monoterpene emissions from the considered conifers is under strict control of leaf temperature, rather than of air temperature *(Fig. 1.23)*. If atmospheric turbulence in cuvettes is not controlled, leaf and air temperature may easily differ by several degrees, thus simulating unrealistic emission rates;
- stomatal conductance, photosynthetic activity and drought stress play a minor role. The realistic air pollutant exposure (O_3, SO_2, single and in combination) has no significant effect on monoterpene emissions from conifers;
- in case of *Quercus ilex* it became evident that this evergreen Mediterranean oak is emitting large amounts of monoterpenes, besides isoprene, though having no detectable content of monoterpenes in leaf or bark. Monoterpene emissions follow rather the physiological activity than the temperature *(Fig. 1.24)*, a pattern that has not yet been reported in literature;
- temperature control can be superimposed by factors like wetting of needles or mechanical stress. For example, biogenic emissions increased more than 10 fold after

***Thymus vulgaris*, Jul. 92**

CONTENT:	EMISSION:
Thymol	Cymene
Cymene	Thymol-methylether
Δ 3-Carene	Camphene
Thymoquinon	Caryophyllene
Carvacrol	
Linalool	
Borneol	
Eugenol	
Caryophyllene	

***Rosmarinus officinalis*, Jun. 92**

CONTENT:	EMISSION:
Myrcene	α-Pinene
Cineol	Camphene
Camphor	Cineol
β-Caryophyllene	β-Pinene
Δ 3-Carene	Camphor
α-Pinene	
Camphene	
α-Tirpenen	
β-Pinene	

***Salvia officinalis*, Apr. 92, flowering**

CONTENT:	EMISSION:
Manool ?	Copaene
Cineol	Thujon
Thujon	Caryophyllene
Caryophyllene	Camphene
Camphor	Cineol
Borneol	α-Pinene
Camphene	β-Pinene
α-Pinene	Borneol
β-Pinene	Bornylacetate
Bornylacetate	

***Salvia officinalis*, Jun. 92**

CONTENT:	EMISSION:
Manool ?	Thujon
Borneol	Camphor
Camphor	
Cineol	
Thujon	
Caryophyllene	
Camphene	
Bornylacetate	
Copaene	
α-,β Pinene	

***Lavandula latifolia*, Mar. 92**

CONTENT:	EMISSION:
Coumarin	Cineol
Borneol	Limonene
Cineol + Limonene	Camphor
Camphor	Camphene
	α- Pinene
	Borneol

***Laurus nobilis*, Mar. 92**

CONTENT:	EMISSION:
Methyleugenol	Alkanes
Cineol	Camphene
Terpenylacetate	α- Pinene
Linalool	Limonene
Eugenol	Cineol
α-,β Pinene	Decanal
Terpineol	β-Pinene

Tab. 1.3 Volatile organics in the leafs compared to emissions at selective Mediterranean shrub species. The top-down grouping of the compounds is according to their relative abundance

application of a strong wind of 10 $m \cdot sec^{-1}$ *(Fig. 1.25)*, and more than 100 fold after mechanical shaking of the canopies *(Fig. 1.26)*. Even with the utmost careful mounting of spruce/pine in a cuvette, biogenic emissions are significantly enhanced for two days.

A second laboratory activity contributing to BEMA was to screen about 15 Mediterranean shrub species cultivated in the greenhouse, for the type and amount of volatile compounds emitted from and stored in the plants. Data are presented in *Tab. 1.3* for the *Lamiaceae-shrubs Rosmarinus officinalis, Thymus vulgaris, Salvia officinalis, Lavendula latifolia* and for *Laurus nobilis*. The results show specific pools and emission patterns of volatile organics for each species. *Figures 1.27* and *1.28* confront the volatile oil pools and the emission patterns of the *Lamiaceae Thymus* vulgaris with external glandular trichomes and of a *Lauraceae* with internal specialised cells (idioblasts) as oil containers. Comparing pools and vapours it becomes evident that the relative composition of the pools is not enough to predict emission types. In case of *Thymus* it was observed that thymolmethylether was emitted instead of the parent compound thymol, indicating the possibility of the plant to convert polar compounds into more volatile ones by methylation. Compared to contents and emissions of conifers, volatile oxygenated terpenoids and phenolics are more frequent in the shrub species examined. During flowering phases, extra compounds are emitted in great quantities, as can be seen with *Salvia*.

Using teflon bag reaction chambers, various aspects of the impact of biogenic compounds, i.e. monoterpenes and isoprene, on atmospheric chemistry have been investigated. Special emphasis was given on the ability of these substances to form ozone in the NO_x-photochemical system. In continuation of the previous work, sunlight irradiations of selected monoterpene hydrocarbons (α-, β-pinene)-NO_x-air, and isoprene-NO_x-air mixtures at part per billion concentrations were carried out. The mixtures were irradiated in a teflon dual reaction chamber outdoor facility *(Fig. 1.29)* and temperature, humidity, sunlight intensity, NO_x-concentration and ozone formation were measured as a function of time. The reactivity of the mixtures in terms of ozone production rate (ppb min^{-1}) ranges from 0.1 to 0.24 and from 0.45 to 0.57 ppb min^{-1} for α-, β-pinene and isoprene respectively.

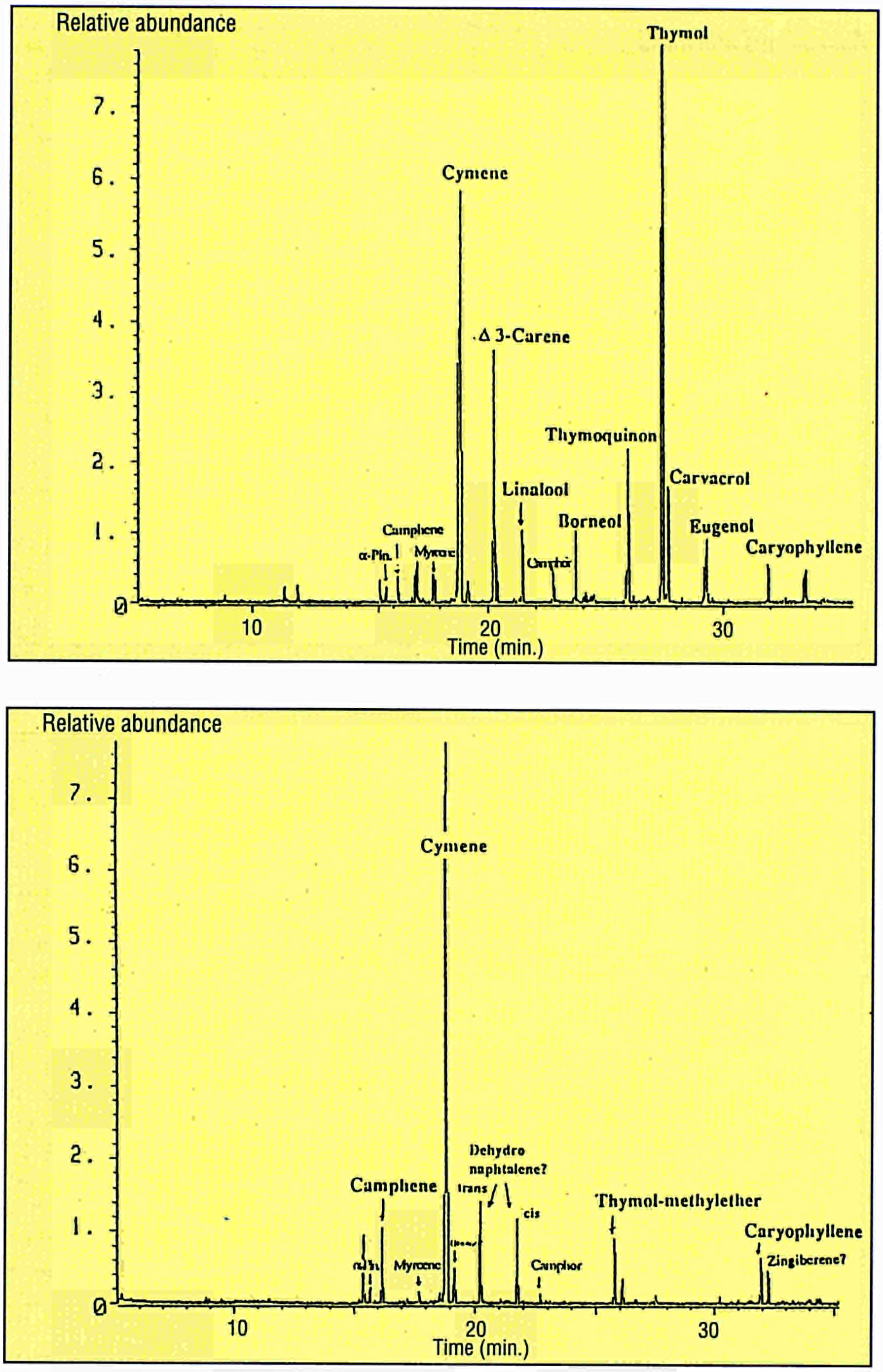


Fig. 1.27 Gas-chromatographic separation of the compounds contained in the leaves (above) and in the vapours (below) of Thymus vulgaris (Lamiaceae).

The major photooxidation products observed during the irradiation of isoprene-NO_x-air mixture were, apart from ozone, aldehydes (formaldehyde, acetaldehyde), ketones (acetone) and aerosols. Yields for formaldehyde and acetaldehyde vary between 50-80 % of the reacted isoprene, depending on the initial reactant conditions. For α-, β-pinene the corresponding yields were found to be less than 5 %, whereas the aerosol formation is clearly favoured.

Removal of Nitrogen Oxides from Flue Gases

Besides the abatement of sulphur dioxide, the JRC conducts research for a combined desulphurisation-denoxing process. During 1991, a process was developed, based on the absorption of NO and the preparation of a concentrated stream of NO and H_2 suitable as a raw gas for the production of hydroxylamine.
Work in this field was continued with a study of the use of Fe(II)NTA instead of Fe(II)EDTA as the complexant. The use of the alternative might be attractive, as NTA has a larger availability and a lower price than EDTA.
Therefore, the chemical equilibrium of the system NO-Fe(II)NTA was studied. The equilibrium constant was determined by absorption experiments in bubble column reactors. All experimental data fit well to an equilibrium constant equation, which covers the temperature range from 22 to 80°C:

$$Kp = 3.05\ 10^{8} \exp(7332/T)$$

The standard reaction enthalpy has a value of -42.4 $kJ.mol^{-1}$. The experimental values for the equilibrium constant are lower than those values found in the literature. However, literature data are extremely scattering and do not seem to be reliable.

Additionally, the absorption of NO in a Fe(II)NTA complex was studied by gas absorption experiments in a 3.75 cm diameter laboratory column. The experiments werecarried out with two types of packing material, i.e. 6 mm and 4 mm Raschig rings. The gas flow rate was varied between 360 and 1400 $l.h^{-1}$ (0.09 and 0.35 $m.s^{-1}$) and the NO concentration in the gas was either 800 ppm or 1600 ppm. The liquid flow rate was varied stepwise between 1 and 25 $l.h^{-1}$. The applied Fe(II)NTA concentration was constant, 10 $mmol.l^{-1}$.

The results showed that the rate of absorption is strongly dependent on the ratio L/G, for low values. This is partly due to the increase of surface

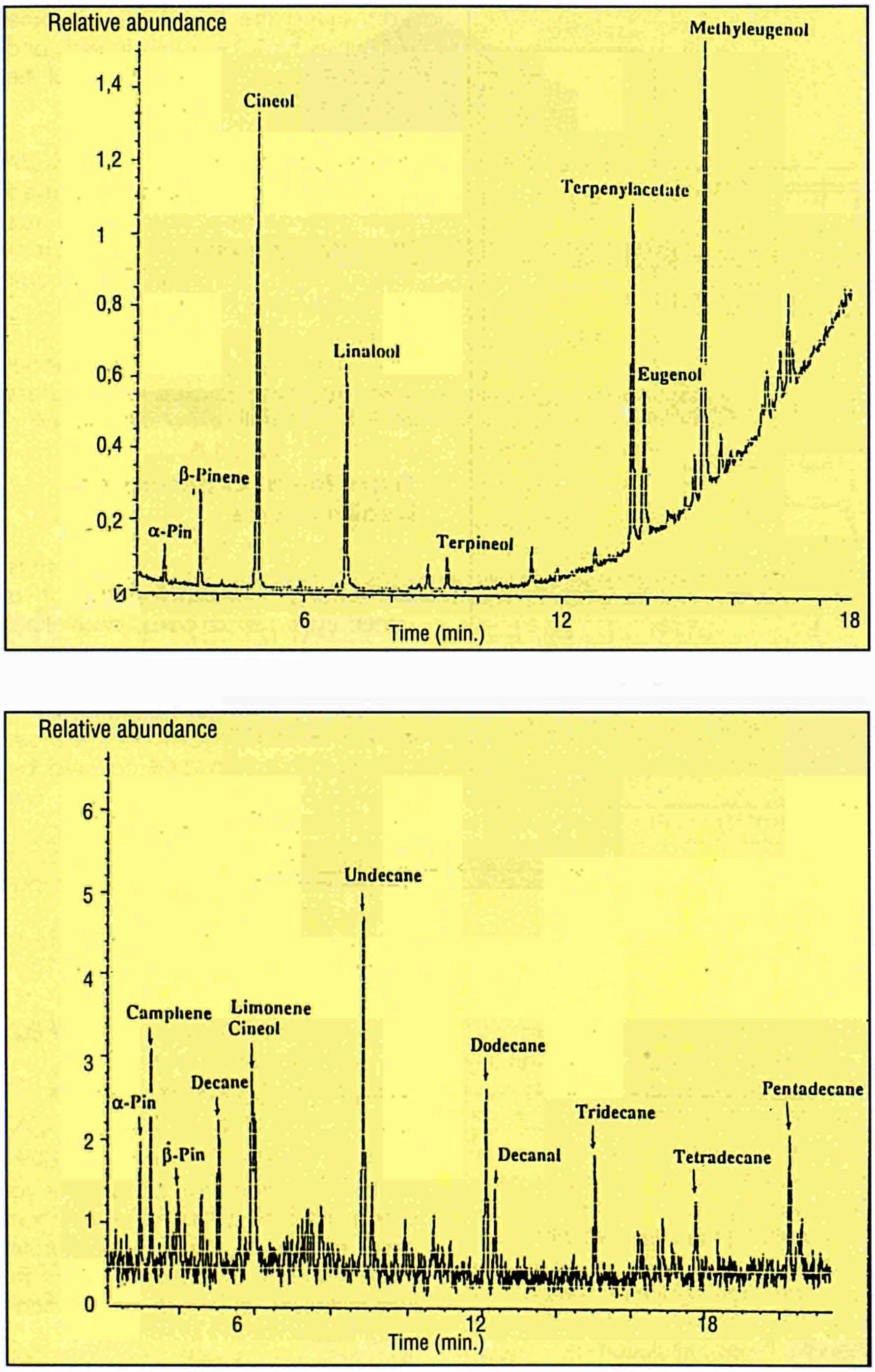


Fig.1.28 Gas-chromatographic separation of the compounds contained in the leaves (above) and in the vapours (below)of Laurus nobilis (Lauraceae).

of interface with increasing liquid flow rate, which favours the rate of absorption. Once the packing is sufficiently wetted, practically no further increase of the interface occurs. Correspondingly, at L/G values >0.05 there is only a slight increase of the absorption rate with increasing L/G.

The rate of absorption appeared to be roughly proportional to the NO gas concentration. Gas side mass transfer coefficients (Kg.a) were calculated for the absorption. The maximum value observed for Kg.a for the 6 mm packing was 0.114 s^{-1}. The smaller packing (due to its higher interfacial area) gives a higher mass transfer coefficient, 0.164 s^{-1}.

The work will proceed during 1993 with a study into the mechanism of the absorption of NO in solutions containing the Fe(II)NTA complex.

ENVIRONMENTAL CHEMICALS

This research area includes a multiplicity of activities grouped under three headings, namely: the Indoor Air Pollution, the Evaluation of Environmental Chemicals and the Soil-Water-Waste.
While Indoor Air Pollution is self-explanatory for what is the aim of the activity, the Evaluation of Chemicals does refer to the management, updating and extension of the Environmental Chemicals Database, on one side, and to Trace Metals in human tissues and their toxicological significance, on the other side.
Soil-Water-Waste encompasses analytical methodologies applied to the different ecosystems as well as the studies on the soil-pollutants interactions, the characterisation of algal blooms in water and the toxic waste management.

ECDIN - Databank

ECDIN is a factual databank created in the framework of the Environment Research Programme of the Joint Research Centre (JRC) of the Commission of the European Communities at the Ispra Establishment (Environment Institute).

A public version of the ECDIN databank is accessible through DIMDI ("Deutches Institut für Medizinische Dokumentation und Information, Koln) and through a host in the USA.

Records are updated continously in collaboration with specialists and research Institutes in and outside Europe with special emphasis on occupational health aspects .

A new version of ECDIN CD-ROM

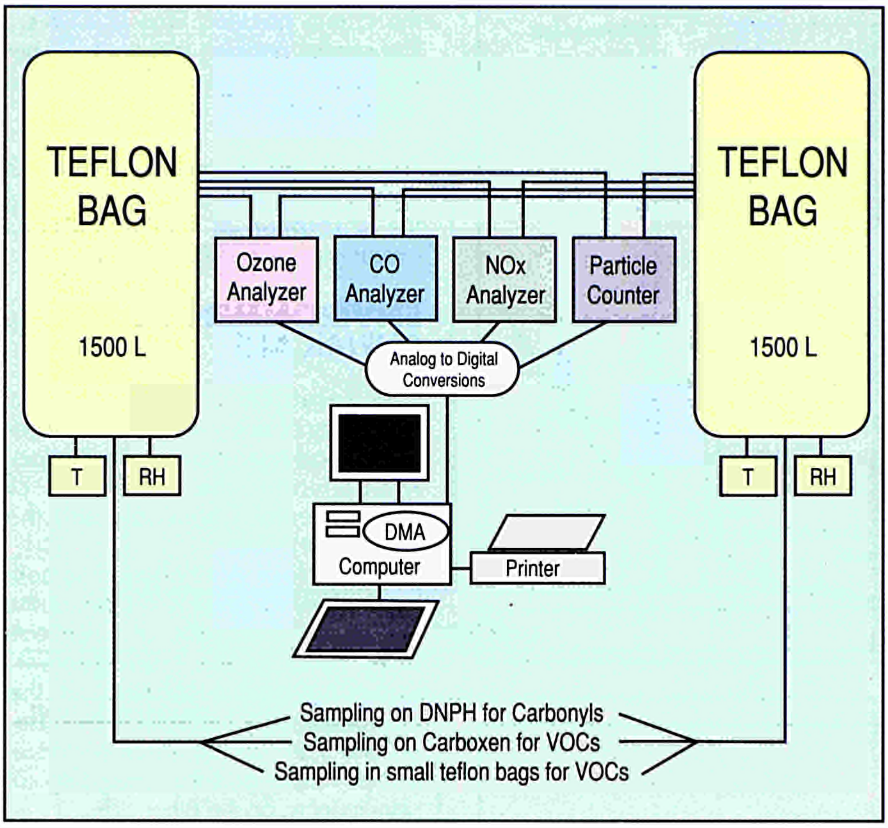


Fig. 1.29 Experimental set-up for the sunlight irradiation of hydrocarbon-NO_X*-air mixtures.*

has been produced during the first 6 months of 1992.

This new version which takes into account the experience and observations obtained from the users of the first version is notably incrased in content. This number of chemical substances included has risen to about 7.500, and the new data files, especially important for the evaluation of environmental toxicity, have been added.

The complete list of the available data files is the following:

- Identification
- Physical ad Chemical Properties
- Uses
- IRPTC Legal Files
- Directive 67/548 EEC (Hazardous Substances)
- Human Health Effects
- Occupational Exposure Limits
- Occupational Poisoning Reports
- Occupational Disease Prevention
- Therapeutic Treatment
- Experimental Toxicity
- Aquatic Toxicity
- Carcinogenicity
- Mutagenicity
- Concentration in Environmental Matrices
- Concentration in Human Media
- Concentration in Animal Media
- Aquatic Bioaccumulation
- Aquatic Biodegradation
- Analytical Methods
- Odour TLVs
- Public Safety Data from B.I.G.

The most significant data added to this version has been specially reserched and updated. In addition, the substances which were included in the first edition have been reviewed.

In the light of the experience gained from using the first edition, some difficulties have been eliminated, and in some areas the presentation of the data has been improved.

It should be noted that the CD-ROM version of ECDIN, although derived from the on-line database, has however, a completely original interrogation and search language and presentation format.

The compact disc is on sale world-wide from specialist distributors acting on behalf of the Commission.

Trace Metal Exposure and Health Effects

The aim of the activity consists essentially in establishing, on a scientifically sound basis, dose-effect relationships in view of preventing potential health hazards from the exposure to trace metals.
To achieve this goal, two topics, linked each other and covered by this more comprehensive theme, are being investigated, i.e.:
- trace metal levels in human tissues of EC general population and occupationally exposed workers;
- metabolism and biochemical effects of trace metals.

Trace Metals in Human Tissues of EC General Population and Occupationally Exposed Workers

This topic is addressed to establish baseline values in general population as the fundamental parameter to assess the biological effects of trace metal exposure on humans.Accurate trace element reference values in human tissues is an important indicator of help

- to understand the pathological states in connection with environmental factors and to identify anomalous trends of essential/toxic elements in the general population;
- to verify or reconsider legal limits of exposure for the protection of the general population;
- to perform the biological monitoring of professionally exposed subjects as basis for prevention measures.

In this context three projects are being developed: EURO TERVIHT,

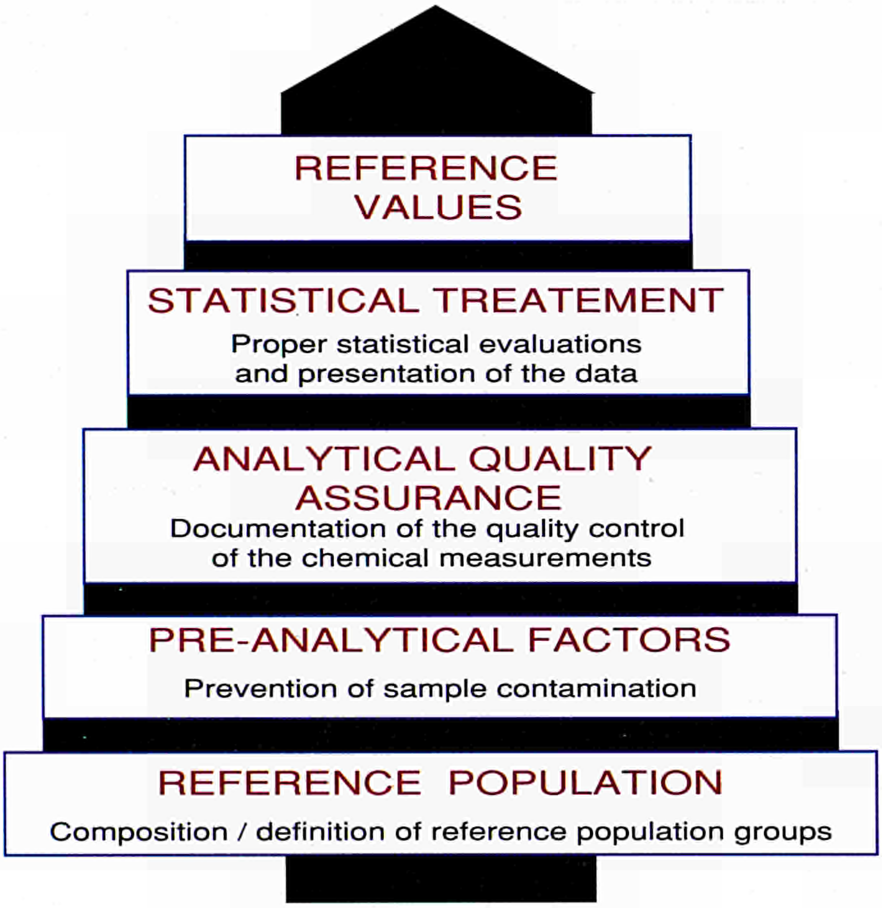


Fig. 1.30 The " Tree " of the Reference Values.

TRACY and HAMBIHT.

The EURO TERVIHT (Trace Element Reference Values in Human Tissue) project is aimed at establishing and comparing trace element reference values (RV) in tissues from inhabitants of the European Community as baseline values for clinical / toxicological assessment studies. The project foresees an international cooperation of specialized chemical / toxicological laboratories for the standardization and harmonization of criteria in establishing RV. For the purpose, criteria for approaching "background" values measurements practised in EURO TERVIHT have been definitively established.
These are based on quality rather than quantity of data and imply the adoption of well defined protocols to satisfy the requirements of the programme stages ("Tree of RV", *Fig. 1.30*). The criteria adopted in the TRACY - project (see the section EUREKA of this report), which have been developed in collaboration with the Scientific Committee on the Toxicology of Metals within the International Commission on Occupational Health (ICOH) and have been recognized by the International Union of Pure and Applied Chemistry (IUPAC), form the basis for the design of the experimental work foreseen in EURO TERVIHT in order to obtain internationally comparable results (*Fig. 1.31*). One of the first steps of the EURO TERVIHT has been that of reviewing and critically evaluating the existing literature on trace element RV in body fluids in the general population of each EC country.
The Institute of Occupational Health of Copenhagen, in cooperation with the JRC, assessed the Danish studies for Al, As, Co, Cr, Cu, F, Hg, Ni, Pb, Se, V, Zn in blood, serum and urine selecting data which were considered to be of significant value as baseline .
It could be concluded that:

- the accuracy of the RV is of the utmost importance, since high-dose environmental or occupational exposure rarely occurs and health risk assessment is mainly connected with long-term low-dose exposure;
- the lack of reliable RV makes it impossible to compare different sub-populations with respect to the general body burden;
- RV for defined subgroups are needed for the selection of geographic areas and the identification of demographic and lifestyle factors, requiring actions to reduce or prevent adverse health effects from long-term exposure to toxic and carcinogenic trace elements;
- RV for children are lacking for all trace elements. These RV must be established to facilitate the assessment of health effects of long-term low-dose exposure;
- although the main focus has been on the toxic and carcinogenic trace elements, the importance of the essential trace elements in relation to the health status of the general population should not be overlooked. The establishment of RV for the essential trace elements for defined subgroups is needed, to provide the scientific basis for future research on the effect of essential trace elements on the health of subjects with different body burdens of e.g. carcinogenic trace elements;
- the environmental exposure to a series of trace elements (e.g. Ga, Ge, In and Te), of recent technological significance, may become a future environmental health problem. Thus RV are also needed for health risk assessment studies. This applies to Pt too, the increased use of which in catalysts for motor vehicles will lead to increased platinum levels in the environment.

As the continuation of the work on the determination of trace elements in body fluids of the general population in northen Italy, the influence of parameters which could affect the experimental ranges of the trace

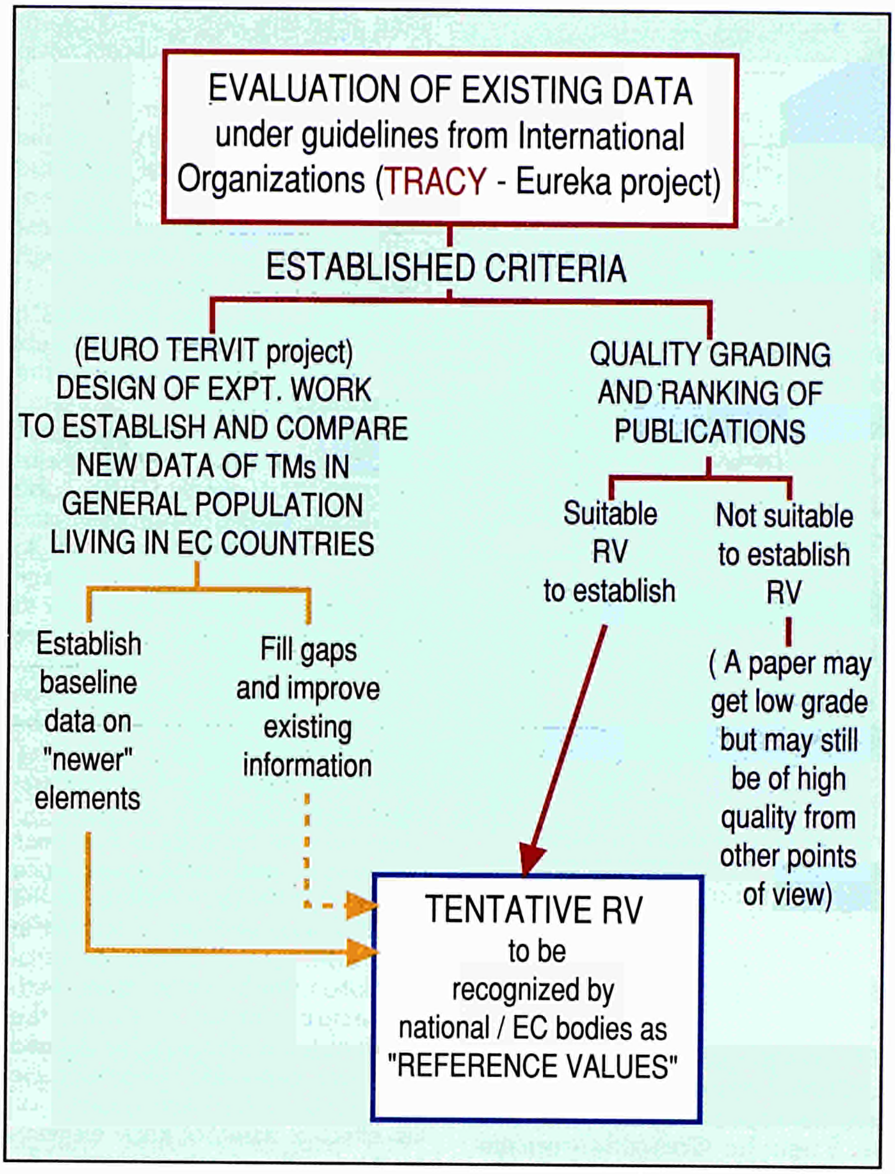


Fig.1.31 Strategy for establishing trace element reference values (RV) for maximum utility in Regulatory Decision Making and related Oriented Research.

elements determined was considered. Since analytical errors were reasonably minimized in previous trace element determinations, the fluctuation of the experimental ranges should be attributed to environmental factors and biological variations which include different exposure (i.e. dietary intake) as well as individual metabolic differences of trace elements in the body. In this context, the importance of the consumption of beverages such as wine, mineral water, beer, tea and coffee, as a possible dietary factor influencing the establishment of trace element RV in the general Italian population was considered.

The study was carried out by means of a 'pool' of advanced analytical methods, (neutron activation analysis, inductively coupled plasma-mass spectrometry, graphite furnace atomic absorption spectroscopy, inductively coupled plasma-atomic emission spectroscopy) which allowed the determination of at least 42 elements.

Table 1.4 summarizes the results (order of magnitude) of the elemental analysis of wine, mineral water, beer, tea infusions and instant coffee. These data were the basis for an assessment study which suggests that beverages could significantly contribute to the total dietary intake of some trace elements with the possibility of influencing the levels in tissues and body fluids. *Table 1.5* identifies the main beverages which contribute to increase the total dietary intake of trace elements of more than 10%. As blood and urinary levels of these elements may depend on the consumption of specific beverages, the knowledge of the degree of variation of the different elements in body fluids and tissues due to dietary factors is of great interest. The availability of 'actual' trace element RV is of paramount importance. This makes retrieval evaluations possible, e.g. to establish the trend of changes of the concentration of trace elements in the different EC countries. *Table 1.6* reports the estimates of the intake of B and Co (wine) and Rb (coffee) in inhabitants of the different EC countries showing that the exposure to the elements considered - as a result of the consumption of the two beverages - is quite different for the inhabitants of the various EC countries.

Obviously the scenario of *Table 1.6* coukd change to possible changes in dietary habits.

These data are also useful from a nutritional point of view. In order to ensure a correct dietary exposure of essential trace elements a more precise knowledge of the alimentary sources of trace metals, is necessary. It might be advisable to consider the extension of the EC directive 80/777, which fixes the limits of trace elements in natural waters, to cover other popular beverages such as wine, beer and particularly mineral water.

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

the project is developed in the framework of EUREKA. (See section 5 of this report).

Beverage (a)	ELEMENT CONCENTRATION (µg l^{-1})			
	>1000	<1000 - 100	<100 - 1	<1 - 0.005
Wine (32)	B,Rb,Zn	Al,Cu,Mn,Sr	Ba,Co,Cr,Li Mo,Ni,Pb,Sc, Se,Sn,Ti,V, W,Zr	As,Cd,Ce,Eu Ge,Hg,In,La, Nb,Sb,Tl
Mineral water (18)	----	B,Sr	Ba,Li,Mn,Rb, Ti,Ag,Al,As, Sc,U,V,Zn Zr	Be,Co,Cr,Cu, Ni,Pd,Sb,Tl, Au,Bi,Cd,Ce, Eu,Gd,Ge,Hg, La,Nd,Pb,Rb, Sn,Th
Beer (17)	----	Al,B;Mn,Rb	Ba,Cu,Sc,Ti, V,Zn,As,Cr, Li,Mo,Ni,Se, W	Be,Ce,Co,Gd, Hg,La,Nb,Pb, Sb,Sn,Zr, Au, Bi,Cd,Eu,Ge, Pd,Rh,Tl,U
Tea (infusion) (10)	Al	B,Mn,Rb,Sr Zn	Ba,Co,Cu,Ni, Ti,Cr,Li,Mo, Pb,Sc,Se,U, V	As,Cd,Ce,Eu, Gd,Hg,La,Nb, Pd,Rh,Sb,Sn, Tl,W,Zr
Coffe (instant) (12)	Rb	Cu,Mn	Al,V,Ba,Co, Cr,Sr,Ti,Zr, As,Li,Mo,Ni, Sc,Se,Sn,W	Cd,Ce,Pb,Sb, Tl,V,Zr

(a) in parenthesis number of samples analyzed.

Table.1.4 *Trace elements in beverages consumed by italian population.*

Element	Beverage
Ag	Mineral water
B	Mineral water, wine
Ba	Mineral water, wine
Co	Wine, tea
Li	Mineral water
Mn	Wine, tea
Ni	Wine, tea
Rb	Wine, coffee
Sb	Mineral water, wine
Tl	Mineral water, wine
V	Mineral water, wine, beer

Table.1.5 *Identification of the main beverages which could contribute to increasing the total dietary intake of trace elements to an extent greater than 10%.*

HAMBIHT (Hard Metal Biomonitoring in Human Tissues)

As a further development of the project aimed at determining hard metal in tissues of professionelly exposed subjects, the biological monitoring of 252 hard metal workers under control of five organizations in northern Italy has been completed. Twenty-five out of them, showed pathological effects. The study has allowed the following conclusions to be reached:

- the determination of Co content in air samples (CoA) represents, perhaps, the best procedure to assess the exposure. However, wide fluctuations of the concentrations of total dusts and Co (from 0.019 to 1.60 mgCo m^{-3}) have been observed. Exposure-effects relationship based on 2 - 4 hrs sampling does not appear to reflect the real exposure by inhalation. The correlation between CoA and urinary cobalt (CoU) ($r = 0.82$, $p<0.001$) tends to be more significant at lower dose exposure. The obvious dispersion of CoU makes this value an indicator of exposure only for a population.
- Determination of CoU on spot samples of urine in comparison to the Co content of 24 h urine showed no increase as a function of inhaled Co during the working week. Taking into account the total amount of Co excreted (and therefore the total volume of urine) there are no drastic variations of CoU during the working week. A decrease in urinary excretion of Co was observed with an increasing period at work *(Fig.1.32)*.
- Co in blood (CoB)as well as CoU are variable parameters and further studies should be necessary to establish their exact significance as possible indicators of exposure, particularly in pathological cases.
- Co content of pubic hair (CoH) and of toenail (CoN) does not seem to be good indicator of Co accumulation in the body.
- Co in bronchoalveolar lavage (CoBAL) is useful, from the qualitative point of view, if an exposure occurred after that the subject was removed from the work ; the

Country	Exposure (mg/indiv. per y) Coffee Rb	Wine B	Wine Co
B	1.58	26.4	0.15
DK	0.79	46.1	0.27
E	2.7	67.2	0.37
F	3.5	106.5	0.59
FRG	2.2	35.6	0.20
G	3.6	48.2	0.27
I	0.34	97.7	0.54
IR	6.4	6.72	0.037
LUX	--	85.8	0.46
NL	1.1	19	0.11
P	1.6	77.3	0.43
UK	9.7	17	0.095

Table.1.6 *Estimated exposure to Rb, B, and Co of adult population living in EC, as result of coffee and wine consumption. [Calculated taking into account for each country the wine (1988 - 1989) and instant coffe (1988) consumption as well as the adult population (from 15 to over 65 years in 1989)]*

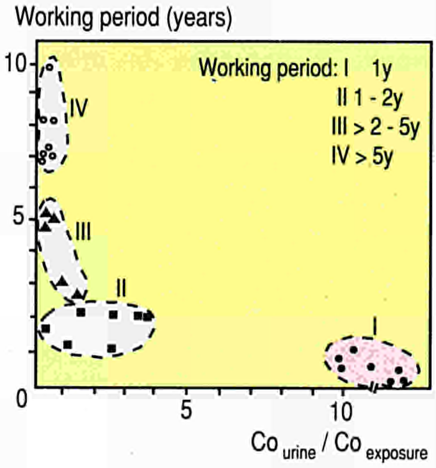


Fig.1.32 *Excretion of Co in urine of hard metal workers with increasing period of exposure at work.*

Subject	Time of Exposure (years)	Metal Content (ng g^{-1} wt.w) Co	W	Ta
		OPEN LUNG BIOPSY		
Pm	13	2,440	107,000	32,500
PA	Many	830	52,000	29,000
		TRANSBRONCHIAL BIOPSY		
FM	7	15,000	101,000	19,000
TF	5	3,900	33,900	1,865
CA	5	2,800	74,000	51,400
CA	20	8,500	134,000	91,500
Control (n=37)		25 - 150	0.1 - 25	0.2 - 30

Table.1.7 *Hard-metal exposure shown by neutron-activation analysis of lung biopsies of workers*

presence of metals such as W and Ta testifies the exposure to hard metals. Very useful for studying possible mechanisms of Co toxicity.

- The following correlations between different biological specimens considered were found: CoU - WU (tungsten urine), $r = 0.86$, $p<0.001$; CoN - WN (tungsten in toenails), $r = 0.85$, $p<0.001$.
- Multielement neutron activation analysis of Co, Ta and W in microsamples of lung tissue (open lung or transbronchial biopsy) collected for clinical purposes is an excellent integrating method to prove the hard metal exposure *(Table 1.7)*.
- Comparable levels of Co, W, Ta were found in the biological samples of diseased and not diseased workers supporting the hypothesis that immunological mechanisms should cause the pathological alterations; i.e. hard metal disease should not be dose-dependent (Co as possible hapten for a coniugation with proteins of the respiratory tract which may lead to an interaction with specific antibodies of B-lymphocytes). Thus, development of the disease should be related to individual predisposing factors more than to environmental conditions.

Trace Metal Metabolism and Biochemical Effects

This topic is addressed to metabolic pathways and to toxicological effects of low doses of trace metals, the studies being performed by both in vivo on laboratory animals and by in vitro toxicity testing as alternative to animal testing.

For the purpose the project AMAMMET (Animal Testing Methods Vs. Alternative Testing Methods in Metal Toxicology) is being developed.

In view of getting more reliable quantitative estimates of the risk to Co exposure, the knowledge of toxicokinetic and metabolic patterns of inhaled and/or ingested Co is of particular interest:

In this context a method for determining inorganic and organically-complexed Co in human urine *in vitro* and rat urine *in vivo* has been developed and applied to urine of hard metal workers.

This has implied the use of different ^{57}Co, ^{58}Co and ^{60}Co- labelled Co compounds (Co-vitamine B12 and Co^{2+} inorganic ions as chloride) for the study of the interaction of Co as well as its biotransformation in urine.

The method has been applied to speciate inorganic and organic form(s) of Co in urine samples of hard metal workers. In nine samples from workers, about 30% of Co in urine, was recovered in the organic fraction suggesting that the inorganic Co inhaled by hard metal workers can undergo biotransformation *in vivo*.

Rats were exposed to $^{57}Co^{2+}$ ions in single intraperitoneal (i.p.)or intravenous (i.v.) doses (from 5 ng Co/rat to 1 mg Co/rat) or to 50 ng Co/rat/day through drinking water for 109 days. Results showed that the target tissue for Co depended on the dosage and route of administration (e.g. lung, kidney or bone). For rats i.v.-injected with 5 ng Co/rat no radioactivity was found in the

Cellular System	End Point	Relevance
• BALB/3T3 Cl A31-1-1 mouse fibroblasts	• Colony forming efficiency • Neoplastic transformation • Cellular uptake	• Cytotoxicity • Carcinogenesis • Uptake / effect relationship
• HepG2 human hepatoma cells	• Neutral red assay • Unscheduled DNA synthesis • Cellular uptake, biotransformation	• Cytotoxicity • Genotoxicity • Metabolic studies
• Normal himan epidermal keratinocytes & HaCat immortalized human epidermal keratinocytes line	• Colony forming efficiency • Inhibition of UV induced DNA repair mechanisms	• Cytotoxicity • Genotoxicity
• NIH/3T3 mouse fibroblast line transfected with human HSP70 promotor + hGH marker gene	• Induction of hGH synthesis = induction of HSP70 stress protein promotor	• Early marker of cellular aggression
• B16 mose melanoma cells	• Effects on melanin synthesis	• Impact on cellular differentiation
• MC3T3-El mouse osteoblast cell line	• Cell survival tests • Effects on alkaline phosphatase • Interference with PGE2 and PTH induced biological effects	• Cytotoxicity • Impact on bone cell function, cell proliferation and on cAPM level
• PC12 rat pheocytochroma cells	• Effects on dopamine synthesis and release • Effects on NGF induced differentiation • Cellular uptake and excretio kinetics	• Neurotoxic effects • Uptake / effect relationship

Table. 1.8 Cell culture lines available at the JRC-Ispra for in-vitro toxicological studies of trace metals.

germinal cells. This suggests that in vivo a blood-test is barrier against the incorporation of the element in sperms may occur. On the other hand, the presence of abnormal amounts of Co in sperma of hard metal workers (both in seminal plasma and germinal cells) suggests that in hard metal workers an excess of Co is able to cross "a barrier" which under physiological conditions does not make its incorporation into spermatozoa possible.

Co has been included in the list of suspected cancerogen to humans by the IARC (International Agency for Research on Cancer). Exposure of BALB/3T3 cell cultures (an in vitro model for the carcinogenic potential of chemicals) to concentrations of cobalt from 100 to 1 μM of Co^{2+} induced a dose dependent cytotoxic response. At 10 μM cell growth was reduced to about 30%. No inhibition was found at 1 μM. Morphological transformation assays gave negative results when the cells were exposed to 100 μM of Co, suggesting a lack of carcinogenic potential of inorganic soluble Co *in vitro*.

As far as it concerns the use of cell culture system in combination with nuclear and radioanalytical techniques seven main cell lines were developed and are currently available *(Table 1.8)* for in vitro environmental and occupational metallotoxicological studies in the following areas: (i) screening test to establish metal toxicity rankings including the carcinogenic potential of metal compounds (ii) setting of uptake - effect relationships of metal exposure (iii) elucidation of molecular mechanisms of metal toxicity.

These *in vitro* toxicity testing were applied to studies of specific metal compounds of environmental and occupational health interest (As, Cd, Co, Cr, Mn and Se) as well as for screening tests of metal toxicity.

Genotoxicological studies

As the complement of the above activities and in order to contribute to genotoxicological investigations on environmental chemical compounds, reserch has been focussed on the constitution of new lines of transgenic mice. The research has been carried out in close collaboration with the

CNR ITBA of Milan (Italy)

A line of transgenic mice with a viral gene under the control of an ubiquitous promoter (SS-TK) inserted in their genome has been derived from a founder obtained by microinjection of the SS-TK DNA construct into fertilized eggs and successive transfer of the micromanipulated embryos in oviducts of foster mothers. Nineteen heterozygous transgenic mice have been derived till now from the founder female mouse. Both the heterozygous and the homozygous mice will be used in genotoxicological investigations.

In addition to the properties that characterize the transgenic mice, this model offer the advantage to carry out a simplified analysis of chemically induced damages. In fact, the stochastically induced mutations that occur on TK viral gene can be put into evidence in the cells derived from different tissues of the treated animal by analytical procedures already described in the scientific literature. These methods foresee the isolation of cells from tissues in order to obtain primary cell cultures and their growth in selective media in which only the cells with the inactivated viral Thymidine Kinase can survive. Since the analysis of the mutational events takes advantage of primary cell cultures derived from transgenic mice, this approach carried out on not-treated transgenic mice will allow their use in *in vitro* experiments thus contributing to *in vivo-in vitro* comparative studies.

In the last period of this year, the methodology for deriving primary cell cultures from liver, kidney and lung of the mouse has been established. These organs are the target of many genotoxic compounds and, therefore, deserve top priority investigation.

Additional research has been focused on transgenic mice for studies on gene expression

Techniques allowing to selectively inactivate any gene in the mouse genome have been set up. This makes possibile to get animal models in which some human hereditary pathologies originated by mutations in well known genes are reproduced. The perfect knowledge of the inserted gene and of its proper genome position offers the opportunity to study the diseases in more accurate manner from the molecular and therapeutic point of view. The technique (called "gene targeting" or "gene knock out") is becoming more and more popular in molecular genetics and then, in the production of the transgenic mice for the above mentioned purposes.

Terminal deoxynucleotidyl Transferase (TdT) gene that codify for an enzyme present in the immature B and T lymphocytes and that characterizes some forms of human leukemias, has been interrupted in murine embryonic stem-cells (ES-cells).The engineered ES cells with the interrupted TdT gene have been introduced in mouse blastocysts *(Fig. 1.33)* that finally have been reimplanted in foster mothers.

Till now, some chimeric mice have been obtained *(Fig. 1.34)*. This means that the microinjected stem cells contributed to the formation of the embryo through the colonization of the Inner Cell Masses. The next step will be to breed these chimeric mice in order to prove that the germ line have been colonized by the engineered ES cells.

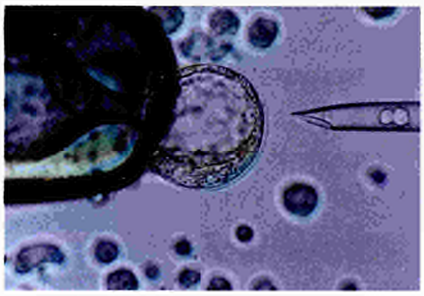


Fig. 1.33 Introduction of engineered ES cells with interrupted TαT gene in mouse blastocyst.

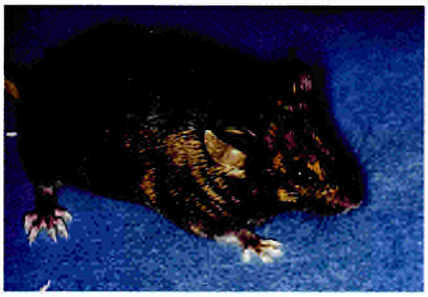


Fig. 1.34 Chimeric mouse.

Indoor Pollution

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

Research activities are focused on the development and validation of methods for the characterization of organic indoor pollution, its sources and sinks. Organic indoor pollutants are of particular concern since many of them are known or suspected to cause carcinogenic, neurotoxic, allergenic, immunotoxic, irritating or sensory effects. In particular volatile organic compounds (VOC) are often suspected and sometimes have been shown to play a role in complaints about inadequate indoor air quality in office buildings or other indoor environments. Building and furnishing materials, household and hobby products are important indoor sources of these compounds.

Work performed in 1992 was aimed at validating a chamber method for the determination of VOC emissions from indoor materials and products, the development of a method for the determination of semivolatile organic compounds (SVOC) in home dust and indoor air and at developing experimental methods and models for the characterization of the deposition of organic vapours on indoor surface materials. In addition a walk-in type environmental chamber of 30 m^3 has been installed and tested.

Validation of a chamber method for the determination of VOC emissions from indoor materials and products.

The most appropriate means of controlling indoor pollution by VOC is to reduce source emissions, e.g. by the choice of low emitting materials and products. A prerequisite are validated standardized methods for emission measurements. An interlaboratory comparison experiment launched in 1991 and aimed at validating a guideline for emission measurements issued in 1990 by the European Collaborative Action "Indoor Air Quality & Its Impact on Man" has been concluded. Twenty laboratories in Europe and in the USA have participated. The experiment included three steps of increasing complexity, requiring the determination in small test chambers of the emission rate(s) of:

- a single compound source (n-dodecane, constant source) whose emission rate could also be determined by weighing as an independent, absolute method;
- the four main compounds (phenol, 1,2,4-trimethylbenzene, n-decane and n-undecane) and the total volatile organic compounds (TVOC) emitted from a PVC tile sample (slowly decreasing source)
- four compounds (α-pinene, linalool, geraniol and α-cedrene) and TVOC emitted from a wax sample (rapidly decreasing source).

The results of the first test have been reported last year. For the second test, each participant received two samples of PVC flooring material. VOC concentrations had to be measured 48 and 72 h after introduction of the material into the chambers.

Statistical analysis of the data reported from the participating laboratories yielded the following more important information:

- data sets were normally distributed after elimination of one run from one laboratory and all TVOC data from another laboratory;
- the steady state emission rate had not yet been reached after 48 h;
- the interlaboratory bias is the most important source of variance of the data (the relative standard deviations ascribed to interlaboratory differences range between 25.7 to 41.7%), followed by the variance between samples; the intralaboratory variance (repeatability of duplicate measurements) was considered satisfactory;
- at the level of variability encountered neither the wide range of chamber capacities (4 l to 1475 l) nor the chamber wall material (glass or stainless steel) introduces any systematic difference in the results.

For the third test a water-based floor wax was distributed. The participants were requested to spread appropriate amounts of wax (depending on chamber volume) on a glass support. Chamber concentrations of emitted compounds had to be measured at ten different times. Using an exponential decay model and non linear regression of the measured data, the initial emission rate (EF)0 and the decay constant k had to be calculated. The results showed extremely large scatter. Therefore only non-parametric summary statistics were calculated. *Table 1.9* shows the results for linalool, the most abundant of the emitted compounds. At least four factors appear to contribute to the large scatter: (a) difficulties in preparing a homogeneous wax layer, (b) sink effects in the chambers, (c) analytical difficulties such as poor GC separation or thermal decomposition of geraniol and (d) difficulties in fitting the experimental data to a decay model due to poor initial guesses of the model parameters.

While the results of the second test were considered satisfactory, further tests with rapidly decreasing sources and the need of a standardized procedure for the application of thin films of liquid or paste materials were agreed upon.

Determination of SVOC and POM in house dust and indoor air

The on-line combination of supercritical fluid extraction (SFE) with gas chromatography (GC) and mass spectrometry (MS) is a promising technique for the analysis of semi-volatile organic compounds (SVOC) and particulate organic matter (POM) in house dust and indoor air. Available techniques require the sampling of large air volumes (100 m^3 and more) and time consuming Soxleth extraction. As a result, research published so far has been limited essentially to the determination of pesticides in indoor air and house dust and of polynuclear aromatic hydrocarbons (PAHs) in indoor air. A commercial instrument for combined SFE-GC had to be further modified in order to improve the efficiency of sample transfer from the SFE extractor to the GC column. The SFE-GC instrument has been coupled to a mass spectrometer in order to investigate:- which classes of SVOC and POM other than pesticides and PAHs are recurrent in indoor air and house dust; - if there are similarities between house dust samples collected in different homes; - if air and dust samples collected simultaneously in the same home show common features.

	$(EF)_0$ ($\mu g\ m^{-2}\ h^{-1}$)	K (h^{-1})
Minimum	1,228	0.4559
25th percentile	13,950	1.964
Median	31,660	4.476
75th percentile	79,990	10.30
Maximum	282,900	13.02

Table.1.9 Distribution of linalool results from the wax test.

Five house dust samples have been collected in four different homes. In one home two samples were collected, one during summer and one during winter. *Fig.1.35* shows the chromatograms of the extracts of the five samples obtained with supercritical CO_2. They show an astonishing similarity. Most of the more abundant constituents are common in all five samples. Their tentative identifications based on mass spectra and elution times are reported in *Table 1.10*. As can be expected, with pure CO_2 mostly

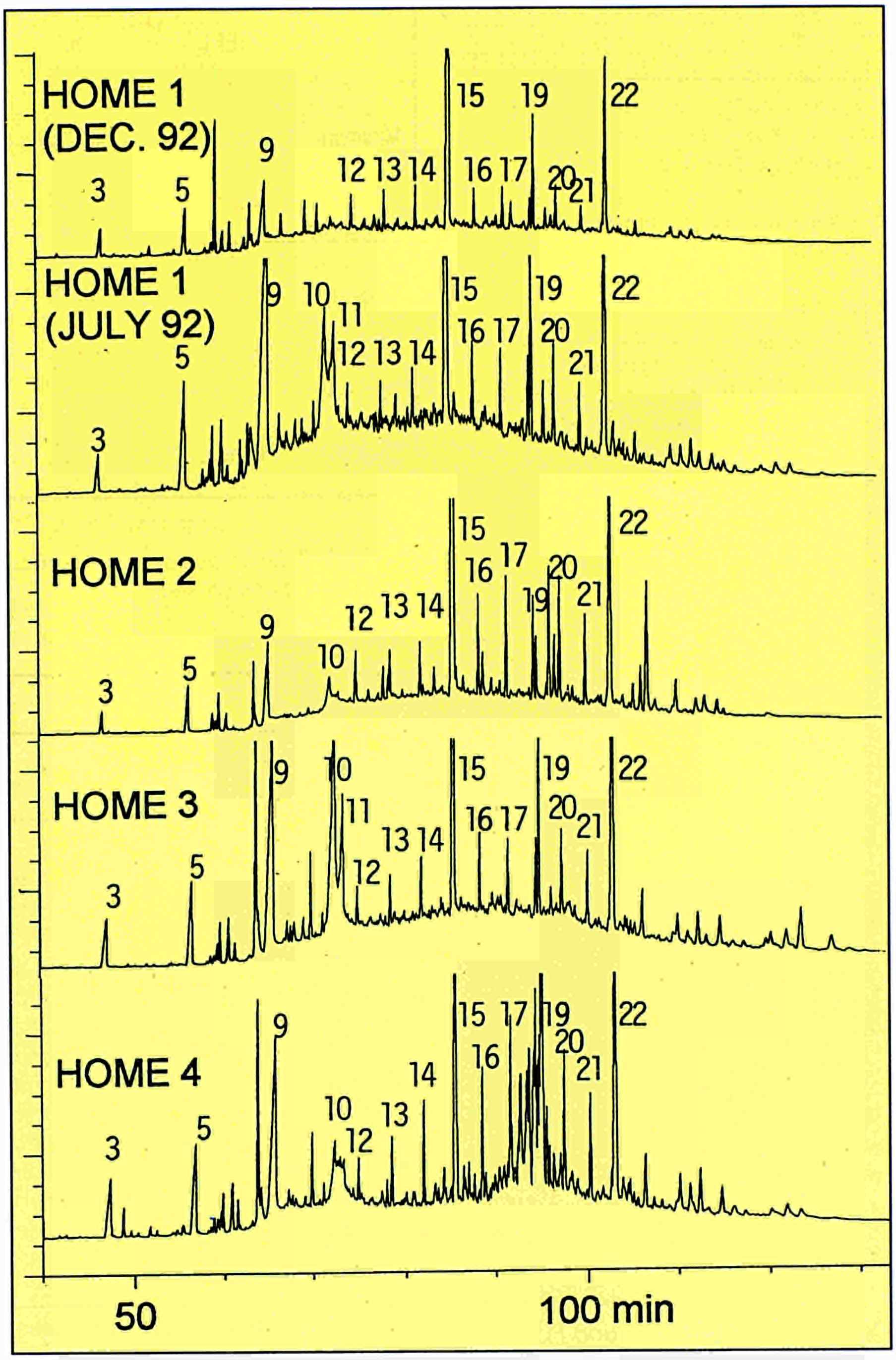


Fig. 1.35 GC - FID chromatograms of five house dust extracts. Numbers of peaks refer to the tentative identification in Table 1.10.

lipophilic compounds or compounds with an important lipophilic moiety are extracted from the samples.
The similarity could be due to extracted compounds which are mostly of outdoor origin or from widespread indoor sources.

Considering the identity of the compounds both hypothesis may partially be true. Fatty acids and long chain n-alkanes are common constituents of outdoor suspended particulate matter (SPM), however, they are also pertinent toindoor sources such as heating, cooking or conservation products. Phthalates and uv-stabilizers as common constituents of plastic materials are more probably of indoor origin.

In the living room of one home 1 m^3 of indoor air was sampled on a polyurethane foam (PUF) plug and immediately afterwards a dust sample was collected. Chromatograms of the extracts of the two samples are shown in *Fig. 1.36* (for the identity of numbered peaks see *Table 1.10*). On top of the figure the approximate elution ranges of VOC, SVOC and POM are indicated.

Interestingly, all compounds identified in the dust extract are also present in the PUF extract, although in the POM range mostly in 4-5 times smaller quantities. Since on the PUF sampler both, vapours and SPM have been collected, it is not yet possible to decide to which extent the compounds eluted in the POM range are in fact associated with SPM. In the SVOC range many more compounds are extracted from the air/PUF sample than from the dust sample. The compounds identified in this range in the dust sample are the more important fatty acids, phthalic acid esters and a uv-stabilizer. All of these compounds contain hydrophilic groups and this may point to the preferred adsorption of hydrophilic SVOC on house dust. Its extraction with a hydrophilic modifier may therfore yield important additional information on its content of organic compounds.

Deposition of organic vapours on indoor surface materials

Adsorption of air pollutants on indoor materials has an impact on the exposure of inhabitants or workers. Adsorption will lower peak concentrations but the subsequent desorption will prolong the presence of indoor air pollutants. Therefore not only characterization of emissions but also of the adsorption capacity of an indoor material is required for indoor exposure estimates and for a rational choice of materials by architects and building companies.

nr.	compound
1	hexanoic acid
2	diethylphthalate
3	dodecanoic (lauric) acid
4	unknown 1
5	tetradecanoic acid
6	butyl-isobutyl-phthalate
7	pentadecanoic acid
8	methanone, (2-hydroxy-4-methoxy-phenil)-, phenil- (uv-stabilizer)
9	hexadecanoic (palmitic) acid
10	unkown 2 (containing long alkenyl portion)
11	octadecanoic (stearic) acid
12	n-docosane (C_{22})
13	n-tricosane (C_{23})
14	n-tetracosane (C_{24})
15	bis-(2-ethylhexyl)-phtalate
16	n-hexacosane (C_{26})
17	n-heptacosane (C_{27})
18	n-octacosane (C_{28})
19	sqalene
20	n-nonacosane (C_{29})
21	n-triacontane (C_{30})
22	cholest-5-en-3-ol, (3.beta)-
23	n-hentriacontane (C_{31})
24	n-dotriacontane (C_{32})

Table.1.10 *Tentative identifications of numbered peaks in Fig. 1.37 and 1.38*

Eight typical indoor pollutants covering a wide volatility range and representing lipophilic and hydrophilic compounds *(Table 1.11)*, and three indoor materials (a carpet with nylon fibre pile and SBR backing, blown vinyl wallcoating, and gypsum board with cartoon finish on both sides) have been selected for a quantitative adsorption study.

The experimental approach consisted in exposing the materials to a constant flow of vapours of the selected compounds in a small test chamber and measuring the concentrations of the compounds as a function of time, until a steady state was attained. The concentration-time data were interpreted by means of

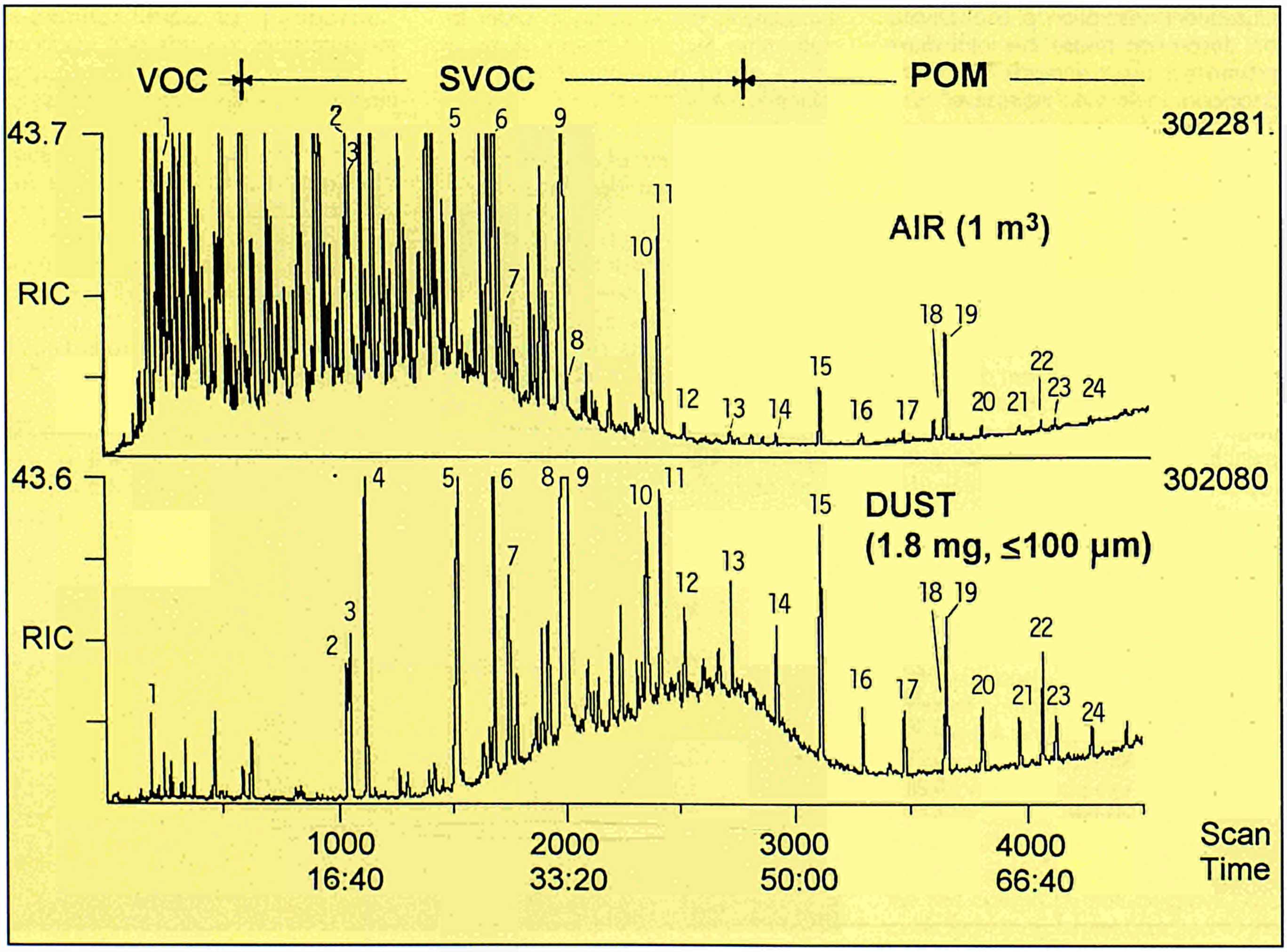


Fig.1.36 *Reconstructed ion chromatograms of organic compounds extracted from an air/ PUF sample (above) and a dust sample (below).*

an existing model based on the assumption of two sinks, one reversible and the other irreversible. *Fig. 1.37* shows as an example experimental concentration data for n-decane in the empty chamber and in the chamber containing a carpet sample. The figure shows also concentration time curves as predicted for an empty chamber without sinks (full line) and obtained by fitting the two-sink model to the experimental data (dashed lines). The difference between the steady state portions of the full line curve and the dashed line curves are interpreted by the model as loss of n-decane in the "irreversible" sink. However an interpretion of this difference in terms of a "slowly reversible" sink appears more appropriate, as was demonstrated by a long term (about 500 h) adsorption experiment with a subsequent desorption phase. During the desorption phase the total mass estimated by the model to have disappeared in the "irriversible" sink was released from the chamber, although very slowly. Therefore a new model will be developed taking in consideration two reversible sinks, a "fast" and a "slow" one.

Adsorption in the reversible sink is best characterized by the ratio k_3/k_4 which is proportional to the distribution coefficient K_e of a compound between the adsorbed and the vapour phase under equilibrium conditions. *Table 1.11* reports the ratios k_3/k_4 for the adsorption of the eight test compounds in the reversible sink of the empty chamber and of the three selected materials.

As can be expected the k_3/k_4 values are smaller for the empty chamber than for the chamber containing one of the materials. The adsorption of most compounds on the studied materials is appreciable and tends to increase with the boiling point. However, obviously other physico-chemical properties of the adsorbed compounds such as their hydro- or lipophilicity, and the nature of the adsorbing materials play also an important role (see e.g. the two alcohols on gypsum board and 1.4-dichlorobenzene on carpet).

In order to confirm the above results in an indipendent way, static experiments are ongoing in order to determine K_e. First results show a fairly good agreement with the dynamic measurements.

Installation and test of a walk-in type environmental chamber "Indoortron"

A 30 m³ walk-in type environmental chamber has been installed and its performance has been tested. The chamber features a double wall design. A stainless steel chamber with electropolished inner walls is surrounded by a second chamber which serves as a thermostat for the inner chamber. Only stainless steel, glass and teflon have been used for the construction of the inner chamber in order to reduce sorption of indoor pollutants on and emissions from the inner walls of the chamber to a minimum.

The chamber temperature can be controlled from 15 to 40°C (±0.5°C) and the relative humidity from 20 to 90 % (± 5%). The chamber can be supplied with clean air at flow rates ranging from 3 to 60 Nm³ h⁻¹ (0.1 to 2 air changes per hour). The inner chamber can be purged with dried and HEPF filtered ambient air with flow rates up to 180 Nm³ h⁻¹ (6 ach).

Fig. 1.38 shows a view through the two doors into the inner chamber where a first experiment is being installed. The chamber can be used for various types of experiments:

- upscaling of small chamber measurements towards real situations for the test of models predicting indoor air pollutant concentrations;

- determination of human exposure during activities giving rise to pollutant emissions;

- emission testing of equipment or large pieces of materials;

- test of equipment for the reduction of indoor air pollution;

- validation of measurement methods by sampling atmospheres with known concentrations of pollutants (low

compounds (ordered by boiling point	empty chamber k_3/k_4	carpet k_3/k_4	blown vinyl k_3/k_4	gypsum board k_3/k_4
tetrachloroethene	0.23	1.15	0.29	4.96
α-pinene	0.29	1.10	0.88	1.22
1,2,4-trimethylbenzene	0.38	6.27	2.83	2.47
2-butoxyethanol	0.23	5.81	3.21	9.18
n-decane	0.28	4.01	1.12	3.06
1,4-dichlorobenzene	0.75	12.50	6.70	5.27
2-ethylhexanol	0.85	8.03	7.14	12.99
n-dodecane	0.91	16.20	8.20	12.54

Table. 1.11 *Ratio k_3/k_4 and k_5 for the compounds and materials tested.*

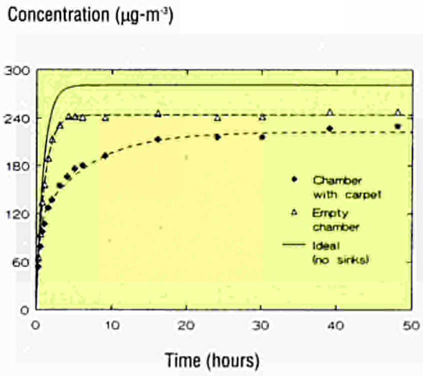


Fig. 1.37 Concentration versus time curves for n-decane under dynamic conditions.

surface to volume ratio, establishment of typical indoor concentrations by direct injection of compounds);

- assessment of acute reversible effects of air pollution by controlled human exposure experiments.

Management of the European Collaborative Action "Indoor Air Quality and its Impact on Man"

The former Concerted Action "Indoor Air Quality and its Impact on Man" (COST project 613) has been included in the Indoor Pollution activity of the JRC Environment Programme as European Collaborative Action (ECA). The ECA is directed by a Steering Committee the members of which have been appointed by competent national authorities.
The Steering Committee has issued a position document which states that the ECA will examine Indoor Air Quality (IAQ) defined as all features of indoor air having an impact on man. The action will incorporate all aspects of the indoor environment including temperature, humidity and other environmental factors which may interact with indoor air quality. It will contribute to prenormative research needed by EC services in their aims of preventing pollution and promoting health, comfort and quality of life.

Evaluation of sources of indoor air pollution (IAP) is a particular focus of the action. A Working Group has been established with the initial task to establish a procedure for the classification of material emissions based on their chemical composition and toxicological relevance.

The ECA published a "Guideline for Ventilation Requirements in Buildings" which introduces new rationales for the assessment of ventilation requirements and has encountered strong interest all over the world. A final draft of a report on "Biological Particles in Indoor Environments" has been prepared.

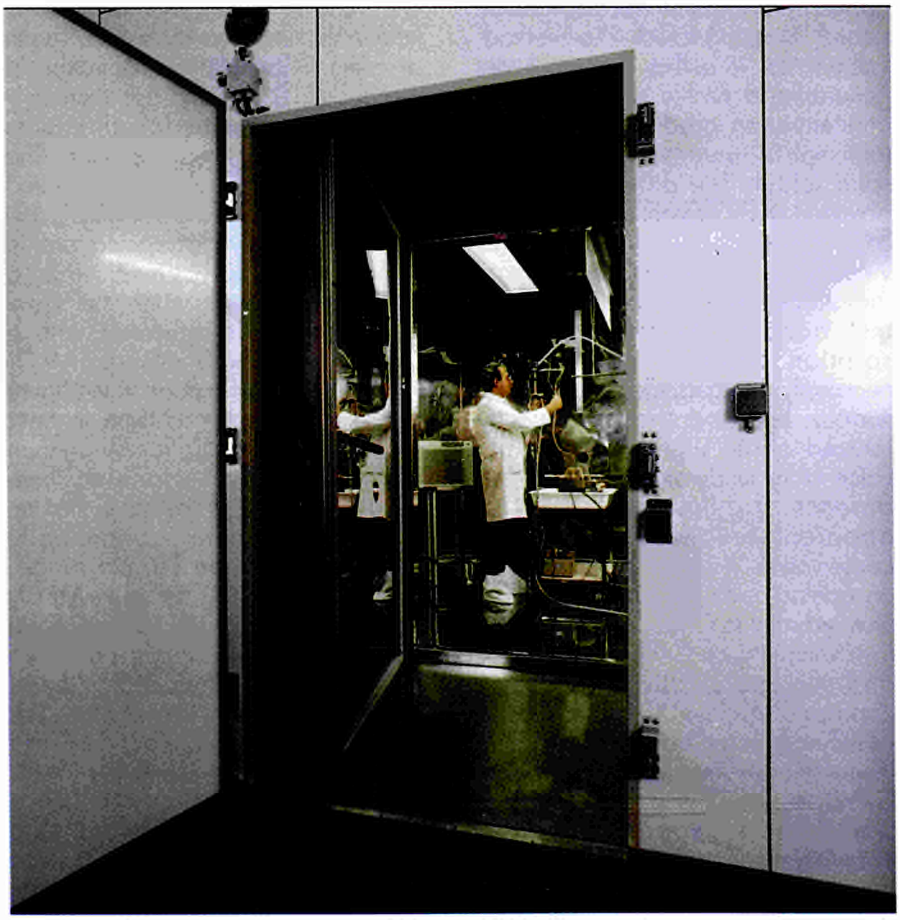


Fig. 1.38 View into the interior of a double-walled walk-in type environmental chamber ("Indoortron") where the testing of an air cleaning device is under preparation.

In the framework of the ECA the JRC organized together with the Danish National Institute of Occupational Health a EUROCOUSES seminar on "Chemical, Microbiological, Health and Comfort Aspects of Indoor Air Quality - State of the Art in SBS". The lectures of this very successful seminar have been published as a book.

Chemical Waste

Soil-Pollutant Interaction Studies

Research activities on pollutant-soil interactions have been oriented to evaluate in different soil types the mobility of organic pollutants having a wide range of water solubility, such as pesticides (atrazine and vinclozolin), tanning agents (chloroanilines) and polychlorinated biphenyls (several PCB congeners). Also trace metals (Cr, As, Se, ...) as mobilized in fly ash leachates have been studied. Laboratory experiments have been performed using batch and column methods.
In order to reach as much as possible environmental applicability and relevance, experiments have been designed in a stepwise scale starting from laboratory columns (dm^3), proceeding with lysimeters (m^3) and finally passing to field sites experiments.
Open-air lysimeters have been constructed and a field site has been identified in the JRC Ispra area.
The lysimeters are equipped with different sampling devices. Samples of aqueous leachate can be obtained by two types of collectors:
- Tension free lysimeter. This consists of a soil column of 500 mm diameter and 950 mm length. Aqueous leachate samples percolated through the soil column by natural gravity are collected by an funnel attached to the bottom of the lysimeter.
- Tension soil-water samplers. These samplers have the form of a candle

(20 mm diameter, 100 mm length) and are made of porous material (ceramic or teflon, pore size 3, 5, or 10 µm). A number of these samplers are placed at different depths. Leachate is sucked out of the soil using a vacuum pump (up to - 0.7 bar). Samples of water leachates can be obtained continuously and from different depths, from the lysimeter columns as well from the field test site.

The objectives pursued for this study are the following:

- to determine wether laboratory data are applicable to field conditions;
- to test the applicability of the different sampling devices for different types of pollutants;
- to better understand the leaching process of pollutants from a field lysimeter.

With the aim of developing direct analytical methods for determining the complexation constant, the study of the competition between Rare Earth (RE) humic acid complexes and Cr(III) has progressed by using fluorescence spectroscopy in the continuous, syncronous and time-resolved mode. As reported previously, the latter mode allowed us to monitor the behaviour of the complexed RE ions, whereas the change of the continuous (fast) fluorescence with increasing metal concentration is related to disappearance of the free humic acid ligand in the solution. The contribution from the uncomplexed metal ion, if fluorescent, can be eliminated with an appropriate offset of the emission wavelength from the exitation wavelength (syncronous fluorescence).

The decrease of the fluorescence signal of the luminescent Tb and Eu complexes with increasing concentration of Cr(III) has been studied as a function of time. Contrary to the fast complexation reactions of Tb and Eu, the results show a slow kinetic of Cr(III) complexation, requiring at least 24 hours to reach equilibrium. This might be due to the slow substitution of water molecules in the first hydration sphere of trivalent Cr. Modelling of the data is underway.

The adsorption of Co and Hg ions onto γAl_2O_3 was studied in the presence of various concentrations of natural humic acid and at different ionic strengths. The surface complexation constant and the stoichiometry of the $Co^{2+}+Al_2O_3$ complex were derived. The adsorption of the two metals was found to increase with increasing humic acid concentration under acidic and nearly neutral conditions, whereas an opposite effect was observed at higer pH. Abrupt changes in the adsorptive behaviour of Hg were induced even by very small humic acid concentrations.

A combination of diffusion and batch-sorption measurements was used to study Cr(VI) interactions with a mixture of clay minerals (Kaolinite and illite), originating from a borehole crossing sediments of fluvio-glacial origin, in which sand and clay layers alternate.

A column experiment, successfully applied previously in tracer migration studies, was adopted. The method, known as in-diffusion, involves generating a profile of radionuclide concentration gradient in a length (column) of water-saturated porous solid (clay). The diffusion profile, obtained at a constant temperature of 5°C after about 10 days, indicates virtually no movement of chromate radiotracer into the column. Taking into account the relatively low sorption capacity of clays for negatively charged species, and that surface hydroxyl groups are fully ionized at the slightly alkaline pH value of groundwater (pH 8.2), the absence of diffusion suggests an apparent breakdown of redox conservation. It seems probable that, on contact with the clay, the Cr(VI) was reduced to Cr(III). Because of the low solubility of Cr(III) compounds, and the high cation exchange capacity of clays, Cr(III) would be expected to have low mobility.

Hypotesis of chemical reduction of Cr(VI) to Cr(III) was subsequently tested in a separate sorption experiment. Distribution ratios, Rd, ranging over $10^4 ml\cdot g^{-1}$ were measured. Following a procedure designed to distinguish Cr(VI) removal from solution due to non-reversible adsorption as opposed to reduction, the clay suspensions were then saturated with phosphate at various pH values. Anionic Cr(VI) is displaced by phosphate, however no such desorption of Cr was observed, suggesting reduction was the case. The mechanism responsible for reduction is not readily apparent, although it could possibly have been catalyzed or mediated through the presence of structural Fe(II) in the clay.

An experimental programme was initiated aiming also at investigating possible mobilizing and scavenging processes for Co in aquatic systems. Of particular interest is the role played by manganese oxides and humic acids.

Columns packed with quartz sand were first pre-equilibrated with a simulated bicarbonatated groundwater at pH 8.3. In one set of experiments, 10 ppm of humic acid were added to the groundwater. The inflow solution was then traced with di-valent ^{58}Co (total concentration of Co about $10^{-10}M$) and approximately 90 pore volumes of this was displaced through each column. The sorption profile of cobalt accumulated on the sand is reported in *Fig. 1.39*. The continuously decreasing profile found in this case was replaced by a well defined peak when the same experiment was repeated with a column containing a layer of δ-MnO_2 enriched sand. The peak in the figure may then be explained by a stronger affinity of di-valent Co for MnO_2 than for the quartz sand. However, there is evidence in the literature that tri-valent Co, thermodynamically unstable in a wide Eh/pH range, can be formed at the MnO_2 interface. Taking into account the generally lower solubility and the stronger interactions with mineral oxides of tri-valent metal ions, the MnO_2 layer may act as an irreversible sink for Co. Experiments are continuing to clarify if such a surface mediated redox transformation can occur under the kinetic constraints imposed by the water flow.

Similar flow-through experiments were conducted in the absence of humic acids. No differences in the shape of the Co sorption profiles were observed with respect to those reported in figure. This indicates that the presence of natural organic substances does not alter the retention properties of the MnO_2 layer. However, the breakthrough profile of Co, i.e. the inlet to outlet concentration ratios, were markedly different in the two cases. The rate of movement of Co through the sand column was found to increase when humic acids were added to the flowing groundwater. This suggests the formation of Co-humic acid species only slightly retarded by interactions with the mineral surface. Also in the study reported above using γAl_2O_3 as solid sorbent, the batch-adsorption of Co(II) has been found to decrease with increasing humic acid concentration in the neutral to alkaline pH region. This appears to be a common feature of humic substances observed for many other metal ions and due to the competition between adsorbed and dissolved humic compounds.

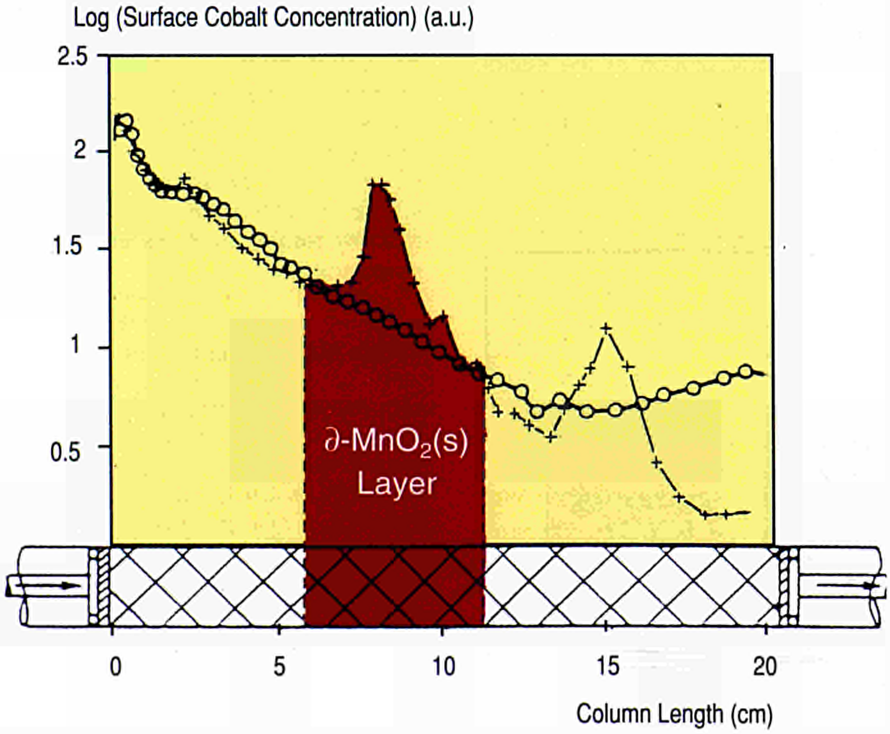


Fig. 1.39 Sorption profile of ^{58}Co in two different columns of quartz sand. The effect of a MnO_2 layer is illustrated (+). Total inlet Co concentration= $1 \cdot 10^{-10}$M. ground water residence time = 1day.

Analytical Development

A systematic study on the application of supercritical fluid extraction (SFE) in trace organic analysis in collaboration with Fisons Ltd. has been carried out. One of the most critical steps in SFE is the trapping of the trace analytes while decompressing the supercritical fluid after ended extraction. Various techniques for trapping have been tested. Collection efficiencies for polychlorinated biphenyls (PCBs) in the range of 90-100% could be obtained by decompressing the supercritical fluid directly into 2,2,4-trimethylpentane *(Fig. 1.40)* or onto a solid impinger e.g. silica, Florisil, and C-18 coated silica. Chlorobenzenes, which are more volatile than PCBs, were purged out of the collection liquid which resulted in non-quantitative recoveries. Solid phase sorption gave collection efficiencies of chlorobenzenes in the range of 90-100%. Based on these results, a new instrument was constructed with on-line coupling of SFE/solid phase sorption/high pressure liquid chromatography *(Fig. 1.41)*. In the testing phase satisfactory results were obtained and a new prototype for a commercial instrument is under construction. This SFE instrument will have the ability of four simultaneous extractions and have been designed with the prospective of on-line coupling to a gas chromatograph and eventually a mass spectrometer. The possibilities of patenting this instrument is under investigation.

A novell extraction technique has been studied for the analysis of semivolatile compounds in drinking water. The method is based on a membrane extraction protocol using inert PTFE membranes with C8 or C18 bonded silica particles emeshed in the fibrillated matrix. The membranes are manufactured in 47mm diameter disks and are easily fitted to existing filtration apparatuses. Major advantage compared to classical solid phase extraction is the much higher flow rate that can be effectivly used during sample extraction. This results in a more then doubled sample throughput. This membranes were successfully applied to the extraction of PCB's, chlorinated pesticides and PAH's at ppb levels from spiked drinking water. Results show good recoveries for PCB's and chlorinated pesticides while poor results were obtained for PAH's.

A completly automated GC-MS system has bee set up for the analysis of Volatile Organic Compounds in drinking water. The system is based on an Ion Trap Mass Spectrometry system coupled to a Purge and Trap and a Gas Chromatograph *(Fig. 1.42)*. The system has been further improved by the addition of a moisture controlling module that efficiently eliminates water background interferences. On-column cryofocu-sing has been achieved by installation of a liquid nitrogen cooling system to the GC oven. The system has been extensivly tested on standard solutions and real samples of drinking water supplies. Detection limits in the ppt range could be

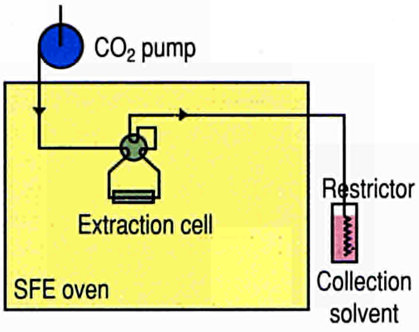


Fig.1.40 *Supercritical Fluid extractor with trapping of analytes directly into a collection solvent.*

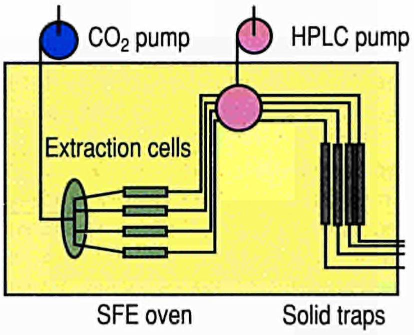


Fig.1.41 *Commercially available prototipe of supercritical fluid extractor developed at the Environmental Institute in collaboration with Fisons.*

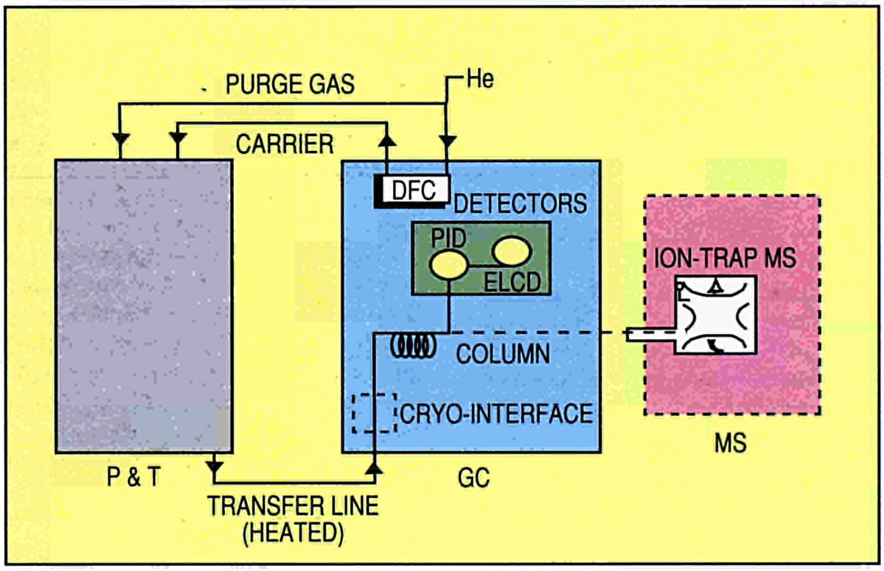


Fig.1.42 *Purge and Trap GC / MS.*

achieved with good linearity *(Fig.1.43)*. The system proved to be extremly prone to contamination by unexpected high concentration (ppm) samples.. Consequently a fast screening procedure was established using an automated Headspace-Gas Chromatography system equipped with ECD-FID detection in series . This system is used for screening incoming water samples before submitting them to Purge and Trap analysis. Future developments on this VOC analysis system will consist in extension of its application to groundwater, surface water, waste water and sludges.

Polychlorinated biphenyls (PCBs) are one of todays's major environmental problems. A total of 209 PCB congeners exist. Due to the great differences in toxicity and environmental occurrence among congeners, the analysis of PCBs as resolved congeners is essential. A major study of methods for the analysis of PCB congeners has been conducted since 1987 and concluded in 1992. This research has lead to the understanding of the gas chromato-graphic retention mechanism of PCB congeners (*Fig.1.44*) and to a complete characterization of the elution profile of technical PCB mixtures on 10 commercially available stationary GC phases. Methods developed under this study have allowed for the isomer-specific analysis of ppt-ppb levels of PCBs in a range of samples including waste-oil, sewage sludge, soil, lake sediments, earthworms, fish and human milk.

The octanol-water partition coefficient (Kow) is known to be an important physico-chemical parameter for the assessment of the environmental fate of trace contaminants in chemical waste. Direct measurements of Kow by the conventional shake-flask method can be laborious due to colloidal formations and adsorption onto glass surfaces, especially for highly hydrophobic compounds such as PCBs. A new technique has been tested in order to circumvent such experimental difficulties. Thus, an octanol solution of PCB was sorbed to a solid support in a "generator column", and the quantity of the PCB in the mobile phase of water, which is passed through, was determined. The Kow of 39 chlorobiphenyl congeners were determined simultaneously in the Askarel PCB mixture, using a modified generator column method and isomer specific analysis by GC-ECD. The obtained data are presently being analysed with advanced statistical analyses and quantitative structure activity relations (QSARs) were developed for the precise prediction of Kow and Kd of all 209 PCB congeners. These data will be used in the design of dynamic mobility studies of PCBs in contaminated soils.

Waste Management

The process of cement matrix solidification of a hazardous inorganic waste mixture containing As_2O_3, $CrCl_3 6H_2$, K_2CrO_4, $CdCl_2$, HgO and $Pb(NO_3)_2$ compounds has been evaluated by performing leach experiments both in static *(Fig.1.45)* and dynamic *(Fig.1.46)* water conditions. Improved physical characteristics of the matrix (i.e. compressive strength, and total porosity) were observed when 12% of waste was blended in cement. In the static leach test the released concentrations of As (III), Cd(II) and Cr(VI) metals were substantially reduced compared with previous

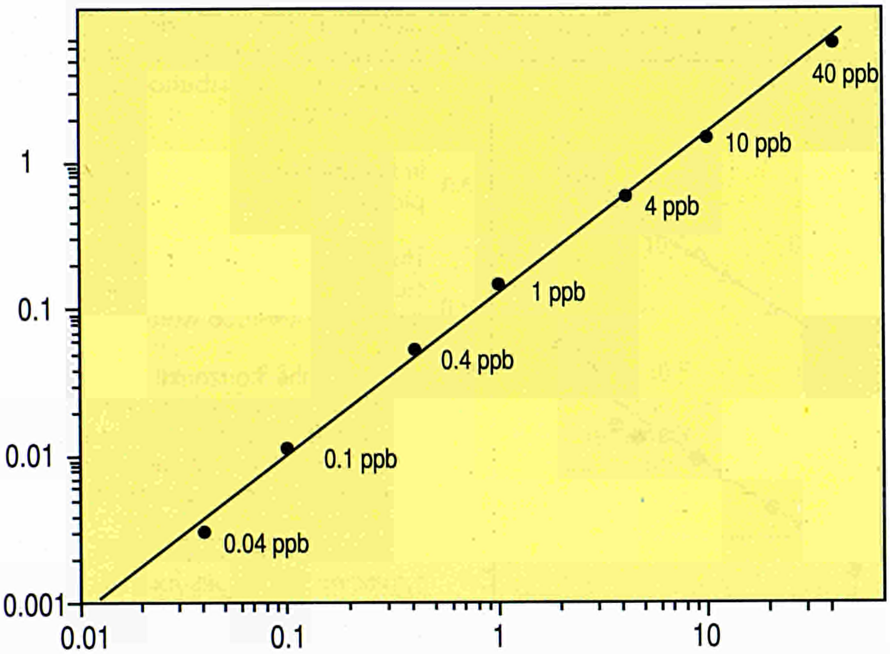


Fig.1.43 Calibration curve from Purge and Trap GC / MS system. Calibration plot for 1,2 Dichlorobenzene coeluted with 5 ppb 1,2 Dichlorobenzene-d4.

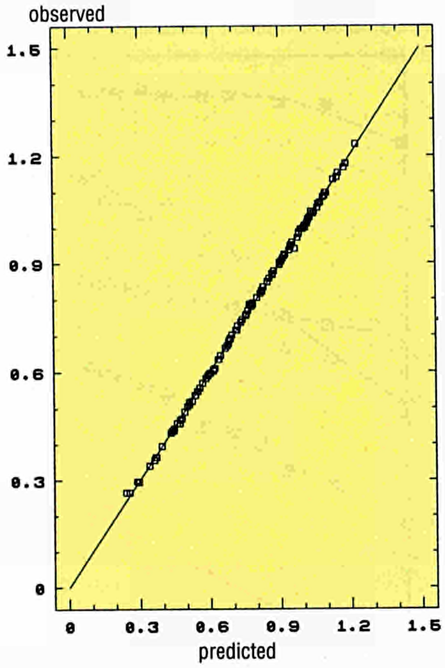


Fig.1.44 Prediction of gas chromatographic retention of 140 PCB congeners from their molecular structure.

investigations in which a single compound of each As(III), Cd(II), Cr(III) and Cr(VI) was immobilized separately in cement. The leachate concentrations of As(III), Cd(II) and Cr(III) were below their permissible limits, reported in the literature for drinking water quality *(Table 1.12)*.

The solidification/stabilization of a synthetic hazardous wase mixture in cement put into evidence some features:

- the physical properties (porosity and compressive strength) of hardened cement are beneficially modified, also considering the reduced water amount used in the cement paste preparation (W/C = 0.4);
- for some elements (As, Cd, Cr), it is not always possible to attribute the leaching process to a diffusion mechanism; Pb and Hg only in static leach condition exhibit a linear dependence of C/Co vs $t^{0.5}$ *(Table 1.13)*;
- As is retained as an insoluble compound and it is not influenced by a carbonation effect, as remarked by previous authors;
- the sequence Cd < Pb < Hg was observed in the leach tests both in static and dynamic water conditions.
- the valence of As^{3+} was not affected by the redox potential of cement matrix as no As^{5+} has been revealed in the leachate within the detection limit of analysis.
- future work is needed to obtain more information concerning the release mechanism, taking into account the boundary conditions during the leach tests and the influence of the matrix composition.

Investigation of water immobilization in cement matrix has been initiated. From the thermogravimetric and differential thermal analyses (TG and DTA) it apperas that the accomodation of water can be arranged by cement modification. Anhydrous aluminium sulfate added to the clinker cement powder will be transformed into ettringite (verified by XRD analysis) with the cement constituents in which 31 water molecules are bound in the compound.

Water Quality

Mito Project

The JRC-Ispra has promoted in close collaboration with institutions of six Member States (the Netherlands, Portugal, Spain, France, Italy and Greece), a Joint European Project on algal blooms: the MITO Project.

The project focuses on :

- *Analytical Cytology of Phytoplankton*: to develop fast and easy-to-use systems for the detection, enumeration and characterization of phytoplanktonic populations at the cellular level to detect changes in populations structure associated with environmental factors.
- *Aquatic Biotoxins*: to develop alternative, sensitive and adequate methods to 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 eco-system effects.

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

The report on the first experimental cruise in Greece was completed. The aims of the exercise were :

- to study the horizontal and vertical distribution of phytoplanktonic communities and their pigments in a dense network of stations, comparing classical and innovative methods of analysis;
- to evaluate the performance of flow cytometric techniques for the analysis of phytoplankton, i.e. biomass and fluorescence distribution of algae;
- to detect changes in population structure associated with environmental factors.

Water samples were analyzed for physical (i.e. temperature, salinity, density and transparency), chemical, (i.e. dissolved oxygen and dissolved inorganic nutrients), and biological characteristics (i.e. quantitative and qualitative composition of the phytoplankton population and chlorophyll-a).

Flow cytometric analysis (FCM) of the phytoplankton was carried out immediately on untreated samples, and later, on preserved samples in the laboratory. At the Joint Research Center a PAS III flow cytometer was used, while analysis at the Delft Technical University was carried out with an Optical Plankton Analyser (OPA).

The evaluation of results suggested that:

- with regards to cell autofluorescence resolution, cells with a diameter of about 1-2 μm (essentially nano-plankton microphytes) and greater (ca. 100 μm) can be measured by FCM;
- with regards to cell concentration, the lower limit of FCM is approximately 10^3 cells·l^{-1}, i.e. very low concentrations of autofluorescent cells. Therefore FCM can be used to measure rapidly and precisely the

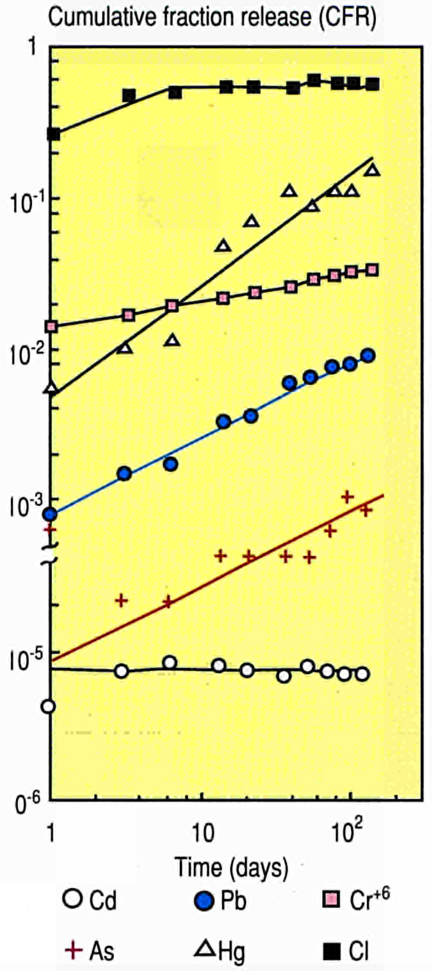


Fig.1.45 *Static leach test. Cumulative fraction release CFR (C/C_o) vs time from cement specomens containing simulated waste; W/C =0.4; SE/C = 0.14*

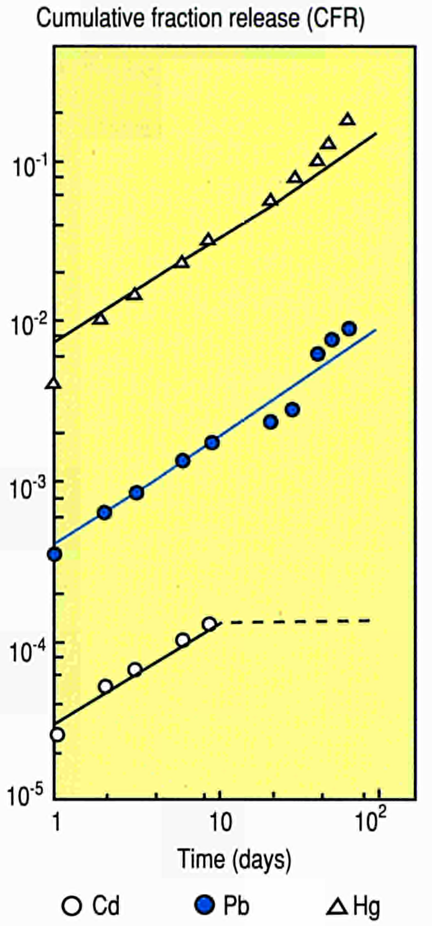


Fig.1.46 *Dynamic leach test. Cumulative fraction release CFR (C/C_o) vs time from cement specomens containing simulated waste; W/C =0.4; SE/C = 0.14*

Element	Static test (*)	Dynamic test	Permissible limit (**)
As(III)	$3.3 \cdot 10^{-7}$	not detected	$6.7 \cdot 10^{-7}$
Cd(II)	$3.1 \cdot 10^{-8}$	$4.4 \cdot 10^{-10}$	$8.9 \cdot 10^{-8}$
Cr(VI)	$1.5 \cdot 10^{-4}$	not detected	$9.6 \cdot 10^{-7}$
Pb(II)	$2.0 \cdot 10^{-5}$	$1.6 \cdot 10^{-8}$	$2.4 \cdot 10^{-7}$
Hg(II)	$3.6 \cdot 10^{-4}$	$3.6 \cdot 10^{-7}$	$2.5 \cdot 10^{-8}$

(*) = The values are calculated on the basis of total flowing volume in 63 days (~454 litres)
(**) = EPA interim Primary Drinking Water Standard

Table 1.12 *Comparison of leached contaminant concentration (Moles ·l^{-1} determined under different leaching conditions. W/C =0.4.*

Element	Static		Dynamic	
	D_e	n	D_e	n
As(III)	$1.3 \cdot 10^{-16}$	0.5	----	----
Cd(II)	----	----	$2.0 \cdot 10^{-15}$	0.73
Cr(VI)	$4.5 \cdot 10^{-11}$	0.17	----	----
Hg(II)	$2.3 \cdot 10^{-10}$	0.65	$3.5 \cdot 10^{-10}$	0.85
Pb(II)	$1.0 \cdot 10^{-12}$	0.5	$6.1 \cdot 10^{-13}$	0.72
Cl(I)	$8.9 \cdot 10^{-8}$	0.45	----	----

Table 1.13 Static and dynamic leaching. Calculated values of De and slope n from Figs. 1.45 and 1.46.

total number of living cells (and their physiological conditions) and to evaluate the phytoplankton biomass present in water samples. This is of paramount importance in monitoring programmes during algal blooms.
The analysis of the state from a second experimental cruise in the Adriatic sea, is in progress.

As a continuation of the modelling activity related to the Adriatic, numerical modelling of the biological activity taking account of the real physical conditions, has been started. The early work in collaboration with IRSA-STI was based on hydrodynamics computer codes developed and released by outside institutes. Since these codes had, especially for applications for the Adriatic, some shortcomings, the development of a new code was started ("ISPRAMIX"). This new hydrodynamics tool was completed in 1992. The essential part for applications in the Adriatic sea is a sophisticated turbulence model, including the influence of density stratification, which allows the computation of realistic turbulent transport properties for all specific seasonal conditions. The hydrodynamic model will be described in a separate paper. The intended application area of the project is the northern Adriatic. Therefore, first a limited topographic model was implemented, which is bounded by a line about 20 km South of the section Rimini-Pula and which has a discretisation grid of 3 km x 3 km. This model has been used for some preliminary verification studies as a "stand alone" model, i.e. using a specific radiation boundary condition at the open sea boundary. A satisfactory agreement of the results with those of earlier studies has been found. Since it must be demonstrated that the use of this specific boundary condition does not adulterate the circulation pattern, a topographic model of the whole Adriatic up to the straight of Otranto has been implemented, which has a more coarse grid of 6 km x 12 km. The testing of this topographic model, and the verification of the reduced topographic model have been started and will be accomplished in early 1993. The next step will then be the coupling with ISPRAMIX of a biological model, which was developed in Ispra in collaboration with the IFM of the University of Hamburg.

The analytical procedures for the evaluation of the noxious properties of the algal toxins have been studied in order to increase their sensitivity and accuracy. In particular, the first goal of the activity was to investigate the possibility to use murine parenchimal cells derived by perfusion of the liver of CD-1 male mice in order to measure the toxic properties of algal extracts with accuracy and with an enhanced sensitivity with respect to the well known "mouse test".For the calibration of the method, the experiments carried out concerned the measurement of the toxicity of Okadaic Acid (OA) as the quantity necessary to kill 50% of the primary murine hepatocytes after 24 h incubation. First results, seems to show that this approach is about 10.000 and 15 times more sensitive than the mouse test and the Aune test respectively. The second attempt concerned the use of the mouse embryos as an analytical tool for evidencing the toxicological properties of metabolic elaborates of algae. Using the OA as calibrating toxic compound. It has been possible to put into evidence the nocivity of this compound at concentrations about 15 times below those necessary in the "mouse test".

Lake Orta

Lake Orta served in the past years as suitable "test laboratory" for the development of predictive metal dispersion models, the results of which might be linked to the studies on point and non-point source evaluation of some of the trace metals, considered by list I and II (Directive 76/464 EEC).
After Cu and Ni, which have been evaluated in the past, Cr introduced into the lake from the same major source as Ni (electroplating industries), has been evaluated in terms of input/output balance.

Contrary to Cu and Ni, Cr shows a strong tendency to particularization, and the dissolved concentrations found in lake, feeding rivers and lake outlet Niguglia are low, but correspondingly high are the concentrations found in the particulate matter *(Table 1.14)*.
Some of the seven monitored tributaries were found to carry high and irregular Cr discharges, which led to an external input of $2.85\ t \cdot y^{-1}$, to which minor sources such as atmospheric deposition $(0.09\ ty^{-1})$

and surface run-off (0.01 $t \cdot y^{-1}$) must be added.

Contrary to Ni and Cu, internal Cr loading seems negligible, as indicated by dialysis cell experiments carried out in the northern part of the lake, although in some pore water samples taken at maximum depth (-130 m) rather high Cr concentrations have been detected, indicating some remobilization potential.

At the lake outlet (river Niguglia), an export rate of 0.51 $t \cdot y^{-1}$ was recorded. The difference to the external loading (2.95 $t \cdot y^{-1}$) of 2.44 $t \cdot y^{-1}$ shall be transported to the sediments, since the mean residence time of Cr in this lake has been quantified to be 0.93y (Cu = 5.1y; Ni = 8.8y).

Background river Toce, draining a similar geological environment, shows much lower dissolved and particulate Cr concentrations (factor 3 and 10, respectively).

It can be concluded, that external Cr loading should be reduced, then the Cr concentration in the lake should decrease in a rather short time.

AQUACON-MedBas-Project

The "Analytical Quality Control and Measurement Error Assessment Studies" Project developed upon request of the EC - Member Countries of the Mediterranean area (Italy, Spain, Portugal, France and Greece) aims first of all at the identification, quantification and elimination / reduction of systematic and random measurement errors, associated with the most critical problem areas of environmental analysis, including sampling errors.

Basically, the AQUACON-MedBas Project includes both intercalibration exercises as well as complex collaborative field and laboratory studies, which include in some cases the testing of sampling procedures and the verification of sampling representativity.

The JRC Ispra takes care of the organizational aspects of the single subprojects, which are offered first of all to the public laboratories, especially in areas where systematic analytical quality control systems are not yet available on a national scale, but might develop as a follow-up of the AQUACON-MedBas activities, also to commercial and industrial laboratories and universities. The participation is free of charge.

The evaluation of the collaborative study on the evaluation of sampling errors for metals in sea water has been completed.

The following major conclusions could be drawn:

- different samplers yielded different results (analysis by reference laboratory);
- the volume of the samplers influence the results, better results being obtained for higher capacity samplers;
- data tend to converge to GO-FLO sampler values after repeated washings, although at least one sampler type is to be discarded.

	n	Cr (dissolved) ($mg \cdot m^{-3}$)			n	Cr in particulate matter ($mg \cdot Kg^{-1}$)			KD ($m^3 \cdot Kg^{-1}$)		
		Mean	Max	Min		Mean	Max	Min	Mean	Max	Min
Whole lake	390	2.6	48	0.1	388	962	5,714	150	706	17,637	16
Lake outlet	32	2.4	12	0.5	32	585	1,499	57	428	1,869	15
Feeding rivers	237	17	510	0.1	28	2,167	17,068	86	470	1,914	1.2
Run-off	27	1.8	4.9	0.5	----	----	----	----	----	----	----
Atmos. deposition	59	2.5	44	0.3	----	----	----	----	----	----	----
Background (Toce river)	35	0.7	3.7	0.1	167		1,239	56	1,182	4,280	115

Table 1.14 Chromium input and output to lake Orta.

The results obtained for the explorative interlaboratory study on Hg determination in fish *(Fig. 1.47)* shows widely scattering results between 1 and 10 $mg.kg^{-1}$, while the target value has been set to 3.55 + 0.05 $mg \cdot kg^{-1}$.

The conclusions from this exercise are that since most countries have maximum allowable mercury concentrations in edible fish, false positives or negatives would have been obtained by many laboratories; in addition test material of the next exercise should be accompanied by some caveat as to the methodologies for dissolving the sample and possible losses and/or contaminations; lastly, in order to distinguish between errors arising from dissolution techniques and the final determination step, a sealed and stabilized mercury solution of unknown concentration to the laboratories will accompany the solid test sample.

The test material for the next run has been prepared (Trout muscle tissue) and is at present under study for its mercury homogeneity.

Five test materials for the subproject "Sediment Analysis (Metals, organochlorine + compounds,PAH's)" have been prepared and the target values for the organochlorine compound concentrations (PCB's N° 28, 52, 101, 118, 138, 153, 170 and 180; o,p-DDT, p,p-DDT, o,p-DDD, o,p-DDE, p,p-DDE, aldrine, dieldrine, and endrine) obtained.

Also the PAH's concentrations (pyrene, benzo-b-naphtho 2, 1-d-thiophen, benz-a-anthracene, benzofluoranthene, benzo-e-pyrene, benzo-a-pyrene), of the test sediments have been obtained.

While the subproject "Freshwater Analysis", to be started with a collaborative sampling error evaluation exercise has been postponed for logistic reasons, the evaluation of results of the first collaborative laboratory study on "Acid Rain Analysis" has been completed. The conclusions are that systematic errors prevail on random errors; calibration techniques, standards solutions and reagents used should be accurately reviewed and certified reference materials analyzed prior to the proficiency testing; further analysis should be tested for ionic balance and measured and calculated conductivity compared; the measu-rement results are scattered to an extent as to require further exercises.

Electrolytic removal of nitrates from waste waters

During 1991 a new, electrolytic process for the removal of nitrates from waste and drinking water was developed. The process is based on the following cathodic reaction:

$$2NO_3+18\ H^++16e\text{->}2NH_3+6H_2O$$

The reaction products are ammonia and, to a small extent, hydroxylamine. The products formed in the cathodic compartment are subsequently transported to the anodic compartment, where they are oxidised anodically in presence of a halogen.

The involved reaction isthe following:

$$2NH_3+\ 6OH\text{-}\ \text{->}N_2 + 6H_2O + 6e$$

The balance of the current between the cathodic and anodic compartment goes to the formation of oxygen:

$$10\ OH\text{->}2.5O_2 + 5H_2O + 10e$$

The sum of the reactions yields the decomposition of nitric acid into nitrogen, oxygen and water:

$$2\ H^+ + 2\ NO_3\text{-}\ \text{->}N_2 +2.5O_2 + H_2O$$

Earlier experiments, carried out at a low current density (0.22 kA.m^{-2}), indicated that the cathodic nitrate decomposition proceeded as a first order reaction. The experimentally found rate constant was approximately 3.5 10^{6} m.s^{-1}.

During 1992 the work was continued with a modification of the original process set-up. The liquid is now first passed through the cathode and then through the anodic compar-tment.The applied cell has an electrode surface area of 500 cm^2. The present bench-scale set-up is shown in *Fig. 1.48*.

With this test rig a number of experiments have been carried out, where the current density, the reagent concentrations and the pumping rate were varied. The most significant results were that the values for the cathodic reaction rate (= mass transfer rate) were confirmed. A typical experiment (Run No. 17, 11.6.92) was carried out with a liquid flow rate of 1.5 l·h^{-1}, a concentration of 45 mmol·l^{-1} NO_3 (2790 mg·l^{-1}) and a current density of 1 kA·m^{-2} (50 A).

The liquid leaving the cathode contained 20 mmol·l^{-1} NH_3 and 25 mmol·l^{-1} NO_3. During the passage through the anodic compartment, the ammonia concentration was reduced to 0.1 mmol·l^{-1}, whereas the nitrate concentration was unchanged. The corresponding value for the cathodic reaction rate constant is 4.9 10^{6} m·s^{1}.

Another typical experiment was carried out with much lower concentrations, nearer to values for drinking water (Run No. 16A, 22.4.92). Here the liquid flow rate was 1.1 l·h^{-1} and the inlet NO_3 concentration was 2.80 mmol·l^{-1}. The liquid leaving the cathode now contained 1.08 mmol·l^{-1} NH_3 and 1.80 mmol·l^{-1} NO_3. During the passage through the anodic compartment, the ammonia concentration was reduced to 0.06 mmol·l^{-1}, the nitrate concentration remaining again unchanged. The corresponding value for the cathodic reaction rate constant is here 2.8 10^{6} mls.

These results show that the electrolytic process can be applied for the treatment of concentrated effluent solutions as wel l for the preparation of potable water.

The experimentally found rate constants indicate that the cathodic reaction is mass transfer controlled. In this case, the application of electrodes with an enlarged surface area, for instance packed bed electrodes, would largely increase the competitivity of the process. Experiments with this type of equipment will be carried out during 1993.

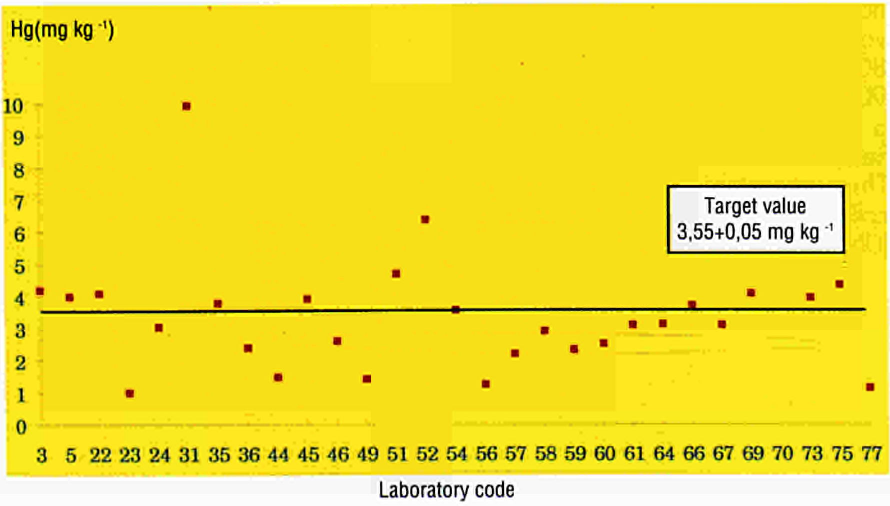


Fig. 1.47 Results of the interlaboratory study for the determination of Hg in fish.

WORKING ENVIRONMENT

The activity is aimed at providing scientific and technical information on a number of issues relating to chemical agents in a work environment,i.e.

1) International Chemical Safety Cards (ICSC)

Part of the information contained in the ICSC has been included in the ECDIN databank, with extended facilities and options for searching and retrieval of data.

Information concerning more than

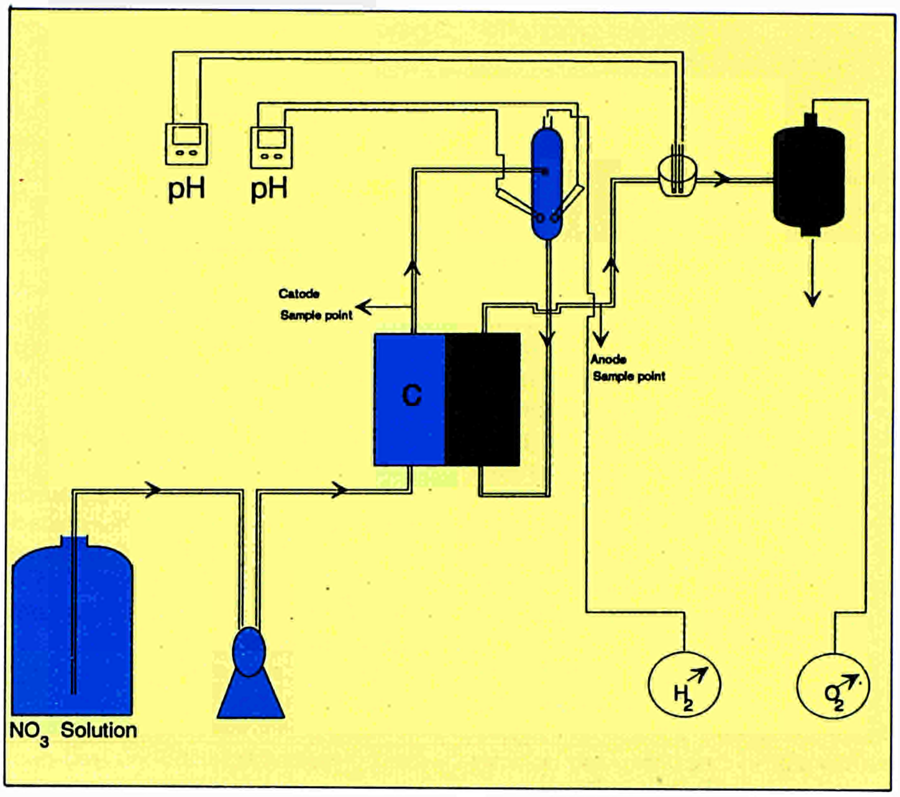


Fig.1.48 *Flux diagram of the* NO_3 *reduction - bench scale plant.*

300 chemicals has been transferred to the data file on Occupational Health and Safety (OHS). Particular attention has been paid to the selection of the following types of data:

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

2) Monographs on Chemicals
With reference to the series on "Biological Indicators for the Assessment of Human Exposure to Industrial Chemicals" work is in progress to extend the information of the monographs to full Criteria Documents (CD).

A CD will be produced in the type preferred by the Scientific Experts Group on the establishment of the EEC Occupational Exposure Limits for each chemical considered by the above series.

3) Occupational Exposure Limits(OEL)
In the frame of the Commission's activities on the establishment of limit values (Council Directives 80/1107/EEC, 88/642/EEC and 90/394/EEC) the JRC is preparing a schedule for data collection in this field.
This exercise is performed in collaboration with other data sources (UNEP - IRPTC data bank).

THE ENVIRONMENT INSTITUTE

Executive Summary
1. Specific Research Programme
2. Scientific-Technical Support to Community Policies
3. Exploratory Research
4. Third Parties Work
5. Participation to EUREKA Actions
6. Appendices

2. Scientific-Technical Support to Community Policies

In the course of 1992 the effort spent by the Environment Institute for the Scientific and Technical Support to Community policies has been furtherly increased .
In particular this has occurred at most in favour of the Directorate General XI (Environment, Nuclear Safety and Civil Protection) and has concerned the areas of Environment (encompassing Atmospheric Pollution, Chemicals, Chemical Waste, Water Quality), of Radioactive Environmental Monitoring (REM) and of the European Centre for the Validation of Alternative Methods (ECVAM).
Worth of stressing that, although the scientific expertise and support have been primarily provided to DG XI, of not lesser significance are to be considered those provided to other Directorates General (I, III, VI, XVII and XXI) or to Services of the Commission (in particular the Consumer Policy Service). The achievements related to the activities in support to these DGs are merged together and presented in the second part of this chapter.

SCIENTIFIC and TECHNICAL SUPPORT to the DIRECTORATE GENERAL XI

Environmental Chemicals

Dangerous Substances

The work directed towards scientific and technical support for the implementation of EC legislation was considerably extended in connection with the forthcoming Council Regulation on Existing Chemicals.
In this context, the Institute received the scientific/technical responsibility for:

- collecting, processing and storing of all data which industry and commerce have to supply to the Commission following the implementation of the Regulation;

- the establishment, management and updating of the European Chemicals Inventory Database (EUCLID);

- providing assistance in the preparation of priority lists;

- participating in the development and application of risk assessment procedure for existing chemicals.

A further extension of the support work for DG. XI in the field of chemicals control was prepared and agreed at the end of 1992, leading to the creation of the European Chemicals Bureau (ECB) at Ispra as an essential scientific unit in support of Community legislation on chemicals.

EUCLID

The EUCLID databank is the primary tool for the risk assessment and management of existing chemicals in the European Community. The data are supplied in standard format in all nine Community languages on diskettes (Harmonized Electronic Dataset). Data are to be collected in 3 phases:

- for high production volume (HPV) chemicals (>1000t/y) in annex 1 of the Regulation within 1 year of taking effect of the regulation;

- for remaining HPV chemicals within 2 years;

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

As part of the data are of a proprietary and confidential nature,

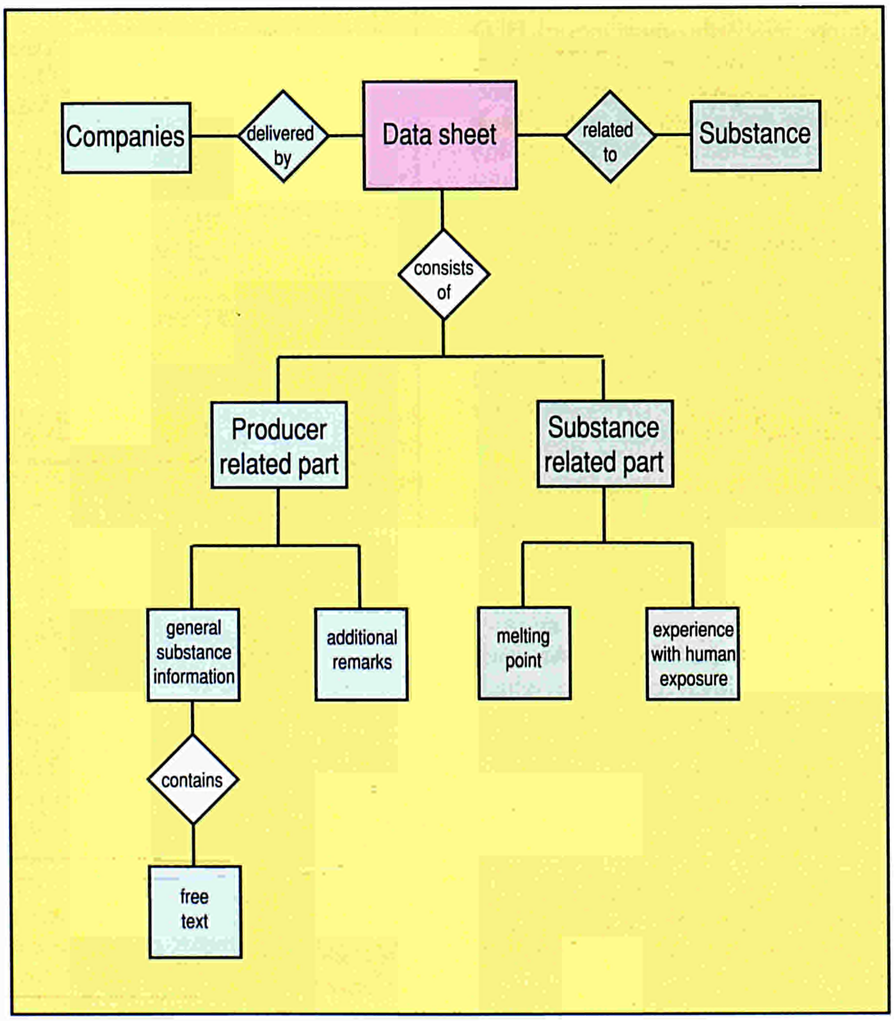


Fig.2.1 Schematic data model for EUCLID.

EUCLID has to be installed and operated in specially protected (controlled access, security surveillance and alarm system) security rooms.

EUCLID is being developed in 3 stages:

- EUCLID 1 contains the data as submitted by industry including confidential data;
- EUCLID 2 is a modified version of EUCLID 1 and is a substance related database;
- EUCLID 3 will also contain data and risk assessments for priority substances.

An overview on EUCLID sofware and displays is given in *Fig.2.1* and *Table 2.1* illustrates the schematic data model for EUCLID.

During 1992 the multilingual HED-Set diskettes and the EUCLID software programms were prepared and tested in collaboration with DG XI and specialist institutions in the member states.

Classification and Labelling

Work was focused on the updating of Annex 1 of the Dangerous Substances Directive especially with respect to the classification, labelling and packaging of organic peroxides and aromatic substances.

In this context, two meetings with experts from national authorities and industry were organized at Ispra.

QSAR

The aims of the work in the fields of QSAR is to develop models which can predict a large number of end points from the chemicals structure and other available data. To achieve this goal several activities have ben undertaken :

- research in the field of statistical model evaluation and validation and in the field of statistical methodologies;

- research in the field of cluster analysis of large numbers of chemicals;

- participation in international efforts to validate, evaluate and recommend models.

In many cases several models designed to predict a given end point for a certain class of chemicals exist. It is therefore necessary to develop methodologies for comparing models. Several such evaluation schemes have been investigated and some new ones developed.

A computer program has been developed and tested for clustering of a large number of structures. The algorithm is able to group sets of chemicals of the size of the EINECS inventory (more than 100,000 chemicals) into groups according to structural similarity.

This program will be applied to develop QSAR models.

Participation in a joint project between the EC and the United States EPA was finalized. Concerning estimates using QSAR and other methodologies in comparison with experimental data for a set of "new chemicals", two project proposals were prepared and accepted. A project proposal supported by DG. XII in collaboration with several research Institutes in the EC on QSARs for predicting fate and effects of chemicals in the environment and

Database Software

Oracle database software for IBM AIX

RDBS	Database kernel
SQL*PLUS	Query language interpreter
SQL*FORMS	Mask generation environment
SQL*REPORT WRITER	Report generation tool
PRO*C	C compiler for integration of SQL into ORACLE
TPO	Transaction processing option
SQL*MENU	Menu generation tool

EUCLID Application

The EUCLID application performs the following tasks:

- editing information about chemical substances including CAS number, EINECS-number, IUPAC name, molecular formular
- initiating reports about substances
- editing reports
- displaying and printing of reports
- executing predefined queries
- exporting and
- importing data sheets on diskettes for the purpose of information exchange with companies and authorities

The program is subdivided in producer related information and substance related information. The whole data set for each substance contains 5 well structured chapters with overall 64 entries (see schematic diagram in *Fig.2.1.*).

The chapters are the following:

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

Table.2.1 *EUCLID software and display system**

a proposal for a collaborative US-EC project on fate and effects predictions for HPV chemicals.

Atmospheric Pollution

Central Laboratory (CL) of Air Pollution

SO_2 Directive

While the harmonization programme has been concluded with the publication of SO_2 and black smoke instruction manuals at the use of network stations, a new action has been launched on the development of a SPM (suspended particulate matter) reference method (Directive 80/779/EEC, amended by Directive 89/427/EEC). A methodology to demonstrate the equivalence of measurement methods for monitoring fine suspended particulate matter has been discussed within the CEN/TC 264 working group. This procedure, concerning in particular the measurement of fine suspended particulate matter up to 10 µm size according to the ISO thoracic convention curve ("PM10"), is in agreement with the following requirements of the Commission:

- an appropriate EC reference method for PM10 should be established;
- EC Member States can use either the reference method under routine conditions, or methods which are equivalent to the reference method (PM 10 equivalent methods);
- Member States should make the necessary steps to ensure that alternative methods are tested by an appropriate EC PM10 reference equivalence procedure.

The above mentioned EC reference equivalence procedure will preferably be based on ambient field testing instead of using the US-EPA wind tunnel methodology because of the considerable differences in sampling performances. To this end, field campaigns will be organized at four different locations characterized by typical aerosol patterns, Ispra being one of the sites selected.

NO_2 Directive: Common Measuring Programme (CMP)

The harmonization programme of the Directive 85/205/EEC, launched in 1990, consists in:

- the definition of a common EC performance test procedure for NO_2 analyzers;
- the intercomparison of different NO_2 primary calibration standards;
- a quality assurance of NO_2 calibration procedures implemented in the Member States;
- a quality assurance of routine NO_2 networks.

In 1992, progress with the above third action has been accomplished, with a first intercomparison of the calibration procedures performed for laboratories of the Northern Europe Member States. This exercise has taken place in May 1992 at the Landesanstalt für Immissionsschutz (Essen, FRG. Ten laboratories from seven Member States (B, DK, F, FRG,L, NL, UK) participated to the exercise.

The Griess-Saltzman wet chemical method was implemented by four laboratories. The other laboratories implemented automatic continuous methods (chemiluminescent instruments) calibrated by the static injection, the dynamic dilution or the permeation method.

The results of the intercomparison will be released after the second exercise, scheduled in April 1993 at the JRC, involving laboratories of the South-Europe Member States.

This first exercise has however shown that the overall precision of the measurements was good, with 90% of the measurements within a confidence limit of about ±10%. The wet chemical method (Saltzman), exhibited, in comparison to the static dilution method, a systematic lower response to increasing NO_2 concentrations (typically 8% at NO_2 concentrations of 350 $\mu m/m^3$). The effect of the relative humidity (R.H.) on the response of the chemilu-minescence analyzer was examined, showing a typical 5% decrease at R.H. levels increasing from 10% to 50%.

Ozone directive : VOC measurement techniques

The EC directive 92/72/EEC of 21 September 1992 on air pollution by ozone, recommends the measurement of volatile organic compounds in selected stations of the networks. The EC intercomparison exercise organised by the CL in 1991 was a first step towards guidelines for harmonised VOC measurements in the EC. The main results of this exercise, were discussed in May and December 1992. Analyses of the results of the intercomparison on VOC measurement, showed that the performance of the laboratories was not sufficient for the achievement of a target value of 15% accuracy, acceptable for the harmonization of VOC measurements. The results for the 15 most volatile compounds were compared to the gravimetric standard: the accuracy averaged 36% over all the participants. This figure contrasted with the good precision observed (5%) within each individual laboratory. A decay in the stability of the sample cylinder was observed for the less volatile compounds, due to absorption on the cylinder walls, and were consequently disregarded in the intercomparison. It appears from this first intercomparison, that gas phase mixtures in cylinders might not be appropriate as calibration standards for these compounds. Additional information on this important problem are expected from the next exercise in programme in 1993.

Application and development of passive samplers: an intercomparison study

Within the framework of a collaboration with the Bavarian Lander, the GSF Institute (Forchungs-zentrum fur Umwelt und Gesundheit Gmbh) carried out an intercom-parison campaign for NO_x, SO_2 and O_3 passive samplers. Aim of this exercise was to determine, after a 6 month intercomparison campaign, the reliability of passive samplers to evaluate transport of pollutants in the alpine region.

The passive samplers were placed in 6 stations of alpine countries (Austria, Germany, Italy, Switzerland) where pollutant measurements and meteorological data were constantly available. The Central Laboratory participated to the intercomparison using NO_2 passive samplers; the EMEP station of the JRC in Ispra was selected as one of the measuring sites.

The results of the intercomparison are expected for early 1993. A statistical analysis applied to the results will provide important information on the limits of applicability of the passive samplers, mostly investigated in urban atmospheres, to rural and remote areas (the Alps).

Monitoring network design

Under request and in collaboration with the Observatoire Regional de l'Air en Midi-Pyrénées (ORAMIP) a survey of NO_2 pollution in Toulouse (France)using passive samplers, has been designed. Using the results of a campaign with 120 tubes spread over the 140 km² of the agglomeration, the maps prepared by the JRC are expected to identify three types of sites:

- sites sensitive to emissions due to traffic;
- sites sensitive to industrial emissions
- sites sensitive to a mixed pollution, likely to be observed, in Toulouse, in particular residential areas. The results will be discussed at a meeting scheduled in 1993.

EMEP Monitoring Programme

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

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

The following parameters are measured:

- in air: SO_2, NO_2, NO, O_3, CO and PAN continuously, non methane hydrocarbons, methane and NH_3, occasionally;
- in atmospheric particulate: SO_4^{--}, NO_3^-, NH_4^+ ,Cl^-, TSP and H^+ on regular basis, heavy metals in 7 days sampling periods:
- in precipitation samples SO_4^{--},NO_3^- ,Cl^-,NH_4^+,Na^+, K^+, Ca^{++}, Mg^{++},pH, electrical conductivity;
- meteorological parameters.

Detailed results of all collected data are reported in annual reports and monthly transmitted to the Norwegian Institute for Air Research (NILU) acting as EMEP Chemical Coordinating Centre, to DG XI, and also to the Italian Ministry of Environment and to the Municipality of Varese. The results obtained have been used for various transboundary transport studies by other Institutes.

Fig.2.2 represents the monthly average concentrations measured at this station during the last six years of O_3, NO_2, SO_2 in air; and of pH, NO_3^- , SO_4^{--} and NH_4^+ in rain. Ten selected EMEP monitoring sites (including the JRC) started a study for the determination of HNO_3/NO_3^- and NH_3/NH_4^+ in atmosphere by annular denuder technique; this study will be based on 20 days continuous measurements in December 1992, March, June and September 1993.

At the end of 1992 the EMEP programme started a discontinuous

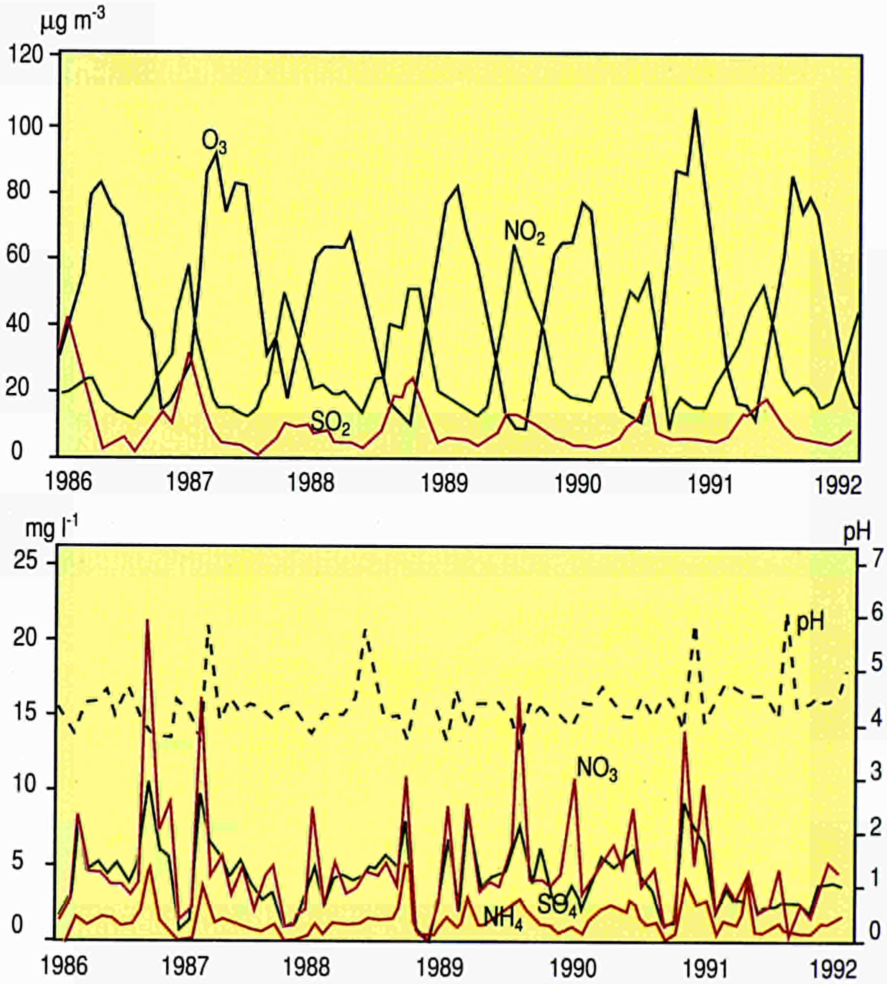


Fig.2.2 Monthly average concentration of O_3, SO_2, and NO_2 in air ($\mu g\ m^{-3}$, above) and of NH_4^+. NO_3^- , and SO_4^{--} in rain (mg l^{-1}, below) measured at the EMEP station. The pH values of the rain samples are also shown.

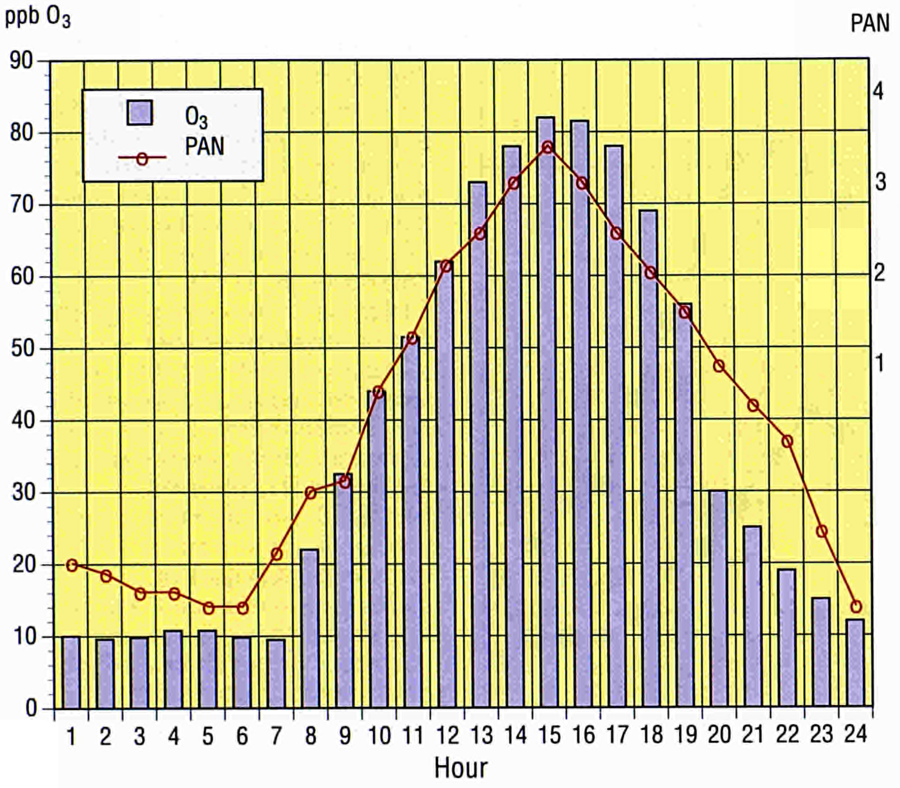


Fig.2.3 Hourly average concentration (pbb/v) of O_3*, (bars) and of PAN (full line) measured at the EMEP station. July 1992.*

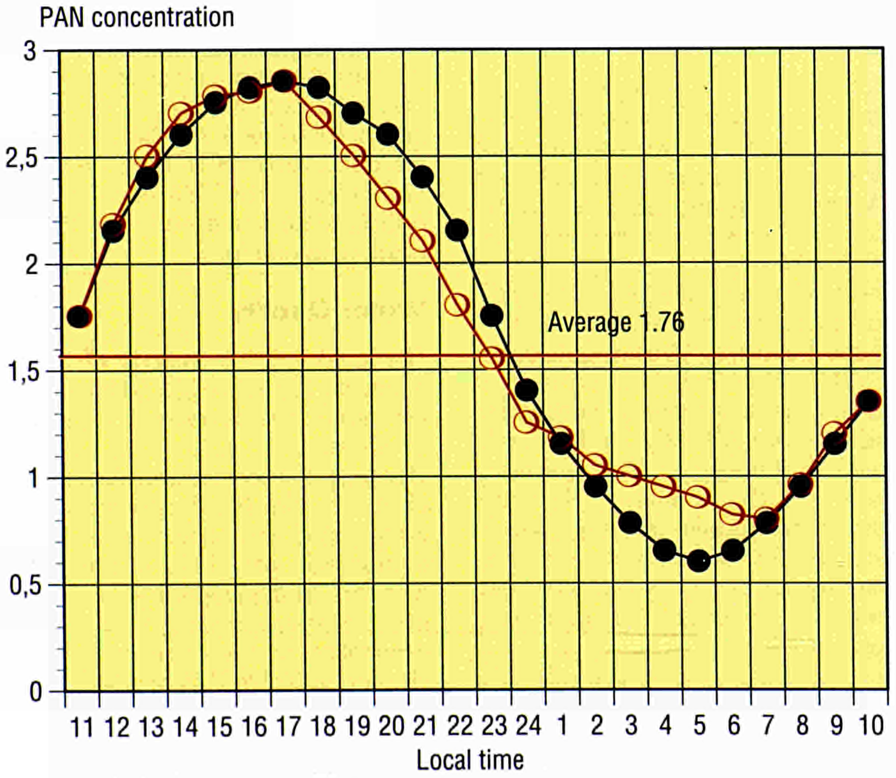


Fig.2.4 Variations of hourly PAN concentrations (pbb/v) measured at the EMEP station in period May - September 1992.

measurement of VOCs in air in ten different sampling sites over Europe NILU and JRC Ispra are responsible for the control of air sampled from these selected sites.

The Environment Institute continue with his participation in intercalibration programme on PAN measurement. For the second time it was shown that transport of PAN standards is possible and the control of these standards can be made with a precision of about 10% by all participating laboratories.
In order to overcome difficulties due to thermal instability of PAN tests were done to show that propyl nitrate can be used to control whether calibrations of PAN is likely to vary over a period. Continuous measurements of PAN during 1992 showed a very good correlation between PAN and Ozone *(Fig.2.3)*. Hourly average variations of PAN concentration during period of a month or longer are sinusoidal *(Fig. 2.4)* and are different from one month to another *(Fig. 2.5)*; both pheno-menon are to be related to U.V. irradiation level.

Prevention and Reduction of Environmental Pollution from Asbestos

In view of implementation of the Directive EC 87/217, the Environment Institute contributed to the development of a ISO standard method using the fibre count method for the determination of fibres in asbestos plant emissions. Final version of the standard method has now been accepted by the Member States.

Very satisfactory results heve been obtained by EI laboratories in the 1992 Fibre Counting Trial organised by "Asbestos International Association" into which 52 laboratories from 27 various countries took part.

Chemical Waste

The establishment of a standard EC method for the analysis of PCBs in waste in connection with the EC Directive 87/101 is under way. A three-steep approach developed at

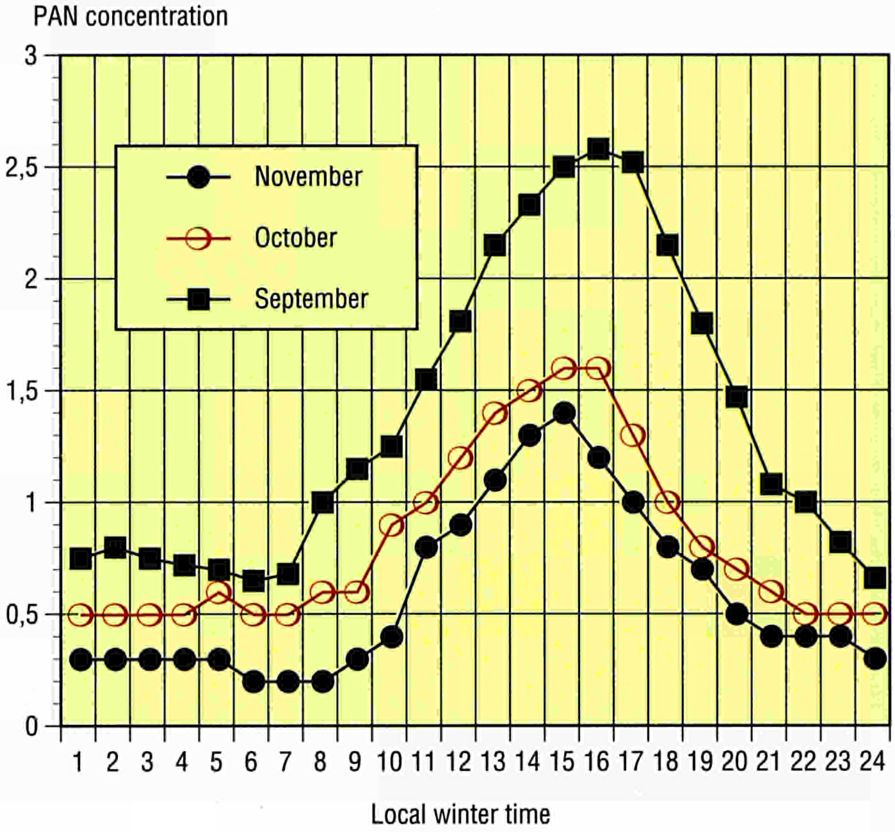


Fig.2.5 Variations of hourly average PAN concentrations (pbb/v) measured at the EMEP station in different periods of time in the year.

JRC, Ispra has been suggested by the Commission to the Member States. In a second phase it is foreseen to discuss this approach among national experts and to organize inter-laboratory comparisons. This phase has been postponed to 1993 due to financial difficulties.

Informatisation of the future European Waste Catalogue

Council Directive 91/156/EEC amending EC Directive 75 / 442 / EEC on waste foresees that the Commission will draw up, not later than 1 April 1993, a list or catalogue of wastes belonging to the categories listed in annex I of the Directive. Council Directive 91 / 689 / EEC on hazardous waste on the basis of three annexes introduced a new definition of hazardous waste. This Directive also prescribes that all categories of hazardous wastes have to be included in the same catalogue.

Actually the catalogue, called European Waste Catalogue (EWC), is elaborated by a working group of independent experts from different Member States and appointed by the Commission. Work is managed by DG XI/A4.
The Environment Institute of the JRC has charged with the informatisation of the European Waste Catalogue (EWC). The research project is carried out as a contract financed by the German Ministry for Research and Technology. The German Federal Environment Agency (Umweltbundesamt) in Berlin, which acts as the representative of the Ministry regarding waste management, supervises the research contract.
The contract shall provide an appropriate and user-friendly product in form of a fully informatised version of the EWC.

The Work programme foresees the following steps:

- Continuous documentation of the drafts of the EWC as elaborated by the experts.
- Documentation of the EWC in English language and in the main languages of the Community. During the first phase French, German and Italian languages will be considered.
- Documentation of the national waste catalogues (B, D, DK, F, I, NL, UK, CH) in their national language and in English language as well.
- Documentation of international waste catalogues and related lists in their English version:
  a) hazard characteristics according to Directive 91/689/EEC;
  b) OECD classification for waste products (International Waste Identification Code, IWIC);
  c) Basel convention on the control of transboundary movements of hazardous wastes and their disposal;
  d) UN transportation code;
  e) hazardous goods according to the European catalogue for hazardous goods;
  f) arising according to economic activities (NACE classification);
  g) arising according to technical processes (OECD classification);
  h) classification and nomenclature of wastes adopted by the custom;
  i) development of computer programmes for a local (PC, MS-DOS) and a central (UNIX work station) system for the documentation of the EWC and its linkage (cross-reference) to the national and international waste catalogues and lists.

Water Quality

The work on the impact of trace elements (Directive 76/464/EEC, list I and II substances) has been continued.
The non-point sources and discharges of As, Pb, Hg, Ni, B, Mo and Sn to the aquatic environment have been evaluated. Very little information appears to be available on these non-point sources, with most information on the elements As, Hg, Pb and Ni *(Table 2.2)* and less on B, Mo and Sn *(Table 2.3)*.

Major sources of As, Hg, Pb and Ni are dredgings, atmospheric deposition and sewage, while B, Mo and Sn appear to be related mainly to

Source	As	Hg	Pb	Ni
Untreated domestic sewage	21.1	1.0-5.8	94.9-580	52.7-232
Domestic sewage via treatment plant	22.6	0.6-3.7	81.4-479.5	79.1-348.3
Sewage sludge (dumping into sea)[1]	1	0.7-1.2	89-166.2	14
Dredgings dumped into sea[2]	148	14.9-16.9	1801-1926	826
Dentistry	-	56.4-64.1	-	-
Hunting	3.5	-	288.1	-
Sportfishing[3]	0.8-1.9	-	194-465	0.8-1.9
Surface run-off due to landfill and agriculture	1.43-1.85[4]	0.2-0.6[5]	22.5-81.9[6]	9.3-16.3[7]
Surface run-off due to deposition	50.8	16.9	1151.6	158.1
Deposition into aquatic environment	16.1	5.4	365.2	50.1
Total	265.3-266.8	96.1-114.6	3795-5210.8	1190-1646.7

\- = no discharge expected.
[1] U.K. only.
[2] B, DK, F, NL, UK only.
[3] NL only.
[4] NL and UK only.
[5] NL, S and UK only.
[6] B, DK, NL, S and UK only.
[7] B, NL, S and UK only.

Table 2.2 *Discharges of As, Pb, Hg and Ni to the aquatic environment in the EC due to non-point sources* $(t \cdot y^{-1})$.

Source	B	Mo	Sn
Domestic sewage			
Sewage sludge (dumping into sea)	5.1-340[1]	0.78-10.3[2]	13.6-238[1]
Dentistry	-	-	22.1-25.1
Hunting	-	-	7.9
Sportfishing[3]	-	-	1.9-5.2
Ship traffic			88
Surface run-off due to landfill and agriculture	0.8-37.3[4]	0.2-0.9[5]	1.6-17.3[6]
Surface run-off due to deposition	1987	10.2	29.4
Deposition onto the aquatic environment	630.1	3.2	9.3
Total	2623-2994.4	14.4-24.6	173.8-420.3

Blank = no estimate available.
\- = no discharge expected.
[1] U.K. only.
[2] U.K. and IRL only.
[3] NL only.
[4] S and UK sludge only.
[5] IRL, NL and UK sewage sludge only.
[6] UK sludge and tin pesticides only.

Table 2.3 *Discharges of B, Mo and Sn to the aquatic environment in the EC due to non-point sources.* $(t \cdot y^{-1})$.

surface run-off and atmospheric deposition (B and Mo) and ship traffic (Sn). Additionally, the discharges of Sb and Sn to the aquatic environment due to point sources have been evaluated.
Sb *(Table 2.4)* derives at a large extent from paint production, textile finishing and emission from power plants, Sn *(Table 2.5)* from basic industries, use in electric power equipment manufactury and shipbuilding (anti-fouling agents).

The Ministerial Seminar of Frankfurt (June 1988) expressed the need for the Commission to prepare a proposal for a future Directive concerning the *ecological quality of surface waters*. Thus, JRC expertise was made available to contribute to the development of this new EC Directive.
A first study on quality assessment schemes for EC lakes was completed in June 1992 and published as EUR Report. The major difficulties in preparing proposals are with the definition of the ecosystem categories, the respective acceptable ecological standards for each of these categories and the classifcation procedures.The study gives a brief summary of the causes of pollution responsible for the impairment of European lakes in recent decades. It examines the various techniques (physico-chemical and biological) for the assessment of lake water quality, reviews some of the more significant approaches used for lake classification in European countries and in the United States, and summarizes the work carried out by the Economic Commission for Europe for the classification of ecological freshwater quality. General guidelines, to be used in the national programmes, for lake assessment are suggested. The primary objectives of a surface water quality monitoring programme are the characterization of the quality of water resources, the identification of problem waters and the evaluation of the effectiveness of pollution control actions. Some indications for the survey network (i.e. number of lakes to be included in a survey programme), sampling procedure, sampling frequency,

Branche of industry	B	DK	F	D	GR	IRL	I	L	NL	P	S	UK	EUR 12
Manifacture basic industry	0.02	0.004	0.06	0.16	0.003	0.002	0.055	0	0.04	0.003	0.02	0.05	0.4
Paint production	7.8	1.6	9.9	47.1	0.4	0.3	0.008	0	3.4	0.7	4.5	3.4	79.1
Manifacture of other. chemicals	0	0.004	0.25	0.8	0.002	0.03	0.1	0	0.2	0.002	0.06	0.2	1.6
Manifacture of starch/ sugar	0.5	0.08	0.2	0.3	0.01	0.15	0.08	0	0.4	0.04	0.09	0.1	1.95
Textile finishing	0.5	0	1.4	2.5	0.1	0.4	3.7	0	1.2	2.6	0.7	1.0	14.1
Non-ferrous industry									0.004			0.5	0.5
Power plants		0.02		2.8					0.2				3.0
Total	**8.8**	**1.7**	**11.8**	**53.7**	**0.5**	**0.9**	**3.9**	**0**	**5.4**	**3.3**	**5.4**	**5.25**	**100.6**

Table 2.4 Total Sb discharges in the EC member states $(t \cdot y^{1})$.

parameters for water quality assessment (physical, chemical, biological) and for habitat assessment (i.e. bottom substrate, water flushing rate, morphology, water stratification) are provided.

A simplified classification scheme for assessing the ecological state of freshwater lakes to be used throughout the European Community, based on generally accepted physico-chemical and biological features such as transparency, dissolved oxygen, chlorophyll-a and phosphorus concentrations, acid neutralizing capacity, algae and macrophytes, macroinvertebrates and fish indices, and, lastly, a sediment index, has been elaborated. Since the ultimate aim of the future Directive should be to reach a high ecological quality (HEQ) in all surface waters and to attain ecological integrity *(Fig.2.6)*, in the proposed lake classification scheme a matrix, giving clear limitations of classes, has been considered taking into account also the morphoedaphic index. This allows the description of lacustrine systems in complying (two classes: excellent, good) and uncomplying waters (three classes: fair, poor, bad) and to follow closely the evolution of the ecological quality of the Community waters, establishing basic (ecological) and minimum (managerial) objectives for lotic environments. The suggested numerical criteria, corresponding to different degree of environmental quality, should allow to check the compliance (and its implementation) of the future Directive into national legislations.

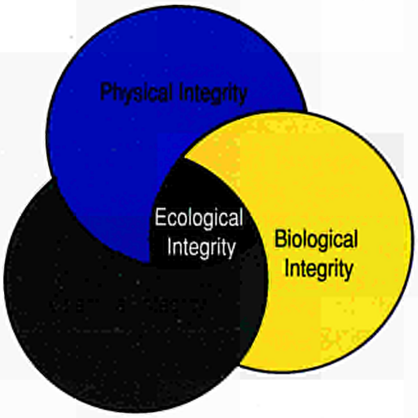


Fig.2.6 Ecological integrity is attainable when physical, chemical and biological integrity occur simultaneously.

A second report was finalized on methodologies adopted for surveying and monitoring the marine environment. The main purpose of the study was rather to analyze the methodological criteria and strategies to be adopted in planning marine researches, mainly depending on the investigated environmental aspects and on the objectives of the research. The marine environment can be surveyed with several descriptive, interpretative or predictive purposes as for instance: to characterize the various components of the system surveyed, to compare the water quality conditions with the standards for different uses, to locate and quantify the biotic and abiotic resources, to understand the environmental phenomenology and the causal relationships among the various components and finally to foresee the positive or negative effects of the proposable interventions. The following aspects were considered: the fundamental processes of the marine environment, the parameters describing the environmental

Branche of industry	B	DK	F	D	GR	IRL	I	L	NL	P	S	UK	EUR 12
Manifacture basic industry	3.7	0.7	12.0	31.4	0.6	0.4	11.0	0	9.3	0.6	4.8	9.3	83.8
Foundries	0.001	0	0.008	0.02	0	0	0.008	0	0.001	0	0.003	0.006	0.05
Metal transformation	0.05	0.03	0.9	0.8	0.003	0.007	0.4	0.02	0.06	0	0.3	0.2	2.8
Manifacture of electrical equipment	0.8	0.4	6.7	12.9	0.1	0.2	4.6	0.02	2.2	0.2	1.2	5.1	34.4
Shipbuilding	0.8- 2.0	0.8- 2.0	2.0- 3.0	2.0- 3.0	4.0- 8.0	0.8	4.0- 6.0	0.8	2.0- 3.0	4.0- 6.0	2.0- 4.0	2.0- 3.0	25.2- 41.6
Non-ferrous industry		0.8							0.1- 2.1*			0.05	0.95- 2.95
TiO_2	0.4		1.8	3.3			0.7				0.6	1.0	7.8
Organotin production			±0***	0.9			0.05		0.9				1.9
Poweder plants		0.01		1.4					0.1				1.5
Miscellaneus									0.2**	0.2			
Total	5.8- 7.0	2.7- 3.9	23-4- 24.4	52.7- 53.7	4.7- 8.7	1.4 22.8	20.8- 17.9	0.8 6.8	14.9- 10.9	4.8- 18.7	8.9- 177.0	17.7-	158.6-

* After reorganization of the production proces the discharge decreased from 2.1 to 0.1 t y^{-1}.

** Manifacture of medical instruments, cleaning companies.

*** After the production of organotin compounds, the tin containg waste is incinerated.

Table 2.5 Total Sn discharges in the EC member states ($t.y^{-1}$).

behaviour and the related analytical methods, the automatic monitoring systems both in situ and from remote sensing, the numerical simulation models, the relating criteria of calibration and their joint utilization with territorial-environmental information systems and finally the water quality standards for various uses. As to the oceanographic aspects, priority has been given to water quality.

Radioctivity Environmental Monitoring (REM)

REM data bank

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

- to keep a historical record of the Chernobyl accident, for further scientific study
- to store the radioactivity monitoring data of the EC Member States in order to prepare the Monitoring Report. By means of this report the Member States are informed of the radioactivity levels in the environment in the European Community, as stated in art. 35 - 36 of the Euratom Treaty.

The information held by the bank covers data from the twelve EC Member States, as well as other European countries for both environmental samples and foodstuffs from 1984 onwards.
Best represented are air, deposition, water, milk, meat and vegetables. The current total number of data records stored in REM is about 500,000.
The data are usually received in the form of national monitoring reports and after being digitised by means of Proteo or EasyProteo *(Fig.2.7)* are exported into the standard REM data exchange format (card image format) and up-loaded in the REM data bank.
Data in the bank are available to external users via the network connection to REM (X.25 or modem).

Because of the planned shut-down of

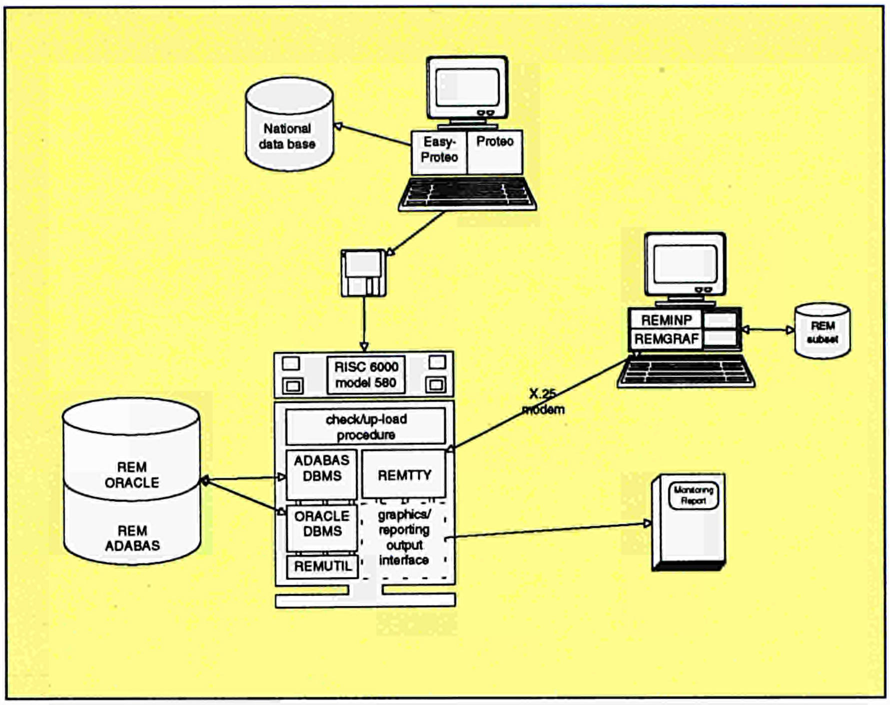


Fig. 2.7 Schematic overview of the REM data bank and its applications (dashed lines indicate future developments).

the JRC mainframe for scientific applications at the end of June 1992, the REM data bank had to be transferred to the UNIX server 'URANO'. For the moment two versions of the data bank exist on the UNIX server: a backup version running under ADABAS 5/NATURAL 2 and a new version under Oracle / SQL, in accordance with the general CEC strategy. The ADABAS version will cease to exist when all the data bank software is rewritten for Oracle, foreseen for 1994.

In the second half year of 1992 the existing ADABAS software - the data loading program, REMUTIL (data management program) and REMNEW (data query program for external users) - was adapted to be used under UNIX. In the mean time the development of software for managing the Oracle data bank was started and the data uploading program was made.

Almost all available data sent by the Member States to be used in the next Monitoring Report (1987-1990), were entered in the bank during the past year. Based on the available 1987-1990 data in the REM data bank, a draft version of the tables and figures for the report was prepared and presented at the meeting of the Member States representatives in Luxembourg (14 - 15 December 1992) *(Fig.2.8)*. Comments from the Member States are expected before publication, foreseen for mid 1993.

One of the major problems experienced in preparing the above monitoring report was the digitalisation and the check of the monitoring data.

To have an input processor better adapted for digitising monitoring data, the development of EasyProteo was started in December 1991 as a follow-up of the earlier developed package Proteo. Because the data cannot be only exported to the REM data exchange format but also to many commercial data formats, this tool is also useful for Member States for entering their monitoring data in their national data bank.

The development was continued during last year. The first official release (16 bit version for AT compatibles, 32 bit version for 80386 or higher and a user manual) was presented and distributed at the above mentioned meeting of the Member States representatives in December.

In the framework of the 'Joint Study Project 1' (JSP1), as a part of the development program CHECIR, DG XII, JRC-Ispra was requested to participate in the set-up of a communication system for the exchange of Chernobyl contamination measurements with the 'Studie Centrum voor Kernenergie' (SCK), Mol, Belgium and 'the Kurchatov Institute of Atomic Energy' (KIAE), Moscow, Russia. KIAE is the co-ordinator of the Chernobyl measurements stored in the data banks of several institutes in the former Soviet Republics.

The complete database system has been upgraded from Oracle-5 to Oracle-6. This implied the redefinition of the database tables to include V6 integrity constraints and the redesign of the software to take advantage of the new Oracle tools delivered with version 6. Exposure data far 1991, supplied by 114 reactor units have been inserted in the database. that now covers the period 1980-1991.

In order to support the Commission in the preparation of the *Exposure Annual Report* and of the *Ten - years experience Report*, a set of procedure has been developed to extract information from the database according to specific formats. The output of the procedures has been used to produce graphs and tables for the above documents.

The definitive version of the Electronic Questionnaire has been developed. The software package has been delivered in seven versions:

1 English version
2 German version
3 Spanish version
4 French version for EDF plants
5 French version for non-EDF plants
6 Dutch version
7 Italian version

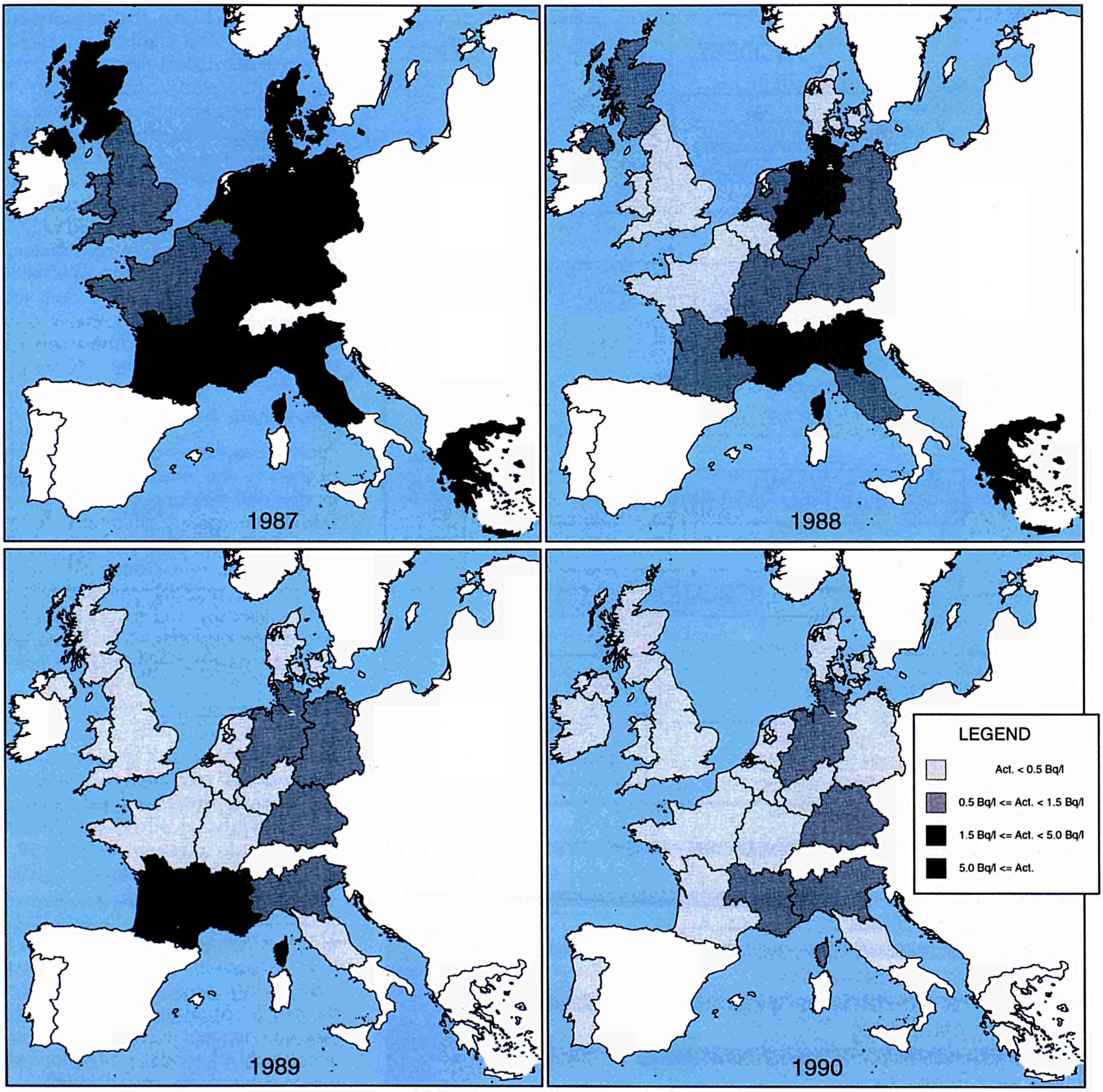


Fig. 2.8 Annual averages of 137Cs contamination in milk in the EC during the four years after the Chernobyl accident (to be published in "Environmental Radioactivity in the EC 1987 - 1990")

The package has been developed under the MS-DOS operating system, and it does not require any run-time support. The diskette contains an automatic installation procedure. The electronic questionnaire has been demonstrated to the utilities during the *Annual exposure experts meeting*, held in November 1992 in Luxembourg. At the same meeting exposure data collected by CEC during the period 1981-1991 have been supplied to the utilities, together with a software tool to query the data. The software has developed under the MS-DOS operating system. Two high density diskettes contain the data, the consultation tool and an automatic installation procedure.

Both CEC and NEA are active in the field of professional radiological exposure although the two databases have different terms of reference. An agreement has recently been reached on a unified data collection, which minimizes the work required to the

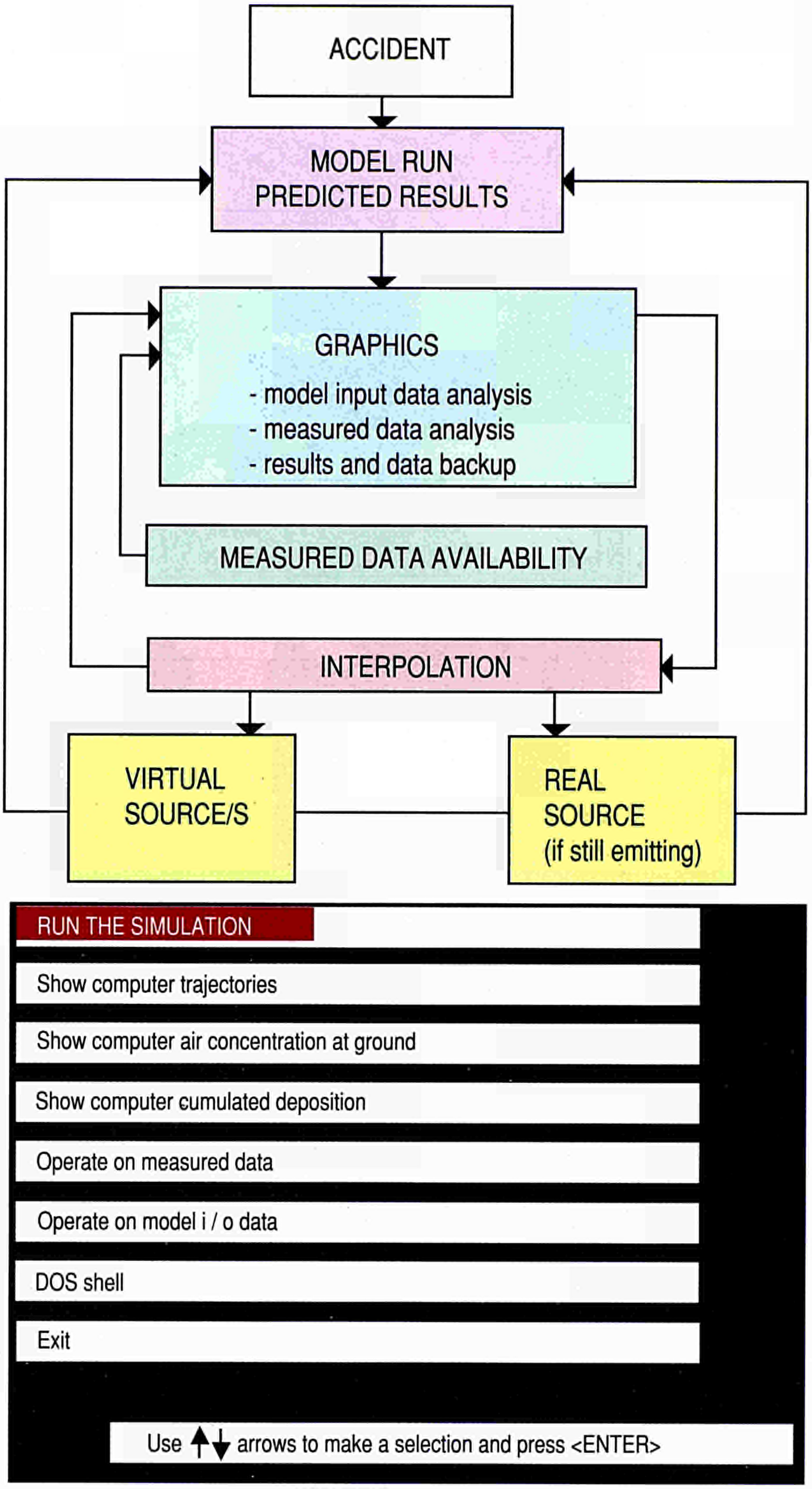


Fig. 2.9 Block diagram of the LORAN procedure (above) and associated main menu (below).

utilities for filing the requested information. The CEPN from 1992 onward will collect the annual data for both organizations using a computerized input module based on MS-Windows. The data will then be imported in the respective databases. The JRC will continue the maintenance of the CEC data bases, a copy of which will be installed at DG XI-A1 in Luxembourg for consultation. The annual task of the JRC will include the preparation of reports for the annual meetings of experts and the distribution of updated sets of data to utilities on magnetic media.

Atmospheric Transport Models

Further progress has been accomplished in the area of long range models and their application.

During emergency situations, following both nuclear and chemical atmospheric emissions, it is very important to quantify immediately the source intensity and to estimate the long range evolution of the cloud, in order to assess the useful countermeasures.

For the purpose, use should be made of all the available information consisting not only of meteorological forecasts, but also of pollution data. For nuclear emergencies, many Countries have installed dense networks for airborne radioactivity measurements, which are avalilable immediately after the accident.

In the past, a technique for pollutants data assimilation has been worked out, based on the idea that a monitoring network is able to describe satisfactorily the cloud evolution and that the major source of uncertainty of model performances are on the input forecasted windfield.

Following this ideas, an automated procedure has been developed, based on the fact that when the observation field becomes available, a function describing this field is fitted and a new area source is used to update the predictions.

Fig. 2.9 shows the conceptual scheme of the procedure with the associated Menu that includes the various selection items.

The procedure incorporates a new version of the code LORAN, which

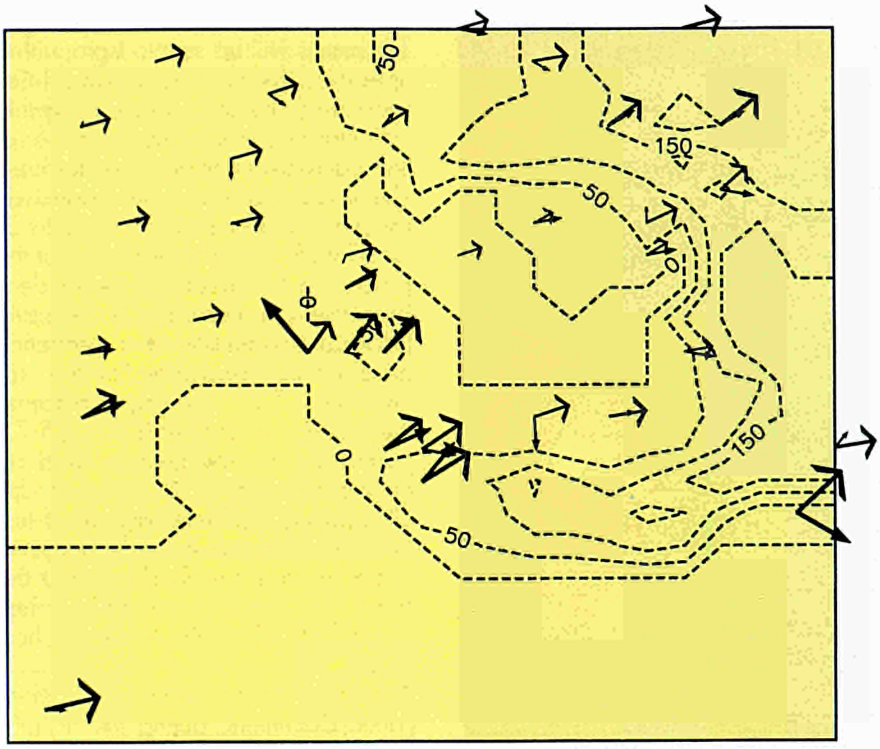


Fig. 2.10 Observations and mesoscale model results in a time interval (12h) for the FOS campaign.

can select from the screen the pressure level of the windfield to be interpolated for the trajectory calculations.
Work is continuing in the direction of introducing simultaneously multiple level trajectories and to produce graphical outputs in the form of contour levels of concentration over Europe and time histories in a number of preassigned localities.

For what it concerns Models for mesoscale distances, in view of studying the evolution of atmospheric emissions, it is sometimes necessary to estimate the circulation of air masses over complex terrains, where the complexity can be due to the presence of mountains or to the effect of large water basins.
To deal with such problems, two circulation models (one RAMS non-hydrostatic primitive equations and the second TVM hydrostatic, three vorticity model) are available. These have been applied to different localities.
Worth of mention the simulation perfomed using the two codes in two different domains. The first was that of the Fos campaign, where the sea-breese is developing over a complex, but rather flat area in the proximity of Marseilles. During the campaign a number of temperature and wind measurements were made and the two codes have been compared with this dataset as well as each other *(Fig.2.10)*. The second was the Athens region, where the local circulation , mainly driven by the sea-land breese is also strongly influenced by a mountainous ridge, fairly close to the sea-shore. During the campaign, only a limited number of measurements were performed.
The results of the comparison show quite a good agreement between the results of the two models during the daytime. The comparison could not be easily extended to the entire period due to the lack of data mainly during night, when the results of the two models show considerable differences *(Fig.2.11)*.

Transport and dispersion of pollutants for short and mesoscale distances can be simulated by Lagrangian particle-in-cell models, in which the motion of each particle is described by the mean wind plus semi-random components accounting for turbulent situations.
During the reporting period a new code (MONTECARLO) has been developed, largely based on routines of an existing code (MCLAGPAR), which have been further improved.
Among the new characteristics of MONTECARLO worth of mention the simulation schemes for describing the inhomogeneous turbulence of the convective boundary layer. The results of these schemes have been critically compared in some standard situations. The results quantify the limitations when using two normal distributions for the vertical wind fluctuations to reproduce the skewness in the vertical eddies.
The model contains furthermore a new effective method for evaluation of buoyant emissions particularly suited for particle models.
An example of the kind of results which can be obtained is shown in *Fig. 2.12*.

ETEX

The Technical Specification Document has been prepared with the description of the model outputs that must be provided by the modellers participating to the exercise. The Document in its present form is only valid for the first dry-run. In fact among the scopes of the dry runs, there are information on the representativeness of the localities selected for the samplers as well as the other general features of the exercise (eg source intensity and duration, sampling intervals,etc.)
Five different concentration data sets will be provided to the Evaluation Team: Every data-set is the result of 60 h calculation of the tracer plume evolution: the first is entirely based on forecasted windfield data, the second is obtained using the first 12h analysed data plus 48 h forecasted

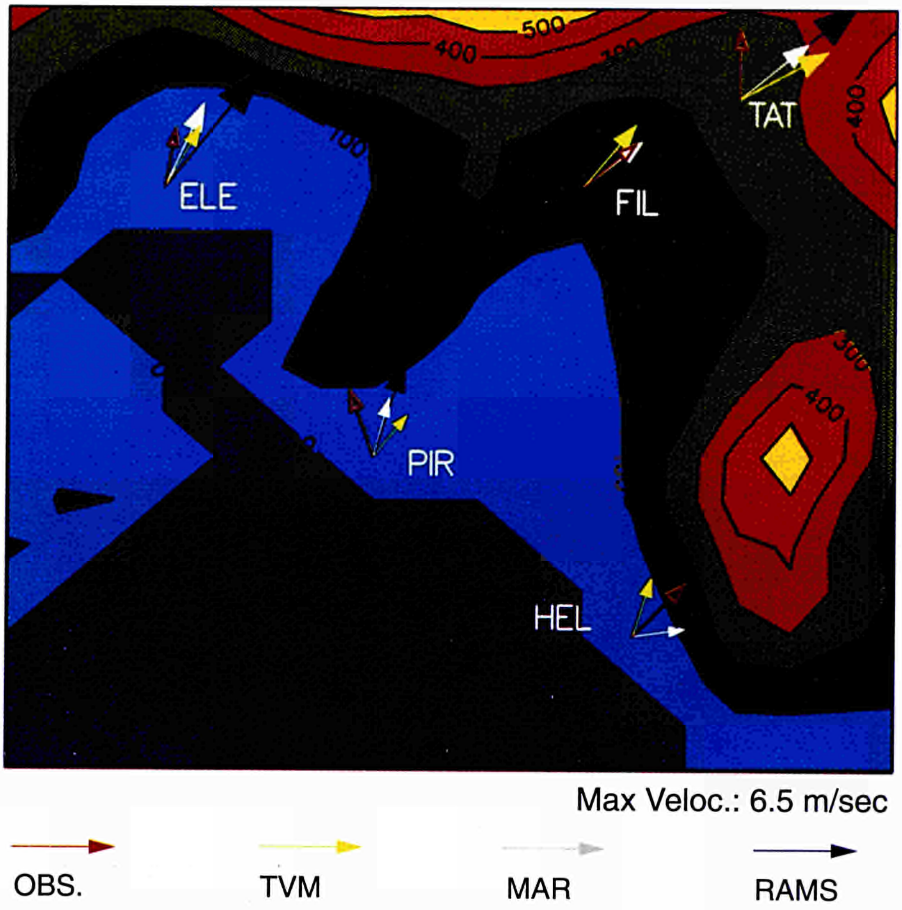


Fig. 2.11 Observations and mesoscale model results in a time interval for the APSIS.

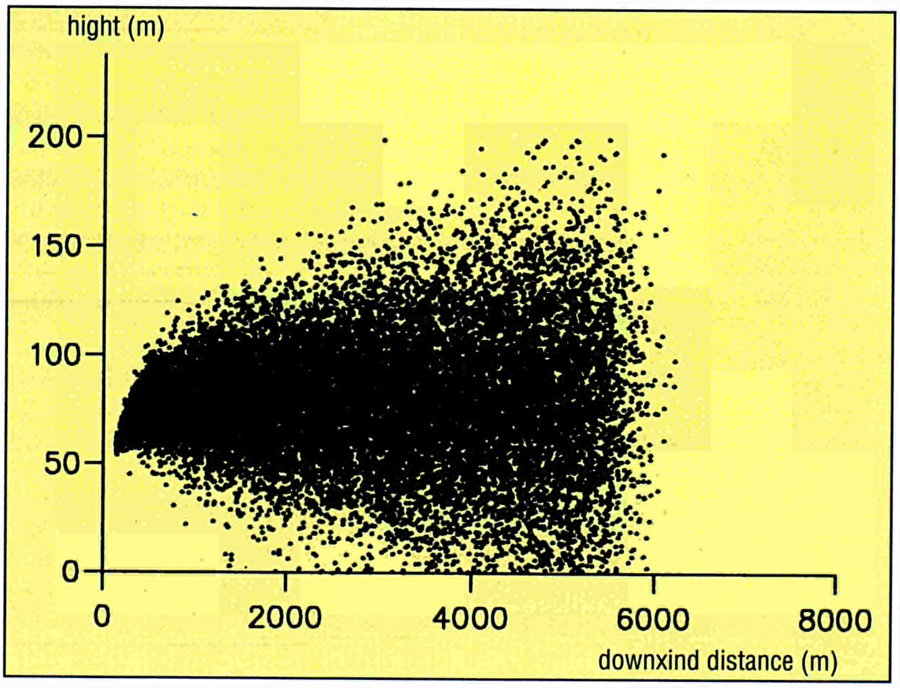


Fig. 2.12 Particle distribution with buoyancy.

data, etc.

The results will be sent to Ispra with a specified format for the localities indicated by the Document within one month from the start-up (either of the real experiment or of the dry-run).

The comparison will be carried on using the same statistical indicators as for ATMES: no further extension of the procedure has been yet demanded. Nonethless, in order to use the same package, selection of a Reference model must be made for the dry runs.This will be done by comparing the box-plots showing the 25-75 percentile distribution obtained by each participant of all the data for all localities and time intervals of first forecast. This has the advantage to select an 'average model ' and the drawback that Evaluation Team has to wait till all results have reached Ispra.

According to the Technical Specification Document, during the dry-run, participants are requested to send by facsimile to Ispra a concentration contour every 24 hours, as a real accident would occur, to anticipate the kind of results that they will then load on floppy disk. An help to the identification of the Reference model will also come from the comparison of faxes. However, as different projections and different formats are used by the participants to the exercise(eg polar stereographic, Lambert conformal conic and rotated spherical), it was then necessary to create a system for converting points and polygons in different projections to the same map. This has been done transforming the maps for a number of participants who have sent samples facsimiles.

ECURIE

ECURIE (European Community Urgent Radiological Information Exchange) is the EEC early warning and exchange of information system, developed in close collaboration with the Member States.

The system consists of a telex communication network between the CEC and the Member State contact points for the transmission of radiological emergency messages

(Fig.2.13). Since Member States belonging both to the IAEA and the EC have to comply with similar obligations it was decided between IAEA and CEC to co-operate. This resulted in an identical code - the Convention Information Structure (C.I.Structure) - into which messages containing radiological information are encoded and sent.
The encoding-decoding software (EDS) has been developed by IAEA (decoding part) and by JRC-Ispra (encoding part).

In order to become and to remain operational, different levels of exercises between the CEC and the Member State contact points exist to test various aspects of the emergency system, i.e.:

level	description
0-1	communication test only
2	contact of radiological duty officer
3	exchange of simulated accident data

The EDS was improved and extended with an interface for automatic mailing by telex (Telexbox3).
It is foreseen to have the software available in the nine official EC languages. As a start the Portuguese and Danish version for preparing a C.I.Structured message were developed and included in the present software.

Until now only telex has been used for transmission of ECURIE messages. The EDS contains an interface to the automatic telex device Telexbox3.

The proposals made by the Environment Institute with respect to harmonising the measurements and reporting of environmental radioactivity in the EC Member States resulted in the creation of two working groups the first dealing with data transfer between the Member States and the CEC and with the establishment of a dense monitoring network, the second one with the establishment of a sparse network of sensitive monitoring stations and with the organisation of intercomparison exercises of measuring techniques of environmental radioactivity.
The intercomparison exercises are performed in collaboration with the International Reference Centre of the World Health Organisation (WHO) at Le Vesinet (F).

The first intercomparison exercise was on the determination of ^{3}H, ^{90}Sr and ^{137}Cs in ground water samples. The results of all laboratories, but one were within 10%.

ECVAM

In October 1991, the Commission decided to set up the European Centre for the Validation of Alternative Methods (ECVAM) as a Special Unit within the Joint Research Centre's Institute for the Environment (Communication from the Commission to the Council and the European Parliament, SEC 91, 1991).

ECVAM will be required to provide support for the Commission in relation to Directive 86/609/EEC, and detailed information for the European Parliament and Member States with regard to the scientific development, pre-validation, formal validation and regulatory acceptability of non-animal tests.

ECVAM will also coordinate and facilitate validation activities at the European level, through the design and management of international interlaboratory studies, though internal pre-validation studies aimed at protocol development and assessment, and through the collection, processing and analysis of *in vitro* , QSAR and *in vivo* data.

ECVAM will collaborate with other organizations, not only by participating into actual validation studies, but also in the selection of appropriate sets of test chemicals for use in blind trials. ECVAM will then purchase,code and supply chemicals to the laboratories participating in such blind trials, and will then receive and analyse the results obtained.

In performing its tasks, ECVAM is assisted by a Scientific Advisory Committee in which are represented all concerned parties, namely: the Member States (12 members), industries (ECETOC, COLIPA, EFPIA, 3 members), the *in vitro* toxicology (ERGATT, 1 member) and animal welfare organizations (EUROGROUP, 2 members).

During 1992, efforts were devoted to the adaptation of present laboratory facilities for *in vitro* toxicology studies and to the planning for a new building specifically designed for ECVAM activities which will be available in the spring of 1994 *(Fig. 2.14)*.

Meetings were organized within the framework of the scientific support to DG XI on the coordination and evaluation of activities aimed at the development and validation of *in vitro* alternative test systems for acute systemic toxicity, the use of cultured hepatocytes, and the establishment of a data base on *in vitro* alternative tests.

OTHER MISCELLANEOUS CONTRIBUTIONS

DG I (External Relations)

The support to the agreement between DG I and IAEA concerning the the technical assistance to the Agency's PACT program has been continued.
Training in various disciplines and/or techniques available at the Environment Institute has been provided to scientists from various developing countries special emphasis being given to analytical and structural chemistry.

DG III (Internal Market and Industrial Affairs)

The scientific and technical support provided to DG III has concerned two major items, i.e.:

- the European Pharmaceutical Databank (ECPHIN);
- chemical products and food.

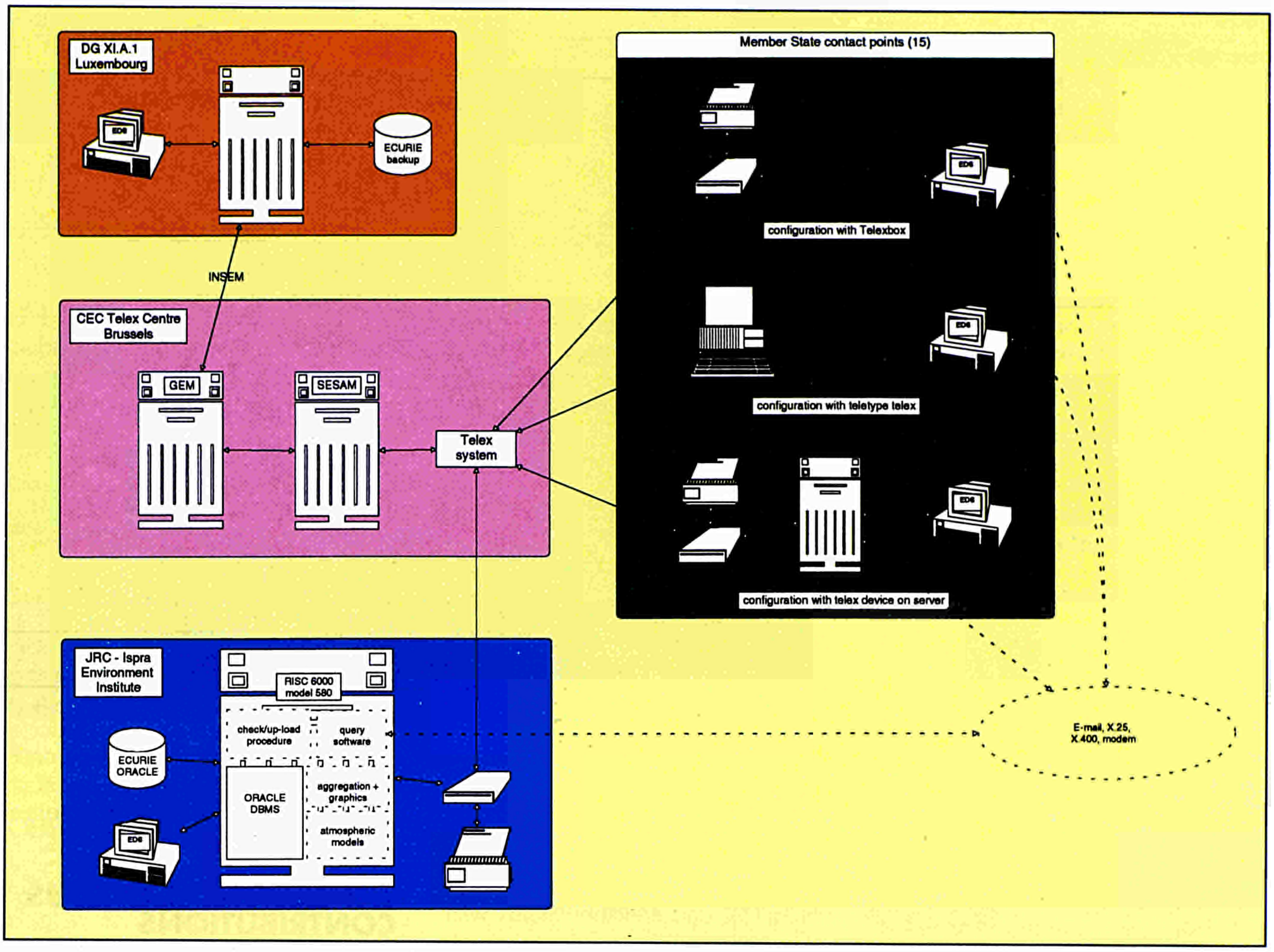


Fig. 2.13 Schematic overview of the ECURIE system (dashed lines indicate future developments).

ECPHIN

The creation of a databank on pharmaceutical products was requested by the European Parliament as an additional measure of market transparency in response to a Commission proposal for a Council Directive related to market transparency regulating prices of pharmaceutics for humans.

After completion of the first phase of data collection from competent authorities of the Member States and storage of the data in the ECPHIN databank, a second development phase was initiated and carried out in 1992. Following the third experts meeting in June 1992, the second phase extended the list of data elements to complete the storage of economic and administrative information and facilitate more comprehensive search possibilities.

Data were received from 14 national authorities in the 12 Member States for phase II. Out of these 14 data sets, 9 were in the agreed format and 5 in either a different format or a format that proved difficult to read. Notwithstanding these complications, all data were loaded in time to give a demonstration on occasion of the 4th progress meeting with national authorities which was held in November 1992 at Ispra.

In addition, data transparency was increased by the definition of equivalences between national terms for pharmaceutical form and route of administration as well as the incorporation of CAS number and ATC codes.

The third phase in 1993 foresees a further expansion of data elements to comprise remaining SPC (Summary Product Characteristics) elements as well as increases transparency of data through modification of the display program and the definition of equivalencies of remaining terms.

Access to the Production Databank is availavble to DG III and other Commission Services and Regulatory Authorities in Member States. This

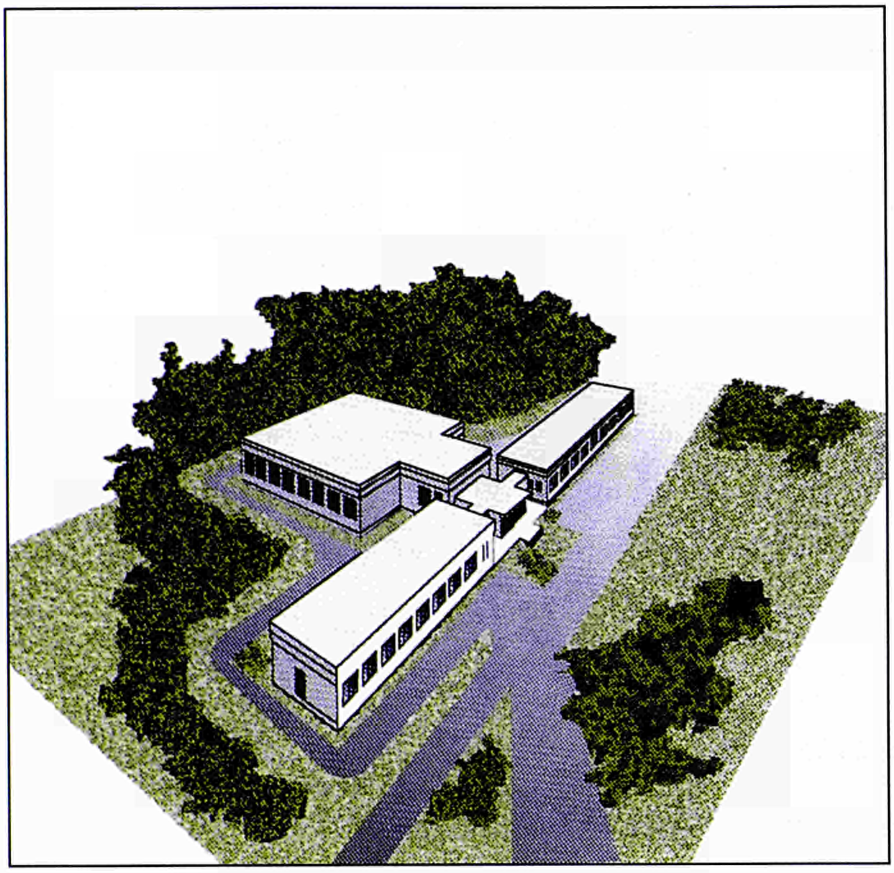


Fig. 2.14 The new ECVAM building planned to be ready on the Spring 1994.

access was available from February 1992 with an interruption during the period July - September due to the transfer of ECPHIN from the AMDAHL mainframe to a UNIX environment

Chemicals products and food

Worth of mentioning the following activities:

- Participation in the activities of the CEN/TC 38/ Working Group 12 "Creosote" charged to develop official standards for methods of sampling and analysis of creosote and creosoted timber. The proposed methods to determine the contents of benzo-α-pyrene and water extractable phenols of creosote must be tested and evaluated by round robin experiments, in which JRC laboratory takes actively part.

- Participation to EC meetings in Brussels concerning the regulation and control of foods. Following the official requests of the Member States concerning the needs of comparison or harmonisation of the various analytical controls for foods (especially after the free circulation of goods in EC), first attempts in collecting data of the existing analytical methods have been undertaken. Some examples for honey and sulphites control have been shown to the responsibles of DG. III.

DG VI (Agriculture)

The agreement between DG VI and Environment Institute concerns two main activities related to dairy products and wine.

In the field of dairy products the following major achievements are worth of mentioning:

- In the study of the EC reference method for detecting cow's milk in ewe's and goat's cheeses some positive interference have been observed for some types of ewe cheeses. The effect of the proteolysis during the ripening of these cheeses seems to be responsible of the interference.

The same method is also applied to goat's cheeses. Research is focused on other proteins present in ewe's and goat's cheeses to be easier separated and detected by isoelectric focusing electrophoresis.

- As far as it concerns the research of the chemical indicators for the evaluation of heat treatment of milk by the determination of the denatured whey proteins (α-lactoalbumine and β-lactoglobuline), seven collaborative trials regarding sterilised and "ultra high temperature" milks have been launched by the ad hoc EC working Group. These determination associated with the lactulose control can differentiate these kinds of milk; investigations on pasteurised milk are under way.

- Within the framework of the determination of the triglyceride profiles in butter, vegetable and animal fats and their mixture in view of detecting non milk fat in butter, following the evaluation of the recommended GC method, the control of some butter of known origin has started. Preliminary attempts to implement the collection of these data have ben undertaken.

As far as the wine is concerned scientific support has been given for the application of NMR technique to the control of wine sugaring (chaptalization). This has implied the active participation into EC meetings of national experts.

In addition the validation of national results (10% of 1,200 samples) for the European wine data bank has been performed, as well as the measurement of wine data bank samples for Portugal, Greece and Luxemburg not yet equipped with nuclear magnetic resonance.

Research on the use of NMR to determine the watering of must and wine as well as the determination of the origin-dependent amount of amino acids in wine were slowed down drastically, due to the budgetary difficulties for the installation of a second NMR spectrometer.

NMR-SNIF (site specific natural isotope fractionation) has been applied for the control of wine ethanol to be sold at the Rotterdam spot market.

Lastly, approximately 50-80 data per wine sample of the 1991/1992 harvest have been prepared for imput into the European data bank.

The Environment Institute has participated into two round robin experiments (FDA and EC) to evaluate the analytical procedures for the detection of lead in wine and, as observer, into an ad hoc group for the detection of watering of wine by MS.

DG XIII (Telecommunications, Information Industries and Innovation)

The agreement between the Environment Institute and DG XIII was focused on the technologies for the abatemenet of sulphur dioxide and of nitrogen oxides from flue gas.

The Ispra Mark 13B Flue Gas Desulphurization Process

A new flue gas desulphurisation process,denominated Ispra Mark 13B, was invented and developed. It is based on the same reaction as the Ispra Mark 13A process, i.e. the conversion of sulphur dioxide with bromine to hydrogen bromide and sulphuric acid:

$$Br_2+SO_2+2H_2O \rightarrow 2HBr+H_2SO_4 \quad (1)$$

The desulphurization is carried out by contacting the waste gases with an aqueous solution, containing both acids and a small quantity of bromine. During the reaction, the two acids are produced simultaneously in the solution.

Subsequently, the acids are separated from the solution in such a way that hydrogen bromide is evaporated, brought in contact with an excess of oxygen (air) and catalytically oxidized to bromine:

$$4HBr+O_2 \rightarrow 2Br_2+2H_2O \quad (2)$$

In this way, the consumed Br_2 is completely recycled and the overall reaction of the process is the formation of sulphuric acid from sulphur dioxide:

$$2SO_2+2H_2O+O_2 \rightarrow 2H_2SO_4 \quad (3)$$

The new process is very similar to the Ispra Mark 13A process, but avoids the regeneration of bromine by electrolysis of HBr. Earlier cost estimations have shown that for the Ispra Mark 13A process, the electrolyzer represents about 25% of the investment and about 30% of the variable operating costs. Replacing the electrolysis by catalytic oxidation will thus lead to substantial cost savings.

A block diagram of the process is given in *Fig.2.15*. SO_2-containing flue gases are treated with the washing solution in the main reactor, which can be any suitable gas-liquid contacting device. The washing liquid is a ternary aqueous solution, containing about 10 wt % H_2SO_4 and 20 wt % HBr and a small amount of bromine (<0.5 wt %). Sulphur dioxide is absorbed in the solution and reacts immediately in the liquid phase according to reaction (1). The formed sulphuric and hydrobromic acids stay dissolved in the washing solution .

The major part of the washing solution is recirculated over the reactor to ensure a sufficient gas-liquid contact, and a relatively small fraction is removed as a sidestream. This stream has to be separated into its acid components to allow:

a) the removal of the produced sulphuric acid from the process,
b) the re-oxidation into bromine of the hydrogen bromide.

The separation of the solution into its main components is carried out by evaporation. The required energy is partly obtained by the use of the sensible heat of the incoming flue gas (150-200°C) and partly from a separate, external heat source.

During evaporation of the ternary solution, the first product to pass into the vapour phase is water, containing a small amount of HBr (approximately 0.3wt %). When removing the water component from the liquid, the acid concentrations of the liquid phase are proportionally and gradually increasing. The vapour phase continues to consist of practically pure water, as long as the acid concentrations in the liquid remain below 15 wt % H_2SO_4 and 30 wt % HBr. This is the first phase of the separation process.

From this point on, there is a sharp increase in the HBr content of the vapour phase, which finally reaches a composition very near to the HBr/H_2O azeotrope, 47.2 wt% HBr. This generally occurs when the H_2SO_4 concentration in the liquid has reached approximately 30 wt %. During this second phase, HBr and H_2O are evaporating simultaneously, until the liquid phase consists only of sulphuric acid and water. This usually occurs at H_2SO_4 concentrations above 65 wt % .

The aforementioned properties are utilized to split the ternary liquid into three fractions. The first fraction consists of water with a small amount of HBr, the second distillate is a rich HBr/H_2O mixture and the third fraction is the residue, concentrated sulphuric acid. To this end, the evaporation is carried out in two stages.

The first stage consists of the evaporation of about half of the present water and a small fraction of HBr. As a rough approximation, 100 parts of the incoming liquid contain 10 parts of H_2SO_4, 20 parts of HBr and 70 part of H_2O. About 34 parts of H_2O are evaporated, together with 2 parts of HBr. The remaining liquid phase consists of 16 wt% H_2SO_4 and 28 wt % HBr. This first stage uses the sensible heat of the incoming flue gases for the energy of evaporation. Control of the flow rate and temperature of the gas stream limits

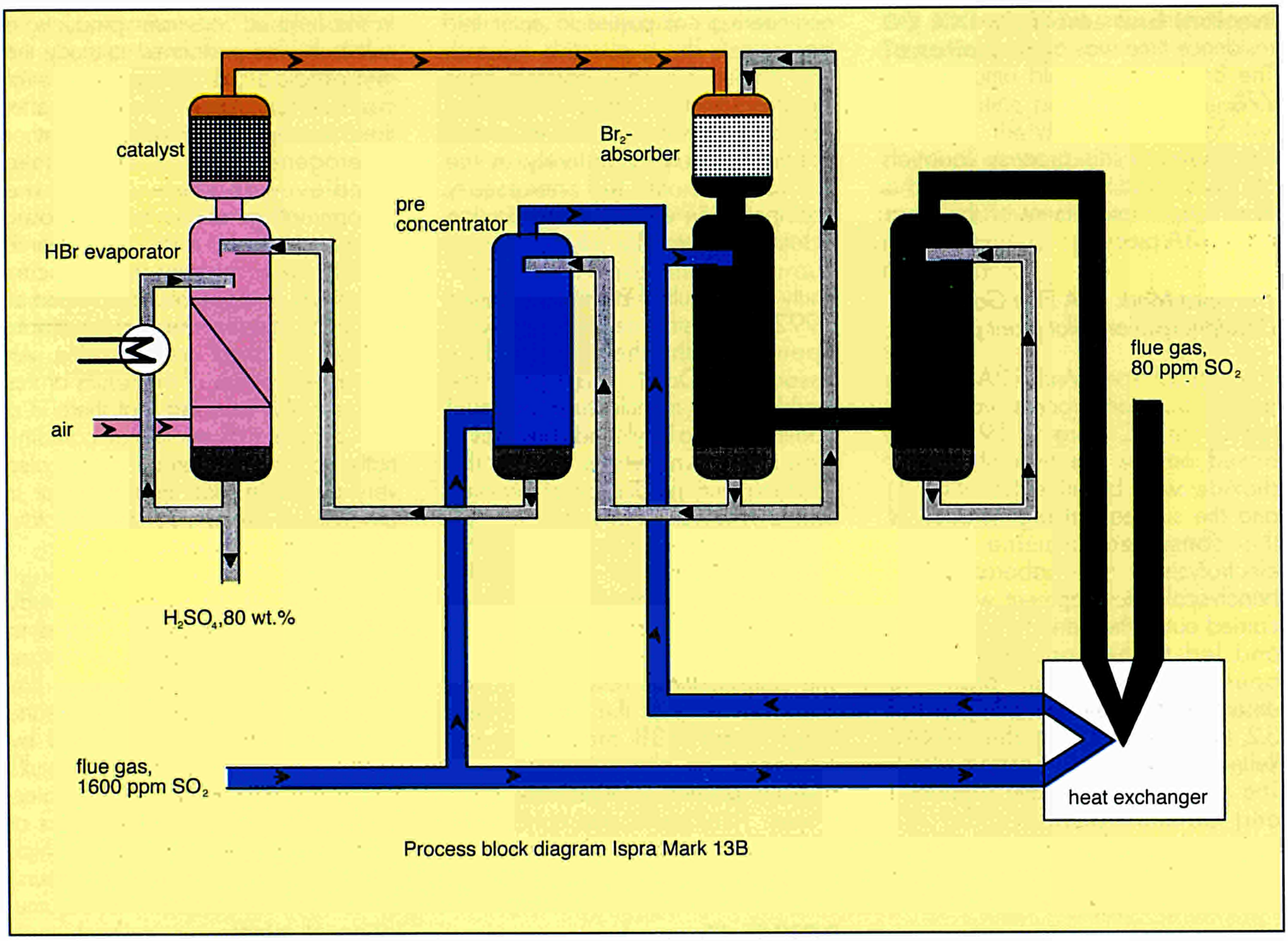


Fig. 2.15 Block diagram of the Ispra Mark 13B flue gas desulphurisation process.

the evaporation to the point where only a relatively small quantity of HBr is present in the vapour phase.

The second stage consists of the evaporation of the remaining water and HBr. The energy needed for the evaporation is furnished by an external heat transfer medium. A small stream of air, containing the required quantity of oxygen needed for the oxidation, is added, so that the resulting vapour phase can directly be passed to the catalytic converter, where reaction (2) takes place.

The catalytic oxidation of HBr occurs at temperatures of 200 to 400°C. A large number of suitable catalysts are commercially available. Required residence times are in the order of 2 to 10 seconds, depending on the reaction temperature. Under these conditions, high conversions (>90%) of HBr into Br_2 can be obtained .

The bromine containing vapour is quenched in the recycling reactor liquid to dissolve the condensable constituents (water and bromine). This yields a solution containing sufficient bromine to be used as the washing solution for the removal of sulphur dioxide from the waste gases in the reactor and completes the recycle operation.

The process has been tried out, first by means of laboratory measurements, followed by experiments in the modified bench-scale plant of the Ispra Mark 13A process. This plant is entirely constructed from technical glass elements and contains all elements of the industrial process. Some results of a typical run are given below.

The plant is fed by flue gas, produced by the combustion of heavy fuel oil in a small burner system. A stream of 8.5 $m^3 \cdot h^{-1}$ was desulphurized from 4.17 $g \cdot m^{-3}$ to 0.63 $g \cdot m^{-3}$, a desulphurization yield of 85%.

The reactor liquid contained 17 wt% HBr and 8 wt % H_2SO_4, and was concentrated to about 28 wt% HBr and 14 wt% H_2SO_4 in the pre-concentrator. Sulphuric acid was produced at the bottom of the HBr-evaporator at a rate of 48 $g \cdot h^{-1}$; the acid had a concentration of 98 wt %, it is limpid and only slightly yellowish.

A commercial catalyst, CuO/Cr_2O_3 on an alumina support was used for the HBr oxidation. The reaction temperature was 400°C and the gas residence time was about 2 seconds. The Br_2 formation yield amounted to 77%.

The results of this process variation are considered very promising and a significant improvement of the Ispra Mark 13A process.

The Ispra Mark 13A Flue Gas Desulphurisation pilot plant project

The original Ispra Mark 13A flue gas desulphurization process was invented at the JRC Ispra in 1980. It is based on the reaction of sulphur dioxide with bromine (reaction 1) and the subsequent regeneration of the consumed bromine by the electrolysis of HBr. Laboratory and bench-scale development work was carried out in the period 1980-1988 and led to the construction and operation of pilot plant to desulphurise a flue gas throughput of 32 000 $Nm^3 \cdot h^{-1}$ at the SARAS Refinery at Sarroch in Sardinia (Italy). The project is financially supported and administratively under the responsability of DG XIII Luxemburg. JRC Ispra bears the responsability for the technical supervision.

The pilot plant in Sarroch was completed during the year 1988 and operation started in the first months of 1989. The plant was in full operation for more than 2000 hours. Several problems with components were encountered. Solving of the problems caused considerable delays in the execution of the experimental programme and caused financial and organizational problems to the main contractor, Ferlini Technology. During 1990, work on the pilot plant project was temporarily suspended and new organization forms for the project were sought.

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

The Commission organised during 1991 an exploration of the willingness of one or more leading European chemical or process engineering companies to enter into the project. This explorative research was carried out on a contract basis by the London based firm Pax Technology Transfer. The JRC Ispra collaborated very actively in the preparation of the necessary documentation and the dissemination of technical details.

Partly as a result of this action, during 1992, promising negotiations were opened with the British firm Associated Octel. This firm is the world-leading manufacturer of petrol additives (Tetra-Ethyl-Lead) and has a significant knowhow about the handling and production of bromine and electrolysis. However, in June 1992 Octel communicated the Commission not to progress the opportunity to complete the Ispra Mark 13A pilot plant project.

The Commission is now investigating if the presence of the new process Ispra Mark 13B may have an influence on the wilingness of potential partners to participate in the project. Final results and conclusions of the affair have to be obtained during 1993.

DGXVII (Energy)

As for the past, the Institute has provided technical assistance to DG XVII-DC in the form of analytical activity on nuclear material samples taken by the safeguards inspectors in different LEU fabrication plants.
In the course of the year some 100 UO_2 pellet and powder samples have been analyzed for U concentration and for 238/235 and 238/234 isotopic ratios.

SPC (Consumer Policy Service)

During 1992 the most part of the activity concerning the agreement between CCR and SPC has been transferred to IRMM (Geel). The activity of the JRC Ispra has been focused on:
- microbiological control of cosmetics, food and water;
- study of analytical methodologies for detecting hazardous α-quartz and amphibole minerals in cosmetic talc.

In the field of cosmetic products, a research was performed to study the microbiological characteristics of cosmetic formulates, before and after their use by the consumer. A rather heterogeneous series of cosmetic samples was subjected to the determination of the total aerobic microbial counts, and to the search and isolation of microbial species potentially pathogenic for man and of bacterial species which are reliable indexes of faecal contamination. An overall evaluation of the results of this first research revealed that there is a real problem of microbial contamination of cosmetic products. It is also very probable that, as the sector is progressively regulated, this problem will be better defined.

As far as food is concerned, a study was carried out on the mycotoxins, a category of toxic substances whose importance in food microbiology has only been recognised in recent years. The mycotoxins, are produced by moulds which can grow on foodstuffs which are extremely poor in water, and are usually immune from risks of contamination by other germs which are pathogenic for man (e.g.: flours, cereals and oil seeds). The accumulation of micotoxins in the human organism has pathogenic or carcinogenic effects. The results obtained in first research, carried out on products intended for animal consumption, revealed a general mean value of positive samples of c.a. 37 %. These products constitute vehicles which can favour the accumulation of mycotoxins in the animals themselves and consequently in man, through foods such as milk and meat.

A study concerning the control of waters intended for human consumption, in connection with Directive EEC 80/778 which lays down the requirements for the quality of these waters, has been performed.

Within the framework of the analytical methodologies for cosmetic talc, several cosmetic talc samples from different countries (Italy, The Nederlands, England, Switzerland) have been collected.

X-ray fluorescence has been used for the quantitative determination of the metals Ti, Fe, Pb, Zn, Cu, Ni, Mn and Cr, while X-ray diffraction served to determine the structural composition.

Quantitative methods have been developed for measuring the amount of chlorite (clinochlore) and of α-quartz and amphibole mineral tremolite (asbestos) which represent an hazard for human health.

Preliminary analysis of cosmetic talc samples did not show detectable amount of tremolite.

Taking into account the calculated limit of detection of the method, the concentration of the sought mineral in all samples is lower than 0,05%.

In the beginning of 1993, using light microscopy, the talc samples will be checked for asbestiform fibrous amphibole minerals.

DG XXI (Customs and Indirect Taxation)

The scientific and technical support concerns the determination of the chemical or structural composition of unknown or not well defined products in view of their characterization and classification for applying the correct customs tarifs.

THE ENVIRONMENT INSTITUTE

3. Exploratory Research

Four projects have been developed in this area, i.e.:

- Absolute Chemical Analysis by Laser Methods;
- Laboratory for Separation Sciences;
- DNA Adducts;
- Aerosol Tracer Technique for Long Range Application;

the first two of them having been funded by the common pot created for the purpose by the JRC Institutes.

The project "Absolute Chemical Analysis by Laser Methods" does represent the evolution of a former exploratory research project, and is aimed at the theoretical evaluation of an absolute methodology of analysis of both atomic and molecular species through the combination of laser sources and spectroscopic techniques.

"Laboratory for Separation Sciences" is the continuation of a project started in 1990 with the wide ranging scope of promoting and stimulating methodological research in support to environmental and food and drug analysis. Focus is placed on hydrophilic substances, biopolimers and biological compounds as well as on sensitive analytical methodologies for environmental pollution monitoring.

Also the project "DNA Adducts" had been started in 1990. The project is aimed at developing methods to detect DNA adducts in microsamples of genomic DNA for direct evidence of exposure to environmental genotoxins.

Through the fourth project "Aerosol Tracer Technique for Long Range Application" it is intended to develop an aerosol tracer technique in view of studying the deposition interaction between aerosols, gases and clouds during transport over 1,000 km.

ABSOLUTE CHEMICAL ANALYSIS BY LASER METHODS

The objective of this work, which has still to be completed, is to evaluate theoretically an absolute methodology of analysis of atomic and molecular species based upon the use of lasers and spectroscopic techniques, in particular fluorescence and ionization.

In spectrochemical analysis, the functional dependence of the variable C (the concentration) upon a given physical parameter X (the signal) has the form X=f(C). If a theoretical expression is known for the function f(C) that is reliable enough to allow a direct calculation of the concentration from a single measurement, in absolute units, of the physical quantity represented by X, then one can speak of an "absolute method of analysis". The idea of challenging laser-based methods, and in particular laser-induced fluorescence, to reach the above goal is justified for the following reasons:

1) laser-based diagnostic methods developed in the past years have led to a much improved understanding of the dynamics of the interaction between the laser radiation and the atomic or molecular system; 2) the analytical sensitivity of laser methods has reached, for atomic species, the parts per quadrillion level; and finally 3) it is extremely difficult, if not impossible, to prepare standard solutions at these low levels.

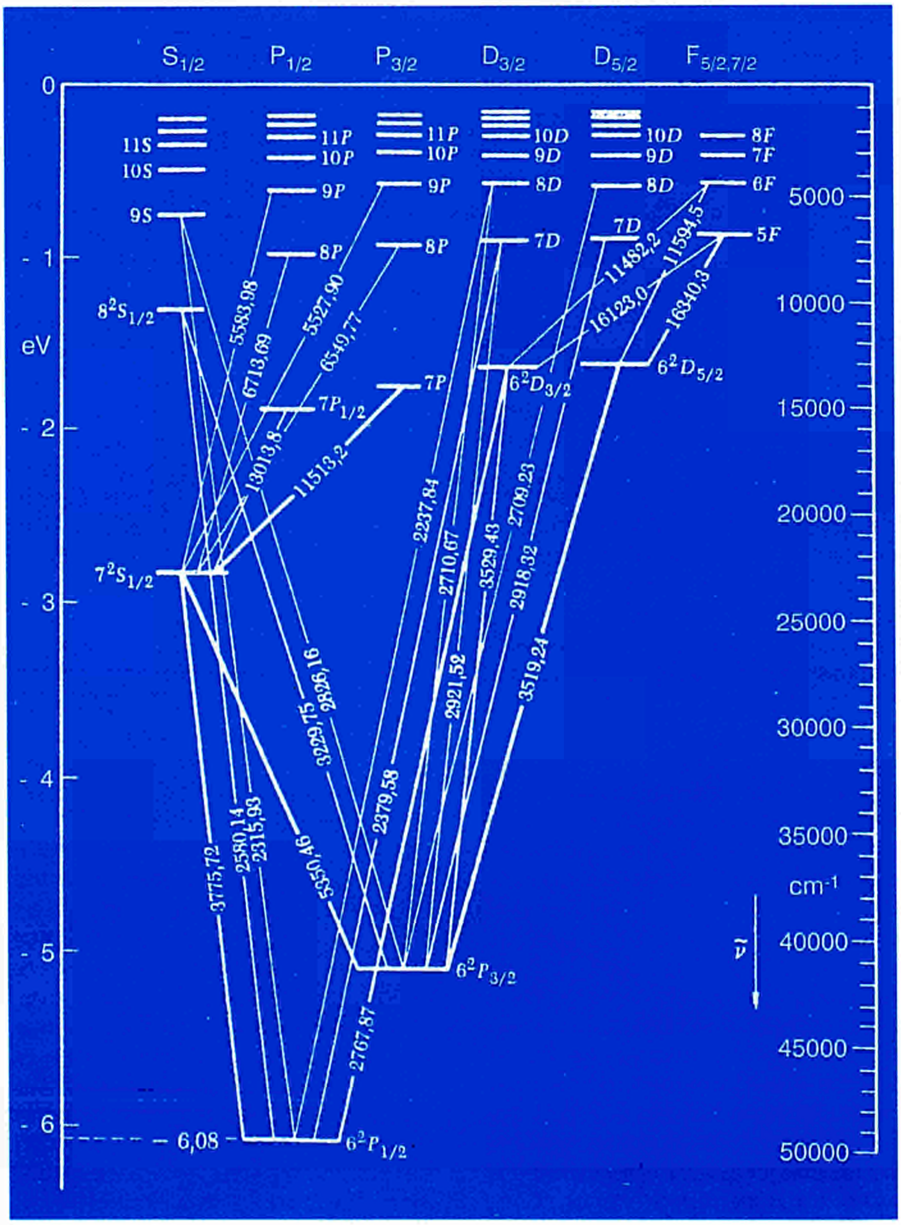


Fig.3.1 *Energy level diagram for the Thallium atom.*

It is clear that, in order to exploit the idea practically, an expression must first be derived for the signal (photon or ions) resulting from the interaction with the laser radiation. This can be done if the atomic system and the laser beam are both fully characterized. Secondly, the overall optical and electronic detection chain needs to be calibrated and finally, an accurate methodology for background correction is needed.

Two test elements were chosen, namely Thallium and Gold. For thallium, only one laser is necessary, since single step excitation can be performed and fluorescence observed from the same excited level or from a nearby level. For gold, a double-resonance excitation scheme is used in which two lasers, spatially and temporally coincident on the sample, excite the atom to a high lying level, while fluorescence is observed in the low ultraviolet region.

The energy level diagram for thallium is shown in *Fig.3.1*.Two excitation / fluorescence processes can be used, namely excitation at 377.572 nm and detection at 535.046 nm or excitation at 276.787 nm and detection at 351.924 nm. In both cases, a three level scheme is adopted for the theoretical modeling of the interaction. However, in order to make a quantitative comparison between the fluorescence signal and the total number of atoms, it is necessary to consider that severe losses of fluorescing atoms may occur due to collisional ionization (which follows laser excitation) and accumulation into the final level reached by the fluorescence radiation ($^2P_{3/2}$) which has a metastable character.

An elegant way to estimate directly the relevance of the above processes is to temporally resolve the fluorescence waveform *during the laser pulse*. To show this, *Fig.3.2* illustrates the different meaning associated to the lifetime (or decay time) of level 2, when this is measured *after* or *during* the laser excitation. If the pulse is long enough (10-20 ns), the decay in the signal observed when the exciting pulse is still on reflects the losses suffered by the population of level 2 towards the ionization continuum and the metastable traps.

Fig.3.3 shows the experimental data obtained with a fast detector (0.2 ns risetime) and a fast (2GHz) digitizing scope for thallium atoms in an argon plasma. The laser excitation was set at 377.572 nm and the fluorescence was monitored at 535.046 nm. The laser power was amply sufficient to optically saturate the transition. A particular outcome seen in this Figure is that, due to these strong saturation effects, enough fluorescence signal persists even when the laser pulse is practically terminated. This allows to evaluate *both decay times* shown in *Fig.3.2*.

In the case of gold, a two-step excitation scheme is used, as illustrated in *Fig.3.4*. In both schemes shown, the two lasers excite the atoms from the ground state to a level which is close to the ionization continuum (approximately 1.5 eV below it), and from which collisional ionization is expected to occur at a significant rate. In addition, collisional transfer (indicated by the double arrows in *Fig.3.4*) from this level to the fluorescing level is necessary in order to measure the radiation at 201.200 nm. It is worth noting that, at such low wavelength, the furnace emission is negligible and a high Signal-to-Noise ratio is obtained. Again, time -resolved information is necessary here in order to quantify the efficiency of the ionization losses and of the collisional transfer.
The performances of our apparatus in resolving temporal differences in the low nanosecond range, such as those expected to occur for collisional transfers between nearby levels, were tested. *Fig.3.5* reports two waveforms due to resonance fluorescence and thermally-assisted fluorescence of thallium in an argon plasma. In the last process, collisions have to transfer the atoms excited by the laser to the fluorescing level, which lies more than 1 eV above the excited level. The difference in the *rise time* of the two curves is indeed perfectly observable.

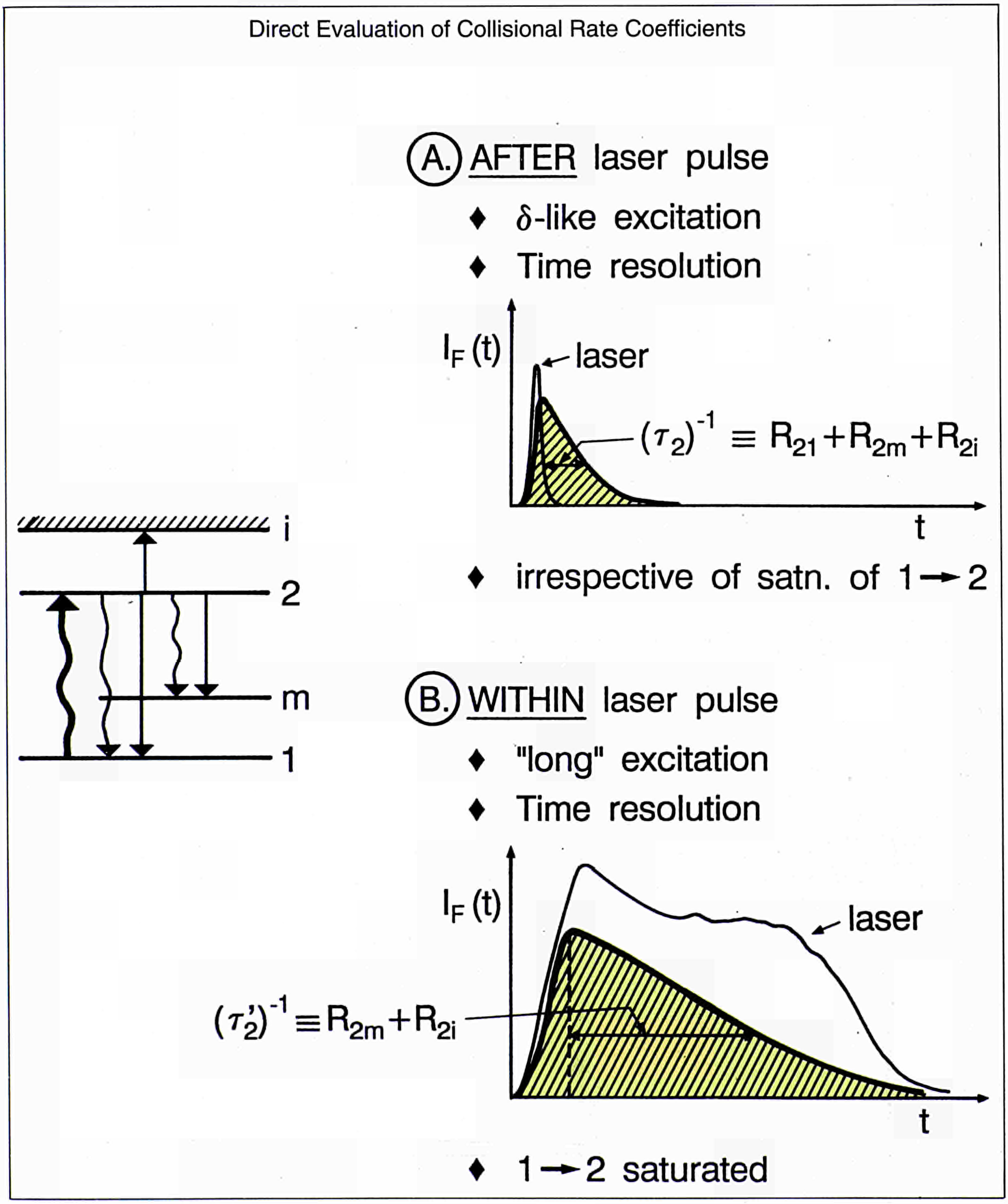
These measurements, which are still in progress in our laboratory, need to be performed in the graphite furnace.

LABORATORY FOR SEPARATION SCIENCES

The application of crossflow membrane techniques in the treatment of wastewaters

Membrane processes as an alternative technique for wastewater treatment allow not only to reject unfriendly liquids for the environment but also to recover products and energy which can be reused in the process or in other applications.
In our case a pilot plant was planned in order to allow the application of various crossflow membrane techniques in the treatment of different types of wastewaters; it combines eight tubular modules and a spiral membrane module.
The tubular group can be equipped with all types of 1.5 m length membranes. At present are installed eight membranes of polivinylidenefluoride (PVDF) with a minimum molecular weight retention of 100,000 dalton and a total active area of 0.9704 m^2.
The spiral group is prepared for working with all kinds of 4" spiral wounded membranes. In this case two different types of membranes are under study: a polysulfone membrane and a composite polyamide membrane. The former has a minimum molecular weight retention of 60,000 dalton and a total active area of 6.5 m^2 and the latter a 15,000 dalton minimum molecular weight retention with an active area of 8.7 m^2.

The plant has been delivered in November 1991 and since than tests on membrane characterization were run regarding the determination of membrane fluxes (pure water permeability tests, (PWP)) and separation characteristics (cut-off tests).
The results obtained for the PWP tests are the following: 0.141 m^3.m^{-2}h^{-1}bar^{-1} (tubular); 0.091 m^3.m^{-2}h^{-1}bar^{-1} (polysulfone); and 0.023 m^3.m^{-2}h^{-1}bar^{-1} (polyamide). These values will be a reference to estimate the state of the membranes and must be



Direct Evaluation of Collisional Rate Coefficients

(A.) AFTER laser pulse

- ♦ δ-like excitation
- ♦ Time resolution
- ♦ irrespective of satn. of 1 → 2

(B.) WITHIN laser pulse

- ♦ "long" excitation
- ♦ Time resolution
- ♦ 1 → 2 saturated

Fig.3.2 Simplified scheme showing the different outcome of time-resolving the fluorescence waveform after *and* within *the exciting laser pulse. In the former case, saturation of the transition is not necessary.*

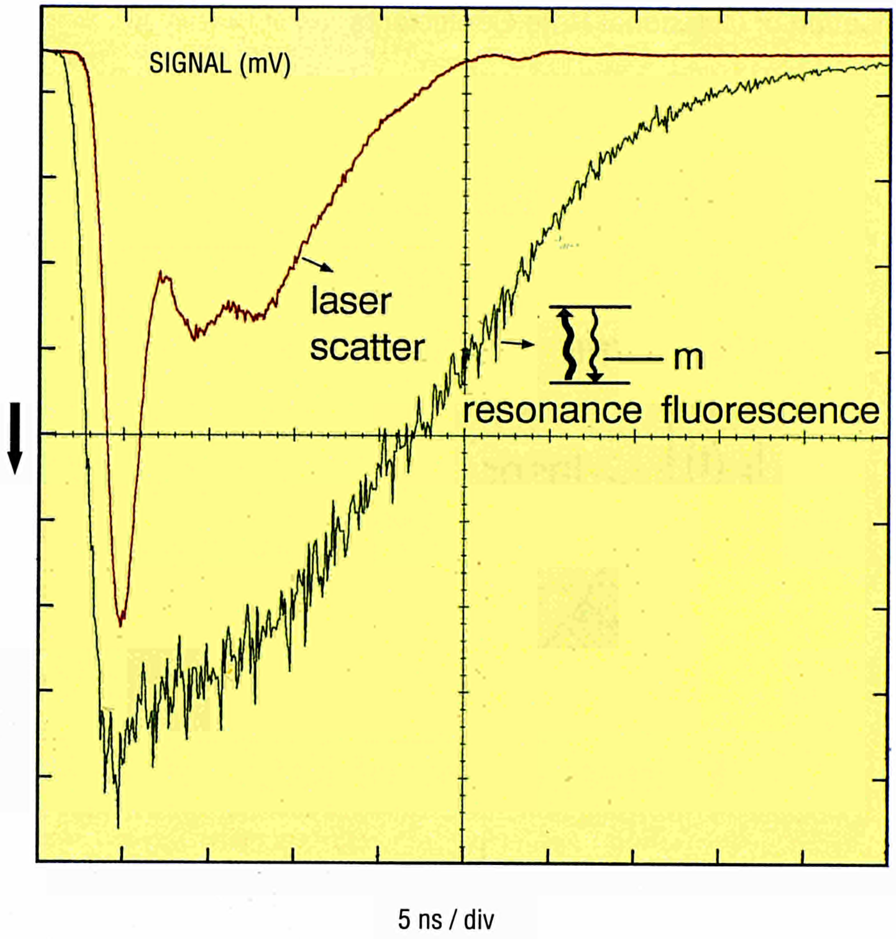


Fig.3.3 Experimental waveforms reproducing the scattered laser radiation and the resonance fluorescence signals for Thallium atoms in an inductively-coupled Argon plasma. Waveforms obtained with a fast microchannel plate photomultiplier.

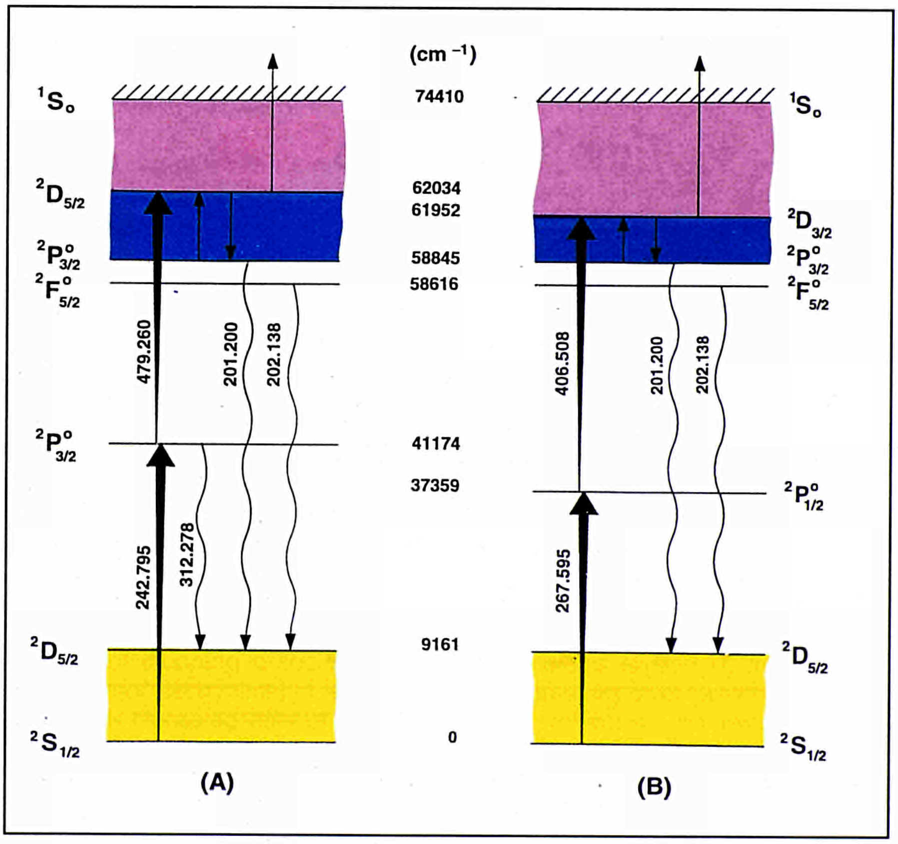


Fig.3.4 Simplified energy level diagram for the Gold atom. In the scheme (A), one single laser, tuned at 242.795 nm can be used to excite the fluorescence which is measured at 312.278 nm. In the scheme (B), only two-step exitation is possible, the fluorescence being observed at 201.200 nm.

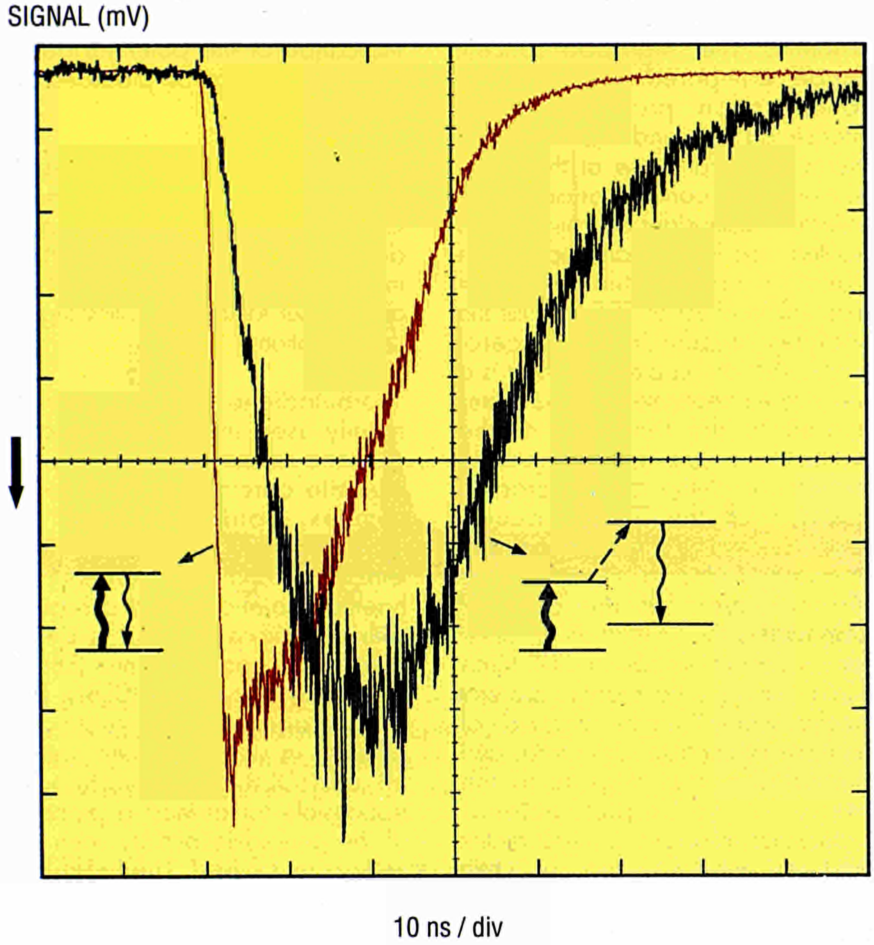


Fig.3.5 Experimental waveforms for the resonance fluorescence and thermally assisted fluorescence signal for Thallium atoms in an inductively coupled plasma. The time lag observed reflects the collisional population of the fluorescence level, as indicated in the insert.

measured between tests. Whenever there is a permeate flux drop, membranes must be cleaned until the initial water fluxes are reached again.

The cut-off is defined as that molecular weight which is 90-95% rejected by the membrane, and the observed rejection coefficient (R) of a solute is defined by the equation:

$$R = 1 - C_{perm}/C_{feed}$$

where C is the concentration of the solute on the feed side and on the permeate side of the membrane.

The tubular membranes showed a rejection coefficient of 80% for a 100 ppm solution of polyvinylalcohol (PVA) Av.Mol.Wt. 30,000-70,000 in the following operating conditions: P = 1.5 bar, T = 25°C, Flux = 3 $m^3 \cdot h^{-1}$. During these tests it was verified a severe decrease of 85% of the initial PWP. These very low pure water permeate fluxes (0.021 $m^3 \cdot m^{-2} h^{-1} bar^{-1}$) can be due to membrane fouling caused by PVA solutions and also to iron hydroxide compounds present in the water used for plant cleanings. According to data found in the literature metal hydroxides (Fe, Mn, Al) may cause a rapid and severe damage of membranes.

A cleaning cycle was run until the initial pure water permeate fluxes were reached again. This operation took more than a week and the water fluxes although higher were very unstable.

The spiral polyamide membrane showed a rejection coefficient of 72% of a 100 ppm solution of PVA 30,000-70,000 Av. Mol. Wt. in the following operating conditions: P = 1.5 bar, T 25°C, Flux = 2.4 $m^3 \cdot h^{-1}$. Also during these tests membrane were very prone to fouling.

In October 1992 a COMETT II Course entitled: "Advanced Separation Technology for Industrial Waste Minimisation: Environmental and Analytical Aspects" was organized at Ispra. During this course technological treatment for different categories of wastewaters were presented by major experts through case studies: Landfill Leachates, Pulp and Paper Industry, Textile, Agro-food and Food Industries, Tanneries and Metal Finishing Industry.

Advanced Separation Techniques

A Capillary Electrophoresis (CE) method was developed to evaluate the possibility of its use for separation, quantitation and further identification of normal and modified nucleosides and nucleotides 3'monophosphates. The advantages afforded by CE include multiple separation modes, high resolution, rapid separation times, and possibility of automation. Micellar Electrokinetic Capillary Chromatography (MECC) separations with a Beckman P/ACE System 2,100 of normal and some modified nucleic acid bases, including deoxy- and ribonucleosides, and deoxynucleotides 5' and 3' monophosphates were achieved. Together nucleosides and nucleotides are a mixture of neutral and charged species, thus the mechanism of their separation is a combination of both electrophoretic migration and partitioning. An interesting result was the deoxyribonucleotides separation from the ribonucleosides and the nucleotides. This cannot be achieved in most chromatographic systems. Substituted nucleotides elute after their unmodified correspondent as substitution decreases their polarity and thus increases their partition in sodium dodecylsulphate (SDS) micelles. As adduct standards are not widely available for the development of analytical methodology, fine tuning of the CE conditions are required for each future system studied. This also requires the availability of synthetic DNA-carcinogen adduct standards representative of different chemical classes.

Capillary Zone Electrophoresis (CZE) has been used for micropreparative applications and the collected fractions have been in some cases characterized and identified by FAB mass spectrometry. After a MECC separation of DNA adducts, micellar separated fractions were collected for preliminary off-line tests. Fractions from multiple runs had to be pooled because of small-diameter capillaries which are limiting the amount of collected material (e.g. sub-picomoles of material). Automated multiple collection of fractions involves optimization of the separation i.e., good retention time repeatability, maximum resolution of the component (s) to be purified from the remaining species at the desired loading levels. Separation conditions (buffer composition, concentration, and pH, capillary treatments, temperature and operating conditions) were previously evaluated for their influence on the retention times, resolution and efficiency on the separation of standard deoxynucleosides and deoxynucleotides 3'-monophosphates. The choice of the 50 mm capillary diameter was based on the resolution required and the high reproducibility of the migration times (<1% RSD) that permits collection of repeated separations into the same set of vials with no cross contamination of adjacent peaks. After the micropreparative sequence completion, the pooled fractions were reinjected to quantify the recovery. The quantitation of each fraction was evaluated either by the external standard or the internal standard method. The recovery values were always >75%.

The fractions collected were then analyzed by FAB-MS. The spectra were generated from the 5 micro-litre collected fractions dissolved in 10 micro-litres of pure glycerol with a VG 70 SEQ high resolution magnetic sector instrument in an EBqQ configuration. A Xenon FAB-gun operated at an accelerating voltage of 8 kV was used in all experiments. The analysis posed, however, several problems. The high SDS concentration, compared to the analyte concentration, produced a very intense background signal with a strong chemical noise at the lower masses. The concentration of the collected nucleosides and nucleotides resulted too low for an appreciable signal, probably due to an ion suppression effect of SDS against the analytes present in the glycerol matrix. The ion suppression effect is a well studied phenomenon. This seems related to the tendency of the hydrophilic compounds to migrate to the interior of the sample droplet, (away from the liquid/vacuum interface) while the hydrophobic compounds tend to migrate to the surface layers of the droplet, suppressing the ionization of other compounds. In our opinion SDS forms a layer on the surface of the glycerol droplet, suppressing the ionization of the more hydrophilic nucleosides and nucleotides, that migrate to the interior of the droplet. Indeed, nucleosides in a pure glycerol matrix produced good FAB spectra, while fractions with SDS, showed no signal even for the glycerol matrix. It seems that these fractions cannot be directly analyzed in FAB-MS mode, without an intermediate step capable to reduce drastically the concentration of SDS. This may, however, have the disadvantage to lead in sample loss and/or eventual modification. We expect an improvement by using a dynamic FAB system, i.e. continuous flow FAB, coupled to a tandem mass-spectrometer.

Moreover, separations of these compounds in Free Zone Electrophoresis were studied with different capillaries and good resolutions for the nucleotides and most of the nucleosides were obtained. This will allow MS analysis avoiding the problem of the presence of SDS in the collected fractions.

DNA ADDUCTS

The formation of DNA Adducts after exposure to genotoxic chemicals is a primary event in cancer initiation. The measurement of carcinogen-DNA adducts can provide both a direct indication of exposure and an early indication of the potential genetic effects which may be produced by a carcinogen.

In collaboration with the University of Swansea (UK), Department of Human Genetoxicology, studies in the detection of DNA adducts in microsamples of human DNA were carried out taking the following into consideration.

1.3-Butadiene (BUT), a chemical mainly used in the production of synthetic rubber, which is a potent multisite carcinogen in mice. In humans, epidemiological data showed an increase in lymphomas, leukaemias and other cancers of the haematopoietic system associated with BUT exposure. BUT is metabolized to 1.2-epoxy-3-butene (EB) and 1.2:3.4-diepoxybutane (DEB). These are mutagenic and genotoxic in different *in vivo* or *in vitro* systems. EB and DEB are thought to be responsible for at least a proportion of the genotoxic activity seen after exposure to BUT.The increased susceptibility of mice, compared to rats, has been attributed to a different metabolism, resulting in the accumulation of the active epoxide intermediates in this species.

Main interest has been focused on investigating DNA alkylation following exposure to DEB, especially in relation to the development of a method for human biomonitoring. Following the reaction of dAMP and poly (dA-dT) with DEB and subsequent HPLC, a major adenine adduct has been identified (see *Fig. 3.6*) and a HPLC/32P-postlabelling (32PPL) method for its detection in DNA samples has been developed . This method and the use of synthetic DEB-dAMP as a reference compound for the optimization of the procedure, permitted the detection of the modified adenine in calf thymus DNA and DNA from treated CHO cells. After phosphorylation and two-dimensional separation, the synthetic standard and the adduct from calf thymus DNA were resolved into two components, probably two isomers of the adduct. The stability of the adduct, the amount formed and its labelling efficiency suggest it will be a suitable indicator of BUT exposure. In addition, with the HPLC conditions used the adduct elutes before the normal nucleotides, thus eliminating cross-contamination for the 32P-postlabelling procedure.

In DNA from CHO cells only one spot, corresponding to the first component of the adduct, was detected on the TLC plate after HPLC and 32PPL. This may be due to a different accessibility of DNA when packaged as chromatin, leading to the formation of only one isomer of the DEB-adenine derivative or to a differential repair of the isomers. Studies on DNA damage and repair following exposure of rodents cells and their mutants defective in DNA excision repair are being carried out to establish whether this lesion persists long enough to be of use as a biomarker of BUT exposure. *In vivo* studies on mice treated with DEB are also underway to investigate the sensitivity of the assay. Biomonitoring studies on humans suspected of exposure to BUT will then proceed.

Studies on the identification of biomarkers in fish were carried out on *in vivo* cat fish and on *in vitro* primary culture of hepatic cells.
In *in vivo* studies, the bile from catfish exposed to 3H-Benzopyrene was collected several days after treatment as analysed by HPLC.

Fig.3.7 shows the identity of HPLC radiochromatogram of 3H BP metabolites and the corresponding fluorescence profile, suggesting that HPLC-Fluorescence analysis of fish bile could be used as biomarker in genetoxicity studies to evaluate exposure to PAH.
In *in vitro* studies, different methods to maintain primary culture of fish hepatocytes were evaluated: in suspension, on microspheres and on monolayers. Several media and attachement factors were investigated. *Fig.3.8* and *Fig.3.9* show the microcarrier and monolayer cultures. *Fig.3.10* shows the corresponding monolayer cultures which were

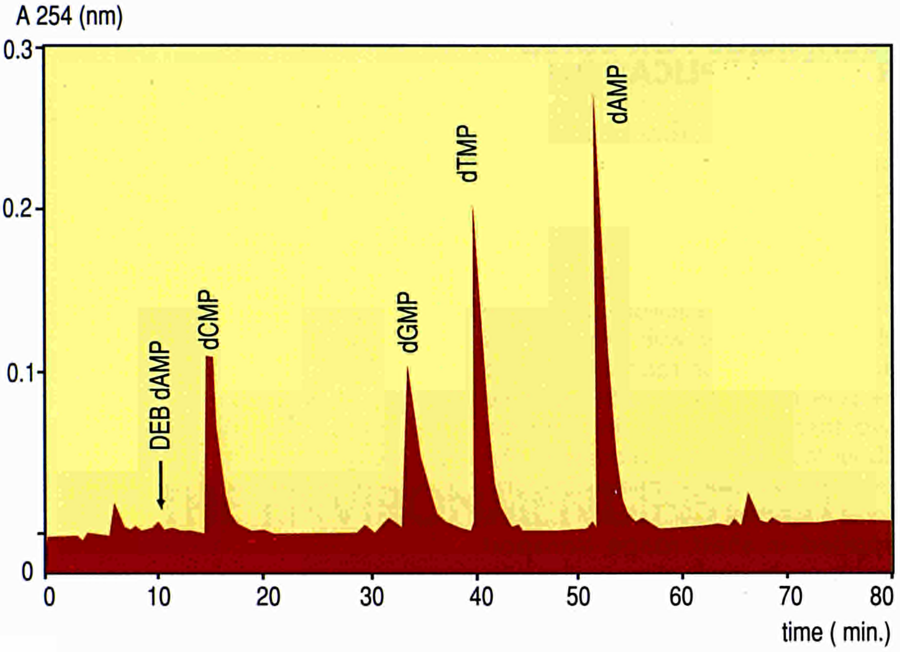


Fig.3.6 *HPLC profile of DEB-treated calf thymus DNA. The location of the adduct is shown. the column was a Spherisorb ODS2 (25 cm x 4.6 mm) ad the eluent 0.1M triethylammonium acetate pH 7; 1% methanol for 20 min; the methanol was increased to 10% in 30 min.*

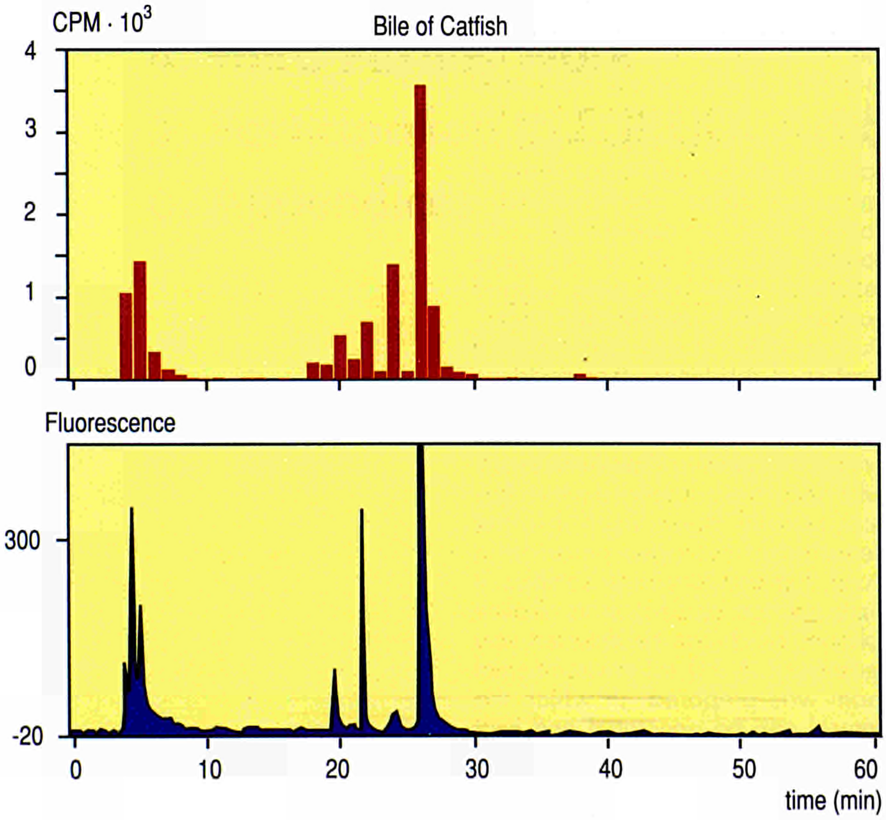


Fig.3.7 *HPLC separation (above) and fluorescence detection (below) of bile from catfish exposed to 3H-Benzopirene.*

evaluated for their vitality by the Neutral Red Uptake method.

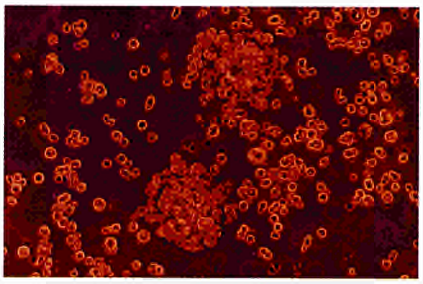


Fig.3.8 Primary culture of catfish hepatocytes on microcarriers.

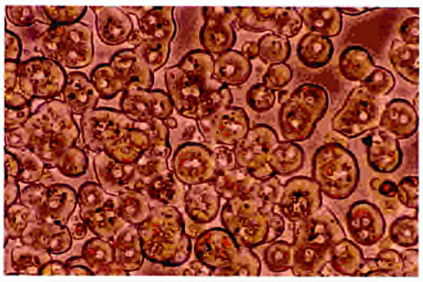


Fig.3.9 Monolayer primary culture of catfish hepatocytes.

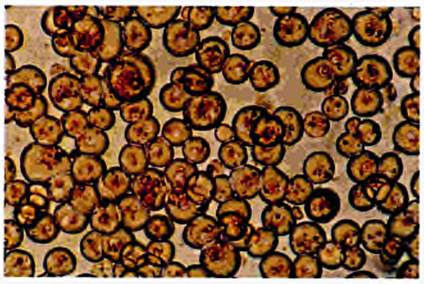


Fig.3.10 Neutral Red Uptake Assay on catfish hepatocytes.

AEROSOL TRACER TECHNIQUE FOR LONG RANGE APPLICATION

Inert perfluorocarbon tracers are presently being used by the Atmospheric Physics Unit for studying transport of air masses up to 1,000 - 2,000 km. Such tracers do not deposit or do not react in the atmosphere. The simultaneous release of an inert tracer with a tracer that does deposit or reacts, and the measurement of the ratio between the two tracers can give information about the deposition process or the reactivity of the atmosphere along the tracer trajectory. This idea has been applied in short range transport problems. Its application on the long range requires the identication of an appropriate tracer.

One way of producing an aerosol tracer is to tag the ambient aerosol itself, e.g. by condensing some tracer material onto the particles. This however would mean processing millions of cubic meters of ambient air (containing the particles), because the ambient aerosol is so dilute and the tracer should not change the properties of the aerosol. The current idea, therefore, is to simulate the ambient aerosol by nebulizing a salt solution, preferably a solution of ammonium sulfate, which is a major component of atmospheric aerosols, containing a small amount of a tracer substance, thus producing tagged particles in the submicron size range.

During 1992 the screening of a number of substances that could be used as a tracer has been started. The most promising idea is the use of luminol or another chemiluminescent substance as a tracer. Luminol has successfully been used for the detection of hydrogen peroxide in cloud, fog and rain water samples. It emits light on oxidization in alkaline solution, which can be detected very sensitively. A 70 m^3 environmental room was prepared, in which the aerosol can be generated and kept for several days, in order to perform the necessary tests on detectability, chemical degradation etc. of the luminol-ammonium sulphate mixture.

THE ENVIRONMENT INSTITUTE

Executive Summary

1. Specific Research Programme
2. Scientific-Technical Support to Community Policies
3. Exploratory Research

4. Third Parties Work

5. Participation to EUREKA Actions
6. Appendices

4. Third Parties Work

This section summarizes the most significant work carried out in 1992 under contract with third parties from which the Institute has earned some 1200 KECUs.
The contracts have concerned the areas for which the Institute possesses particular know-how or facilities or equipments. As the consequence most of the executed work has dealt with issues in the area of Air Pollution, Environmental Chemicals, Water Quality, Analytical Services.
A brief description of only the most significant contracts is given in the following.

Air Pollution

Within the framework of the ongoing contract with the Regione Lombardia (1990-1993), a consultacy support to regional authorities in air quality problems has been provided.
In addition the validation of a representative set of air quality monitoring stations of the regional sub-networks has been performed.
During the second year of activity, the tasks scheduled for this period of the contract were fulfilled, thirthy one stations having been validated.

In the frame of the reasearch contract with CNR/ENEL on tropospheric ozone in the prealpine region, ground-level ozone data recorded at 17 stations distributed at different altitude in the pre-Alpine and Alpine regions in Italy, Switzerland (Ticino) and Austria (Tyrol) have been collected and organized in a database. The ozone patterns at different sites and altitude as well as the observed episodes has been partially analysed. Contacts have been in the meantime established with new groups, active in the field, in Switzerland and Austria in order to expand the database to other sites of the Alpine region. The data acquisition is in progress.

Results of the studies on the nighttime degradation of biogenically emitted compounds, with special relevance to mechanisms responsible for the tropospheric ozone budget, were pursued, as discussed in the pertinent section of the first chapter of this report.

A study contract with the Polish Ministry of the Environment, in the frame of the PHARE project of the CEC has been signed in February 1992. This contract was been focused on the evaluation of the transboundary transport of air pollution (SO$_2$ and NO$_2$) from Czechoslovakia to Poland across the Brama Morawska gate. An experimental campaign took place in March April in Upper Silesia (Katowice and Bielsko-Biala), a region rich of coal mines, cokeries, steel and metallurgical plants and highly polluted. A JRC mobile unit equipped with conventional monitors (SO$_2$, NO$_x$, NO, NO$_2$, CO and aerosols) and optical remote sensors (Cospec V for measurement of vertical burdens of SO$_2$ and NO$_2$) moved up and down parallel to the borderline. Under favourable wind directions, a mean pollution income from Czechoslovakia was evaluated: specific area sources have been identified and their individual emissions have been calculated. The final report, including data treatment and the most significant maps of pollution distribution, was ended in October 1992.

The contract named "Convenzione CNR-ENEL per le ricerche sulla interazione dei sistemi energetici con la salute dell'uomo e con l'ambiente", granted by the Italian electricity board (ENEL), entered its second year of activity. One of the Institute's duties was the development of pollutant dry deposition measuring methods. A new fast-response ozone sonde, specially designed for the determination of ozone deposition, was purchased. A field study was conducted at the Ispra site in July 1992. The results indicate that the deposition of ozone, mainly due to the penetration of that substance into vegetation through the stomata, is close to zero during the night, the stomata being closed, starts up in the morning and decreases in the afternoon. A typical average daytime value is found to be 0.3 $\mathrm{cm \cdot s^{-1}}$.

Tracer experiments have been performed in the framework of REKLIP/MISTRAL project.

REKLIP is a regional climate project agreed as a joint effort of French, German and Suisse public or private research institutions.In the frame of REKLIP the subproject MISTRAL has been conceived which is aiming to develop a real time system for emergency planning and emergency management in case of hazardous emissions of chemicals in the Basel region.A network of about 50 metereological ground stations with high temporal and spatial resolution allows for the calculation of three-dimensional mass consistent wind-fields which are further used for a Monte Carlo simulation of the atmospheric transport from well defined emission sources.For a large set of metereological situations transfer coefficients will be calculated which will give in case of a real hazardous chemical emission a realistict and quick overview of the affected aereas and the time evolution of the expected immissions.
For the validation of this combined historical wind data - modeling approach three tracer experiments in the MISTRAL test area were performed on 21,24 and 26 September 1992. For each experiment 16,2 kg of per-fluorcarbon tracer were released. At 50 different sites ,selected according to predicted wind fields,air samples were collected in six half-hours periods. Moreover two aircrafts collected another 150 samples with special regard to vertical concentration profiles.
Whilst the first experiment was a complete fiasco due to a unfortunate selection of the release point,the other two were fully successful. Tracer concentrations were measured over a range of 4 orders of magnitude showing on a first glance the extreme complexity of the Basel aerea.
Fig.4.1 shows that the surface concentration of tracer has not been influenced by the southerly geostrophic wind but only by the regional easterly wind in the Rhine valley and the thermally induced local winds of the side valleys.At higher altitudes however a combination of geostrophic, regional and local wind systems with turbulent mixing processes leads to a rather

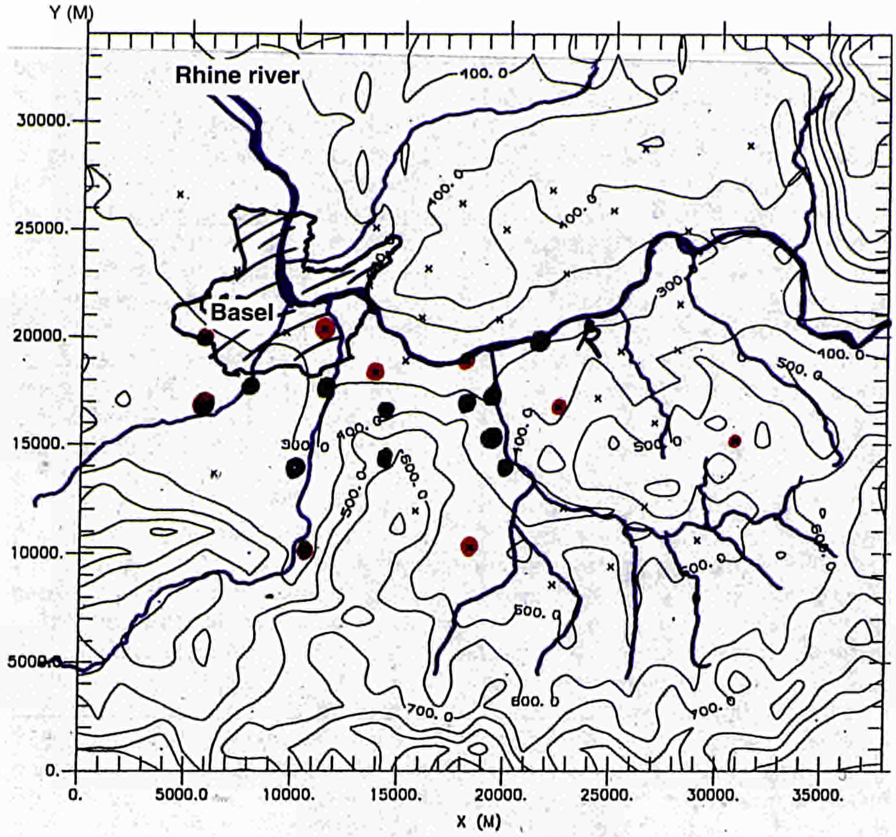


Fig.4.1 REKLIP / MISTRAL TRACER EXPERIMENT. Surface concentrations of tracer 3 hours after release.

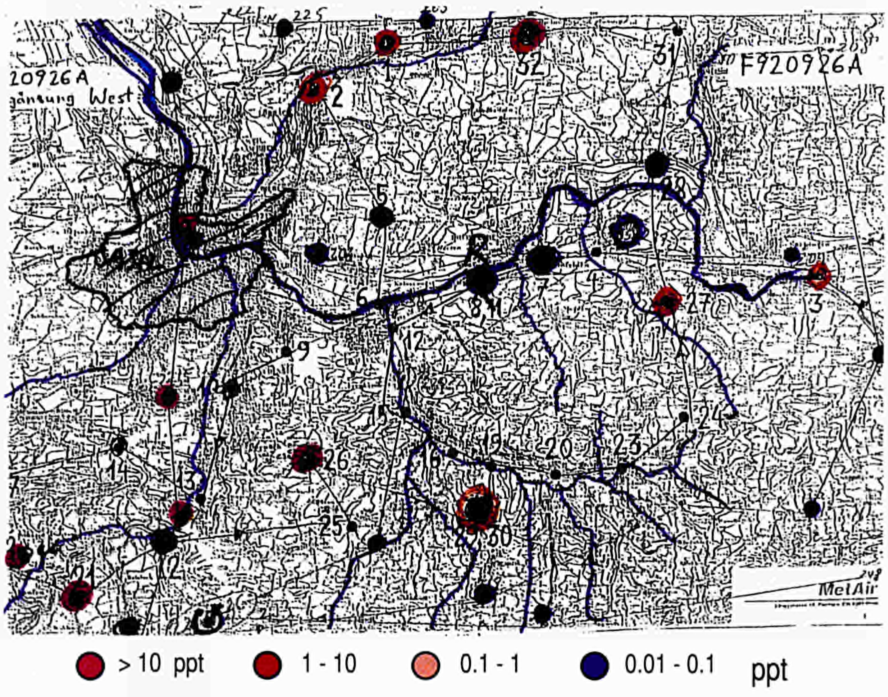


Fig.4.2 REKLIP / MISTRAL TRACER EXPERIMENT. Tracer concentrations at 500 m above ground 3 hours after release.

uniform distribution across the whole test area.(See *Fig.4.2* with aircraft measurements of tracer about 500 m above ground)

Indoor Air Pollution

In 1992 two projects have been partially or entirely supported by third parties:

- Deposition of organic vapours on indoor surface materials. This project has been partially supported by the CNR-ENEL project 'Interactions of energy systems with human health and environment', Rome, Italy, and has been described in the specific Programme section.

- Assessment of indoor pollution by volatile organic compounds (VOC) in buildings of the European Parliament (EP). This activity consisted of two parts:

(a) As a follow-up of previous efforts to assess the possible contribution of VOC to complaints on indoor air quality in EP offices, in collaboration with an external epidemiologist a sample of offices in the building with most complaints (IPE-2 in Strasbourg) was selected and monitored for VOC concentrations. The result of this small scale survey was used to estimate the size of a study which would be needed to detect an association of VOC concentrations and complaints. Because of the low and uniform concentrations detected, an unacceptably large size resulted for this study. The project was therefore abandoned.

(b) The exposure to VOC of employees in four printing shops of the EP was assessed. Short term and weekly average VOC samples have been collected. The results show that the main pollutants are solvents (chlorinated hydrocarbons and alkanes), whose concentrations in no case exceeded the treshold limit value (TLV). However, in a few rooms concentrations are relatively high and suggestions have been made to reduce them.

Water Quality

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

A study was performed to fill the gaps existing in the knowledge of the limnological conditions of four Briantei lakes (Italy).

The research concerned the main ecosystem components:

- physical, chemical and biological characteristics of the lake waters;
- structure of the phytoplanktonic and zooplanktonic populations;
- lake sediments with reference to the content of eutrophicating substances and their bioavailability, heavy metals, organochlorinated compounds and radionuclides.

The picture which emerges from this research shows how the trophic state of lakes Briantei has been heavily modified over the last 20 years and it is such as to classify the evolution of the four lakes from a natural trophic condition of mesotrophy to a situation at the upper limit of eutrophy *(Fig.4.3)*.

The results have been published by the JRC-Ispra in the Series

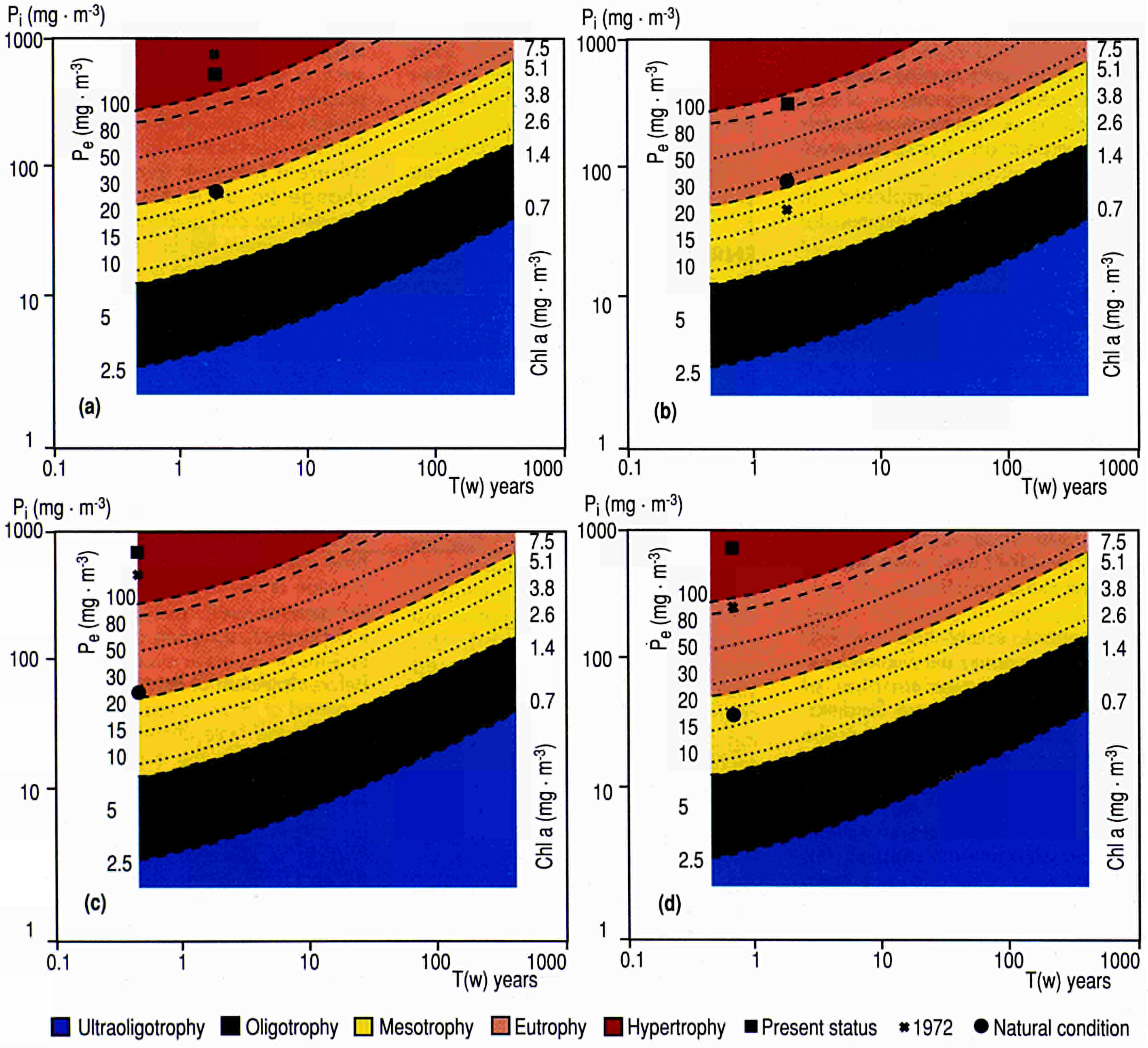


Fig.4.3 *Synthesis diagram correlating the total in-flowing Phosphorus concentration (Pi) with the total Phosphorus (Pe) and Chlorophyll-a concentration, as a function of the theoretical water renewal time, in (a) lake Alserio; (b) lake Annone East; (c) lake Annone West; (d) lake Pusiano.*

"Environment and Quality of Life" as EUR Report in 1992.

A contract has been signed with the Regione Lombardia, in the framework of the cooperation with the Italian Ministry of the Environment, to study the recovery and management of lake Como.
The research concerned :
- assessment of trophic evolution over the last 20 years;
- quantification of internal loadings and their role in determining P levels in lake waters;
- definition of water quality objectives for management purposes;
- application of mathematical models for the prediction of lake recovery times.

The study was completed in December 1992, and submitted for approval to the commitment.

A contract has been signed with the Regione Veneto, in the framework of the cooperation with the Italian Ministry of the Environment, to set up a safeguarding plan of lake Garda.
The study concerned :
- quantification of internal loadings from sediments;
- evolution of P levels in lake waters by models.

The study was completed in December 1992 and submitted for approval to the commitment.

The contract, established in 1990 with Ente Autonomo del Flumendosa, Cagliari, the major supplier of drinking water to Southern Sardinia, and aiming at the evaluation of the concentrations of harmful substances in the top sediment layers of lakes Flumendosa, Mulargia and Simbirizzi, as well as the fluxes of nutrient elements and metals through the sediment-water interface, has been completed.

The joint field study on Lake Stechlin (D), performed in the framework of a cooperation agreement with GSF Neuherberg, has been completed with the analysis of the sediments for DDT, DDE, γ-HCH, dieldrine and the PCB - congeners 28, 52, 101, 153 and 180.
The spatial distribution mapping of these compounds in the lake sediments showed that the PCB's were released by the nuclear power station, while DDT and lindane derive from extended spraying operations in the surrounding forests during the eighties.

A contract has been concluded with Azienda Comasca Servizi Municipalizzati (ACSM), Como, aiming at the inventory-taking of harmful substances, present in the sediments of the southernmost part of Lake Como and the assessment of their fluxes through the sediment-water interface. Sediment sampling has been performed and the elaboration of the spatial distribution maps are currently in progress.

ENRESA

The contract with Empresa Nacional de Residuos Radioactivos S.A. concerns the geochemical investigation carried out both in-situ at El Berrocal uranium mine and at JRC Ispra trought laboratory experiments. The activity has been mainly devoted to the preparation of a second cross-hole tracer test based on critical evaluation of the results of the first trial carried out in Sept.-Oct 91. This first approach must be considered as a preliminary experiment aiming to verify the feasibility of migration test using isotopic tracers (^{79}Br). This verification may be considered successful, but the next phase, aiming to produce significant hydrologic parameters, requires a more sophisticated set-up.
On the basis of the experience gained from this preliminary experiment, a new conceptual design for the next tracer test has been proposed which is expected to fulfill the requirements pointed out during the El Berrocal Project coordination meeting.
The final layout for this new test strongly depends upon the understanding of the permeable fracture geometry, which is not yet well defined in the neighbourhood of borehole n°1. Neither it is known exactly at what depth the fracture intersects the well, nor whether many branches of the same fracture exist which intersect the borehole at different depths.
It has been agreed that British Geological Survey would have taken charge of a characterization test (pressure interference test) aiming to clarify the channelling between the two boreholes.
Waiting for the characterisation results, a preliminary design was proposed, based on the assumption that the two wells are connected by a single fracture or fracture zone, in such a way as only one "double packer" (isolating 2 to 4 metres stretch) may be used in each well. Further information of a possible different fracture geometry may change (to a certain extent) the planned test configuration.
The experiment set up is reported in *Fig.4.4*. The fracture is isolated by a double packer in both wells. The groundwater is pumped continuously from the section between packers in the well S1. The constant flow rate necessary for the test is searched (and mantained) through a discharge valve (1) in a close circuit mounted on the withdrawal well. To the same circuit an automatic sampler is connected (2).This system will allow: a) better control of the withdrawal flow rate from S1, b) the homogenization of the tracer concentration in the arrival well and c) to set up independent sampling and pumping systems on a unique circuit.
Before injection of the tracer solution a period of trials is required to find a discharge rate allowing a steady-state regime for the experiment.This will be indicated by the pressure stabilization between packers in both injection and withdrowal wells. Possibly an automatic system may be set up (3) allowing a direct control on the discharge valve by pressure tranducer (4).
Once equilibrium is reached, the injection is made in well S7 through a second close circuit having a threefold purpose: a)to inject the tracer, b) to homogenize the "source reservoir"and c) to check the tracer concentration in the source by periodic samplings.

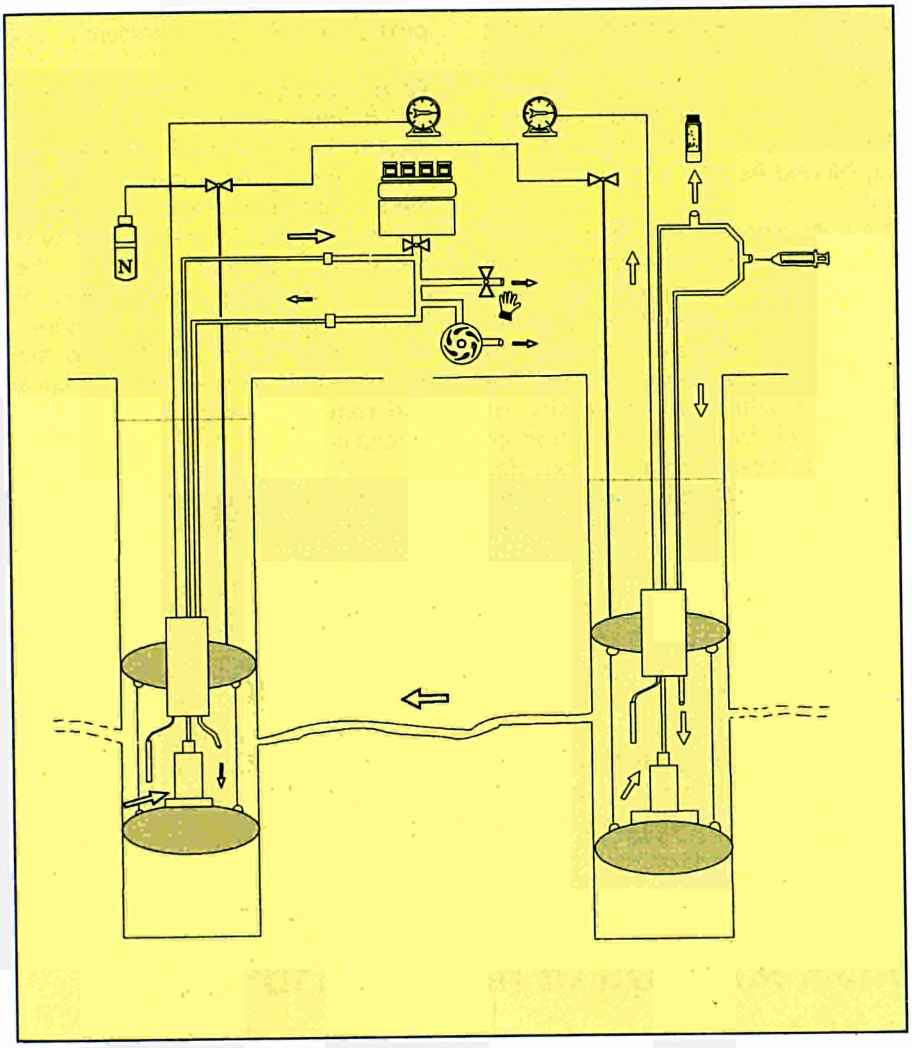


Fig.4.4 Cross-hole migration setup.

Environmental Chemicals

In the frame of the on going contract with the german Ministry of Environment / German Federal Environment Agency, the data collection and evaluation on a second list of high production volume chemicals was continued, focussing on the data files and categories which are covered in the ECDIN data bank.
An interim report was prepared and accepted.

A contract has been established with the italian Electricity Board (ENEL) for the evaluation of the embriotoxicity of NO_2
The effects induced by NO_2 on mouse embryos have been studied in vivo treating pregnant females (CD-1 strain) with atmospheres of air added with NO_2 up to 10 ppm. The procedures of inhalation have been carried out for the first three days of the pregnancy (8 hours·day^{-1}). This period corresponds to the preimplantation phase of the murine embryo development.
The embryocydal effect of the NO_2 has been evaluated by scoring the percentage of the healthy blastocysts that could be recovered from the uteri of the NO_2 treated females in comparison with the control ones that have been exposed to the air only.
Moreover, the potential deleterious effects due to the exposures that were not lethal for the cleavage stages of the murine development, but that could result harmful in the successive stages, have been assessed by growing *in vitro* the blastocysts until the differentiation into ecto- and entoderm layers of their Inner Cell Mass.
Even at the maximal doses of treatments, the formation of the blastocyst and its successive development with the formation and the differentiation of the Inner Cell Mass was not impaired.
The most probable chemical species that originates in the body fluids of the treated mice by exposures to Nitrogen Dioxide, the NO_3 , was used in in vitro experiments in order to evaluate its deleterious properties.
The embryos have been recovered at the 2-cell stage and treated in vitro with $NaNO_3$ up to tens of millimolar concentrations.
As in the case of the in vivo experiments, no effect have been detected neither on the blastocyst formation, nor on the Inner Cell Mass formation and its differentiation.
The levels of NO_2 present in the atmospheres delivered to the mice were up to 20-75 times the average concentrations detectable in an urban area or about 100 times the indoor levels where there are unvented gas combustion appliances (Oxides of Nitrogen. Environmental Health Criteria #4. WHO Geneva, 1977).
From the results here reported, it seems that these concentrations of NO_2 in the air cannot be considered detrimental for the first period of the mouse embryo development.
Although more and specific studies must be carried out in this particular field of the NO_2 toxicology, it is likely that these conclusions could also be valid for the human embryos in the stages of the preimplantation and the first postimplantation development.

Analytical Measurement Quality Control and Measurement Services

The EI received in the last year numerous requests to assist groups of Italian laboratories in their attempts to improve measurement quality. A contract was concluded in 1992 with CNR Rome, which trusted to the EI the analytical quality control management of the Venetian Lagoon Project.
This project foresees, amongst others analytical studies on many chemical parameters in the water, the sediments and biota of the Lagoon by some thirty Italian institutes. Task of the EI was to assure the precision, accuracy and comparability of the analytical data obtained by the different institutes.

The activities in the framework of the contract with Regione Emilia-Romagna (proficiency testing of drinking water laboratories) has been continued. The second interlaboratory comparison showed that laboratories gained sufficient accuracy in several cases (anions, phosphorus, copper, zinc) but there is still need to improve the analysis for NH_4^+, Hg, Cd, Pb, Cr, Ni and As.

The competence of the EI in the field of environmental reference material production prompted national laboratories to request the preparation of candidate reference materials and proficiency testing samples. The contract with the University of Osnabruck for the preparation of 7.000 bottles of cabbage powder has been completed as well as the preparation of 1.000 bottles of mussel tissue for ENEA Casaccia.

Two contracts were concluded with Laboratorio Cantonale di Lugano and CNR Pallanza, for the determination of mercury in 50 fish samples from lake Lugano and in 87 samples from Lake Maggiore respectively. The work was sponsored by the "Commissione Italo-Helvetica per la protezione delle acque comuni".

As a part of the collaboration with the BOREX network (see Annual Report 1991) aimed at detecting solar neutrinos, the need of measuring radiochemical impurities at ultratrace level in the waters was required. *Table 4.1* shows, the values of the g/g concentrations of Th/U in the water of the japanese KAMIOKA detector following the improvements in the detection limits and requirements of the analytical procedure.

A research contract concerning the antimicrobial behaviour of some chemical products has been established with the firm ECOFORM (Milan).

A project to carry out the quality control of all the analytical procedures involved in the italian network rain (RIDEP) has been presented to the Italian Environment Ministry.

SAMPLES	Th	U
Underground water	$2\ (\pm0.2)\cdot10^{-12}$	$765\cdot10^{-12}$
Distilled water	$5.2(\pm0.8)\cdot10^{-12}$	$585\cdot10^{-12}$
Redistilled underground water	$1.5(\pm0.2)\cdot10^{-12}$	$3(\pm0.3)\cdot10^{-13}$
Detector water	$1.5(\pm0.2)\cdot10^{-13}$	$3(\pm0.5)\cdot10^{-13}$
Distilled residual	$3.3(\pm0.5)\cdot10^{-13}$	$3.2(\pm0.05)\cdot10^{-14}$
Redistilled detector water	$1.5(\pm0.05)\cdot10^{-13}$	$9(\pm1)\cdot10^{-14}$
Blank	$1\text{-}3\cdot10^{-14}$	$3\text{-}4\cdot10^{-14}$

Table 4.1 Radiochemical impurities in waters at ultratrace level g · g^{-1}

THE ENVIRONMENT INSTITUTE

5. Participation to EUREKA Actions

The participation of the Environment Institute into EUREKA environmental projects has been continued in 1992.
This has mainly concerned EUROTRAC and EUROENVIRON.
The first is a joint european research effort to investigate the effects of human activities on the complex tropospheric chemistry; the second is a wide-scope project aimed at developing new technologies, processes and/or services all addressed to improve the protection of the environment.
Each of the above projects is subdivided into a series of subprojects dealing with different features of the more general and comprehensive parent project.
The achievements obtained in the course of 1992 for the subprojects EUROTRAC-TRACT, EUROTRAC-LACTOZ, EUROENVIRON - TRACY and EUROENVIRON - MOBILE ANALYTICAL LABORATORY are summarized below.

EUROTRACT/TRACT

The TRACT campaign (Transport over complex terrain) was designed to study the transport, diffusion, chemical transformation and deposition of air pollutants over complex terrain in a mesoscale area. The German "Land" (federal state) of Baden-Wuerttemberg with extension to Alsace and Northern Switzerland, was considered to be an ideal place for such a study, because of its dimensions (tipically mesoscale, i.e. 300 x 300 km approximately), and topography (it includes the mid-altitude mountain ranges of the Black Forest, the Vosges and Schwaebische Alb, reaching 1400 m a.s.l. at its highest top).

The campaign took place from Septemher 9 to 23, 1992, with the participation of a number of research groups from nine European countries, under the coodination of Prof.Fiedler from the Unversity of Karlsruhe. The JRC Environment Institute was present with two of its groups : the JRC atmospheric tracers group and the JRC atmospheric surface layer observation laboratory.

Tracer experiment

In collaboration with the I.M.K. Karlsruhe, A.S.P.A.Strasbourg and the T.U.Braunschweig a meso-scale tracer experiment was performed on September 16,1992 in the aerea extending from Baden-Baden to Offenburg in north-south and from Wasselonne (Alsace) to Freudenstatt across the Hornisgrinde(Top of Northern Black Forest) in west-east direction.
The aim was to check whether

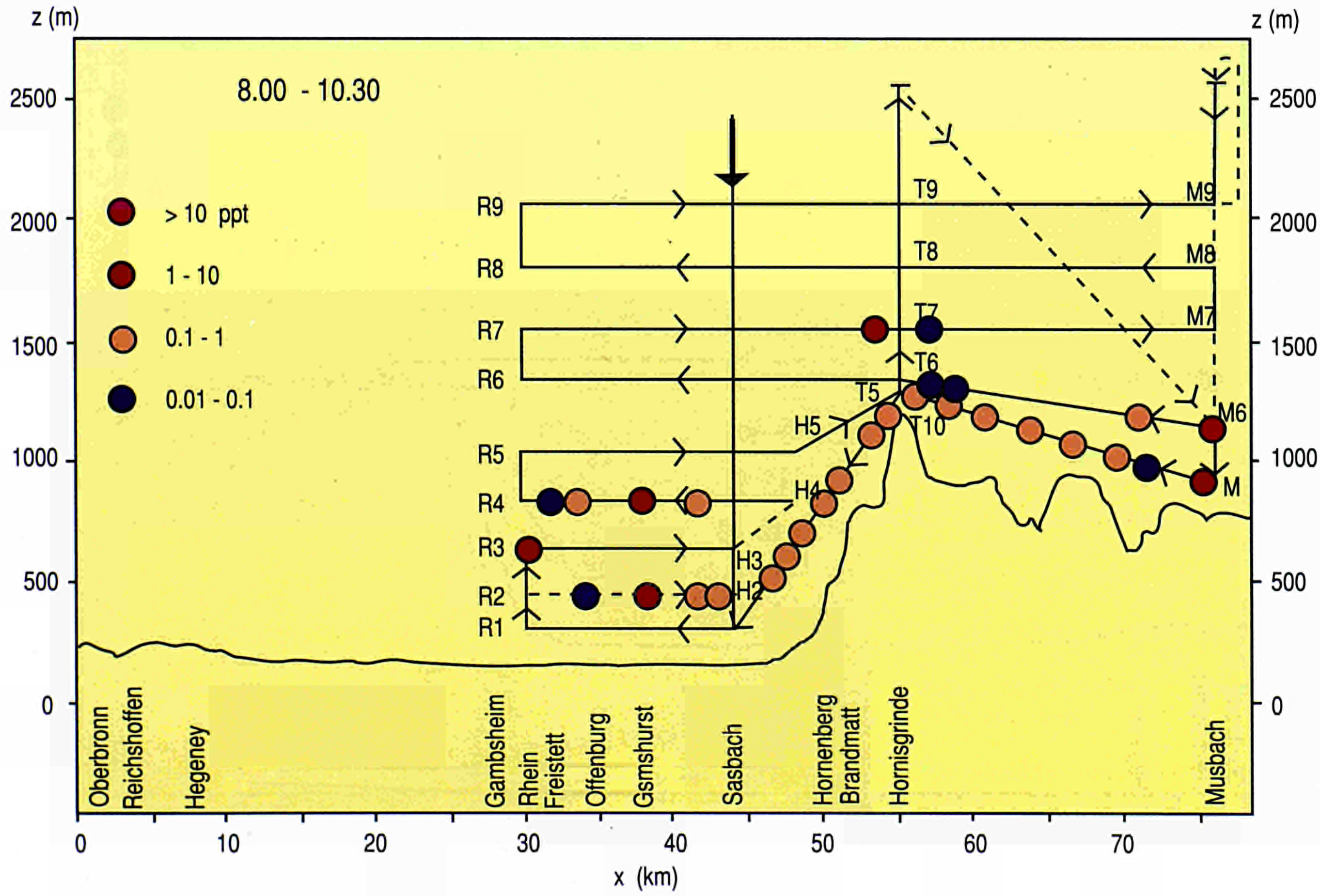


Fig.5.1 Morning flight (8.00 - 10.30 h). Vertical distribution of tracer across Rhine - Valley and Black Forest.

polluted air masses in the Rhine valley can be transported across the ridge of the 1000 m higher mountains from the mixing layer to the free troposphere and this for convective weather conditions with low wind speeds and sufficient sunshine to allow for turbulent vertical mixing.

A network of 20 sampling stations with a total of 28 samplers has been set up.A total of 224 ground samples has been collected with 1/2 h sampling periods.In view of the specific objectives of this campaign great effort was put on air-borne sampling.

The research aircraft of the Braunschweig University was equipped to sample air in 4 l plastic bags with a frequence of about 30 sec to1minute. A total of 700 samples were collected in the course of four flights. At the same time metereological parameters like wind vector,temperature,humidity and ozone mixing ratios were measured.

In *Fig.5.1* to *Fig.5.3* the flight passes are displayed as cross sections from the Rhine over the release point at Sasbach,the top of the Black Forest to Musbach at the eastern edge of the mountains.Besides11 horizontal legs,vertical profiles were flown at three different sites giving in this way a comprehensive picture of the atmospheric structure.

The color coded tracer concentrations show clearly the first conclusions which can be drawn from this experiment: In the morning the vertical dffusion was restricted by the elevated inversion at 1200 m a.s.l..Due to the upslope winds from westerly directions tracer gas has been already transported from the Rhine Valley to the eastern part of the investigation area. At noon and in the later afternoon the tracer field becomes more and more homogeneous and the observed increase of tracer concentration up to 1000 m above the boundary layer verifies the efficiency of mountains in atmospheric handover processes.

Surface layer observations

The JRC atmospheric surface layer observation laboratory is a mobile station designed for the measurement of a variety of turbulent variables characterising the surface layer. The station was located during the campaign at a point called "Klippeneck" (48°6'N, 8°46'E, 985 m a.s.l.), on a high plateau covered with short grass serving as landing area for gliders. The scope of the measurements was twofold:

- to record all kind of turbulent variables characterising the surface layer and necessary for subsequent

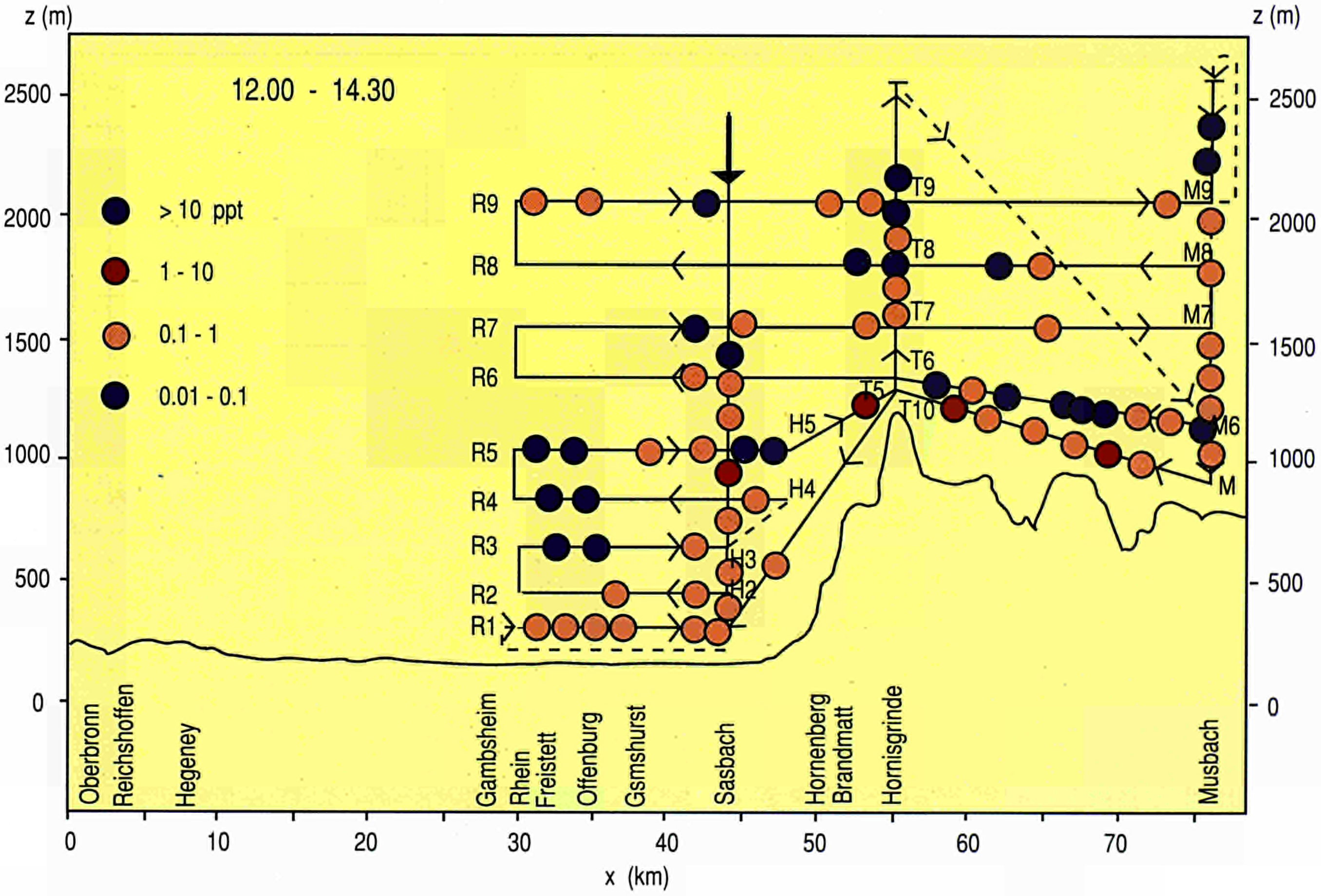


Fig.5.2 *Noon flight (12.00 - 14.30 h). Vertical distribution of tracer across Rhine - Valley and Black Forest.*

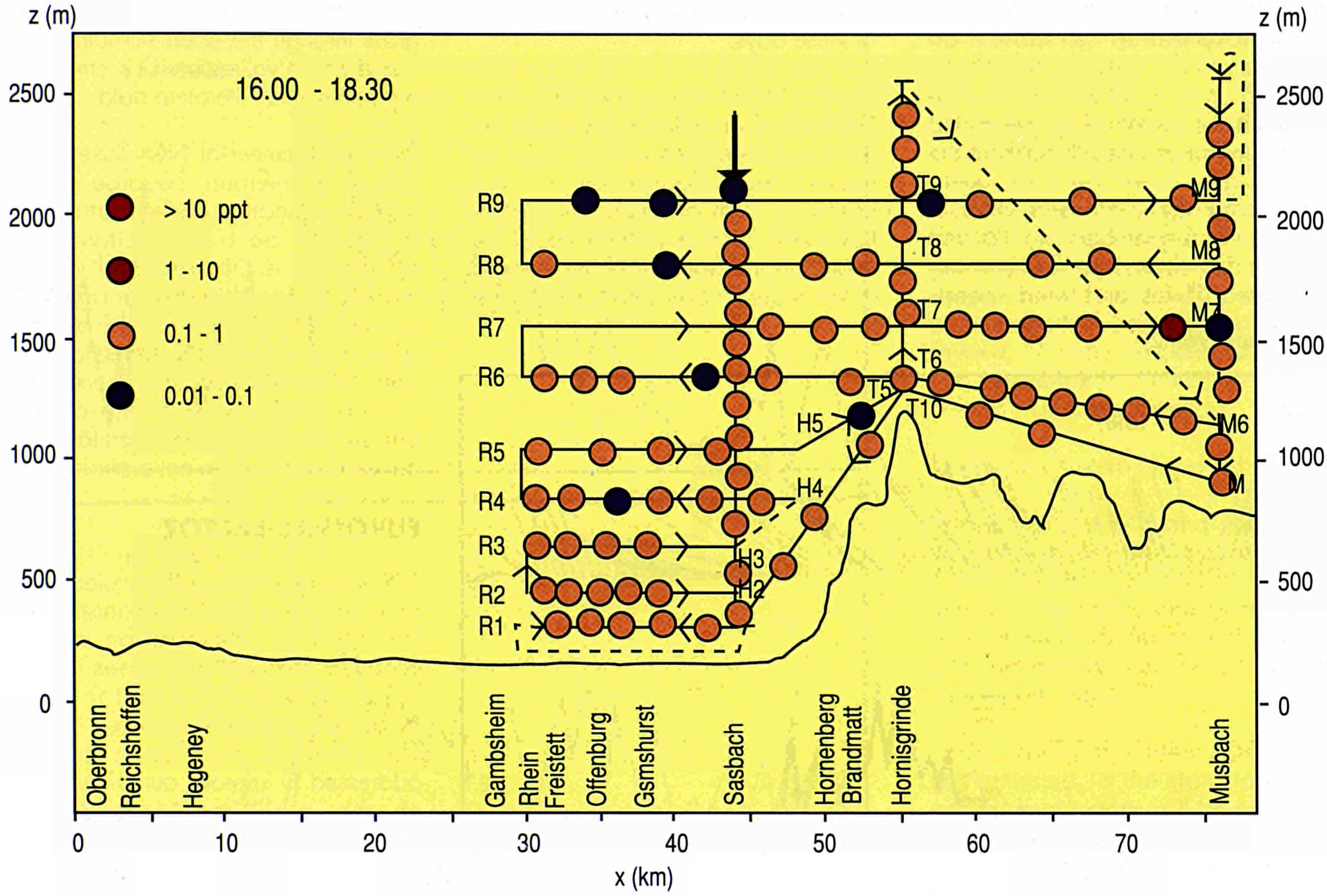


Fig.5.3 Afternoon flight (16.00 - 18.30 h). Vertical distribution of tracer across Rhine - Valley and Black Forest.

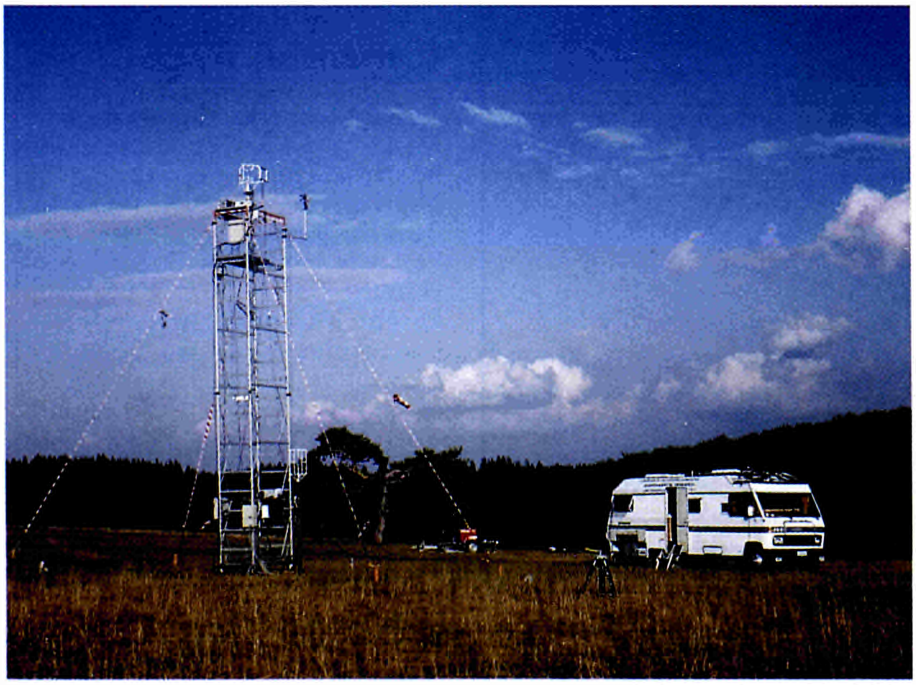


Fig.5.4 General view of the mobile laboratory setup.

modelling work; sensible and latent heat fluxes, stability parameters, etc.;
- to measure dry deposition rates (which was one of the main goals of the campaign).

Two sonic anemometers mounted on a tower at 2 and 8 m above ground level and fast-response sensor for the measurement of humidity, ozone and NO_2 concentrations, mounted at 8 m were employed. Data on temperature, humidity, the three components (E-W, N-S, vertical) of the wind vector, ozone an NO_2 concentrations were recorded.

The sensible and latent heat fluxes obtained were terms of the surface energy balance equation. In order to get the remaining terms, i.e.the net radiative flux and the soil heat flux, a net radiometer placed a 1 m height and four soil temperature probes were operated.

A general view of the mobile laboratory set-up is shown on *Fig.5.4.*

Although the system was measuring on a continuous basis throughout the campaign, three periods were chosen for their intensive measurement, i.e. September 11, 16 and 21. *Fig.5.5* shows the sensible and latent heat fluxes and wind speeds and directions observed during two of these days.

Fig.5.6 shows the ozone deposition velocities. Deposition starts up in the morning, reaches a maximum at noon, and decreases in the afternoon, with an important scatter, however. Such a pattern could be related to the aperture of the stomata of the vegetal cover (short grass), and due to the pollutant penetration in the grass through the open stomata. Typical daytime values are 0.3 $\mathrm{cm \cdot s^{-1}}$, in agreement with literature data.

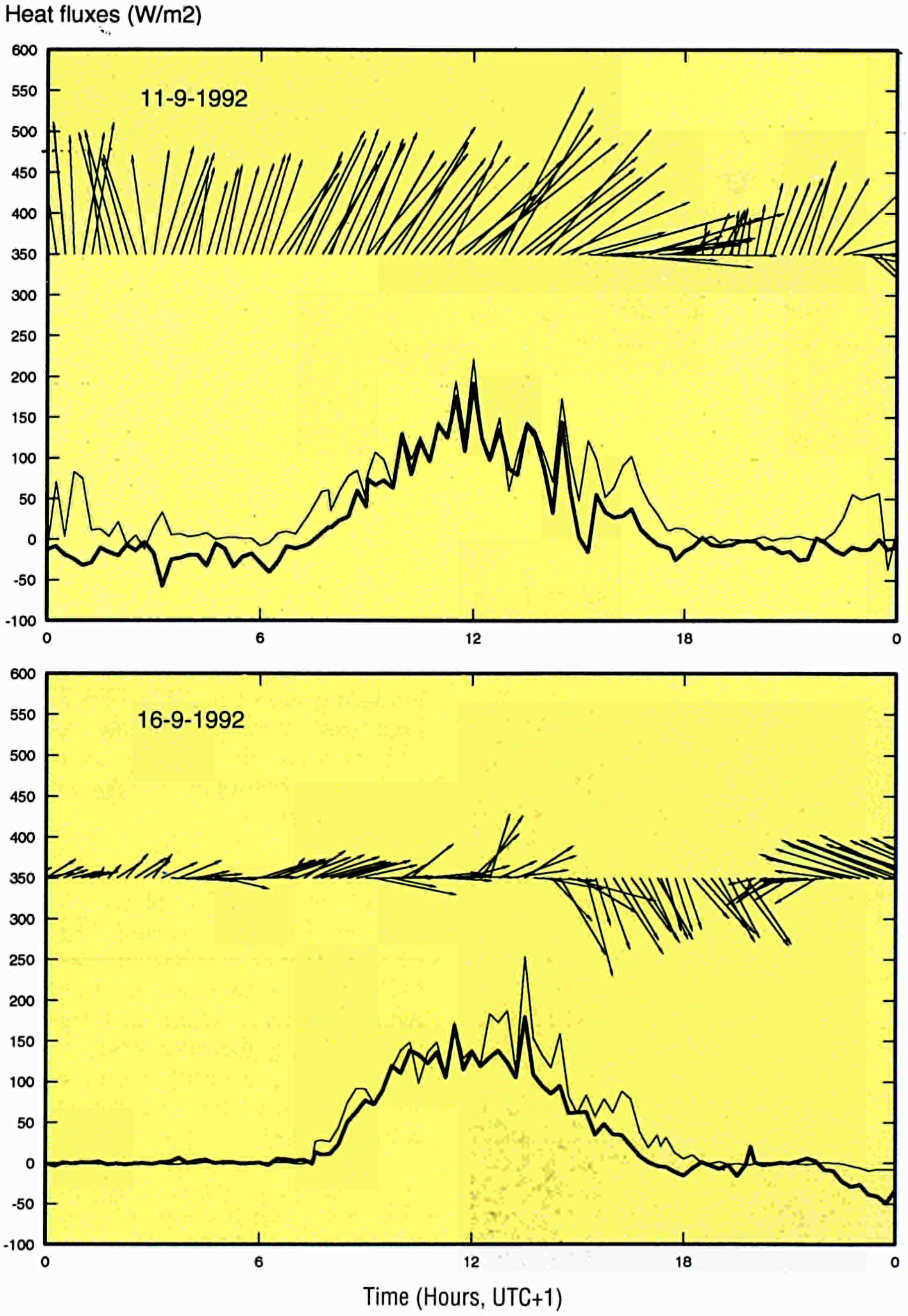


Fig.5.5 *Sensible (bold line), and latent (thin line) heat fluxes, as observed during two days of the TRAC campaign at Klippeneck, Germany. The arrovs represent the wind.*

The measurement of NO_2 fluxes was difficult to interpret, because of the important scatter of the data. The fluxes can be both positive and negative (i.e. upward and downward): a possible explanation of upward NO_2 fluxes could be the already proved NO emission by soils, followed by rapid conversion to NO_2 by reaction with the ozone present. But instrumental artifacts or advective effects are not excluded.

EUROTRAC-LACTOZ

The main objective of this project is to provide kinetic and mechanistic dat for a proper description of the complex chemical processes which lead to ozone formation and destruction in the troposphere.
The attention has been mainly addressed to improve our knowledge of the nighttime degradation processes (oxidation by the nitrate radical (NO_3) of isoprene and aromatics. Further studies have been dedicated to the kinetics of the radical-radical reaction NO_3+HO_2. The main results are described in the first section of this report.

EURENVIRON/TRACY

The project (Database of Toxic Metals in Human Tissues and Fluids) has been jointly developed by Norway (Dag Brune Consultant), Sweden (University of Umea and National Institute of Occupational Health, Solna) and CEC Joint Research Centre - Ispra in close cooperation with the Scientific Committee on the Toxicology of Metals within the International Commission on Occupational Health (ICOH) and has been further recognized by the International Union Pure and applied Chemistry (IUPAC) - Commission on Toxicology.
The aim of TRACY is the systematic collection and critical evaluation of the published information concerning trace metals in human tissues and fluids. The data will be stored in a

computerized data file for the derivation of "reference values", accessible to users. The published data are judged and graded according to the criteria established in accordance with an IUPAC expert group.
In 1992 three meetings of the expert group were held (two in Stockholm, January 17 and May 30; one in Ispra, November 13-14), with the participation of scientists from Italy, Finland, Norway, Sweden, Denmark, The Netherlands, United Kingdom, Belgium, USA and Canada.

The meetings were aimed at:

- developing criteria and phases for evaluation of the published data (for each element: pilot phase and relevant criteria; consensus between two (or more) independent evaluators; review by the TRACY group; final report) *(Fig.5.7)*.

- evaluating the elements to be implemented in the database (Cd and Cr final reports will be prepared before end 1993; Ni and Se consensus phase; Co, Pb, V pilot phase).

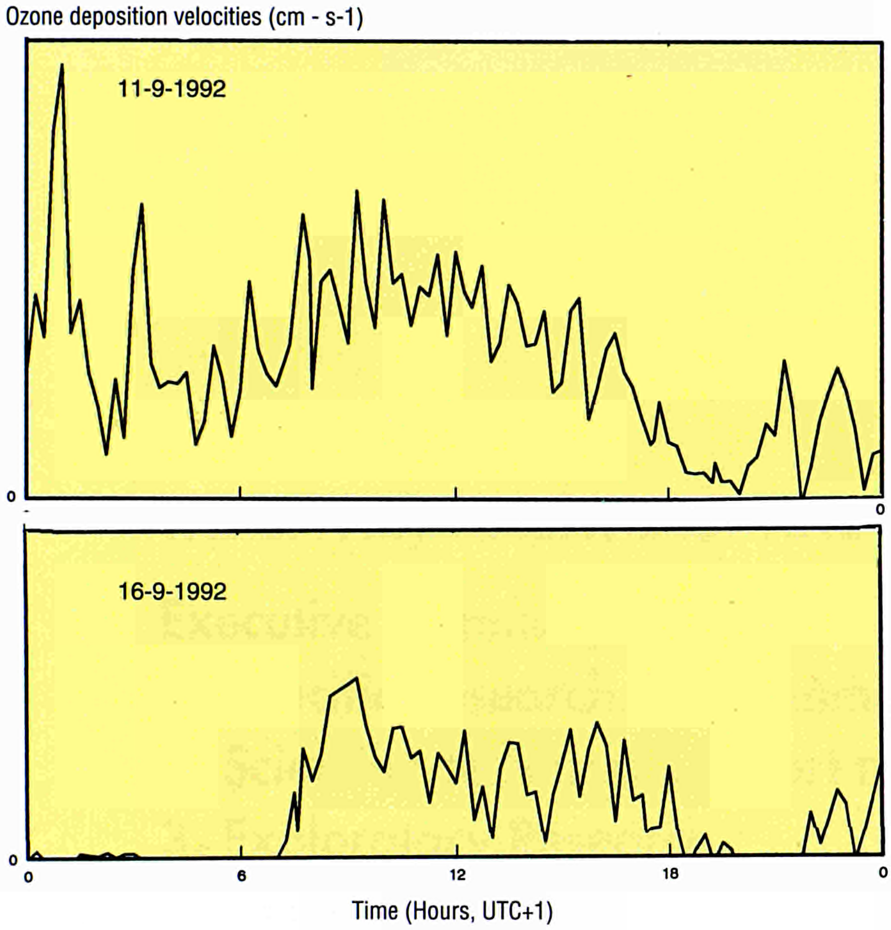
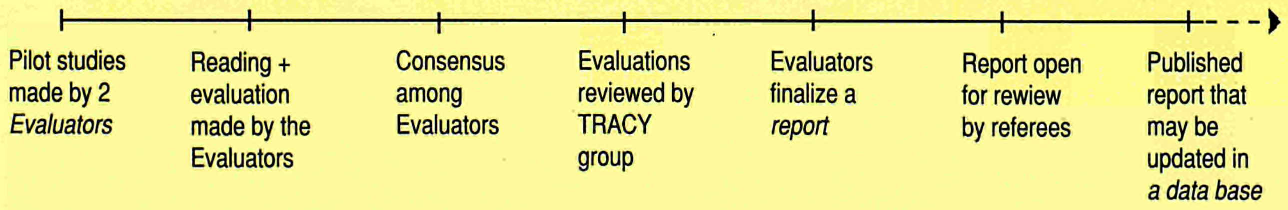


Fig.5.6 Deposition velocities, as observed during two days of the TRAC campaign at Klippeneck.



In co-operation with ICOH and IUPAC the TRACY-group chooses for each element at least 2 Evaluators, who each perform a pilot study to get experience and to find the relevant criteria for the element studied. The TRACY-group then confirms the criteria and the Evaluators tasks. The publications are allocated by computerized literature search. The Evaluators read and evaluate them indipendently. Then they meet to arrive at consensus documents for the evaluations, which should contain proposals for tentative reference values for the element studied, if possible derived by meta analysis. The documents are then reviewed by the TRACY-group. The Evaluators then prepare one common evaluation report, which is made available for review by journal referees and other experts. If the published reports are present in a data base they may easily be upgraded over a period of years to take account of relevant comments and also the subsequent evaluation of additional publications.

Fig.5.7 Proposed phases for evaluation of publications in the TRAC-project for producing reference values of trace elements in samples from humans.

EURENVIRON/MOBILE ANALYTICAL LABORATORY

Within the framework of Eureka project EU674 (Mobile Analytical Laboratory) belonging to EURENVIRON, two mobile units were planned and ordered in July '92 to be delivered to Ispra by the end of April '93. The required analytical instrumentation and Standard Operating Procedures to be adopted by the Mobile Laboratory have been decided.

A round robin exercise to determine the suitability of various preparation techniques, against analytical methods for inorganic analysis, has been carried out.

THE ENVIRONMENT INSTITUTE

6. Appendices

Publications, Conferences

SPECIFIC RESEARCH PROGRAMME

Air Pollution

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Glossary of Acronyms and Abbreviations

AMAMMET
Animal Testing Methods vs. Alternative Testing Methods in Metal Toxicology

ATC
Anatomic Therapeutic Class

ATMES
Atmospheric Transport Models Evaluation Study

BAL
Broncho Alveolar Lavage

BEMA
Biogenic Emissions in the Mediterranean Area

BIG
Belgian Fireman Brigade

BUT
1.3 Butadiene

CAS
Chemical Abstract Service

CCN
Clouds Condensation Nuclei

CD
Criteria Document

CD-ROM
Compact Disk Read-Only-Memory

CE
Capillary Electrophoresis

CEN
European Normalisation Commission

CEPN
Study Centre for Nuclear Protection

CN
Condensation Nuclei

CNR
Italian National Research Council

COLIPA
Committee of the Association of Perfume, Cosmetic and Toiletry Industries

CPC
Condensation Particle Counter

CPM
Community Measuring Programme

CSTR
Continuous Stirred Tank Reactor

CSS
Canadian Scientific Ship

CZE
Capillary Zone Electrophoresis

DDD
Dichloro-Diphenyl-Dichloroethane

DDE
Dichloro-Diphenyl-Ethilene

DDT
Dichloro-Diphenyl-Threechloroethane

DEB
1.2:3.4 Di-Epoxy Butane

DIDMI
Deutsche Institüt für Medizinische Dokumentation

DMS
Di-Methyl-Sulphide

DMSP
Di-Methyl-Sulphonio-Propionate

DNA
Desoxyribo Nucleic Acid

DTA
Differential Thermal Analysis

EB
1.2 Epoxy-3 Butane

EC
European Community

ECA
European Collaborative Action

ECB
European Chemical Bureau

ECD
Electron Capture Detector

ECDIN
Environmental Chemical Data Information Network

ECETOC
European Chemical Industry Ecology and Toxicology Centre

ECPHIN
European Pharmaceutical Database

ECURIE
European Community Urgent Radiological Information Exchange System

ECVAM
European Centre for the Validation of Alternative Testing Methods

EDF
French Electricity Board

EDS
Encoding-Decoding Software

EDTA
Ethylene-Diammino-Tetracetic Acid

EF
Emission Flow Rate

EFPIA
European Federation of Pharmaceutical Industries Association

EMEP
Evaluation Monitoring European Pollution

EP
European Parliament

EPA
Environmental Protection Agency

ERGATT
European Research Group for Alternatives in Toxicity Testing

ES
Embryonic Stem-cells

ESAOE
European Arctic Stratospheric Ozone Experiment

ET
East Transit

ETEX
European Tracer Experiment

Glossary of Acronyms and Abbreviations

EUCLID	European Chemicals Inventory Database
EUREKA	European Research Coordination Agency
EWC	European Waste Catalog
FAB-MS	Fast Atom Bombardment - Mass Spectrometry
FCM	Flow Cytometry
FDA	Food & Drug Administration
FID	Flame Ionization Detector
FTIR	Fourier Transform Infra Red Spectrometry
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
HAMBIHT	Hard Metal Biomonitoring in Human Tissues
HEQ	High Ecological Quality
HEFP	High Efficiency Particulate Filter
IAEA	International Atomic Energy Agency
IAP	Indoor Air Pollution
IAQ	Indoor Air Quality
IARC	International Agency for Research on Cancer
ICOM	International Commission on Occupational Health
ICSC	International Chemical Safety Cards
IRPTC	International Registry of Potentially Toxic Chemicals
ITBA	Italian Institute of Advanced Biological Techniques
IUPAC	International Union of Pure and Applied Chemistry
IWIC	International Waste Identification Code
MBL	Marine Boundary Layer
MECC	Micellar Electrokinetic Capillary Chromatography
MITO	Microphyte Toxins
MS	Mass Spectrometry
MSA	Methane-Sulphonic Acid
NACE	General Nomenclature of the Economical Activities in the European Communities
NASA	National Aeronautics and SpaceAdmnistration
NEA	Nuclear Energy Agency
NH	Northern Hemisphere
NILU	Norsk Institut Luftorskning
NMR	Nuclear Magnetic Resonance Spectrometry
NTA	Nitril-Threeacetic Acid
OA	Oxadaic Acid
OECD	Organization for Economic Cooperation and Development
OHS	Occupational Health Office
OPA	Optical Plankton Analyzer
ORAMIP	Regional Air Observatory in Middle Pyrenees
PAH	Poly-Aromatic Hydrocarbons
PAN	Peroxy-Acetyl-Nitrate
PCB	Poly-Chloro-Biphenyl
PHARE	Poland and Hungary Assistance for Economics Recovery
POM	Particulate Organic Matter
PUF	Poly-Urethane Foam
PVA	Poly-Vinyl-Alcohol
PVC	Poly-Vinyl-Chloride
PVDF	Poly-Vinyli-Dene-Fluoride
PTFE	Polychloro-Three-Fluoro-Ethylene
PWP	Pure Water Permeability Test
QSAR	Quantitative Structure-Activity Relashionship
RAMS	Regional Atmospheric Model System

Glossary of Acronyms and Abbreviations

RE	Rare Earths
REM	Radioactivity Environmental Monitoring
REMPI	Resonance Enhanced Multi-Photon Ionization
RIDEP	Italian Rain Monitoring Network
RV	Reference Values
SBR	Styrene-Butadiene Rubber
SDS	Sodium Dodecyl Sulphate
SFE	Supercrityical Fluid Extraction
SH	Southern Hemisphere
SPC	Summary Product Characteristics
SPM	Suspended Particulate Matter
SVOC	Semi Volatile Organic Compound
TdT	Terminal deoxynucleotidyl Transferase
TERVIHT	Trace Element Reference Value in Human Tissues
TG	Thermogravimetry
TK	Thymidine Kinase
TLV	Treshold Limit Value
TVM	Threedimensional Vorticity Model
TVOC	Total Volatile Organic Compound
UNEP	United Nations Environmental Program
UV	Ultra Violet
UV-VIS	Ultra Violet-Visible (spectrometry)
VOC	Volatile Organic Compound
WHO	World Health Organization
WT	West Transit

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This is the "Annual Report of the Environment Institute" of the Joint Research Centre - Ispra Site - of the Commission of the European Communities.

The report summarizes the major achievements in the projects developed by the Institute in the course of the year 1992, i.e., the first of the three year (1992-1994) Specific Research Programme of the Joint Research Centre.

The activities have been focused essentially on the program "Environmental Protection", the projects included in it having concerned the areas of air and water pollution, indoor air pollution, environmental chemicals, chemical waste and food & drug analysis. The contribution to the subprogramme "Working Environment" has concerned a number of issues related to chemical agents in a working environment.

A section of the report is dedicated to the progress accomplished in the activities performed as the scientific and technical support to various Commission' Services.

For the largest part this has concerned the Directorate General XI (Environment, Nuclear Safety and Civil Protection) in the areas of chemicals, air and water pollution, chemical waste, radioactive environmental monitoring (REM) and the validation of toxicity testing methods alternative to those implying the use of animals.

Main achievements in exploratory research, within the frame of the participation to EUREKA projects, as well as in the contractual work for third parties are also presented.

The data on the Institute structure and its human and financial resources completement the report and assist in assessing the value of the contribution of the Institute to the implementation of the EC research policy.