

Environment and Quality of Life

1987
Programme Progress Report

Environmental Protection

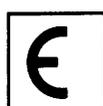


Commission of the European Communities
Directorate-General for Science Research and Development
Joint Research Centre, Ispra Establishment

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INTRODUCTION

Since 1973 Environmental Protection is one of the major tasks of the European Communities.

More recently, the Single European Act, adopted in February 1986 by the Conference of the Representatives of the Governments of the EC Member States, stresses the action by the Community relating to the Environment with the following objectives:

- to preserve, protect and improve the quality of the environment;
- to contribute towards protecting human health;
- to ensure a prudent and rational utilization of natural resources.

The execution of the EC environmental policy is relying on legislative and regulatory actions and on scientific information from its environmental research programmes executed as shared-cost/concerted actions as well as (direct research) in the Commission's own Joint Research Centre (JRC).

The principal scope of the JRC "Environmental Protection" programme is to provide, together with the JRC programmes «Application of Remote Sensing Techniques» and «Industrial Risk» and the related Indirect and Concerted Action Programmes, scientific support to the Community's Programme of Action on Environment (1987-1992).

The table displays an overview of the major links of the Action Programme managed by DG XI (Directorate-General for the Environment, Consumer Protection and Nuclear Safety) at Brussels with the programmes of the Research Action Programme (RAP) Environment.

For the definition of the programme content besides available skills and competences the following JRC specific tasks were considered:

- to act as a co-ordinator for certain environmental issues likely to have short term impact for the regulation work of the Commission (e.g., «acid deposition»);
- to pursue medium and long term studies in order to inform the Commission and Member States on environmental trends and to maintain the role of JRC within the European environmental research;
- to provide scientific support to other Commission services in implementing Council Directives (e.g., EINECS, Central Laboratory for Air Pollution).

This report, which is the sixth and last progress report of the four years 1984-87 programme, essentially covers the main results of the year 1987, with more emphasis on activities which already have come to a certain conclusion. For the reader in hurry a summary of results of the year 1987 is given at the beginning of this report.

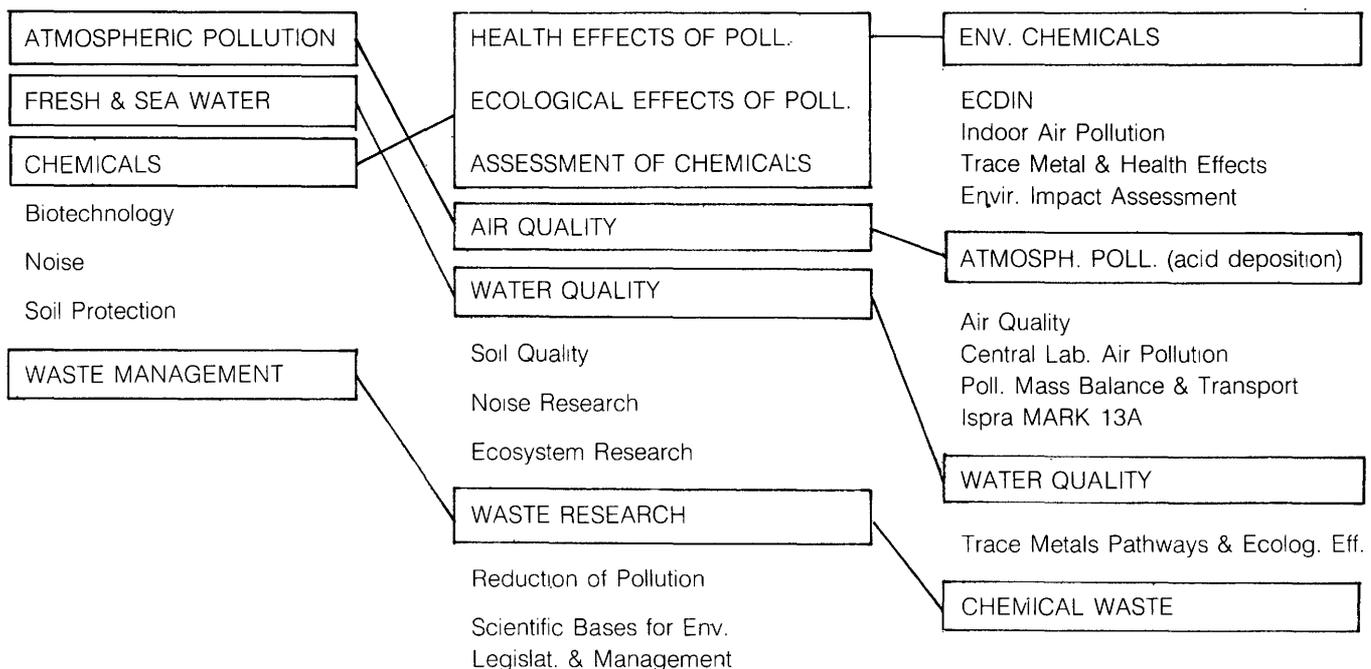
4th ENVIRONMENTAL ACTION PROGRAMME

**(REGULATORY ACTION)
DG XI (1987-1992)**

ENVIRONMENTAL PROTECTION RESEARCH PROGRAMMES

**(SHARED COST & CONC. ACTION)
DG XII/E (1986-1990)**

**(DIRECT ACTION)
DG XII/JRC (1984-1987)
(1987 revision)**



SUMMARY OF MAIN RESULTS

1. ENVIRONMENTAL CHEMICALS

The operation of the ECDIN (Environmental Chemical Data Information Network) data bank has been continued although only limited funds were available for extending data coverage and data updating. The number of users was still slightly increasing due to an increasing interest from USA, Japan and Australia. The B.I.G. data base (Belgian Fire Brigade Information Centre on Dangerous Substances) has been incorporated to ECDIN to make available detailed information on first measures in case of road accidents involving chemical substances.

The support to other Commission services by supplying information, consultancy and technical assistance within the ECDIN project has continued. Examples of supporting activities are the improvement of the hazardous substances list for DG III, biological monitoring and professional exposure for DG V, environmental impact and disposal of toxic substances and the implementation of the on-line display programme for EINECS (European Inventory of Existing Chemical Substances) for DG XI and finally the translation of chemical names of the Customs list for DG XXI.

The cost concerted action «Indoor Air Quality and its Impact on Man», led by JRC has established its initial working programme: preparation of guidelines for formaldehyde emissions, investigation of problem buildings and measurements of indoor pollutant levels. The experimental activities of JRC were presented at three international fairs and at these occasions the carbonyl compound content in active and passive cigarette smoke was demonstrated.

A number of mutagenic species have been detected in the smoke of more than 40 different cigarette brands and it has been demonstrated that more than 90% of the total pollutant mass is contained in passive smoke.

On request of the European Parliament, indoor air quality has been assessed during three measurement campaigns in the Parliament buildings at Strasbourg, Brussels and Luxembourg.

Within the activity on «Exposure and Health Effects of Trace Metals» further results have been obtained on the in-vitro distribution of different trace metals in human blood and on the dose-effect relationships of inorganic arsenic compounds in cell cultures.

Systematic work on the determination of trace metals in lung tissues, blood and urine of the general population continued in order to establish baseline reference values. Neutron activation analysis continued to be applied for the study of clinical case reports and the diagnosis of the trace metals induced lung diseases.

In the frame of the activity on «environmental pathways» work for the characterization of soil and soil-pollutant interaction was started.

Series of experiments with soils sampled at the Ispra site and interacting with different trace metal species have demonstrated the unique possibilities of the radio tracer methods. A finite element model was applied to the trace metal mobilization in ground-water from a coal fly ash repository. One result is that the arsenic concentration in ground-water 20 m beneath the repository will persist for 60 years above the maximum permissible concentration level, as defined in EC 80/778 directive on drinking water quality (50 µg/l).

2. ATMOSPHERIC POLLUTION (ACID DEPOSITION)

The role of naturally emitted substances, like terpenes and pinenes in chemical and photochemical transformation processes of air pollutants to acidic compounds was further investigated. The reaction of β -pinene with O_3 in presence of SO_2 leads to sulphur containing particulate matter, from which at least 75% are sulphate. This finding is similar for dark and sunlight irradiated conditions. In similar experiments with natural terpene mixtures a rapid oxidation of sulphur dioxide to sulphate was found.

To contribute to the understanding of the role that NO_3 radicals play in the night-time chemistry of atmospheric pollutants, reactions between NO_3 radicals and unsaturated organic hydrocarbons of biological origin have been studied using FT-IR and GC-MS techniques. Under laboratory conditions main products are nitrate, pernitrate and carbonyl functional groups.

Normal air quality levels and severe pollution episodes were monitored around the city of Varese during the winter period with out mobile laboratory for remote sensing of air pollutants. As main pollution sources sulphur containing fuel for domestic heating and dense traffic were identified.

On request of the Greek Ministry for the Environment, in September the same mobile unit performed extended air pollution measurements in Greece (Athens and Thessaloniki). Especially high values of SO_2 were observed. Data evaluation will continue as soon as meteorological parameters will be available.

A new dual-trap tracer analyser with a detection limit of 0.01 ppt for perfluorocarbons was purchased and tested. The mobile laboratory for «in-field» release, sampling and analysis of atmospheric tracer is now assembled and ready for field campaigns.

A 3D-Doppler acoustic radar (SODAR), capable to determine vertical wind vector profiles, has been purchased and works now at the Ispra site on a continuous routine basis. Another meteorological instrument, a 3 D sonic thermo-/anemometer coupled with a fast response NO_2 analyser has been successfully tested in a joint exercise with the Fraunhofer Institute for Atmospheric Research near Reising (Bavaria) for dry deposition measurements.

The JRC contribution to the COST concerted action 611 «Physicochemical behaviour of atmospheric pollutants» has continued and JRC scientists have been deeply involved in the definition phase of the EUREKA environmental project EUROTRAC.

The Central Laboratory for Air Pollution, set up for the implementation of the EC 80/779 directive on limits and guidelines for SO_2 and suspended particulates, continued its mission on behalf of DG XI with the check of station instruments in Italy and Greece. Examples for inefficient sampling lines, giving rise to completely false measurements were encountered and underline the need for calibration exercises on routine measuring stations. The JRC-EMEP station was run continuously at the Ispra site and the data were made available in the frame of the programme on the Evaluation and Monitoring of European Pollution.

The construction of the pilot plant for the ISPRA MARK 13A desulphurisation process at the SARAS refinery, Sarroch (Sar-

dinia) has been continued and the plant operation will start in the second half of 1988.

Laboratory work for extending the ISPRA MARK 13A process for flue gas desulphurisation to a combined desulphurisation/denoxing process continued. Electrolytic reduction of nitrous oxide via an iron-EDTA complex gave promising results. Preliminary experiments showed a reduction of the nitrous oxide at the cathodic compartment of the electrolytical cell and a significant formation of ammonia. At the same time, in the anodic compartment of the same cell, bromine, to be used for oxidising sulphur dioxide to sulphuric acid could be regenerated from the hydrobromic acid formed in the actual ISPRA MARK 13A process.

3. WATER QUALITY

In enclosure experiments on Lake Comabbio, a shallow water body with periodical mass-mortality of fish during the critical stratification period, the amelioration of physical, chemical and biological parameters by artificial oxygenation was followed. For testing the ecotoxicity of nickel at low concentrations (50 $\mu\text{g/l}$) the mortality and reproduction rate of *Daphnia Magna* proved to be a valuable bioindicator.

A further assessment of the flow cytometric method developed at Ispra showed that it is possible to identify algal classes by photopigment autofluorescence and to quantify number and size of cells within populations which would allow to assess water quality in a objective and comparable way. For the modellistic prediction of the recovery of Lake Orta, a highly polluted water body, a systematic inventory of trace metals (Cu, Cd, Pb, Cr, Ni, Zn) in dissolved, particulate and sedimented phase was performed.

4. CHEMICAL WASTE

To study the fate and environmental pathways of highly toxic compounds contained in chemical waste specific analytical procedures for extraction and analysis of polyhalogenated aromatic compounds from environmental samples were developed. These methods were further verified by use of ^{14}C radio-labelled dioxines and polychlorinated biphenyls.

Risk assessment procedures for human exposure to these compounds which may be contained in soot, incinerator fly ash, polluted soils and industrial wastes were established by assigning toxicity equivalent factors to each compound and considering source-composition and bio-availability as well.

The Chemical Emergency Management (ChEM) decision support system has been further developed. The first module is now operating and capable to identify the levels of threat related to the most common types of accidents involving PCBs.

Support to DG XI for the modification of EC directives on chemical waste, on updating of the toxic substances list and particularly on the EC directive on PCBs has continued.

RESEARCH AREAS

1. Environmental Chemicals

In drafting directives and laws for the protection of human health and the natural environment the Commission and national authorities need validated scientific information on environmental chemicals (e.g. production and use patterns, toxicity, concentration in environmental matrices, biodegradability, etc.).

The importance of «acceptable» data is further underlined by the fact that the economic consequences of setting environmental standards for certain pollutants (e.g. Cd in reclaimed soils, Pb in gasoline) or banning certain products (use of carbonyl compounds or asbestos in residential dwellings) may be important. Having this general objective in mind, JRC regrouped the data bank ECDIN activities on Indoor Air Pollution, «Exposure and Health Effects of Trace Metals and, Environmental Pathways» under the common heading Environmental Chemicals.

1.1 ECDIN

(Environmental Chemical Data Information Network)

Introduction

The ECDIN project is concerned with the development of a data bank for «Environmental Chemicals», that is chemicals that actually or potentially may affect man and/or the environment as a consequence of their manufacture, transport, use and disposal. Since 1980 the collected data had been loaded into a data base designed to utilize the ADABAS data base management system.

An important part of the data collection and some of the software development was funded by the E.C. Indirect Action Environmental Research Programme.

The principal medium term objectives are the following:

- To make ECDIN progressively operational, giving priority to the needs of the Commission services in selecting chemicals to be covered and data fields to be implemented.
- To make this service easily accessible to public and private users via the international informatics networks.
- To build up within the Member States a network of ECDIN partners for continuous input and updating of data.
- To carry out research, essentially on ranking of chemical substances, structure/activity relationships, and evaluation of chemicals.

To achieve these objectives, it will be necessary to perform the following tasks:

- Continued data collection and regular updating where necessary.
- Further development of the ECDIN system in order to scope with the users' needs, mainly in terms of retrieval language.
- Follow-up of technical progress in the field of retrieval languages and user's interface systems.
- Continuous contacts with people in research and management of the environmental protection domain, in order to quickly adapt the system to the evolution in that field.
- Continuous contacts with the relevant Commission services in order to follow the Commission's priorities and to store the information referring to the EEC directives.
- Critical data evaluation, at least in the more crucial fields.

RESULTS

1. The Public Available ECDIN

In the reporting period the public access to ECDIN has continued, through the external host, Datacentralen IS (Copenhagen).

The number of subscribers is still slowly increasing, but the cumulative access time is stagnating (see fig. 1).

These evidences are only apparently contradictory: in fact the overall interest for an information tool such as ECDIN is increasing worldwide, but the limited amount of funds available for updating makes the system less interesting for «old» users. They have already extracted the relevant information of their interest, but find very few «new data» on the same subject. Another time limiting factor could be the increased skill of users, allowing them to get the same information by a shorter search. So it is not surprising that the most active users are now coming from Japan and Australia, recently better linked with the marketing host. One important new acquisition has been the incorporation of the Brandweer Informatiecentrum Gevarlijkestoffen (B.I.G.) data base into ECDIN as a new Data Category.

This data category stores all relevant information with regard to first aid in case of road accidents during transport of chemical substances.

The data bank B.I.G. has been developed by the Ministry of Internal Affairs of Belgium, the University of Leuven, and the fire station of the city of Geel (Belgium)

Originally B.I.G. was implemented in 4 languages (Deutsch, French, English, German), and has been translated to Spanish, Italian, Portuguese and Danish on behalf of J.R.C. Ispra.

The data contained in the data bank give detailed information to firemen who are involved in clearing accidents with chemical substances, in a clear and readily understandable language. Figure 2 represents the first page of the data display with language selection menu and overview of the different data files. Other files have been in the meantime readjusted, improved and (or) updated, but the total size of these improvements has not been sufficient to maintain the excellent level previously reached by ECDIN. The fig. 3 gives the situation of the loaded records at the end of 1987.

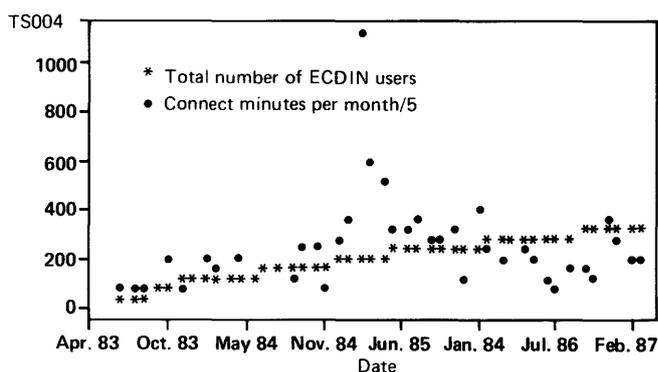


Fig. 1. ECDIN use statistics

THIS FILE IS MADE AND MAINTAINED BY:

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FOR THE COMMISSION OF THE EUROPEAN COMMUNITIES

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| | |
|-----------------|---------------|
| ? | ? |
| NL - NEDERLANDS | I - ITALIANO |
| F - FRANCAIS | E - ESPANOL |
| S - DEUTSCH | P - PORTUGUES |
| GB - ENGLISH | DK - DANSK |

Select Language = = = = = >

**** Available Data ****

?
A Type of Hazard
B Emergency Action - Methodes
C Personal Protection
D Properties - Appearance
E First Aid - Symptoms
F First Aid - Measures
G General Precautions
H Remarks
I Literature

Select details required (CR=all) =>

Fig. 2. The HAZARDS INFORMATION data Category

*** E C D I N *** LOAD STATUS STATISTICS *** 01/12/87 ***

| FILE | RECORDS | COMPDS |
|---|---------|--------|
| 1 Chemical Synonyms | 94482 | 62338 |
| 2 Physicochemical Properties | 31229 | 4157 |
| 3 Transport and Handling | 0 | 0 |
| 4 Chemical Structure Diagram | 50695 | 50693 |
| 5 Chemical Producers | 16084 | 6092 |
| 6 Chemical Processes | 1387 | 1644 |
| 7 Uses | 8535 | 8535 |
| 8 Production and Consumption Statistics | 5637 | 924 |
| 9 Export Statistics | 237 | 52 |
| 10 Import Statistics | 103 | 48 |
| 11 Occupational Health and Safety | 14001 | 2613 |
| 12 Occupational Exposure Limits | 8744 | 1665 |
| 13 Directive 67/548/EEC | 932 | 762 |
| 14 Classical Toxicity | 42061 | 18369 |
| 15 Aquatic Toxicity | 27381 | 1021 |
| 16 Mutagenicity | 3940 | 656 |
| 17 Carcinogenicity | 2348 | 196 |
| 18 Odour and Taste Threshold Limits | 1073 | 574 |
| 19 Effects on Soil Microorganisms | 3631 | 173 |
| 20 Concentration in Environmental Matrices (Cost 64b) | 19053 | 1626 |
| 21 Analytical Methods | 1797 | 1285 |
| 22 Legislation | 31798 | 4845 |
| 23 Teratogenicity | 0 | 0 |
| 24 Concentration in Human Media | 5814 | 617 |
| 25 Concentration in Animal Media | 2714 | 120 |
| 26 Metabolism in the Aquatic Environment | 0 | 0 |
| 27 Metabolism in Soil | 2637 | 183 |
| 28 Bioaccumulation in the Aquatic Environment | 1979 | 251 |
| 29 IRPTG WASTE | 630 | 546 |
| 30 BIG | 5297 | 5297 |

Fig. 3

2. Development of ECDIN

During 1987 work started on the development of a new user-interface for the ECDIN-databank.

This ECDIN-ACCESS project, is funded by the INSIS programme of DG-XIII with the scope to improve the electronic communication between the institutions of the European Community and extending this communication to the member state administrations, and to facilitate the access to data collections under the responsibility of EC institutions. At the beginning of the year a contract was granted to a consortium consisting of two Danish and one Italian company to carry out a feasibility study.

The study recommends an interface consisting of an user front-end implemented on an intelligent terminal, the Common Command Language (CCL) possibly extended with some functions to facilitate the interrogation and display of retrieval data, and a CCL-ADABAS module. The user front-end will comprise help modules, which allow the user to formulate current CCL commands without any knowledge of the database structure.

The information contained in ECDIN is used more and more by other Commission Services for other research and evaluation activities, like evaluation of Chemical Risk, Structure Activities Relationships, searches for specific toxicological and analytical problems.

3. Support to other Commission Services

EINECS. The inventory of existing chemicals was definitively established at the end of 1986; a provisional issue of the English version has been printed and distributed at the start of the reporting period.

In 1987 the overall list has been made available on-line, through the main Ispra computer, to the authorized services of the Commission and of the Member States.

Data Concerning the compounds in EINECS, the European Inventory of Existing Chemical Substances, have been loaded into the data bank and have been made available through the ECDIN display programme as a new file A(C): Identifiers.

This version of the Display Programme has since the summer been available on the computer in Ispra for the Commission Services and for the competent authorities of the member states. A reorganisation of the synonym file has been carried out during autumn 1987.

The complete file of synonyms maintained by the Custom Union Service is now accessible through the new ECDIN Display System.

In addition to the work for EINECS, ECDIN provided a continuous support to several Commission services, by supplying information, consultancy and technical assistance.

For DG III assistance for the improvement of the hazardous substances list was given.

For DG V work on the biological monitoring of adverse effects for professional exposure to chemicals continued. DG XI relied on assistance in several actions concerning chemical impact and disposal of toxic/substances) and DG XXI in translating chemical names of the Customs list.

Evaluation of Chemicals

The availability of reliable physico-chemical and biological/toxicological data is one of the limiting factors in the overall risk assessment of chemicals. In many cases, such data are often sparse or lacking entirely.

To some extent, this difficulty may be overcome by introducing estimation or calculation methods which allow to derive essential physico-chemical data from some basic properties or from structural correlations.

To this end, a project has been started in collaboration with GSF, München, Neuherberg (project group Environmental Hazard Potential of Chemicals) to assess the potential use of such estimation methods and implement their practical application. In a first step, an available calculation programme («Chemest») has been transcribed to be compatible with the ECDIN host computer in view of a future application to increase the physico-chemical data base.

In a second phase, estimated vapour pressure and water solubility data have been derived for selected groups of chemicals and compared to available experimental data.

An example is given in Table I, where the estimated parameters are confronted with the (few) available experimental figures for the monochloroalkanes. It appears, that in the most cases, satisfactory agreement can be obtained between experimental and calculated results with a slight bias towards overestimation of calculated values. In case, where different estimation methods are available, variations are rather insignificant (methods 1 and 2 for vapour pressure estimation).

At this stage, it is evident that at least for the extrapolation of results from the first members of a homologue series of chemicals of less complex structure to members of higher Mw the estimation methods can be quite useful.

For 1988, it is planned to extend these studies systematically to chemical series of more complex structure and to add other important parameters (for instance octanol/water partition coefficient).

REFERENCES

O. NORAGER, M. BONI, W. PENNING, R. ROI
New Development in the ECDIN Databank, 10th International On-Line Meeting, Learned Information (Europe) Ltd., 24 December 1986, London (UK).

Table I. PC - Estimation (Chemest) - Alkylchlorides

| Compound | Form. | Mw | M.p. (°C) | B.p. | Vapour Pressure (Torr) (25 °C) | | | Water Solub. (g/l) (20°) | |
|-----------------|-----------------------------------|-------|--------------|-------|--------------------------------|---------------------|---------------------|--------------------------|---------------|
| | | | | | (experim.) | Meth. 1 (estim.) | Meth. 2 (estim.) | experim. | estimated |
| Chloromethane | CH ₃ Cl | 50.5 | -98 | -24 | 4.8-5.0 atm. | 5.3 atm | | 9 | (60) |
| Chloroethane | C ₂ H ₅ Cl | 64.5 | -138.7 | 13.1 | 1000 | 1150 | | 5.74 | 7.6(1) 9.5(2) |
| 1-Chloropropane | C ₃ H ₇ Cl | 78.5 | -122.8 | 46.8 | 280 | 346 | 343 | 2.7 | 2.5 |
| 1-Chlorobutane | C ₄ H ₉ Cl | 92.6 | -123 | 74.8 | 80/110 | 119 | 116 | 0.6 | 0.79 |
| 1-Chloropentane | C ₅ H ₁₁ Cl | 106.6 | -99 | 102.8 | | 32 | 29 | | 0.25 |
| 1-Chlorohexane | C ₆ H ₁₃ Cl | 120.6 | -83 | 132 | | 12 | 10 | | 0.079 |
| 1-Chloroheptane | C ₇ H ₁₅ Cl | 134.6 | -69.5 | 159 | | 3.6 | 3 | | 0.025 |
| 1-Chlorooctane | C ₈ H ₁₇ Cl | 148.7 | -57.8 | 182 | | 1.3 | 1.1 | | 0.008 |
| 1-Chlorononane | C ₉ H ₁₉ Cl | 162.7 | -39.4 | 203.4 | | | | | 0.0025 |

Commission of the European Communities:
Biological Indicators for the assessment of human exposure to industrial chemicals: Arsenic, Cobalt, Vanadium, Endrin, Aldrin and Dieldrin.
Edited by L. Alessio, A. Berlin, M. Boni, R. Roi for the CEC as EUR Report 1987 (EUR 11135 en).

Commission of the European Communities and International Commission on Occupational Health.
Proceedings of the «1st International Workshop on Data Banks in Occupational Health».
Edited by L. Parmeggiani, R. Roi as EUR rep. n. 11022EN, 1987.

1.2 INDOOR POLLUTION

INTRODUCTION

Since the early 70's increasing evidence has become available that indoor air in residential and other non-industrial closed environments (in addition to diet, drinking water, outdoor and industrial workplace air) makes a major contribution to population exposure to a wide range of environmental chemicals. Such evidence includes health and comfort complaints due to indoor air pollution (IAP), the detection of major indoor sources of air pollutants and of indoor concentrations of a wide range of air pollutants which are higher and sometimes considerably higher than the corresponding outdoor concentrations. In particular, volatile organic compounds (VOC) occur indoors consistently at higher concentrations than outdoors /1, 2, 3, 4/ and it has been shown that population exposure to this class of chemicals to which belong many irritating, toxic and cancerogenic compounds is predominantly due to indoor air exposure /3/.

This activity aims at enlarging knowledge about air quality in closed environments with the scope to assess its relevance for human health and comfort. In particular, environments with high population residence times (e.g. residential dwellings, schools, office buildings) or presumably high air pollution levels (e.g. new buildings) are taken in consideration.

Pollution by VOC is at the centre of interest in view of the:

- high concentration levels found indoors compared to outdoors,
- high complexity of this type of pollution requiring a widespread effort of assessment,
- potentially important health relevance,
- experience in the field of environmental organic analysis existing at the JRC.

The complexity of IAP (Indoor Air Pollution) and the scarcity of dedicated research capacities calls for collaboration of European laboratories working in this field.

An essential part of the effort of the JRC therefore is dedicated to the management and scientific coordination of the Concerted Action «Indoor Air Quality and Its Impact on Man».

The final goal of this action is to contribute to

- human total exposure assessment,
- a scientific basis for the establishment of indoor air quality criteria, and
- a control of indoor pollution sources affecting human health and comfort.

ACHIEVEMENTS AND RESULTS

1. Concerted Action «Indoor Air Quality & Its Impact on Man»

The most important event for the indoor activity was the commencement of the Concerted Action. In two Concertation Committee meetings organized in March and November at Ispra an initial working programme has been prepared. Three Working Groups have been established:

- Working Group 1 is going to prepare a guideline for problem building investigations with special reference to the question how to identify and to approach buildings affected by the «Sick Building Syndrome» (SBS); a preliminary draft has been produced in 1987;
- Working Group 2 will prepare strategies/guidelines for indoor measurements;
- Working Group 3 is charged to prepare a guideline for formaldehyde emission measurements, which has been drafted in 1987.

In order to assist Commission Services in evaluating the opportunity of regulatory action in the field of indoor air quality it was further decided to prepare three summary reports on existing knowledge in the field of exposure to and health effects of indoor radon, formaldehyde and NO₂ in Community countries. Preliminary drafts of these reports have been discussed during the second Concertation Committee meeting.

In August «Indoor Air '87», the fourth International Conference on Indoor Air Quality and Climate was held in Berlin under the auspices of the CEC represented by the JRC. Bernd Seifert, the chairman of the Concertation Committee was the president of the conference and many members of the Concertation Committee including JRC staff were involved in the organization of this most important scientific event in the indoor air field in 1987, to which the JRC contributed also three scientific communications /5, 6, 7/.

2. Indoor Air Quality Measurements in Buildings of the European Parliament

A) EXPERIMENTAL PROCEDURES

Temperature and humidity were determined by a dry and wet thermometer psychrometer.

Air exchange rate was determined by sulphur hexafluoride (SF₆) dilution: a small quantity of the gas (~ 1 cm³ each 50 m³ of room volume) was released in the room and, after a delay for mixing, air samples were collected and SF₆ measured by a portable gas-chromatograph. The tracer gas is completely inert. The results are reported in terms of numbers of room volumes changed each hour.

Respirable particulate material. The concentration of the suspended particles with diameter smaller than 4 μm was measured by a nephelometer (light scattering) type instrument GCA model RAM-1.

Formaldehyde, heavier aldehydes and Ketones. The procedure used consists in sampling about 30 l of air through a reagent solution (dinitrophenyl-hydrazine in acetonitrile), of which an aliquot is carried to the laboratory. Here the separation of the reacted compounds (hydrazones) is performed by liquid chromatography and the different compounds detected by an ultra-violet scanning photometer.

Volatile organic compounds (VOC). The compounds with boiling points ranging from n-hexane to about the alkanes with 13 carbon atoms are trapped in a sampling column containing an adsorbent, either a synthetic porous polymer (Tenax) or graphitized carbon black (Carbotrap).

The sampling columns are carried to the laboratory. Here they are thermally desorbed cryogenically preconcentrated and injected into a gas-chromatograph where they are separated using capillary columns and detected by flame ionization (GC-FID analysis) or mass spectrometry (GC-MS analysis).

An indication of the total amount of VOC present in air, including also those more volatile than n-hexane (and therefore not retained by the sampling system described above) is obtained through a portable photo-ionization detector (Photovac mod. TIP). Since the response of this instrument depends strongly on the chemical composition of a compound no quantitative data can be obtained for mixtures. However the reading of this in-

strument is useful as an indication of situations of elevated pollution, where duplicate samples are taken in order to carry out GC-FID as well as GC-MS analyses.

The «total >C6» reported in Tables II and IV refers to the sum of the detector responses to all compounds recorded during GC-FID analysis, converted into mass (mg) using the mean instrument response factor for the hydrocarbons present in a calibration mixture.

A more detailed description of these procedures may be found elsewhere /8/.

B) RESULTS

The results of all the measurements performed on the site and in the laboratory are presented in Tables I-II and III-IV respectively for Brussels and Luxembourg. Formaldehyde,

acetaldehyde, benzaldehyde and acetone are reported separately from the VOC (though they are also volatile organic compounds) because they have been measured through a different technique. Under the heading VOC are reported the three most abundant single compounds and the «total <C6» concentration, obtained as explained above.

C) COMMENTS

Temperature and humidity. As already observed at Strasbourg in 1986 (see PPR 1986), some rooms had temperatures between 24 and 25°C and one even in excess of 25°C. The temperature observed in room n. 212 of the new building (De Gasperi or BAK) in Luxembourg was presumably elevated (26.8°C), because the air conditioning system was not operating and the sun entered through a wide window. The observed range for the relative humidity is 39-57%.

TABLE I. Physical parameters in the buildings in Brussels

| Building and Room | Volume (m ³) | air change rate (h ⁻¹) | respirable particulate matter (mg/m ³) | Temperature (°C) | Relative Humidity (%) |
|------------------------|--------------------------|------------------------------------|--|------------------|-----------------------|
| BELLIARD | | | | | |
| 63 | 50 | 1.05 | 0.13 | 22.4 | 47 |
| travel agency | 100 | 1.44 | 0.36 | 22.4 | 45 |
| telephone exchange | 120 | 0.84 | 0.12 | 21.6 | 50 |
| 201 | 75 | 0.68 | 0.22 | 23.3 | 48 |
| 256 | 70 | 1.60 | 0.010 | 21.6 | 39 |
| 341 | 110 | 0.35 | 0.016 | 20.2 | 44 |
| 378 | 60 | 0.94 | 0.010 | 23.2 | 45 |
| 436 | 105 | 0.86 | 0.025 | 20.4 | 51 |
| 472 | 50 | 1.72 | 0.017 | 22.4 | 40 |
| 736 | 62 | 0.64 | 0.018 | 22.6 | 48 |
| 766 (filing room) | 200 | 0.76 | 0.018 | 24.0 | 43 |
| 801 + 817 | 190 | 0.77 | 0.025 | 21.4 | 49 |
| 810 | 38 | 0.45 | 0.020 | 22.8 | 48 |
| meeting room No. 52 * | 1000 | 0.39 | 0.020 | 23.0 | 42 |
| NL interpreter cabin * | 20 | 0.74 | 0.080 | 24.0 | 43 |
| meeting room No. 61 * | 830 | 1.39 | 0.020 | 23.4 | 39 |
| F interpreter cabin * | 20 | 1.52 | 0.020 | 25.0 | 44 |
| REMORQUER | | | | | |
| 105 | 30 | 0.30 | 0.050 | 22.2 | 54 |
| ARDENNES | | | | | |
| 307 | 50 | 4.67 | 0.040 | 19.6 | 51 |
| 717 | 100 | 3.40 | 0.35 | 20.8 | 49 |
| EASTMAN | | | | | |
| printing workshop | 360 | 1.09 | 0.080 | 22.6 | 55 |
| " " " " | 120 | 0.78 | 0.17 | 24.6 | 54 |
| 306 | 70 | 0.79 | 0.050 | 22.0 | 57 |
| REWARD | | | | | |
| 612 | 90 | 1.20 | 0.028 | 20.6 | 56 |
| OUTDOORS | | | | | |
| BEL roof - 13 Oct | - | - | 0.020 | 14.4 | 70 |
| " " - 14 Oct | - | - | 0.015 | 14.8 | 86 |

* = forced ventilation not in operation

TABLE II. Chemical parameters in the buildings in Brussels

| Building and room | VOC (mg/m ³) | | | | formal- dehyde (mg/m ³) | acetal- dehyde (mg/m ³) | benzal- dehyde (mg/m ³) | acetone (mg/m ³) |
|------------------------|--------------------------|--------------------------------|------------------------------------|------------------------------------|---|---|---|---------------------------------|
| | total >C ₆ | main compound ^{a)} | 2nd main compound ^{a)} | 3rd main compound ^{a)} | | | | |
| BELLIARD | | | | | | | | |
| 63 | 0.18 | TEC 0.022 | TOL 0.019 | B | 0.030 | 0.007 | b | 0.007 |
| travel agency | 0.35 | 2MP 0.038 | TOL 0.027 | U-2 0.020 | 0.071 | 0.035 | b | 0.019 |
| telephone exchange | 0.21 | TOL 0.027 | B | B | 0.062 | 0.019 | b | 0.012 |
| 201 | 0.25 | TOL 0.019 | B | B | 0.078 | 0.016 | b | 0.013 |
| 256 | 0.25 | TOL 0.017 | B | B | 0.029 | 0.009 | b | 0.005 |
| 341 | 0.30 | U-2 0.028 | TOL 0.028 | 2MP 0.014 | 0.043 | 0.008 | b | 0.006 |
| 378 | 0.016 | ACA 0.028 | HEA 0.019 | TOL 0.010 | 0.021 | 0.015 | b | 0.005 |
| 436 | 0.18 | ACA 0.029 | HEA 0.014 | TOL 0.011 | 0.050 | 0.004 | b | 0.007 |
| 472 | 0.16 | TOL 0.010 | B | B | 0.028 | 0.002 | b | 0.005 |
| 736 | 0.30 | TOL 0.013 | U-2 0.011 | B | s | s | s | s |
| 766 (filing room) | s | s | s | s | 0.066 | 0.004 | b | 0.005 |
| 801 + 817 | 0.081 | U-3 0.011 | B | B | 0.021 | 0.004 | b | 0.005 |
| 810 | 0.047 | B | B | B | 0.021 | 0.004 | b | 0.005 |
| meeting room No. 52 + | 0.20 | TOL 0.030 | ACA 0.020 | HEX 0.010 | 0.005 | 0.003 | b | 0.004 |
| NL interpreter cabin + | 0.22 | U-1 0.039 | TOL 0.032 | PIN 0.012 | 0.46 | 0.16 | b | 0.033 |
| meeting room No. 61 + | 0.87 | TCE 0.64 | TEC 0.17 | TOL 0.022 | s | s | s | s |
| F interpreter cabin + | 0.51 | U-2 0.12 | 2MP 0.059 | TOL 0.049 | 0.32 | 0.011 | b | 0.006 |
| REMORQUER | | | | | | | | |
| 105 | 2.04 | HEX 1.73 | TOL 0.089 | B | s | s | s | s |
| ARDENNES | | | | | | | | |
| 307 | 0.087 | B | B | B | 0.024 | 0.010 | b | 0.003 |
| 717 | 0.10 | TOL 0.016 | TEC 0.010 | B | 0.055 | 0.022 | b | 0.007 |
| EASTMAN | | | | | | | | |
| printing workshop | 139 | TEC 56.7 | HEP 16.0 | MCH 9.8 | 0.053 | 0.013 | b | 0.008 |
| " " " " | 133 | * | * | * | s | s | | s |
| 306 | 2.51 | TEC 1.25 | 1TC 0.21 | HEP 0.21 | 0.056 | 0.013 | b | 0.012 |
| REMAR | | | | | | | | |
| 612 | 0.42 | TOL 0.11 | XYL 0.020 | BEN 0.016 | 0.057 | 0.009 | b | 0.018 |
| OUTDOORS | | | | | | | | |
| BEL roof - 13 Oct. | 0.11 | TOL 0.011 | XYL 0.007 | TEC 0.007 | 0.009 | 0.019 | b | 0.008 |
| BEL roof - 14 Oct | 0.90 | HEX 0.76 | MCP 0.015 | 3MP 0.012 | 0.003 | 0.005 | b | b |

B = below 0.01 mg/m³
^{a)} for abbreviations see Table 5

b = below detection limit
s = sample lost

* = composition very similar to that observed in the sample above.
+ = forced ventilation not in operation

Air change rate. The values observed for this parameter range between 0.30 and 6.46 h⁻¹ and their distribution is presented in Fig. 1a. Since some values are lower than 0.5 h⁻¹, which is usually considered a minimum value, also the number of cubic meters per hour available to each room (obtained by multiplying the air change rate by the room volume) has been determined. The distribution obtained for this parameter is represented in Fig. 1b. Three rooms show values below 25 m³/h, which in some countries is considered the minimum fresh air requirement for one person /9/. One of the three rooms is an interpreter cabin in the Belliard building, where the air conditioning system was not working when the survey was made and presumably has a much higher air change rate when the system is working. The two other rooms (Belliard 810, Remorquer 105) deserve further attention.

Respirable particles. Most values observed for this parameter are very low, i.e. below 0.050 mg/m³; higher values are found in rooms of smokers and in the printing workshop in the Eastman building. For comparison, particle concentrations observed in outdoor air with the same instrument are as high as 0.20 mg/m³.

Formaldehyde, heavier aldehydes and ketones. The distribution of the formaldehyde concentrations observed is represented in Fig. 2. The two highest values have been detected in the already mentioned interpreter cabins where forced ventilation was temporarily switched off. However in six other rooms the formaldehyde concentration exceeded, though by little, the guideline value for 24 hour exposure of 0.10 mg/m³ recently established by the World Health Organization for indoor and ambient air /10/. Interestingly

TABLE III. Physical parameters in the buildings in Luxembourg

| Building and Room | Volume (m ³) | air change rate (h ⁻¹) | respirable particulate matter (mg/m ³) | Temperature (°C) | Relative Humidity (%) |
|-------------------------|--------------------------|------------------------------------|--|------------------|-----------------------|
| TOUR | | | | | |
| 014 (audio visual) | 70 | 2.76 | 0.010 | 23.8 | 43 |
| med exam room | 70 | 2.47 | 0.034 | 23.0 | 48 |
| 221 | 40 | 4.77 | 0.008 | 22.0 | 50 |
| 235 | 40 | 3.17 | 0.010 | 23.0 | 52 |
| 726 | 30 | 5.18 | 0.037 | 25.4 | 47 |
| 2128 | 70 | 2.91 | - | 23.4 | 48 |
| 2134 | 70 | 3.80 | - | 23.8 | 46 |
| SCHUMAN | | | | | |
| 126 (print w secr) | 100 | 1.67 | 0.020 | 24.2 | 43 |
| 342 | 40 | 0.68 | 0.020 | 23.0 | 48 |
| 388 | 55 | 0.48 | 0.018 | 23.0 | 52 |
| 3113 | 40 | 0.71 | 0.035 | 23.4 | 48 |
| 3121 | 40 | 0.82 | 0.035 | 23.4 | 52 |
| meeting room No.601 | 900 | 6.46 | 0.026 | 18.6 | 58 |
| meeting room No.603 | 250 | 1.59 | 0.015 | 23.2 | 52 |
| NEW HEMICYCLE | | | | | |
| Office (print. w. -5) | 45 | 1.13 | 0.018 | 23.4 | 39 |
| 357 | 60 | 0.70 | 0.026 | 22.0 | 47 |
| 340 | 60 | 1.02 | 0.025 | 24.6 | 39 |
| SENNINGERBERG | | | | | |
| 18 | 40 | 0.73 | 0.070 | 24.0 | 43 |
| DE GASPERI (BAK) | | | | | |
| 212 | 50 | 0.57 | 0.080 | 26.8 | 41 |
| OUTDOORS | | | | | |
| parking centre | | | | | |
| européen | | | | | |
| " " " - 16 Oct | - | - | 0.018 | 12.0 | 82 |
| " " " - 17 Oct | - | - | 0.033 | 15.0 | 76 |
| " " " - 19 Oct | - | - | 0.050 | 15.8 | 54 |

enough all these rooms are in the Schuman building. The only room in the same building where formaldehyde shows a much lower concentration had a lower temperature and a much higher ventilation rate. This finding suggests that particle board emission is the source of the elevated formaldehyde concentrations (the emission of formaldehyde depends strongly on temperature).

Apart from the interpreter cabin, the highest concentration of acetaldehyde is observed in the room with the highest particle concentration (travel agency, Belliard); both pollutants are caused by cigarette smoking and their parallel behaviour is a good confirmation of their common origin. There are no guideline values for acetaldehyde in indoor air; the limits fixed for professionally exposed people are a hundredfold higher than the corresponding values for formaldehyde.

Consequently the concentrations of acetaldehyde observed in this survey are presumably not critical by themselves. Environmental tobacco smoke, however, of which they are an indicator, is considered a human carcinogen.

Benzaldehyde which has been detected in all but one building in Luxembourg (but not in Brussels) deserves a special comment due to an abnormal sampling effect. Air samples pass through two impinger bottles in series. Ideally compounds to be

analysed are completely or nearly completely trapped in the first bottle and the second bottle serves only as a control for potential losses from the first bottle. Benzaldehyde, however, was prevalently or even only detected in the second impinger bottle. We have tested several hypotheses for this abnormal behaviour but have not yet found an explanation. As a consequence it is not possible to calculate air concentrations of benzaldehyde, even though GC-MS measurements of VOC indicate, that the compound, which is used as flavouring agent in cleaning products, was present. It can, however, be concluded from these last measurements, that concentrations were considerably lower than the threshold limit for workplace air of 20 mg/m³ in Italy (no value is defined in other Community countries).

Acetone, widely used as a solvent, presents the highest value (0.127 mg/m³) in room n. 212 of the new building in Luxembourg, where works were still under way, like fixing moquette by means of glues. All other values are below 0.050 mg/m³, which may be compared with the legal limit of 1000 mg/m³ for professional exposure.

Volatile organic compounds. In 15 rooms duplicate samples have been collected for analysis by both, GC-FID and GC-MS (see section «Experimental Procedures»). All other samples were

TABLE IV. Chemical parameters in the buildings in Luxembourg

| Building and room | VOC (mg/m ³) | | | | formal- dehyde (mg/m ³) | acetal- dehyde (mg/m ³) | benzal- dehyde (mg/m ³) | acetone (mg/m ³) |
|------------------------------|--------------------------|--------------------------------|------------------------------------|------------------------------------|---|---|---|---------------------------------|
| | total > C ₆ | main compound ^{a)} | 2nd main compound ^{a)} | 3rd main compound ^{a)} | | | | |
| TOUR | | | | | | | | |
| 014 (audio visual) | 0.11 | BEN 0.016 | B | B | 0.021 | 0.006 | + | 0.006 |
| med exam room | 0.11 | TOL 0.022 | 2PR 0.020 | B | 0.021 | 0.010 | + | 0.014 |
| 221 | 0.11 | ACA 0.013 | B | B | 0.011 | 0.003 | b | 0.005 |
| 235 | 0.11 | TOL 0.012 | B | B | 0.034 | 0.008 | b | 0.011 |
| 726 | 0.32 | TOL 0.035 | U-4 0.033 | PIN 0.026 | 0.031 | 0.014 | + | 0.022 |
| 2128 | 0.22 | 2PF 0.070 | 1TC 0.041 | TOL 0.011 | 0.028 | 0.009 | + | 0.008 |
| 2134 | 0.24 | 2PF 0.12 | 1TC 0.015 | TOL 0.010 | 0.018 | 0.005 | + | 0.005 |
| SCHUMAN | | | | | | | | |
| - 126 (office printing work) | 0.86 | BUT 0.57 | OCT 0.024 | HEP 0.020 | 0.138 | 0.010 | + | 0.019 |
| 342 | 0.41 | TEC 0.086 | HEP 0.019 | TOL 0.015 | 0.111 | 0.019 | + | 0.021 |
| 388 | 0.57 | TEC 0.012 | HEP 0.025 | TOL 0.017 | 0.126 | 0.023 | + | 0.032 |
| 3113 | 0.82 | TEC 0.16 | 2MX 0.076 | 1TC 0.067 | 0.123 | 0.021 | + | 0.039 |
| 3121 | 0.38 | TEC 0.099 | HEP 0.015 | B | 0.132 | 0.025 | + | 0.043 |
| meeting room No.601 | s | s | s | s | 0.035 | 0.007 | + | 0.005 |
| meeting room No.603 | 0.63 | TEC 0.25 | TCE 0.24 | MCH 0.027 | 0.101 | 0.013 | + | 0.010 |
| NEW HEMICYCLE | | | | | | | | |
| Office (print. work. -5) | 2.63 | TCE 0.61 | TEC 0.75 | HEP 0.093 | 0.051 | 0.009 | b | 0.018 |
| 357 | 0.33 | TEC 0.061 | XYL 0.011 | B | 0.063 | 0.014 | b | 0.022 |
| 340 | 0.18 | TEC 0.060 | B | B | 0.085 | 0.016 | b | 0.025 |
| SENNINGERBERG | | | | | | | | |
| 18 | 0.013 | B | B | B | 0.049 | 0.022 | + | 0.031 |
| DE GASPERI (BAK) | | | | | | | | |
| 212 | 0.35 | TOL 0.016 | PED 0.013 | TED 0.011 | 0.063 | 0.022 | + | 0.127 |
| OUTDOORS | | | | | | | | |
| parking centre européen | | | | | | | | |
| " " - 16 Oct | 0.12 | TEC 0.014 | TOL 0.006 | HEX 0.005 | 0.003 | 0.002 | b | 0.001 |
| " " - 17 Oct | 0.052 | TOL 0.004 | B | B | 0.010 | 0.006 | + | 0.002 |
| " " - 19 Oct | 0.050 | TOL 0.004 | XYL 0.002 | ETB 0.002 | 0.008 | 0.008 | + | 0.002 |

B = below 0.01 mg/m³
a) for abbreviations see Table 5

b = below detection limit
s = sample lost

+ = detected, but not quantifiable (see the text)

analyzed by only one of these techniques. Results are reported in Tables II and IV, respectively for Brussels and Luxembourg, in terms of «total >C₆» (see Experimental Procedures) and of the three most abundant compounds, whenever their concentration exceeded 0.01 mg/m³.

The «total» data compare well with the values reported in the literature for indoor air with, however, two exceptions, namely the two halls of the printing workshop in the Eastman building in Brussels. The high vapour concentration present in these spaces influences probably the air of the whole building, as may be understood from the concentration and the composition observed in the only other room (n. 306) of this building included in the survey. Results qualitatively similar to those of room n. 306 are also observed in the office of the printing workshop in the New Hemicycle in Luxembourg.

24 individual compounds (mostly solvents) have been detected at a concentration greater than 0.01 mg/m³, among which four compounds the identity of which could nor or not completely be established. Their concentrations have been derived using the mean instrument response factor for hydrocarbons and can

be underestimated if the compounds contain hetero-atoms (like oxygen, nitrogen or sulfur).

For an evaluation of these data with respect to their health significance two different criteria must be used. The results observed in the Eastman printing workshop can be compared with the limit values established for professionally exposed workers, because exposure in these rooms results from the working activity. Concentration of the main pollutant in this space, tetrachloroethene, is about half the lowest limit value fixed in a Western European country (Sweden), i.e. 135 mg/m³; the concentrations of the two next abundant compounds, n-heptane and methylcyclohexane, are about hundred times lower than the corresponding occupational limits. For all other rooms, where, as a principle, the exposure is not due to the working activity, a different criterion must be used. The recent WHO guideline document cited above /10/ includes also guideline values for a few organic compounds. Among these, in addition to benzene, for which «no safe level can be recommended as benzene is carcinogenic to humans», are three of the compounds observed in this survey, contributing altogether almost

Table V Identification of the compounds reported in tables II and IV

| | |
|-----|-------------------------|
| ACA | acetic acid |
| BEN | benzene |
| BUT | 1-butanol |
| DOD | n-dodecane |
| ETB | ethylbenzene |
| HEA | hexanal |
| HEX | n-hexane |
| HEP | n-heptane |
| MCH | methylcyclohexane |
| MCP | methylcyclopentane |
| 3MP | 3-methylpentane |
| 2MX | 2-methylhexane |
| 3MX | 3-methylhexane |
| 2MP | 2-methyl-1-propanol |
| OCT | n-octane |
| PED | n-pentadecane |
| PIN | α -pinene |
| 2PF | 2-propyl-furane |
| 2PR | 2-propanol |
| 1TC | 1,1,1-trichloroethane |
| TCE | trichloroethene |
| TEC | tetrachlorethene |
| TED | n-tetradecane |
| XYL | 1,3-xylene + 1,4-xylene |
| U-1 | unknown alcohol |
| U-2 | unknown alcohol |
| U-3 | unknown compound* |
| U-4 | unknown compound |

* most likely one of the following three:
1-butanol, 2-propylfurane, cyclohexane

half of the reported values, namely toluene, trichloroethene and tetrachloroethene. The WHO guideline concentrations are 1 mg/m³ for trichloroethene, 5 mg/m³ for tetrachloroethene and 7.5 mg/m³ for toluene. The highest concentrations observed are 0.64 and 0.61 mg/m³ for trichloroethene (64% and 61% of the guideline value); 1.25 mg/m³ for tetrachloroethene (25% of the guideline); 0.11 mg/m³ for toluene (1.5% of the guideline). The rooms where these higher concentrations occur are respectively: the Belliard meeting room n. 61 (where the air conditioning system was not working); the office attached to the printing workshop in the New Hemicycle; room n. 306 (Eastman), already mentioned above; room n. 162 (Remard, new building in which finishing works were still in progress). As the WHO guideline values refer to 24 hour exposure, whereas the employees will in general be exposed for only 8 hours/day, the maximum concentrations observed can be regarded as acceptable, but it must be borne in mind that relatively large fluctuations may occur from day to day, depending on the environmental conditions (weather, air conditioning, opening or closing of the doors, etc.) and due to human activities inside the building. The latter aspect is particularly important in the case of the buildings (Eastman, New Hemicycle) where the printing workshop may influence the air of the whole building.

D) CONCLUSIONS

The air change rate in room n. 810, Belliard building, and n. 105, Remorquer building, should be controlled, also in relation to the number of occupants.

The Schuman building shows formaldehyde levels slightly above the guideline concentration recently issued by the WHO for indoor air; this guideline however refers to 24 hour exposure. The printing workshop in the Eastman building, though considered as an industrial work-place, presents pretty high concentrations of VOC: these could become critical in comparison with legal limits under conditions different from those realized

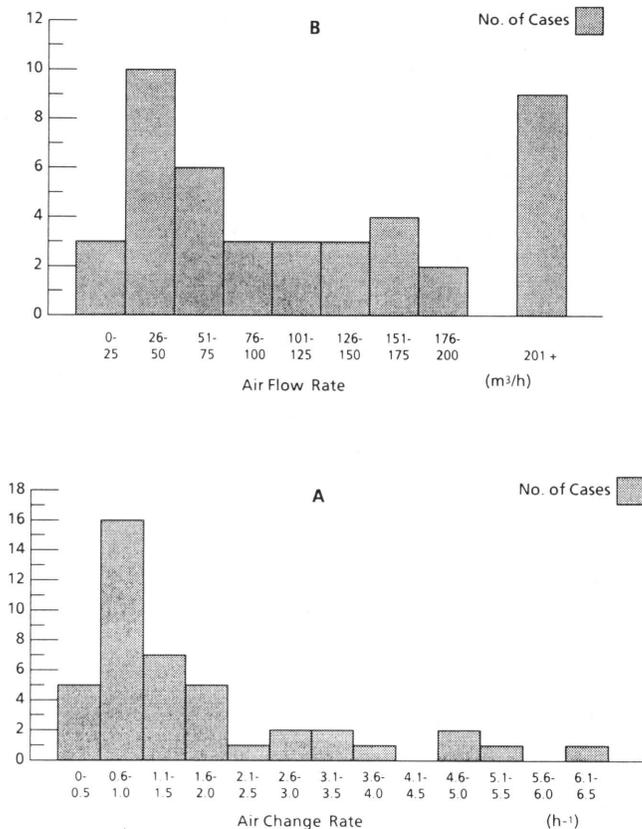


Fig. 1. Distribution of the air change rate and of the air flow rate.

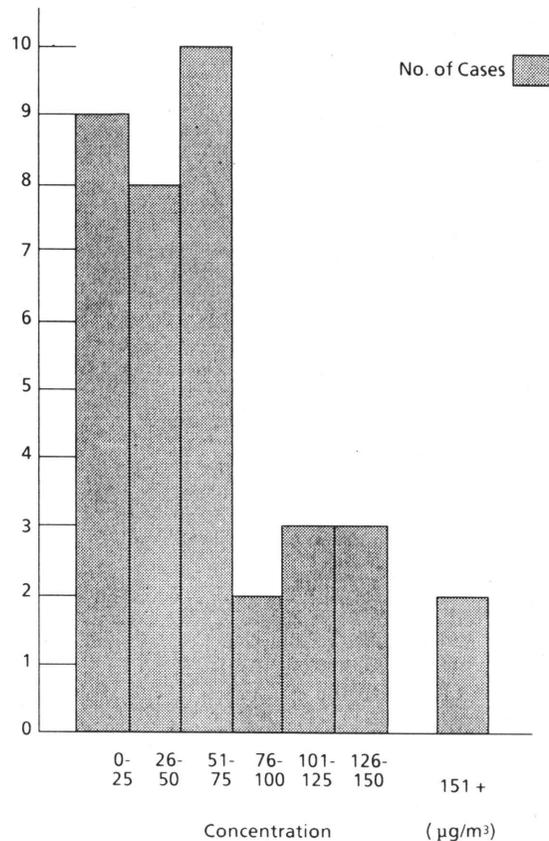


Fig. 2. Distribution of the formaldehyde concentrations observed.

at the moment of sampling for this survey. Moreover there are indications that vapours diffuse outside of the workshop and may pollute the air of other rooms in the building.

3. Participation in Exhibitions

The JRC presented its indoor activity at three exhibitions, in Milan (April 1987), Ghent (May 1987) and Madrid (September 1987). As an example of environmental analysis the determination of carbonyl compounds in mainstream and sidestream cigarette smoke was demonstrated with the scope to sensitize visitors for the problem of indoor air quality. As a spin off of the demonstrations a systematic investigation of carbonyl compounds in cigarette smoke has been performed. Results of this activity, which was partially performed during the exhibitions and partially in the laboratory, are presented in a separate topical report (see following pages).

REFERENCES

- /1/ L. LEBRET, H.J. VAN DE WIEL, H.P. BOS, D. NOIJ and J.S.M. BOLEIJ,
Volatile organic compounds in Dutch homes. *Environment Int.* 12, 323-332 (1986).
- /2/ M. DE BORTOLI, H. KNÖPPEL, E. PECCHIO, A. PEIL, L. ROGORA, H. SCHAUBURG, H. SCHLITT and H. VISSERS
Concentrations of selected organic pollutants in indoor and outdoor air in Northern Italy. *Environment Int.* 12, 343-350 (1986).
- /3/ L. WALLACE
The Total Exposure Assessment Methodology (TEAM) Study: Summary and Analysis, Vol. I, ORD, U.S. EPA, Washington DC 20460 (1987).
- /4/ C. KRAUSE, W. MAILAHN, R. NAGEL, C. SCHULZ, B. SEIFERT and D. ULLRICH
Occurrence of volatile organic compounds in the Federal Republic of Germany. IN: INDOOR AIR '87 (B. SEIFERT et al. eds.) Vol. 1, Institute for Water, Soil and Air Hygiene, p. 102-106 (1987).
- /5/ H. KNÖPPEL and H. SCHAUBURG
Screening of Household Products for the Emission of Volatile Organic Compounds. IN: INDOOR AIR '87 (B. SEIFERT et al., eds), Vol. 1, Institute for Water, Soil and Air Hygiene, p. 27-31 (1987).
- /6/ M. DE BORTOLI, H. KNÖPPEL, E. PECCHIO and H. VISSERS
Performance of a Thermally Desorbable Diffusion Sampler for Personal and Indoor Air Monitoring. IN: INDOOR AIR '87 (B. SEIFERT et al., eds.) Vol. 1, Institut for Water, Soil and Air Hygiene, p. 139-143 (1987).
- /7/ M. OEHME and H. KNÖPPEL
Analysis of Low Volatile (>C15) and Particle Bound Indoor Pollutants: Assessment of a Sensitive Method and First Results. IN: INDOOR AIR '87 (B. SEIFERT et al., eds.) Vol. 1, Institute for Water, Soil and Air Hygiene, p. 210-214 (1987).
- /8/ M. DE BORTOLI, H. KNÖPPEL, E. PECCHIO, A. PEIL, L. ROGORA, H. SCHAUBURG, H. SCHLITT and H. VISSERS.
Measurements of indoor air quality and comparison with ambient air», report n. EUR 9656, CEC 1985.
- /9/ International Energy Agency: «Energy conservation in buildings and community systems programme» Annex IX: Minimum ventilation rates, Final Report, August 1983.
- /10/ World Health Organization, Regional Office for Europe, «Air Quality guidelines», WHO Copenhagen 1987.

Carbonyl Compounds in Mainstream and Environmental Cigarette Smoke

Topical Report by H. Schlitt and H. Knöppel

INTRODUCTION

Carbonyl compounds, i.e. aldehydes and ketones, are an important class of indoor pollutants. Most attention has been focused on formaldehyde due to the high concentrations often found in indoor environments, its strong irritation potential and its suspected carcinogenicity. However, many other aldehydes and ketones have been detected in indoor air /1, 2/.

Several aldehydes and ketones have also been detected in mainstream cigarette smoke together with many other volatile organic compounds (VOC) using Tenax trapping and gas chromatographic-mass spectrometric detection /4/.

Due to the extremely complex pattern of VOC contained in cigarette smoke, however, the identification and quantitative analysis of single compounds by this technique is difficult and minor constituents may easily be overlooked.

In view of the important role of cigarette smoke as an indoor pollution source on one side and on the other side of the strong irritation potential of many carbonyl compounds as well as the mutagenic properties of several of them /3/ we have applied a specific analytical method to the selective detection of carbonyl compounds in mainstream (MS) and sidestream (SS) or environmental cigarette smoke.

The study consists of two parts. In part A carbonyl compounds in MS smoke of 34 cigarette brands available on the Italian market have been determined. For one «strong» cigarette (without filter) and one «light» cigarette (with filter) the delivery of carbonyl compounds as a function of the number of puffs has been measured. In addition the reproducibility of the emission measurements in MS and SS smoke has been determined, analyzing 5 cigarettes of the «light» brand under the same experimental conditions.

In part B carbonyl compounds in MS smoke have been compared with those in SS (or environmental) smoke of the above mentioned «strong» and «light» cigarettes in terms of absolute amounts of average concentrations. The latter are also compared with available MAWC's (maximum admitted workplace concentrations). In addition the influence of the air velocity on these quantities has been determined.

EXPERIMENTAL

Cigarettes were tested using the experimental set-up shown in Fig. 1.

For the analysis of MS smoke cigarettes were lighted and attached to sampling train A. The personal pump D (Du Pont, type Alpha 1) was adjusted to a constant flow rate of 500 mL/min. In the open position of electrovalve F only a negligible amount of air was drawn through the cigarette. The valve was closed for two seconds per minute yielding a cigarette puff of 16.7 mL (compared to 35 mL of a standard puff /5/). Cigarettes without filter were smoked up to a remaining length of about 8 mm, filter cigarettes up to about 2 mm (in addition to the filter length), yielding 10 ± 2 puffs/cigarette. The cigarette smoke passed through the impinger bottles C, where carbonyl compounds were absorbed and reacted. The trap E contained water and served to protect pump D from acetonitrile evaporating from the impinger bottles C (see below).

For the analysis of both, mainstream and sidestream smoke, the cigarette was inserted into the Plexiglas^R tube J (14 cm diameter).

A controlled air flow ranging from 3.5-35 L/min was passed through the flow meter H and the Plexiglas^R tube by means of the adjustable bellows pump G, corresponding to linear air velocities of 4-38 mm/sec in case of a laminar flow (as a matter of fact the flow was turbulent as the good mixing of the cigarette smoke in tube J showed; see section «Results and Discussion»

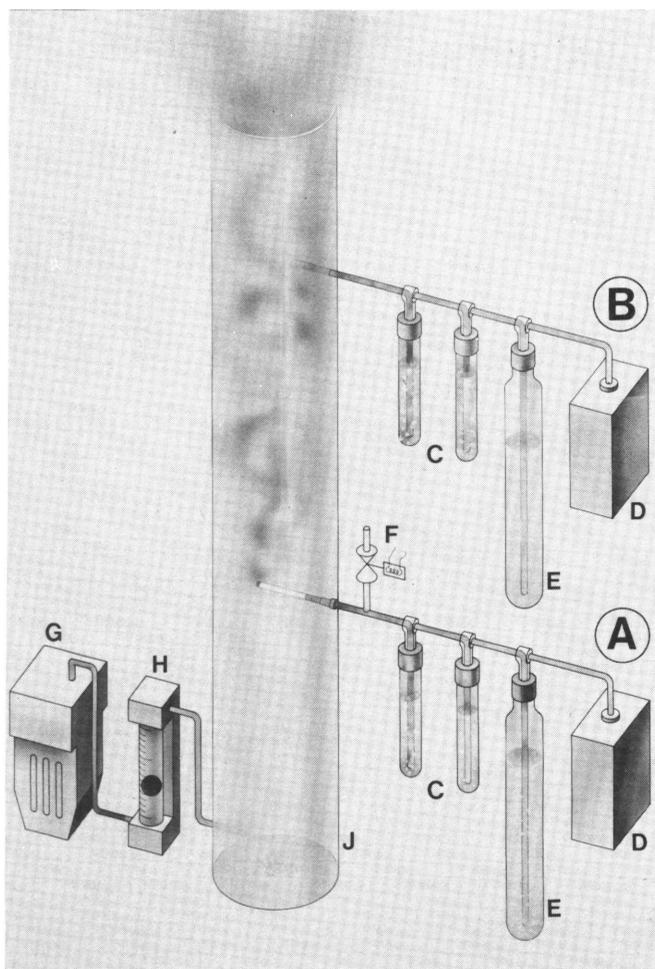


Fig. 1. Experimental set-up for the determination of carbonyl compounds in mainstream (MS) and sidestream (SS) cigarette smoke. A = sampling train for MS smoke. B = sampling train for SS smoke. C = impinger bottles containing DNPH in acetonitrile; D = constant flow personal pumps; E = water traps preventing acetonitrile from entering the personal pumps; F = bypass valve; G = bellows pump; H = flow meter; J = plexiglas tube

below). An aliquot of the diluted SS smoke was drawn through sample train B with a flow rate of 500 mL/min during the entire smoking period. The distance between the cigarette and the sampling position of SS smoke was 50 cm.

Carbonyl compounds in MS and SS smoke were determined through their reaction with dinitrophenylhydrazine (DNPH) following the method of LIPARI et al. /6/. The impinger bottles C contained each 15 mL of a solution of 1 mg DNPH in 1 mL of purified acetonitrile. Instead of 1 N HClO₄ as used by LIPARI et al. 250 μL of 10 N H₃PO₄ were added to each impinger bottle. The second impinger bottle served as breakthrough control and contained in none of the experiments more than 5% of the detected carbonyl compounds. After sampling the remaining volume was determined and 10 μL injected on top of two (initially one) HPLC columns in series (2x Supelcosil RP-18, 25 × 0.48 cm, Supelco Inc., Bellefonte, PA). Hydrazones, the reaction products of DNPH with carbonyl compounds, were eluted using a water/acetonitrile gradient starting with 50% CH₃CN and increasing to 90% CH₃CN in 40 min. A scanning UV detector (Hewlett-Packard, model 1040A) was used for the detection and identification of the hydrazones. Known amounts of hydrazones of all identified carbonyl compounds have been produced reacting pure carbonyl compounds with DNPH. They were used as standards for quantitative analyses and to establish a library of UV spectra. Figure 2 shows a typical HPLC chromatogram of carbonyl compounds (resp. their hydrazones) in sidestream cigarette smoke.

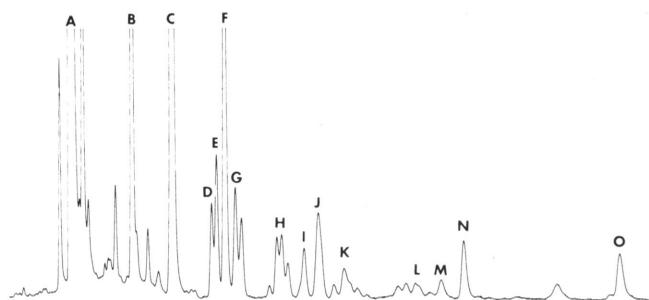


Fig. 2. HPLC chromatogram of the carbonyl compounds (resp. their hydrazones) typically present in tobacco smoke. Column: 2 × 250 mm × 4.6 mm, 5 μm Supelcosil LC 18 columns; mobile phase: gradient from 50% acetonitrile in water to 82% acetonitrile in 40 min.; flow: 1.0 ml/min.

A = unreacted DNPH, B = formaldehyde, C = acetaldehyde, D = furfural, E = acrolein, F = acetone, G = propanal, H = crotonaldehyde (2-butenal), I = methyl-vinyl-ketone, J = butanone, K = benzaldehyde, L = 3-methyl-butanal, M = n-pentanal, N = methylglyoxal, O = betanedione.

RESULTS AND DISCUSSION

A. Carbonyl compounds in mainstream cigarette smoke

Mainstream cigarette smoke of 34 different cigarette brands (9 Italian and 25 international, 10 without and 24 with filter) has been analysed for its carbonyl compound content. Table I reports the quantities of 13 carbonyl compounds and their total amount in μg/cigarette. Acetaldehyde is by far the most abundant single constituent contributing 57 ± 15% to the total. With one exception (cigarette F) acetone is the second abundant constituent followed by butanone and propanal with rather similar abundances. However, whereas butanone has been detected in the MS smoke of all cigarettes propanal has not been detected in four of them (B, P, Q, Z). The next abundant compounds is acrolein, detected in the MS smoke of all but one (DD) cigarette. In these experiments acrolein could not be separated from furfural, which contributes about 20% to the reported acrolein values. Acrolein is one of the strongest known irritants (see section B). Other fairly frequently detected compounds are crotonaldehyde, methyl-vinyl-ketone, 3-methyl-butanal and n-pentanal.

Formaldehyde is only a minor constituent of MS cigarette smoke and could not be detected at all in the MS smoke of 10 cigarettes. Other occasionally detected minor constituents are butanedione (= dimethyl-glyoxal), methyl-glyoxal and benzaldehyde. In order to assess the amount of carbonyl compounds inhaled by a smoker of a «light» filter cigarette (brand EE) and a «strong» cigarette without filter (H) as a function of the puff number, after each second puff and after each of the two last puffs 10 μL of the trapping solution in the first impinger bottle of sampling train A were injected onto the HPLC column and analyzed for their carbonyl compound content. The logarithms of the sum of the detector counts of all carbonyl compounds are plotted in Fig. 3 against the puff number for the «light» resp. the «strong» cigarette together with the calculated linear correlation lines. In addition the correlation coefficients *r* are given.

The results show that the cumulative amount of carbonyl compounds in mainstream cigarette smoke increases nearly exponentially with the puff number. It results in particular that the last two puffs contain about the same amount as all preceding ones.

The variation of the emission between cigarettes of the same brand is shown in Table II. The table reports the results of the analyses of the carbonyl compounds contained in MS and SS smoke of five cigarettes of the same brand (the «light» filter

TABLE I. Amounts of carbonyl compounds released into mainstream smoke by cigarettes of 34 brands commercially available in Italy ($\mu\text{g}/\text{cigarette}$)

| Compounds ¹⁾ | National Italian commercial brands without filter | | | International commercial brands without filter | | | | | | | National Italian commercial brands with filter | | | | | |
|-------------------------|---|-----|-----|--|------|-----|-----|-----|-----|-----|--|-----|-----|-----|-----|-----|
| | A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P |
| Formaldehyde | 16 | 5.1 | 0.9 | * | 8.0 | 2.1 | 2.0 | 6.2 | 4.1 | * | 3.3 | 4.1 | 3.7 | 4.0 | 2.5 | * |
| Acetaldehyde | 747 | 462 | 375 | 896 | 622 | 548 | 493 | 413 | 315 | 272 | 339 | 308 | 230 | 203 | 175 | 55 |
| Acrolein ³⁾ | 83 | 28 | 16 | 48 | 53 | 12 | 22 | 39 | 22 | 19 | 12 | 19 | 17 | 13 | 10 | 2.6 |
| Acetone | 325 | 95 | 170 | 215 | 215 | 51 | 151 | 189 | 111 | 120 | 44 | 140 | 109 | 73 | 62 | 18 |
| Propanal | 122 | * | 47 | 101 | 94 | 59 | 63 | 58 | 41 | 34 | 35 | 42 | 33 | 26 | 22 | * |
| Crotonaldehyde | 62 | 8.5 | 7.3 | 16 | 20 | * | 14 | 29 | 11 | 15 | * | 14 | 14 | 3.8 | 4.4 | * |
| Methyl-Vinyl-Ketone | 39 | * | * | 18 | 11 | * | 7.6 | 17 | 4.7 | 8.3 | * | 12 | 5.7 | 2.0 | * | * |
| Butanone | 136 | 59 | 93 | 118 | 86 | 43 | 68 | 71 | 47 | 61 | 26 | 55 | 45 | 23 | 24 | 6.9 |
| Benzaldehyde | 15 | * | 5.7 | * | 3.8 | * | * | * | * | * | * | * | * | * | * | * |
| 3-Methyl-Butanal | 36 | 16 | 22 | 28 | 17 | 14 | 15 | 13 | 11 | 15 | 4.4 | 8.1 | 6.6 | 5.1 | 5.6 | * |
| n-Pentanal | 55 | 31 | 37 | 51 | 34 | 31 | 29 | 30 | 21 | 23 | 12 | 17 | 14 | 9.0 | 7.9 | * |
| Methyl-Glyoxal | 5 | * | 7.2 | * | 2.7 | * | * | 3.5 | * | * | * | * | * | * | * | * |
| Butanedione | 21 | * | 24 | * | 1.5 | * | * | 15 | * | * | * | 6.3 | 4.7 | * | * | * |
| TOTALE | 1662 | 695 | 722 | 1491 | 1168 | 760 | 865 | 884 | 588 | 567 | 476 | 626 | 483 | 362 | 313 | 83 |

¹⁾ see fig 1. ²⁾ Menthol taste ³⁾ together with Furtural * not detected

TABLE I (continued)

| Compounds ¹⁾ | International Commercial Brands with Filter | | | | | | | | | | | | | | | | | |
|-------------------------|---|-----|-----|-----|-----|-----|-----|-----|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | Q | R | S | T | U | V | W | X | Y ²⁾ | Z | AA | BB | CC | DD | EE | FF | GG | HH |
| Formaldehyde | 4.3 | 6.9 | 4.2 | 4.3 | * | 4.2 | 2.8 | 4.4 | 3.2 | 1.2 | * | * | * | 1.8 | 2.0 | * | * | * |
| Acetaldehyde | 372 | 314 | 294 | 271 | 265 | 228 | 204 | 170 | 142 | 109 | 105 | 96 | 95 | 77 | 64 | 63 | 60 | 34 |
| Acrolein ³⁾ | 24 | 25 | 15 | 19 | 24 | 17 | 10 | 9.6 | 8.6 | 6.1 | 5.6 | 4.9 | 4.2 | * | 1.9 | 2.5 | 3.3 | 1.8 |
| Acetone | 169 | 99 | 99 | 113 | 96 | 87 | 95 | 74 | 64 | 34 | 47 | 41 | 38 | 21 | 14 | 29 | 27 | 13 |
| Propanal | * | 37 | 32 | 51 | 38 | 31 | 26 | 19 | 19 | * | 14 | 12 | 11 | 6.4 | 3.9 | 7.5 | 6.9 | 3.6 |
| Crotonaldehyde | 13 | 5.7 | 9.9 | 13 | 1.4 | 8.6 | 12 | 7.7 | 6.0 | * | 5.4 | * | 4.5 | * | * | * | * | * |
| Methyl-Vinyl-Ketone | 13 | 7.5 | 5.6 | 9.5 | 9.2 | 3.3 | 8.7 | 7.2 | 5.7 | * | * | * | * | * | * | * | * | * |
| Butanone | 62 | 32 | 34 | 44 | 47 | 32 | 36 | 32 | 26 | 12 | 19 | 16 | 16 | 6.4 | 4.1 | 11 | 10 | 5.1 |
| Benzaldehyde | * | * | * | * | 3.0 | * | * | * | * | * | * | * | * | * | * | * | * | * |
| 3-Methyl-Butanal | 9.7 | 9.2 | 6.3 | 6.9 | * | * | 9.6 | 4.5 | 4.5 | * | * | * | * | * | * | * | * | * |
| n-Pentanal | 26 | 14 | 16 | 15 | * | * | 14 | 10 | 8.2 | * | * | * | * | * | * | * | * | * |
| Methyl-Glyoxal | * | * | * | * | 3.1 | * | * | * | * | * | * | * | * | * | * | * | * | * |
| Butanedione | 6.6 | * | * | 5.6 | nd | * | 13 | * | * | * | 5.7 | * | * | * | * | * | * | * |
| TOTALE | 700 | 550 | 516 | 552 | 527 | 411 | 431 | 338 | 287 | 162 | 202 | 170 | 169 | 113 | 90 | 113 | 107 | 58 |

¹⁾ see fig 1. ²⁾ Menthol taste ³⁾ together with Furtural * not detected

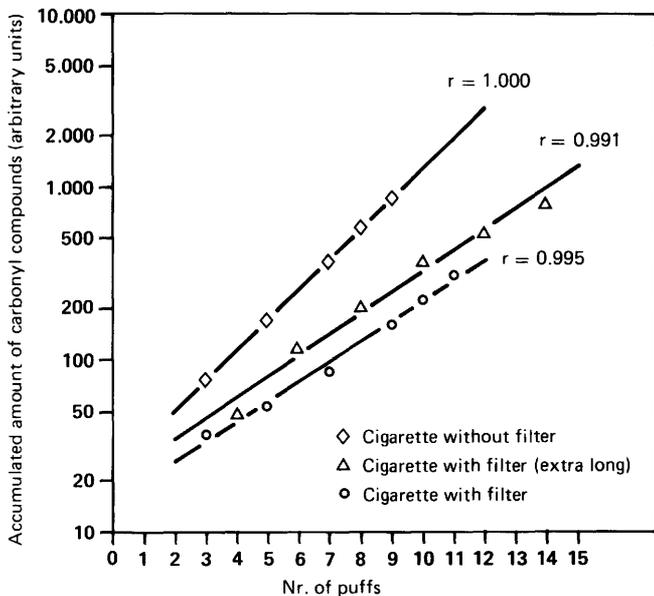


Fig. 3. Semi-logarithmic plot of the total amount of carbonyl compounds accumulated in the first impinger bottle of sampling train A (see Fig. 1) as a function of puff number for cigarettes of three brands.

TABLE II. Mean value and standard deviations of the amounts per cigarette of carbonyl compounds in MS and SS smoke of five cigarettes of the same brand

| Compound | SS | | MS | |
|---------------------|---------------------------|--------------------|---------------------------|--------------------|
| | mean value (µg/cigarette) | Standard deviation | mean value (µg/cigarette) | Standard deviation |
| Formaldehyde | 2360 | ± 28% | 3.2 | ± 18% |
| Acetaldehyde | 4830 | ± 5% | 95 | ± 49% |
| Acrolein + Furfural | 1090 | ± 18% |) |) |
| Acetone | 1620 | ± 10% | 24 | ± 52% |
| Propanal | 390 | ± 10% | 4.6 | ± 51% |
| Crotonaldehyde | 280 | ± 4% | * | * |
| Methyl-Vinyl-Ketone | 260 | ± 9% | * | * |
| Butanone | 660 | ± 18% | 8.5 | ± 28% |
| Methyl-Glyoxal | 160 | ± 64% | * | * |
| TOTAL | 11640 | ± 10% | 135 | ± 48% |

) only two values >0 * not detected

cigarette mentioned above). Variations in SS smoke in terms of standard deviation are of the order of 10-20% (with the exception of formaldehyde and methyl-glyoxal, a minor constituent). They are considerably smaller than those in MS smoke, where major constituents show a standard deviation of about 50%. The strong increase of the carbonyl compound concentration in MS smoke with the puff number may be a reason for the greater variation.

B. The comparison of MS and SS cigarette smoke with respect to its content of carbonyl compounds has been performed using cigarettes of the «light» and the «strong» brand mentioned above. The total amounts of carbonyl compounds released into MS and SS smoke are compared in Table III. In order to determine the amount released into SS smoke, the amount trapped in the impinger bottles of sampling train B was multiplied by

TABLE III. Amounts of carbonyl compounds released into MS and SS smoke of a «light» filter cigarette and a «strong» cigarette without filter and ratios of the amounts in SS and MS smoke

| Compound | Amounts (µg/cigarette) | | | | Ratio SS/MS | |
|---------------------------------|------------------------|-------------|------------|-------------|-------------|----------|
| | MS "light" | MS "strong" | SS "light" | SS "strong" | "light" | "strong" |
| Formaldehyde | 2.4 | 15 | 2200 | 2300 | 920 | 150 |
| Acetaldehyde | 95 | 590 | 4700 | 6100 | 49 | 10 |
| Furfural | 0.7 | 11 | 340 | 240 | 490 | 22 |
| Acrolein (= 2-propenal) | 3.2 | 41 | 820 | 880 | 260 | 21 |
| Acetone | 21 | 120 | 1600 | 2000 | 76 | 17 |
| Propanal | 5.5 | 56 | 420 | 560 | 76 | 10 |
| Crotonal (= 2-butenal) | 1.1 | 19 | 340 | 430 | 310 | 23 |
| Methyl-Vinyl-Ketone | 1.1 | 7.5 | 280 | 290 | 250 | 39 |
| Butanone | 8.5 | 60 | 740 | 930 | 87 | 16 |
| Benzaldehyde | --- | 1.9 | 78 | 78 | --- | 41 |
| 3-Methyl-Butanal | 0.5 | 13 | 66 | 100 | 130 | 7.7 |
| n-Pentanal | 0.5 | 13 | 66 | 100 | 130 | 7.7 |
| Methylglyoxal | 1.1 | 4.4 | 350 | 300 | 320 | 68 |
| Butanedione (= dimethylglyoxal) | --- | 3.6 | 240 | 240 | --- | 67 |

the ratio of the air flow through the Plexiglas^R tube J (as determined by the flow meter H, see Fig. 1) and the flow through the sampling train. At the total flow of 30 L/min applied in these experiments, sampling at different positions across the Plexiglas^R tube section yielded differences comparable to the differences between individual cigarettes of the same when samples were taken at the same position (see Table II). It was therefore concluded that the SS smoke at 50 cm distance from the cigarette was fairly well mixed and homogeneous.

Table III shows two interesting results: (a) in the described experimental conditions (puff volume 16.7 mL, 10 ± 2 puffs/cigarette) the amount of carbonyl compounds released to the environment is from about 10 to 1000 times higher than that inhaled by a smoker (for the standard puff volume of 35 mL these factors have to be divided by two). As may be expected this difference is greater for filter cigarettes than for cigarettes without filter. It is particularly high for formaldehyde. (b) Whereas carbonyl compounds in MS smoke are 5-10 times more abundant for cigarettes without filter compared to filter cigarettes, no such difference exists for SS smoke. This result underlines the fact that filters protect to a certain extent the «active» but not the «passive» (i.e. involuntary) smoker and that so-called «light» cigarettes are of no benefit with respect to indoor pollution by environmental tobacco smoke.

In Table IV the average concentrations of carbonyl compounds in MS and SS smoke of a «light» and a «strong» cigarette are compared to one another and to maximum admitted workplace concentrations (MAWC's). Like the total amounts (see Table III), also the average concentrations in the SS smoke of the two cigarette types differ only modestly from one another (50%), whereas the concentrations in MS smoke are about 20 times higher than those in SS smoke for the «light» cigarette and nearly 120 times higher for the «strong» cigarette. If one compares, however, the inhaled volume of MS smoke for one cigarette (about 0.35 L for 10 standard puffs of 35 mL each) to the breathing volume of a «passive» smoker during the burning time of a cigarette (about 100 L in 10 min), it follows that in case of the «strong» cigarette a «passive» smoker at 50 cm downwind the cigarette may inhale 2.4 times the amount of carbonyl compounds inhaled by an «active» smoker and even 14 times this amount in case of a «light» cigarette.

TABLE IV. Average concentrations and relative contributions to the total amount of carbonyl compounds in MS and SS smoke of a «light» filter cigarette and a «strong» cigarette without filter. Comparison with MAWC values

| Compound | "light cigarette" | | | | "strong cigarette" | | | | M.A.W.C. ²⁾ µg/L or mg/m ³ |
|------------------------------------|--------------------------|---------------------|--------------------------|---------------------|--------------------------|---------------------|--------------------------|---------------------|---|
| | MS µg/L ¹⁾ | MS % of total | SS µg/L ¹⁾ | SS % of total | MS µg/L ¹⁾ | MS % of total | SS µg/L ¹⁾ | SS % of total | |
| Formaldehyde | 13 | 1.7 | 6.7 | 18 | 100 | 1.6 | 8.4 | 15 | 1.2 |
| Acetaldehyde | 519 | 68 | 14 | 38 | 3930 | 62 | 23 | 42 | 90 |
| Furfural | 4 | 0.5 | 1.0 | 2.7 | 70 | 1.1 | 0.9 | 1.7 | 20 |
| Acrolein (= 2-propenal) | 17 | 2.2 | 2.5 | 6.8 | 272 | 4.3 | 3.2 | 5.9 | 0.25 |
| Acetone | 115 | 15 | 4.9 | 13 | 805 | 13 | 7.4 | 14 | 2400 ³⁾ |
| Propanal | 30 | 3.9 | 1.3 | 3.5 | 375 | 5.9 | 2.1 | 3.9 | 5 |
| Crotonal (= 2-butenal) | 6 | 0.8 | 1.0 | 2.7 | 128 | 2.0 | 1.6 | 3.0 | 0.5 - 6 ⁵⁾ |
| Methyl-Vinyl-Ketone | 6 | 0.8 | 0.8 | 2.2 | 50 | 0.8 | 1.1 | 2.0 | 0.1 ⁴⁾ |
| Butanone | 46 | 6.0 | 2.3 | 6.2 | 395 | 6.2 | 3.4 | 6.3 | 590 |
| Benzaldehyde | * | * | 0.2 | 0.5 | 13 | 0.2 | 0.3 | 0.6 | 20 ⁶⁾ |
| 3-Methyl-Butanal | 3 | 0.4 | 0.2 | 0.5 | 89 | 1.4 | 0.4 | 0.7 | * |
| n-Pentanal | 3 | 0.4 | 0.2 | 0.5 | 87 | 1.4 | 0.4 | 0.7 | 175 ⁷⁾ |
| Methylglyoxal | 6 | 0.8 | 1.1 | 3.0 | 29 | 0.5 | 1.1 | 2.0 | * |
| Butanedione (= dimethylglyoxal) | * | * | 0.7 | 1.9 | 24 | 0.4 | 0.9 | 1.7 | * |
| TOTAL | 768 | | 369 | | 6367 | | 542 | | |

Key to Table IV (of topical report):

- 1) Mean value.
- 2) Maximum admitted workplace concentration.
Where not otherwise indicated, values issued in 1985 in the FRG are given.
- 3) 600 in Denmark
- 4) Defined only in USSR
- 5) Limit varying between countries. Since 1985, no limit in the FRG due to reasonable suspicion of cancerogenicity
- 6) In Italy
- 7) TWA in the U.S.A.

* No value defined

Of the compounds for which MAWC values are defined all but acetone, butanone and benzaldehyde exhibit average MS concentrations higher than the MAWC values, whereas in SS smoke at 50 cm downwind the burning zone only the average concentrations of formaldehyde and acrolein exceed MAWC values defined in Community countries. It should, however be mentioned, that in the FRG crotonaldehyde is considered a suspected human carcinogen and therefore no MAWC value is defined. In the USSR a MAWC value for methyl-vinyl-ketone of 0.1 µg/L has been established, which is exceeded in both, MS and SS smoke.

Table IV reports also the relative contributions of the single carbonyl compounds to the total mean concentration. The largest difference between MS and SS smoke exists for formaldehyde, the relative contribution of which is about 10 times higher in SS

smoke for both, the «light» and the «strong» cigarette. Methylglyoxal and butanedione are also significantly more abundant in SS smoke of both cigarette brands whereas furfural, acrolein, and crotonal are significantly more abundant only in SS smoke of the «light» cigarette.

The influence of a variation of the air flow through the Plexiglas[®] tube J (see Fig. 1) from 4 to 35 L/min on the amount of carbonyl compounds released into MS and SS smoke is shown in Fig. 4. As may be expected, the amount of carbonyl compounds per cigarette in MS smoke is essentially independent of the air flow, i.e. variations are of the same magnitude as those

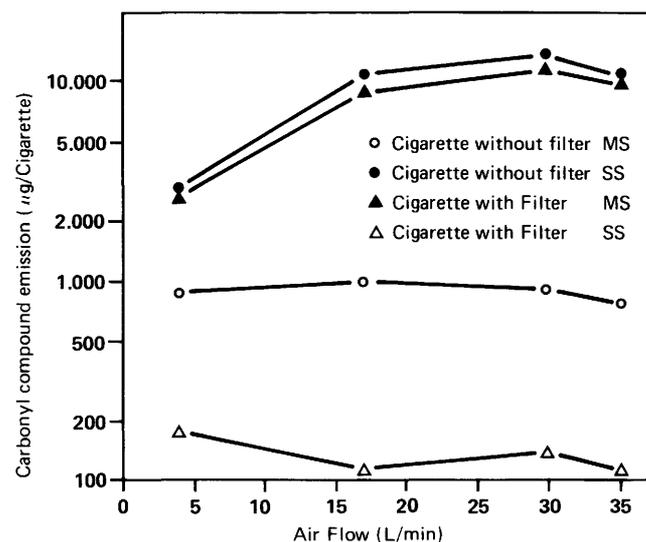


Fig. 4. Total amount of carbonyl compounds (µg/cigarette) released into MS and SS smoke by a cigarette with and without filter as a function of the air flow through plexiglas tube J (see Fig. 1).

between individual cigarettes of the same brand. The amount of carbonyl compounds per cigarette in SS smoke shows an increase by about a factor of 3 between 4 and 17 L/min and remains essentially constant between 17 and 35 L/min. The reported measurements has been performed in this range.

CONCLUSION

Acetaldehyde is the most prominent carbonyl compound in both, MS and SS cigarette smoke accounting for $57 \pm 15\%$ of the total and is a good indicator of smoking in an indoor environment. All but one of the 10 aldehydes and 4 ketones which have been identified are known irritants. Among them acrolein, crotonaldehyde and methyl-vinyl-ketone are highly toxic compounds and lachrymators, acrolein even a severe one, and, hence, deserve particular attention. In addition, acetaldehyde, crotonaldehyde and formaldehyde are suspected carcinogens. These and a few other detected aldehydes have shown mutagenic activity in the Ames salmonella test, as will be outlined in a later report.

Concentrations of carbonyl compounds in MS smoke increased exponentially with the puff number. As a result under standard smoking conditions the last two of an average of 10 puffs/cigarette contain about the same amount of carbonyl compounds as the preceding 8 ones.

Cigarettes with and without filter, «light» and «strong» ones, release comparable amounts of carbonyl compounds to sidestream smoke, i.e. to the environment. This amount is under standard smoking conditions (35 mL/puff, 1 puff/min) from 4 to 500 times higher than that delivered to MS smoke, i.e. to the smoker, depending on the compound and cigarette type. In particular a «passive» smoker at 50 cm downwind a cigarette may inhale more than 10 times the amount «actively» taken up by the smoker.

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REFERENCES

- /1/ M. DE BORTOLI, H. KNÖPPEL, E. PECCHIO, A. PEIL, L. ROGORA, H. SCHAUBURG, H. SCHLITT and H. VISSERS
Concentrations of selected organic pollutants in indoor and outdoor air in Northern Italy. *Environ. Int.* 12, 1986, pp. 343-350.
- /2/ B. BERGLUND, U. BERGLUND and T. LINDVALL
Assessment of discomfort and irritation from the indoor air. In: *Proceedings of «AIQ '86. Managing Indoor Air for Health and Energy Conservation»*. Atlanta, GA: American Society of Heating, Refrigerating and Air Conditioning Engineers, Inc. (ASHRAE), 1986, pp. 138-149.
- /3/ R. BARALE
Private communication
- /4/ C.E. HIGGINS, W.E. GRIEST and G. OLERICH
Application of Tenax trapping to analysis of gas phase organic compounds in ultra-low tar cigarette smoke. *J. Assoc. Off. Anal. Chem.* 66, 1983, pp. 1074-1083.
- /5/ C.E. WYNDER and D. HOFFMAN (1967)
Tobacco and Tobacco Smoke. Academic Press, New York, NY, p.318.
- /6/ F. LIPARI and S.J. SWARIN
Determination of formaldehyde and other aldehydes in automobile exhaust with an improved 2, 4-dinitrophenylhydrazine method. *J. of Chromatography* 247, 1982, pp. 297-306.

1.3. TRACE METAL EXPOSURE AND HEALTH EFFECTS

Introduction

Trace metal pollution is of major concern for European health and environmental policies. Due to high industrialisation, intensive agriculture and increasing coal burning for energy production, trace metal levels are widespread and increasing.

The setting of exposure limits and standards of environmental quality, although a matter of policy decision, is relying on the creation of new scientific information in the field of environmental toxicology.

Especially low level-long term exposure /vs. effects relationships have to be established and the concentration of trace metals in critical organs and indicator media (blood, urine) determined. The following JRC activities on trace metals like Cd, As, V, Tl, Hg are contributing to this task:

- quality assurance for sampling, handling, storage and biochemical fractionating of human tissues;
- systematic multielement microdeterminations by NAA (Neutron Activation Analysis) in human samples at different exposure levels;
- metabolism of trace metals by long term-low dose laboratory animal experiments;
- assessments of the toxicological significance of trace metals in exposed and unexposed populations.

Results

With in this general frame pointed out above in 1987 results on the following items were gained which are still of preliminary nature or will be published in special scientific journals and are therefore not reported extensively in this annual report. (On the contrary a metallo-biochemical study on the metabolic reduction of pentavalent to trivalent arsenic in cell cultures is presented in the following topical report):

- bioavailability of arsenic in cooked shrimps which have been spiked with ^{73}As -labelled arsenobetaine;
- ratio of ingested vs. inhaled tetravalent and pentavalent vanadium in laboratory animals;
- in vitro distribution of trace metals in human blood;
- uptake and effects of iron in melanoma cells;
- determinations of trace metal concentrations in the lung, blood and urine as reference values for the normal population.
- determination of trace metal concentrations in tissues and body fluids of subjects affected by lung and liver disorders (sarcooidosis, pneumoconiosis and tumors);
- neutron activation analyses of bronchoalveolar lavage for the establishment of clinical case reports and clinical diagnosis of trace metal induced lung diseases.

Cellular uptake and metabolic reduction of pentavalent to trivalent arsenic as determinants of cytotoxicity and morphological transformation

Topical Report by F. Bertolero*, G. Pozzi, E. Sabbioni, U. Saffiotti**

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INTRODUCTION

Conclusive epidemiological evidence exists for an increased risk for lung cancer and for non-melanotic skin cancer following exposure to inorganic arsenic (1). A possible carcinogenic effect was recently reported in hamster lungs (2), but most animal experiments have, so far, resulted in negative findings (3).

This discrepancy may be due to species-specific metabolic differences between human subjects and laboratory rodents. Studies have shown significantly different arsenic metabolism in rats as compared with humans and other mammals (4). In human as well as in rabbits, inorganic arsenic is methylated *in vivo* through pathways which have not yet been identified and the methylated metabolites were shown to have a very low affinity for macromolecules and to be rapidly excreted (5). Arsenic methylation is, therefore, regarded as a detoxification mechanism. The increase in cancer risk observed in epidemiological occupational studies has been attributed mainly to the presence of inorganic trivalent arsenic (6).

Experimental toxicity studies have shown that trivalent arsenic is more toxic at equimolar concentrations than pentavalent arsenic (7). On the other hand, the observation that inorganic pentavalent arsenic can be reduced *in vivo* to the more toxic trivalent form (8) may have major implications in carcinogenesis. At the present time, since an adequate animal model to study the mechanisms of arsenic-induced carcinogenicity is still lacking, *in vitro* systems are mostly used to determine the cellular effects of inorganic arsenicals (9).

A recent study with Syrian hamster embryo cells reported that inorganic arsenic induced cell transformation and chromosome damage, but no gene mutations over a similar dose range (10). Also in these assays, trivalent arsenite was more active than pentavalent arsenate.

In the present study, we determine toxicity and morphological transformation induced in the mouse embryo cell line BALB/3T3 clone A31-1-1, by both trivalent and pentavalent inorganic arsenic. We also investigated the biotransformation of pentavalent arsenate to trivalent arsenite in these cells and correlated the absorbed dose and the toxic effects with the oxidation state of intracellular and extracellular arsenic.

RESULTS

Cellular uptake

The rate of ^{73}As -arsenic uptake by BALB/3T3 cells after incubation with either sodium arsenite (Figure 1) or sodium arsenate (Figure 2) was dose-dependent in both cases. It was highest during the first hour of exposure and decreased thereafter, more so in arsenate than in arsenite treated cells, suggesting a possible release of incorporated arsenic. Incubation for 1 h with equimolar (3×10^{-6} M) concentrations of arsenite or arsenate resulted in a 4-fold higher incorporation of arsenic in cells exposed to arsenite (Figure 1) as compared to arsenate (Figure 2).

Cytotoxicity

A colony forming assay was used to estimate the cytotoxicity effect after 24 or 72 h of exposure to arsenite or arsenate (Figure 3). The inhibition of CFE was dose-dependent with all treatments. Trivalent arsenic was more toxic than pentavalent arsenic at both

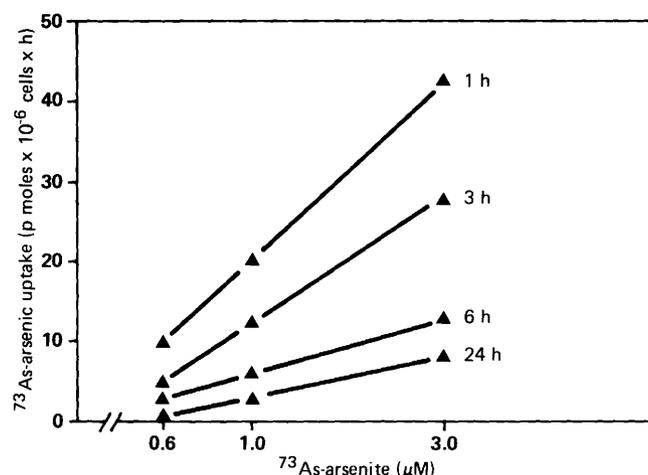


Fig. 1. Rate of ^{73}As -arsenite uptake by BALB/3T3 cells.

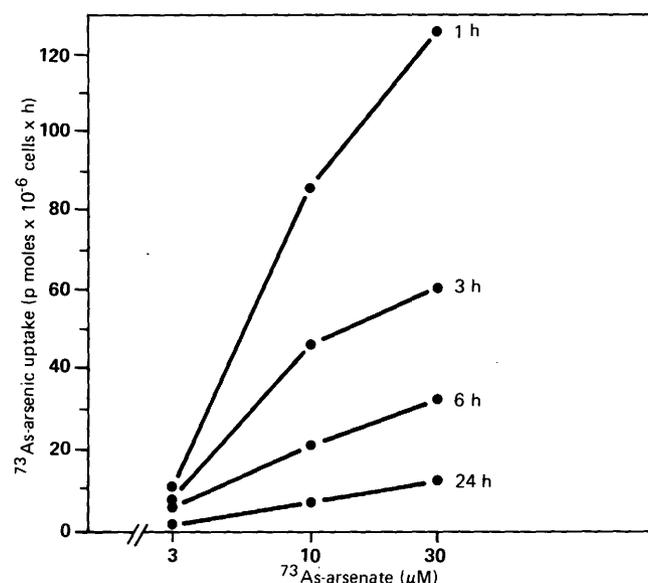


Fig. 2. Rate of ^{73}As -arsenate uptake by BALB/3T3 cells

exposure times. In contrast, when CFE inhibition was correlated not to be external dose as in Figure 3, but to the total cellular arsenic burden (Figure 4), a linear decrease in CFE was found with a logarithmic increase of the absorbed dose for both arsenic forms. Regression analysis indicated that the two parameters, CFE and absorbed dose, were highly correlated and no significant difference in the resulting dose-response curve was observed for treatments with either form of arsenic (Figure 4).

Intracellular arsenic speciation

The intracellular partition and speciation of absorbed arsenic was examined after exposure to different concentrations of either arsenite or arsenate (Table I). Already after 1 h incubations, more than 90% of the cell associated ^{73}As -arsenic was recovered in the cytosol (105,000 g supernatant), practically in all cases and independently from the valence state of the arsenic administered (Table I). At all times between 1 and 24 h and for both arsenic forms, more than 99% of cytosolic arsenic was inorganic and no methylated arsenic metabolites could be detected by ion exchange chromatography.

The speciation of the valence state of intracellular inorganic arsenic is reported in Table II. In cells exposed to arsenite from 1 h to 24 h, intracellular arsenic was all in the trivalent state,

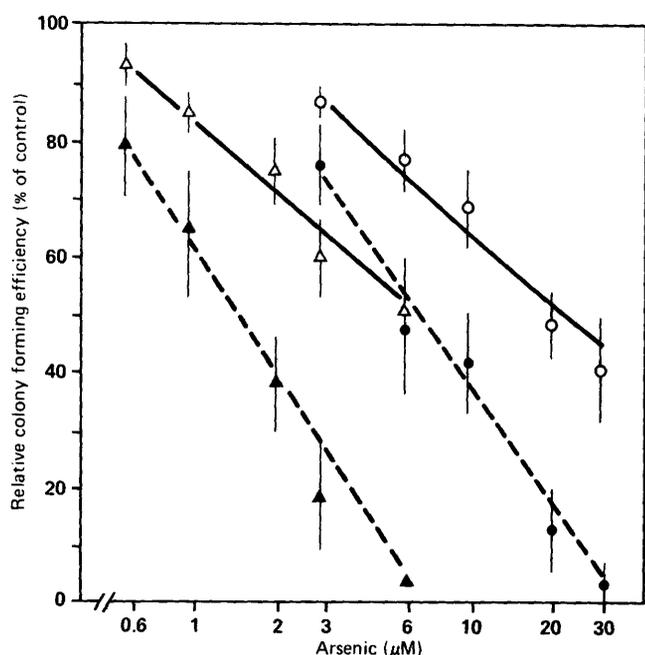


Fig. 3. Arsenic induced cytotoxicity. BALB/3T3 cells were plated (200/60 mm dish) in MEM + 10% FBS; 24 h after seeding, the medium was removed and the stated concentrations of sodium arsenite (Δ - Δ , 24 h exposure; \blacktriangle - \blacktriangle , 72 h exposure) or sodium arsenate (\circ - \circ , 24 h exposure; \bullet - \bullet , 72 h exposure) were added for 24 h or 72 h of exposure, after which experimental media were replaced with regular medium.

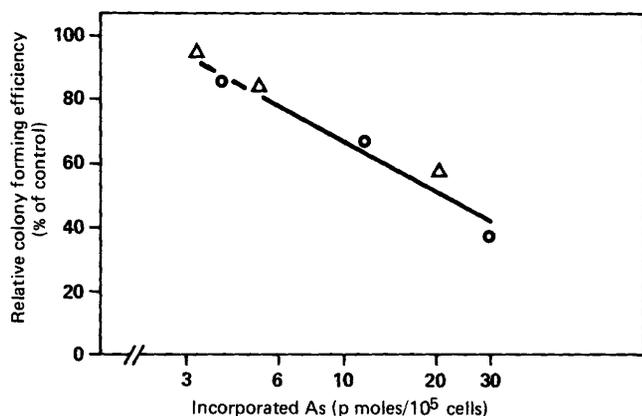


Fig. 4. Comparison of the extent of cytotoxicity with intracellular ^{73}As -arsenic concentrations in BALB/3T3 cells exposed to sodium arsenite (\blacktriangle) or sodium arsenate (\circ).

whereas in cells exposed to arsenate, more than 70% of the cytosolic arsenic was trivalent and the rest was pentavalent inorganic arsenic, indicating a high rate of intracellular metabolic reduction of pentavalent to trivalent arsenic.

Arsenic forms in the medium

After 24 h incubation in cell-free medium, inorganic trivalent arsenic was partly oxidized to the pentavalent form (up to 30% of the dose) (Table III).

As shown by incubation of arsenite with BALB/3T3 cells, the spontaneous oxidation of arsenite to arsenate occurred to a significantly lower extent (4%) than in the corresponding cell-free system (30%). Inorganic pentavalent arsenic incubated for 24 h in cell-free medium was recovered unchanged, whereas when BALB/3T3 cells were incubated with arsenate, an amount of trivalent arsenic, increasing with time, was detected in the medium, reaching approximately 5% of the dose within 24 h. The cumulative release of trivalent inorganic arsenic by BALB/3T3 cells exposed to arsenate was dose-dependent (dose range tested: from 3×10^{-6} to 3×10^{-5} M) and in a log/log relation with time between 3 h and 24 h of exposure (Figure 5). Methylated forms of arsenic were not detected in the incubation media under any of the experimental conditions described above.

Effect of diethylmaleate (DEM) on arsenate reduction

DEM, a known glutathione depleting agent, was incubated with BALB/3T3 cells simultaneously to 1×10^{-5} M ^{73}As -labelled sodium arsenate. DEM inhibited the reduction of arsenate to arsenite up to levels of 25% of controls (Table IV). Cell survival at the highest tested dose of DEM (3×10^{-4} M) was approximately 50% of controls. These results show that the reduction of arsenate in the cells is partly dependent on glutathione.

Morphological transformation

Transformation assays were conducted on BALB/3T3 cells exposed to three different concentrations of either sodium arsenite or sodium arsenate. Both trivalent and pentavalent arsenic were found positive in the transformation assay (Table V). The relative effectiveness, measured as the molar concentrations required to induce the same level of biological response, was higher for sodium arsenite than for sodium arsenate by an estimated factor of approximately 5-fold.

DISCUSSION

In this study, both sodium arsenite and sodium arsenate gave positive results in the morphological transformation assay with the BALB/3T3 Cl A31-1-1 cells, thus confirming the *in vitro* oncogenic activity of inorganic arsenic salts observed by others in embryo cells from a different species (10).

Comparing the relative transforming activity of sodium arsenite and sodium arsenate, we found that the trivalent form is approximately 5-fold more potent than the pentavalent form. This fin-

Table I. Relative intracellular partition of absorbed arsenic after exposure of BALB/3T3 cells to ^{73}As -labelled sodium arsenite or sodium arsenate

| Incubation time (h) | Absorbed As recovered in the cytosol (% of the total cellular uptake) | | | | | |
|---------------------|---|------------------------|------------------------|---------------------------------------|------------------------|------------------------|
| | NaAsO ₂ (M) | | | Na ₂ HAsO ₄ (M) | | |
| | (6×10^{-7}) | (1×10^{-6}) | (3×10^{-6}) | (3×10^{-6}) | (3×10^{-5}) | (3×10^{-5}) |
| 1 | 95 ± 3 | 95 ± 3 | 81 ± 16 | 97 ± 1 | 98 ± 1 | 99 ± 1 |
| 12 | 96 ± 2 | 97 ± 1 | 90 ± 2 | 97 ± 1 | 92 ± 7 | 96 ± 4 |
| 24 | 96 ± 1 | 93 ± 3 | 92 ± 3 | 97 ± 1 | 90 ± 7 | 97 ± 1 |

Table II. Speciation of arsenic forms in the intracellular soluble fraction of BALB/3T3 cells exposed ^{73}As -labelled sodium arsenite or sodium arsenate

| Incubation time (h) | Percent of absorbed ^{73}As -arsenic recovered as trivalent As | |
|---------------------|---|--|
| | Exposure to NaAsO_2 | Exposure to Na_2HAsO_4 |
| 1 | 100 | 76.7 \pm 0.2 |
| 3 | 100 | 72.8 \pm 0.3 |
| 6 | 100 | 76.9 \pm 0.7 |
| 12 | 100 | 72.4 \pm 5.9 |
| 24 | 100 | 80.6 \pm 1.0 |

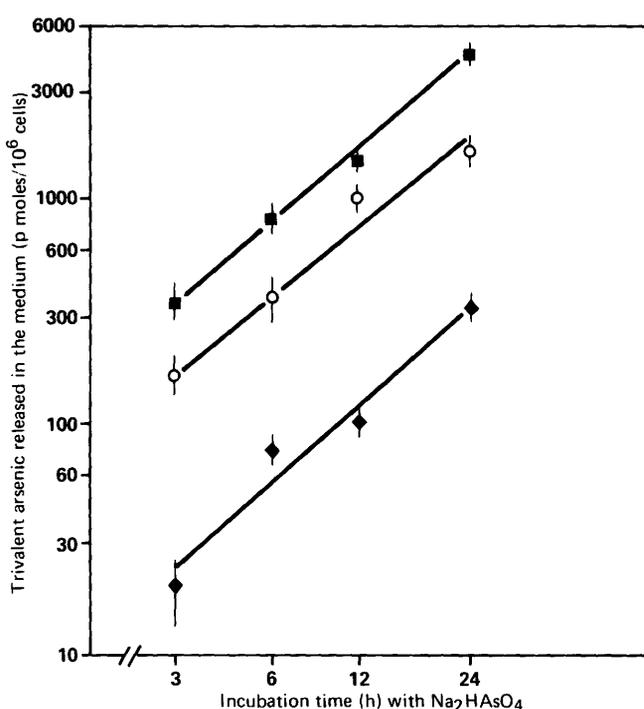


Fig. 5. Dose-dependent release of trivalent arsenic from arsenate exposed cells. BALB/3T3 cells were plated (2×10^6 /T75 flask) and 48 h later incubated with $3 \times 10^{-5}\text{M}$ (■), $1 \times 10^{-5}\text{M}$ (○), or $3 \times 10^{-6}\text{M}$ (◆) ^{73}As -labelled sodium arsenate of known specific activity.

ding is compatible with the 10-fold higher activity observed in Syrian hamster embryo cells by Lee et al. (10). The biphasic response for CFE, reported by these authors for Syrian hamster embryo cells with 7-day exposures, showing CFE enhancement at the dose ranges of 0.7-3.0 μM arsenite and 10-50 μM arsenate followed by a logarithmic decrease at higher doses, was not observed in the present cell system after 24 or 72 h exposures at the same dose ranges. The present results show, at both exposure times and for both forms of arsenic, a linear decrease in CFE with logarithmic increase in exposure concentration. The mechanisms responsible for these different levels of biological activity of arsenic species were investigated here in relation to the chemical form and to the biotransformation of arsenic. Arsenate was absorbed and retained by the cell less effectively than arsenite. This finding contributes to explain why higher external concentrations are required to induce an equivalent cytotoxicity and transformation frequency for arsenate as compared to arsenite.

The difference in exposure to pentavalent versus trivalent arsenic salts, required to induce a given toxicity, was previously reported in studies with soluble inorganic arsenicals, both in vitro (11) and in vivo (12). We have shown that, in the tested dose-range, the cytotoxic dose-response curves were not significantly different for arsenite and arsenate when the effect was correlated to the internal cellular arsenic burden instead of the external exposure level. This finding strongly suggests that the same intracellular chemical form of arsenic is responsible for the effect, independently from the valence state of the inorganic arsenic present in the culture medium. The possibility that arsenate was reduced to arsenite in vivo had already been reported, but such studies either did not provide clear evidence of the reduction (8) or they did not correlate the biotransformation to any effect. In the present study, arsenite exposed cells retained only trivalent arsenic, whereas arsenate exposed cells converted most of the cytosolic arsenic to the trivalent form. BALB/3T3 cells were thus shown to reduce arsenate to arsenite (Table II) and to release the reduced form in the culture medium (Table III). The mechanism of arsenate reduction explored in the present in vitro system appears to some extent analogous to that reported for the cellular reduction of chromate, where this carcinogenic metal is partly reduced by enzyme-catalyzed reactions (13) and partly by non-enzymatic components such as glutathione (GSH) (14). When the present cells were incubated simultaneously with arsenate and DEM, a well-known GSH depleting agent (15), the reduction to trivalent arsenic was inhibited, thus showing that at least part of the biotransformation of arsenate can be attributed to this non-enzymatic pathway. It should be noted that BALB/3T3 cells, under the conditions tested, did not methylate inorganic arsenic to any detectable extent. This process of biotransformation is generally regarded

Table III. Speciation of arsenic forms in cell-free medium and in medium after incubation of BALB/3T3 cells with ^{73}As -labelled sodium arsenite or sodium arsenate

| Incubation time (h) | Exposure to NaAsO_2 | | Exposure to Na_2HAsO_4 | |
|---------------------|--|------------------------|--|------------------------|
| | As ⁺⁵ recovered (% of the dose) | | As ⁺³ recovered (% of the dose) | |
| | Cell-free medium | Cell-containing medium | Cell-free medium | Cell-containing medium |
| 0 | 0.0 \pm 0.0 | ND | 0.0 \pm 0.0 | 0.0 \pm 0.0 |
| 3 | 4.0 \pm 0.9 | 2.0 \pm 0.2 | ND | 0.2 \pm 0.1 |
| 6 | 6.0 \pm 1.3 | 2.3 \pm 0.6 | 0.0 \pm 0.0 | 0.8 \pm 0.2 |
| 12 | ND | 3.1 \pm 0.4 | ND | 2.3 \pm 0.3 |
| 24 | 30.1 \pm 7.6 | 4.0 \pm 1.1 | 0.0 \pm 0.1 | 4.9 \pm 0.8 |

as a detoxification mechanism of inorganic arsenic in vivo (15). Species variability and differences in the balance between reduction and biomethylation in more complex in vivo systems may explain the difficulty of establishing an adequate model to study arsenic carcinogenicity in vivo. In vitro models, using clonal populations of target cells, may be useful in elucidating specific steps in the mechanisms of arsenic carcinogenicity. In interpreting results obtained with BALB/3T3 cells or similar lines, it is important to remember that these lines are not comparable to normal cells, since they are aneuploid and have unstable karyotype (16).

We are planning to extend these studies to a recently developed epithelial cell culture system that represents a major target tissue of carcinogenesis, and particularly arsenic carcinogenesis, namely the epidermis (17).

REFERENCES

1. A.M. LEE and J.F. FRAUMENI (1969) Arsenic and respiratory cancer in man: an occupational study. *J. Natl. Cancer Inst.*, 42, 1045-1052.
2. G. PERSHAGEN, G. NORDBERG and N.G. BJÖRKLUND, (1984) Carcinomas of the respiratory tract in hamsters given arsenic trioxide and/or benzo(a) pyrene by the pulmonary route. *Environ. Res.* 34, 227-241.
3. C. BARONI, G.J. VAN ESCH and U. SAFFIOTTI (1963) Carcinogenesis tests of two inorganic arsenicals. *Arch. Environ. Health*, 7, 54-60.
4. F.T. HUNTER, A.F. KIP and Jr. J.W. IRVINE (1942) Radioactive tracer studies on arsenic injected as potassium arsenite. *J. Pharmacol. Exp. Ther.*, 76, 207-220.

5. G.K.H. TAM, S.M. CHARONNEAU, F. BRYCE, C. POMROY and E. SANDI (1979) Metabolism of inorganic arsenic (^{74}As) in humans following oral ingestion. (*Toxicol. Appl. Pharmacol.*, 50, 319-322).
6. P.J. LANDRIGAN (1981) Arsenic - State of the art. *Am. J. Med.* 2, 5-14.
7. K.S. SQUIBB and B.A. FOWLER (1983) The toxicology of arsenic and its compounds. In Fowler, B.A. (ed.), *Biological and Environmental Effects of Arsenic*, Elsevier, Amsterdam, pp. 233-269.
8. J.M. GINSBURG (1965) Renal mechanism for excretion and transformation of arsenic in the dog. *Am. J. Physiol.* 208, 832-840.
9. J.A. DI PAOLO and B.C. CASTO (1979). Quantitative studies of in vitro morphological transformation of Syrian hamster cells by inorganic metal salts. *Cancer Res.*, 39, 1008-1013.
10. T.C. LEE, M. OSHIMURA and J.C. BARRETT (1985) (Comparison of arsenic induced cell transformation, cytotoxicity, mutation and cytogenetic effects in Syrian hamster embryo cells in culture. *Carcinogenesis*, 6, 1421-1426.
11. A.B. FISHER, J. P. BUCHET and R. LAUWERYS (1985) Arsenic uptake cytotoxicity and detoxification studied in mammalian cells in culture. *Arch. Toxicol.*, 57, 168-172.
12. W.R. BYRON, G.W. BIERBOWER, J.B. BROWER and W.H. HANSEN (1967) Pathologic changes in rats and dogs from two-year feeding of sodium arsenite and sodium arsenate. (*Toxicol. Appl. Pharmacol.*, 10, 132-147).
13. S. DE FLORA, A. MORELLI, C. BASSO, M. ROMANO, D. SERRA and A. DE FLORA (1985) Prominent role of DT-diaphorase as a cellular mechanism reducing chromium (VI) and reverting its mutagenicity. *Cancer Res.*, 45, 3188-3196.
14. H.J. WIEGAND, H. OTTENWÄLTER and H.M. BOLT (1984) The reduction of chromium (VI) to chromium (III) by glutathione: an intracellular resox pathway in the metabolism of the carcinogen chromate. *Toxicology*, 33, 341-348.
15. F. BERTOLERO, E. MARAFANTE, J. EDEL-RADE, R. PIETRA and E. SABBIONI (1981) Biotransformation and intracellular binding of arsenic in tissues of rabbits after intraperitoneal administration of ^{74}As -labelled arsenite. *Toxicology*, 20, 34-44.

Table IV. Effect of diethylmaleate (DEM) on arsenate reduction by BALB/3T3 cells

| DEM (M) | Cells/flask (% of control) | As ³⁺ released in the medium | |
|----------------------|----------------------------|---|----------------|
| | | (picomoles 10 ⁶ cells) | (% of control) |
| 0.0 | 100 | 1675 ± 150 | 100 |
| 1 × 10 ⁻⁴ | 80 | 1252 ± 145 | 75 |
| 2 × 10 ⁻⁴ | 71 | 421 ± 62 | 25 |
| 3 × 10 ⁻⁴ | 53 | 465 ± 89 | 28 |

Table V. Arsenic induced cytotoxicity and transformation in BALB/3T3 cells

| Arsenic form | Exposure | | No. of Type III foci/ No. of dishes | No. of Type III positive dishes/ No. of dishes | Transformation frequency × 10 ⁻⁴ cells |
|-----------------------------------|----------------------|---------|-------------------------------------|--|---|
| | Dose (M) | CFE (%) | | | |
| NaAsO ₂ | 1 × 10 ⁻⁶ | 74 ± 8 | 0/18 | 0/18 | 0.0 |
| NaAsO ₂ | 3 × 10 ⁻⁶ | 19 ± 3 | 2/18 | 2/18 | 0.6 |
| NaAsO ₂ | 6 × 10 ⁻⁶ | 5 ± 2 | 3/18 | 3/18 | 4.1 |
| Na ₂ HAsO ₄ | 1 × 10 ⁻⁵ | 54 ± 3 | 0/18 | 0/18 | 0.0 |
| Na ₂ HAsO ₄ | 2 × 10 ⁻⁵ | 23 ± 3 | 10/18 | 6/18 | 2.4 |
| Na ₂ HAsO ₄ | 3 × 10 ⁻⁵ | 7 ± 2 | 8/18 | 7/18 | 7.9 |
| Bi-distilled H ₂ O | 0.1% (v/v) | 100 ± 6 | 0/21 | 0/21 | 0.0 |

16. U. SAFFIOTTI, M. BIGNAMI and M.E. KAIGHN (1985) Parameters affecting the relationships among cytotoxicity, genotoxicity, mutational, and transformational responses in BALB/3T3 cells. In Barrett, J.C. and Tennant, R.W. (eds.), *Carcinogenesis*, Vol. 9, Mammalian Cell Transformation, Raven Press, New York, pp. 139-151.
17. F. BERTOLERO, M.E. KAIGHN, M.A. GONDA and U. SAFFIOTTI (1984) Mouse epidermal keratinocytes. Clonal proliferation and response to hormones and growth factors. *Exp. Cell Res.*, 155, 64-80.

1.4. ENVIRONMENTAL PATHWAYS (Environmental impact assessment)

Introduction

The projected increase of the use of coal for electricity generation in Europe suggests to assess the potential environmental impact of coal fired power plants (CFPP).

Within the past programme an assessment study on the emissions and pathways of trace metals (TM) from CFPP and, for comparison, from other anthropogenic sources such as incinerators and fertilizers has been undertaken. Thereby emphasis was laid to the atmospheric emissions of TM from CFPP. However improvement of filter technics for the retainment of particulate matter and the installation of flue gas desulphurization plants in a near future should reduce TM emissions by the stack. Also fluidized bed combustion (FBC), a promising technology developed in order to lower both NO_x production and SO₂ emission, to be employed in a near future requires the addition of up to 20% of limestone to the coal. In consequence the quantities of the solid wastes, such as fly ash from the filters, desulphurization sludge and gypsum and spent sorbent/ash mixtures from FBC-boilers will increase substantially. Most of these wastes are disposed of in some way, e.g. in landfills, or used for amendement of agricultural soils.

So water leaching of TM from these waste products could be an important pathway of certain TM to the environment.

The objectives of this activity therefore are:

- to determine trace metal concentrations in aqueous leachates from fly ash, desulphurization sludge and gypsum and to relate them to the EC 80/778 directive on drinking water quality;
- to assess the potential impact on fresh water resources by modelling of environmental pathways.

RESULTS

LABORATORY WATER LEACHING STUDIES

Water leaching studies of TM from coal fly ash on a laboratory scale have been continued.

During the reporting period two fly ashes sampled from the electrostatic precipitator hoppers of two French coal-fired power stations have been investigated. Columns of these fly ashes of 10, 25, 50 and 100 cm length have been leached with water. Fly ashes and leachates have been analysed for their trace metal concentrations by instrumental neutron activation analysis. Trace metal content of the two fly ashes, called fly ash V and fly ash LH, are reported in Table I, whereas trace metal concentrations of the aqueous leachates from the 50 cm column experiments in function of percolated pore volumes are shown in Fig. 1 to 4. An other series of leaching experiments have been performed, whereby column length have been increased continuously during the leaching process in order to simulate the increasing height of a real fly ash deposit during its build-up.

Table I. Trace metal concentrations in fly ashes V and LH as determined by INNA

| Trace Metal | Fly ash V [ppm] | Fly ash LH [ppm] |
|-------------|-----------------|------------------|
| As | 10.1 | 13.3 |
| Cr | 118.5 | 119 |
| Mo | 10.95 | 11.1 |
| Sb | 8.30 | 5 |
| Se | 6.21 | 9.9 |
| V | 236 | 175 |
| W | 3.60 | 7.5 |
| Zn | 93.6 | 96 |

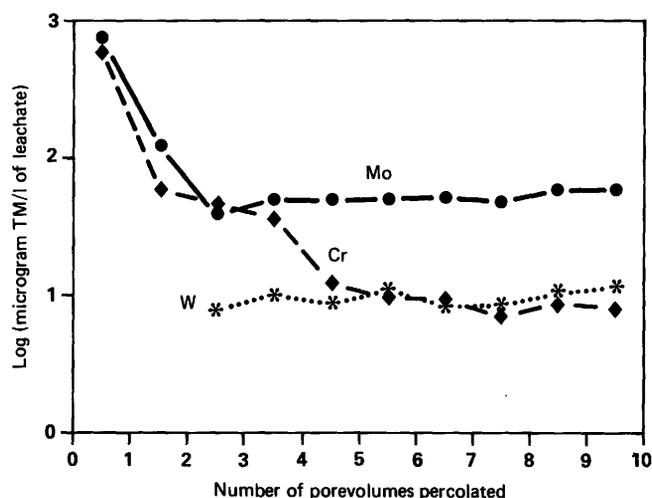


Fig. 1. Trace metal leaching from fly ash V, chromium, molybdenum, tungsten

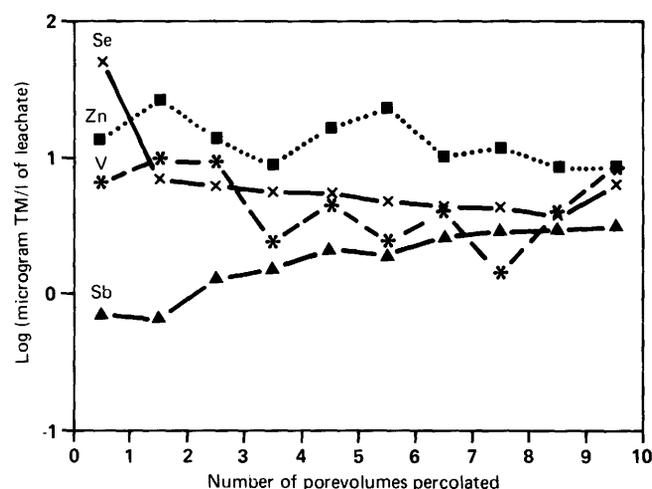


Fig. 2. Trace metal leaching from fly ash V, selenium, zinc, vanadium, antimony

A first column of fly ash A of 8.5 cm is leached with one pore volume of water. Then a second fly ash column is superposed over the first column and leached. In this way the leachate from the second column enters the top of the first column. This procedure have been continued until six columns of 8.5 cm per leaching experiments have been superposed. Then leaching of the six superposed columns has been carried on for some time in order to simulate the leaching behaviour of a final fly ash repository.

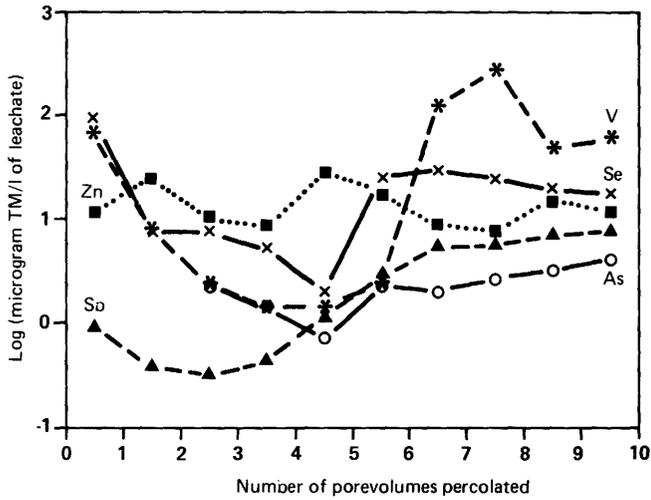


Fig. 3. TM leaching from fly ash LH, vanadium, selenium, zinc, arsenic, antimony

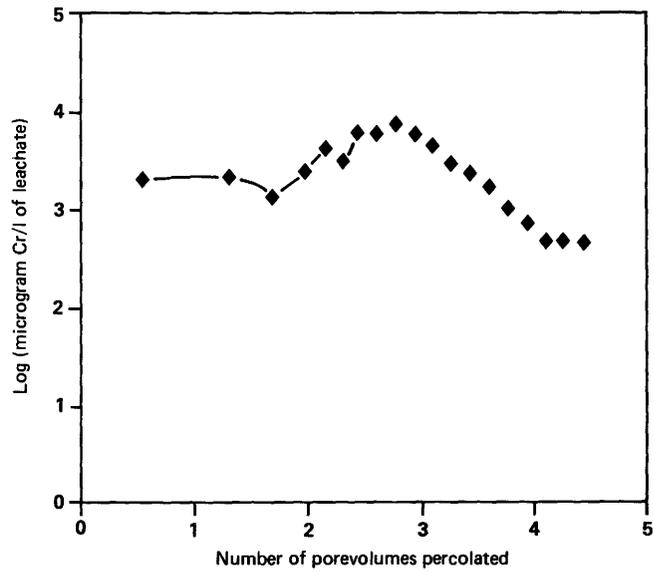


Fig. 5. Chromium leaching from fly ash A, 6 superposed columns of 8.5 cm each

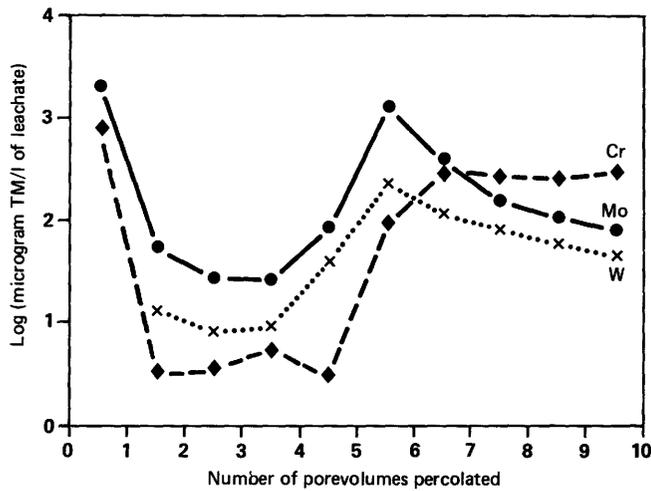


Fig. 4. Trace metal leaching from fly ash LH, chromium, molybdenum, tungsten

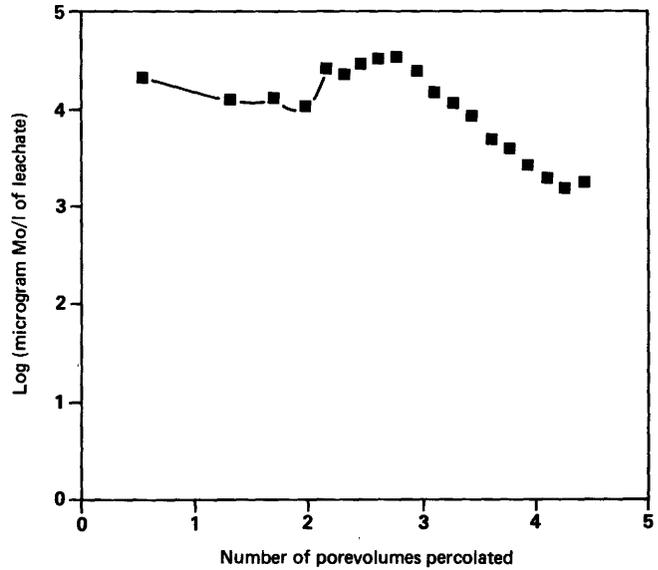


Fig. 6. Molybdenum leaching from fly ash A, 6 superposed columns of 8.5 cm each

Leachate fractions always were taken on the outlet of the first (the lowest) column and analysed for their trace metal content. The number of percolated pore volumes have been calculated for the respective total column length, so that the single fractions in chronological order correspond to 1, 1/2, 1/3, 1/4, 1/5, 1/6, 1/6, 1/6, 1/6, 1/6, 1/6, pore volumes. Resulting concentrations of Cr, Mo, W, Se, Sb, V in the aqueous leachates in function of pore volumes percolated are shown in Fig. 5 to 10. As can be seen in the figures 5, 6 and 7 concentrations of Cr, Mo and W show a similar course. During the phase of increasing column height concentrations are increasing slightly. During the leaching phase of constant fly ash column height concentrations decrease continuously confirming the results previously obtained. Also a rapid release of Se in the beginning of the leaching process and the slowly increase of Sb concentration with ongoing leaching is confirmed.

Trace metal speciation by ion chromatography

Trace metal speciation is an important and promising task in trace metal pollution research. Modern high performance ion-chromatographic techniques are powerful tools in resolving some of trace metal speciation problems. During the reporting period high performance anion chromatography combined with radiometric detection has been used in radiotracer quality control studies and speciation studies of coal fly ash leachates. For this end the eluate of the

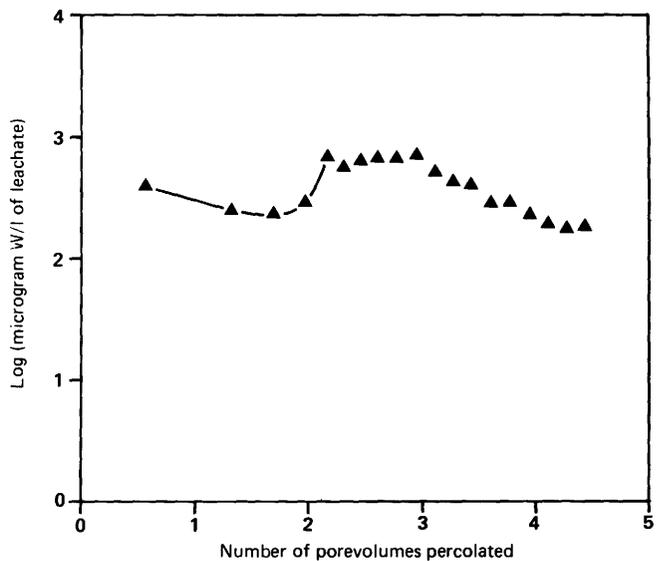


Fig. 7. Tungsten leaching from fly ash A, 6 superposed columns of 8.5 cm each

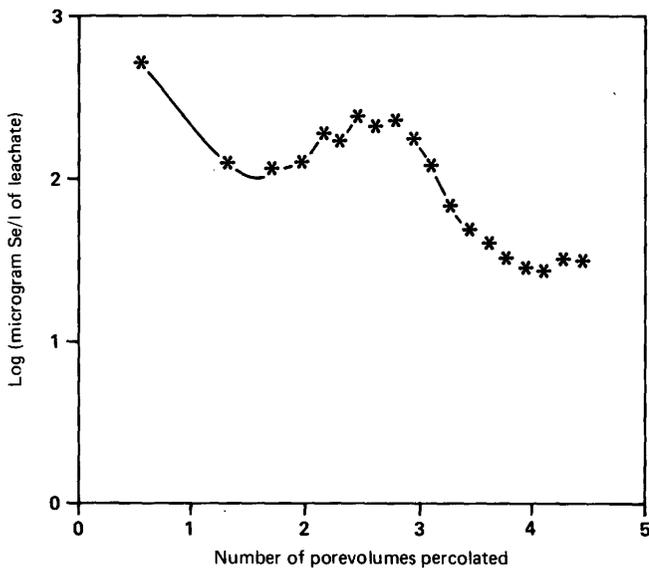


Fig. 8. Selenium leaching from fly ash A, 6 superposed columns of 8.5 cm each

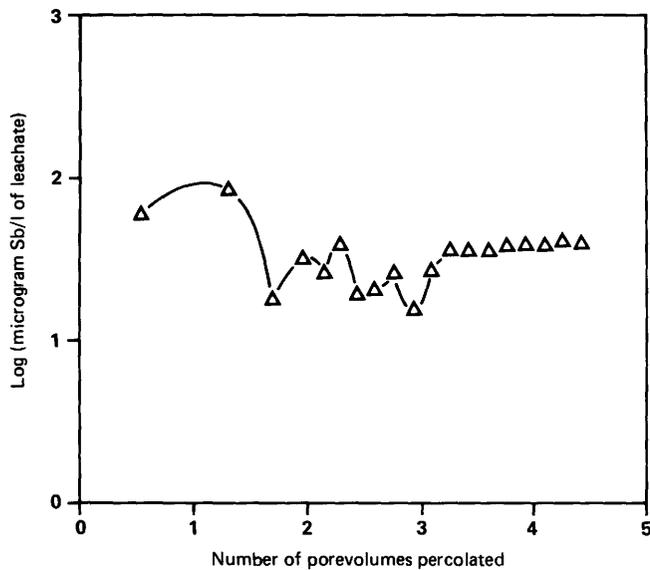


Fig. 9. Antimony leaching from fly ash A, 6 superposed columns of 8.5 cm each

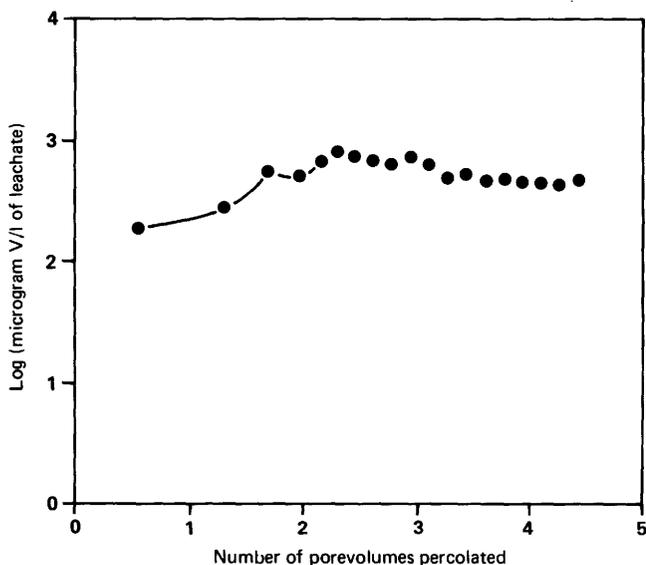


Fig. 10. Vanadium leaching from fly ash A, 6 superposed columns of 8.5 cm each

chromatographic column is fractionated and collected by a fraction collector and the specific radioactivity of the fractions is determined by gamma counting.

The chemical form of purchased radiotracer solutions of sodiumselenite, sodiumselenate, sodiumchromate and chromous chloride has been determined by this method injecting 50 microliters portions of solution. The obtained ion chromatograms are given in Fig. 11, 12 and 13. Purchased ^{75}Se selenite tracer has been found to consist of 95.3% of ^{75}Se selenite and 4.7% of ^{75}Se selenate (Fig. 11). An other charge of purchased ^{75}Se selenite has been analysed for 91.4% ^{75}Se selenite and 8.6% of ^{75}Se selenate. Purchased ^{75}Se selenate tracer, however, has been found to be rather pure ^{75}Se selenate (99.9%) containing only 0.1% of ^{75}Se selenite (Fig. 12). Ion chromatographic analysis of purchased ^{51}Cr chromous chloride tracer gave no response for ^{51}Cr chromate. So this tracer can be considered to be pure trivalent ^{51}Cr . On the other hand purchased ^{51}Cr chromate tracer originally contained only 35.8% of ^{51}Cr chromate (Fig. 13). After oxidation of the rest of ^{51}Cr in solution with some hydrogenperoxide practically all of the ^{51}Cr (99.7%) has been found as chromate species. An other charge of purchased ^{51}Cr chromate tracer originally contained only 31.4% of hexavalent ^{51}Cr .

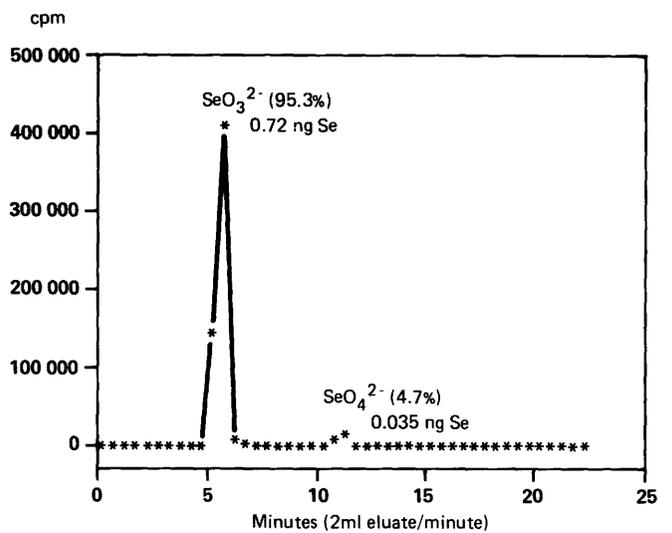


Fig. 11. Ionchromatographic separation of a purchased ^{75}Se selenite tracer

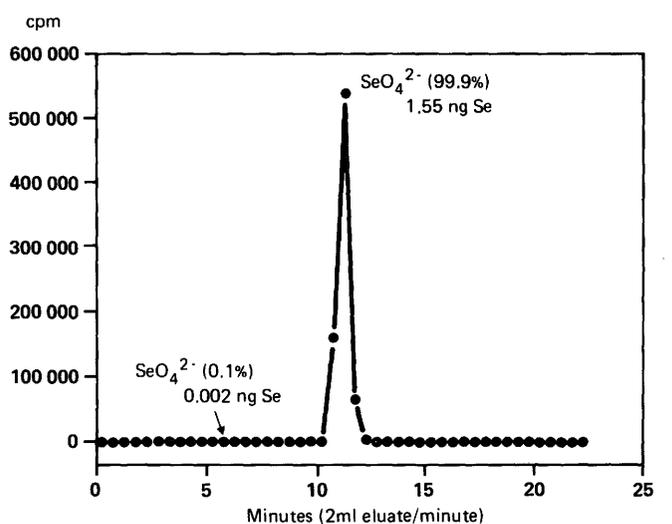


Fig. 12. Ionchromatographic separation of a purchased ^{75}Se selenate tracer

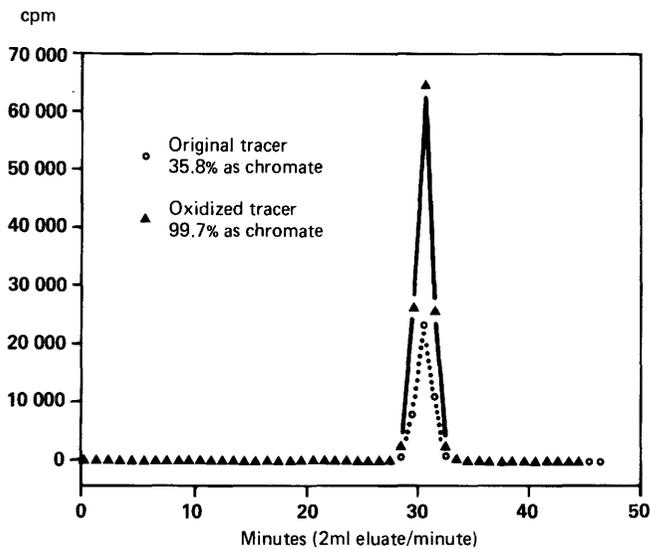


Fig. 13. Ionchromatographic separation of a purchased ^{51}Cr chromate tracer

Considering the concentrations of some ppb of Se and Cr species in the solutions investigated and the given specific radioactivity of the two tracers one can conclude that with this method speciation of $^{75}\text{Se}(\text{IV})$, $^{75}\text{Se}(\text{VI})$ and $^{51}\text{Cr}(\text{VI})$ should be possible down to concentrations of some ppt. Moreover by means of a preconcentration column a factor of about 500 can be gained although the recovery by the preconcentrator columns has been found in the 90% range. An example performed with ^{51}Cr chromate of low specific radioactivity is given in Fig. 14.

Fig. 15, 16, 17 show ionchromatographic speciation analysis of neutron activated sodiumselenite, sodiumselenate and potassiumchromate. Irradiations has been carried out in the nuclear reactor LENA of the University of Pavia. Solid samples of the three salts have been irradiated in air filled polyethylene containers with 2×10^{17} neutrons. After 100 hours of annealing at room temperature they have been dissolved in water. Obtained specific radioactivities are rather low. Irradiating sodiumselenite 77% of ^{75}Se selenite and 23% of ^{75}Se selenate has been found in the solution. In the case of irradiated sodiumselenate these values are 4.2% of ^{75}Se selenite and 95.8% ^{75}Se selenate. Only 65% of ^{51}Cr has been found as ^{51}Cr chromate after irradiation of potassiumchromate. It has not yet checked whether the bulk of the non-activated Se and Cr ions remains in the original chemical form or if it is also

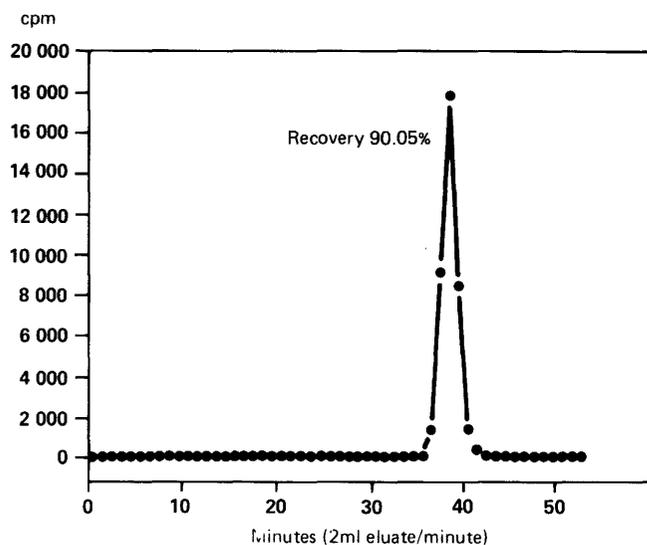


Fig. 14. Ionchromatographic separation of ^{51}Cr chromate after preconcentration of 2.8 ng of chromate contained in 2 ml of aqueous solution

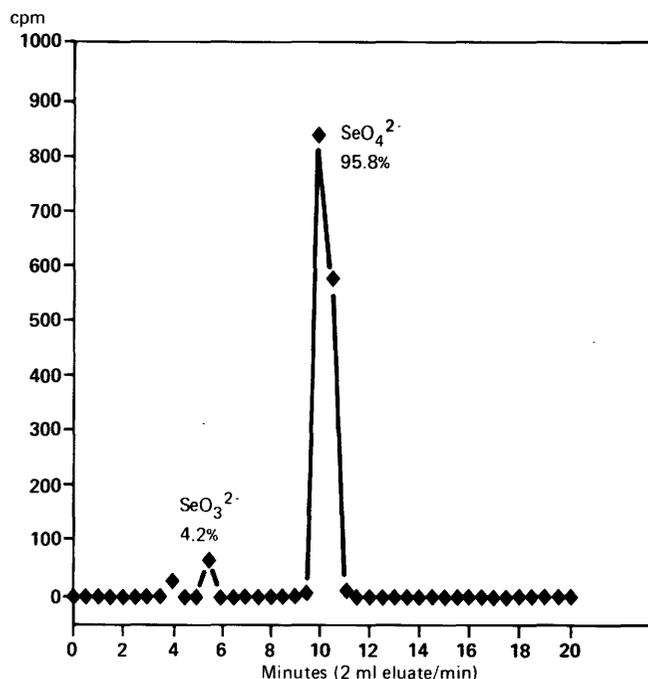


Fig. 15. Ionchromatogram of neutron activated sodium selenate

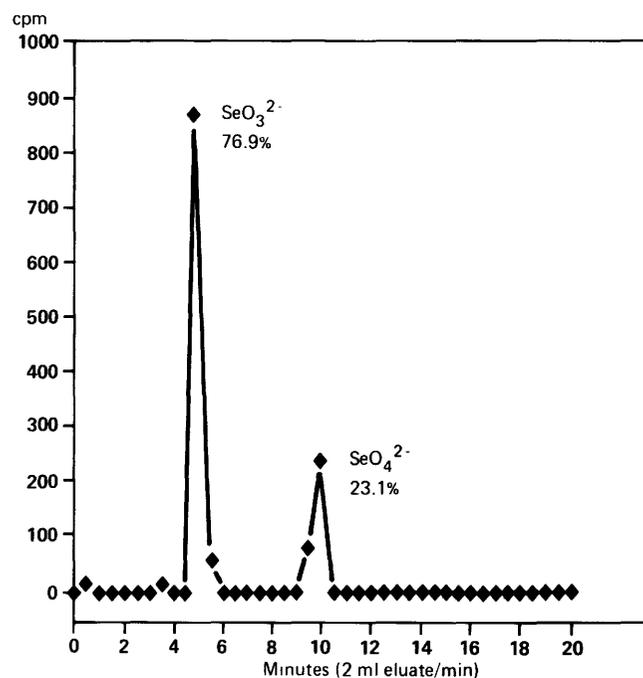


Fig. 16. Ionchromatogram of neutron activated sodium selenite

transformed to other oxidation states in the same extent as the activated atoms. If there should be an selective effect on activated atoms (Szilard Chalmers reaction) and isotopic exchange in aqueous solution should be negligible, high performance ionchromatographic separation could be used as a preparative method for isolating ^{75}Se (or ^{51}Cr from irradiated $\text{Cr}(\text{III})$ salts) of somewhat higher specific radioactivity by using short irradiation periods.

When ^{75}Se selenite/selenate tracer is brought together with a slurry of fly ash A and water (1:5) a disproportionation of the two chemical forms occurs (Fig. 18/20). In fact selenite in great part is absorbed by the fly ash. Moreover part of the selenite probably is oxidized to the selenate form which remains in solution. This finding confirms the results obtained in selenium speciation of fly ash column leachates as described in PPR86 (pag. 99), where selenate has been found to be the dominant chemical form.

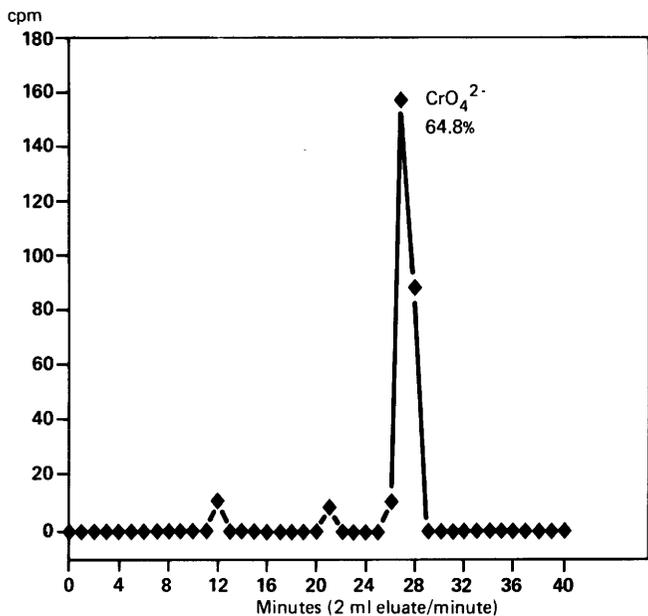


Fig. 17. Ionchromatogram of neutron activated potassium chromate

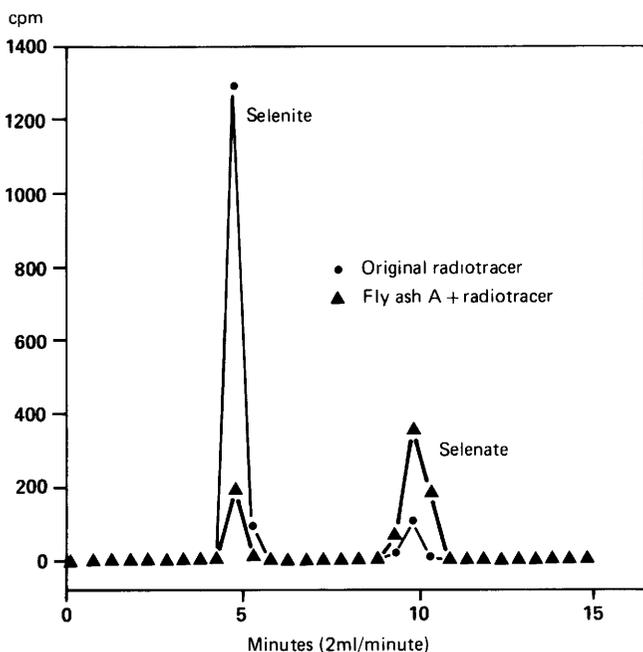


Fig. 18. Disproportionation of ^{75}Se selenite in a fly ash-water slurry (1:5) as determined by ionchromatography

Soil classification

Since June this research activity has laid more emphasis to experimental soil pollution research. The choice of soils to be studied will be clearly oriented to the characteristic mayor soils as they are found in the territory of the Member States of the European Community. For practical reasons it is intended to sample these types of soils nearest to the Ispra Establishment. Therefore a comparative inventory of European and Italian soil types is needed.

In Europe there is a big variety of soils with very different morphologic and pedologic characteristics. For the present studies eleven major types of soils have been selected (Table II) which are in association with other types of soils as shown in Table III. Those 11 dominant soil types cover 53% of the total terrestrial surface of Europe and in various associations 94% of the Italian territory. So a vast collection of soils in different associations exists comprising a variety ranging from acidic to alkaline soils,

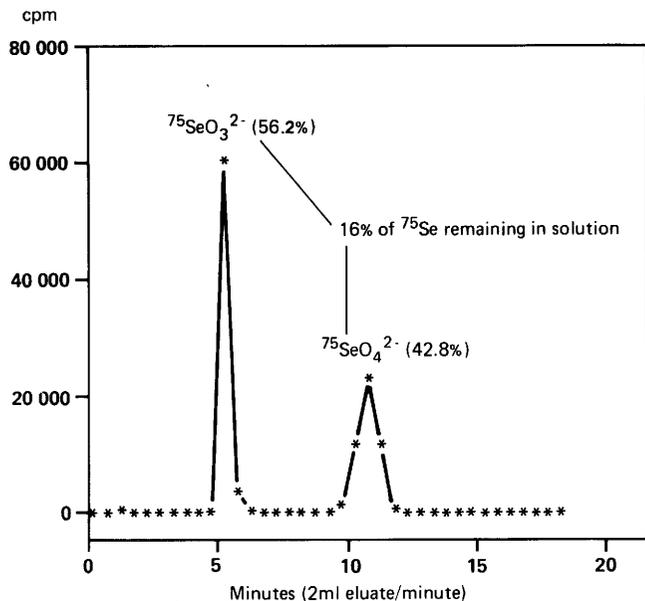


Fig. 19. Absorption and disproportionation of ^{75}Se selenite tracer in a fly ash-water slurry (1:5) as determined by ionchromatography

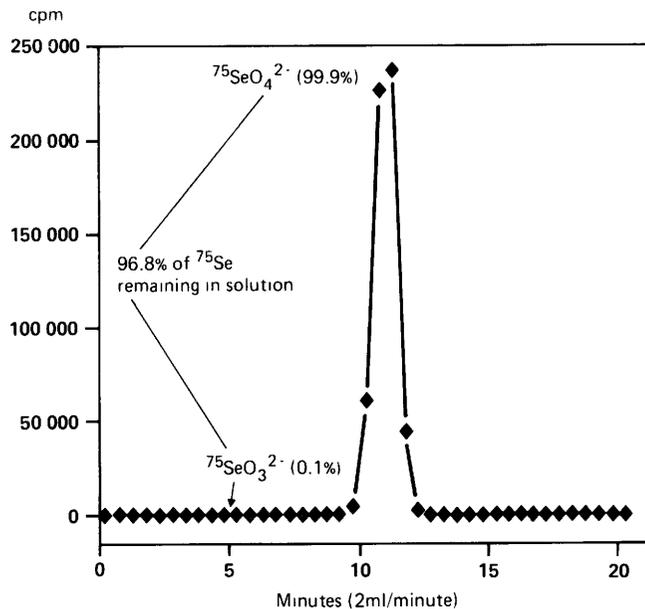


Fig. 20. Absorption and disproportionation of ^{75}Se selenate in a fly ash-water slurry (1:5) as determined by ionchromatography

from coarse texture soils to fine pine sand together with different kinds of parent materials which can be alluvial deposits, metamorphic and eruptive rocks.

Chemical and physical analysis of typical European soils

Part of analytical techniques for chemical, physico-chemical and physical soil characterization procedures has been already checked on a 10 cm horizon of a top soil sampled at the Ispra Establishment and characterized according to the Soil Map of the European Communities as an orthic luvisol: Lo 2/4 ab (45% luvisol, 25% stagno-gleyic luvisol, 20% eutric cambisol or distric cambisol (Bd), less than 10% Bg-gleyic cambisol and Re-eutric regosol).

- Physical characteristics:

Soil samples were air dried and sieved to 2 mm grain size. Overall soil particle density has been determined by pycnometer weighings. Bulk density and porosity have been measured by column (5 x 10 cm high) percolation experiments using tritiated water as a tracer. For texture class determinations organic matter

Table II. Main European soils present in Italy

| Dominant soil unit | km ² Italy | % in Europe | % in Italy | % Italian soils in Europe | Country |
|----------------------|-----------------------|-------------|------------|---------------------------|-------------------------|
| Je Eutric Fluvisols | 5,100 | 3.49 | 2 | 7 | All except GR |
| Rc Calcaric Regosols | 30,000 | 2.54 | 12 | 56 | BNL, F, FRG, GR, I, UK |
| Id Dystric Lithosols | 11,800 | 1.27 | 5 | 44 | F, GR, P, IRL, I, E |
| Eo Orthic Rendzinas | 13,500 | 5.00 | 5 | 13 | F, FRG, I, UK |
| Be Eutric Cambisols | 100,700 | 13.20 | 40 | 56 | All |
| Bd Dystric Cambisols | 35,800 | 12.07 | 14 | 14 | All except DK |
| Lo Orthic Luvisols | 11,700 | 8.21 | 5 | 7 | All except E |
| Lc Chromic Luvisols | 10,500 | 3.80 | 4 | 13 | F, FRG, GR, I, P, E, UK |
| Lg Gleyic Luvisols | 6,800 | 2.30 | 3 | 14 | BNL, F, I, P, E, UK |
| Pl Leptic Podzols | 4,500 | 0.80 | 2 | 27 | F, I |
| Vp Pellic Vertisols | 4,500 | 0.44 | 2 | 48 | F, GR, I, P, E |
| Total | 234,900 | 53.12 | 94 | | |

has been destroyed with hydrogen peroxide. Remaining mineral fraction was washed, sieved, dried and weighed. Sand, silt and clay fractions have been determined by sedimentation analysis.

Obtained results are summarized in Table IV.

- Physico-chemical characteristics:

pH was measured by a glass electrode in soil/water slurry and in aqueous slurry saturated with potassium chloride and nitrogen as well. Electric conductivity which roughly indicates total salt content was determined by a conductometer. Total nitrogen, organic matter and carbonates were determined according to standard procedure (Jackson 1979). Obtained results are shown in Table V.

- Elements in mobile phase:

Mobile Na, K, Ca were extracted by 1-normal ammonium acetate solution at pH 7. Mobile Fe, Cu, Mn, Cd, Cr, Pb and V were extracted by 0.05 molar NaEDTA solution. After dilution metal concentrations were determined by the following methods: Na, K, Ca, Mg, Fe, Cu, Mn by inductively coupled plasma emission spectrometry (ICP); Cr, Cd, Pb, V by graphite furnace atomic absorption spectrometry (GFAAS). Table VI reports the concentration values of mobile elements as found for the two soil samples investigated.

Laboratory experiments on soil-pollutant interactions

Batch experiments using radiotracers have been carried out in order to evaluate the absorption of different chemical forms of Cr and Se on two samples of soil and on pure sand in function of equilibration time and initial trace metal concentrations in solution. As an example Fig. 21 demonstrates the results of chromate absorption on one of the soil samples investigated. Due to competition reactions on the free absorption sites, with increasing chromate concentration absorption of chromate on the soil particle surface decreases. Equilibration time is in the order of 10 to 40 hours. In Fig. 22 distribution coefficients for chromate taken from Fig. 21 at 40 h equilibration time are plotted against initial chromate concentration of the solution. Fig. 23-25 show absorption curves of selenate on the two soil samples investigated and on pure sand in function of equilibrium time.

Selenate concentration is equal in all experiments (1.47 micromol/liter). Absorption capacity of sand has been found about one order of magnitude lower than that of the two soil samples.

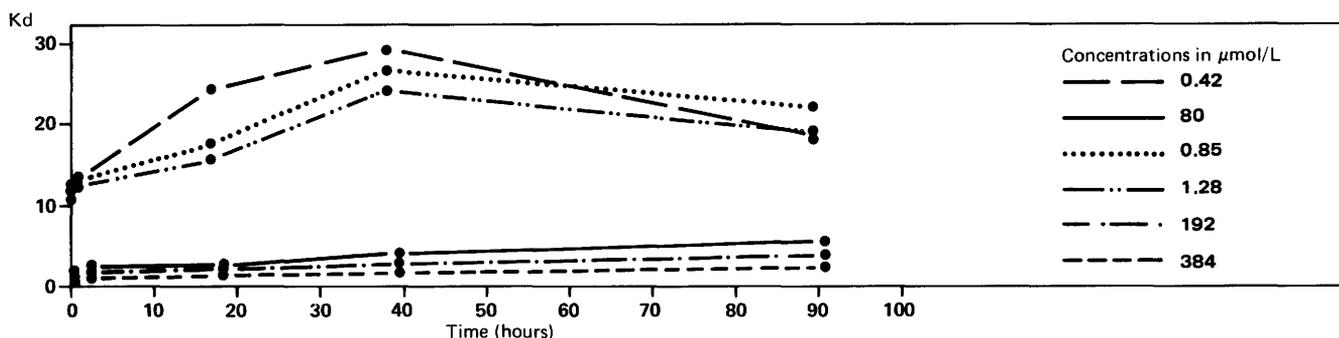


Fig. 21. Ispra 2 soil: Determination of Chromate-Soil Distribution Coefficient K_d by Batch Experiments

Table III.

| Dominant soil unit | Association N. | Italian Region | Parent Materials | General Characteristics | Associated soils |
|------------------------------|----------------|--|--|--|--|
| Bef Flyvi-Eutric Cambisols | 39 | Plain | Alluvial deposits | plains along several rivers | |
| Bd Dystric Cambisols | 46 | Italian Alps | Acidic rocks, gneis, granite, sandstone and shale | Texture from coarse to medium fine | |
| Bd Dystric Cambisols | 51 to 56 | Piedmont Alps Central Italy Calabria, Sicily | 56 from volcanic rocks | | |
| Lo Orthic Luvisols | 19 | Piedmont Northern Italy | Old alluvium | Argillic B horizon | |
| Lc Chromic Luvisols | 34 | Lazio | Effusive rocks proclastic products | Brown to red argillic B horizon texture from medium to fine | 55% chromic Luvisols 40% Ando-Eutric Cambisols Vitric Andosols |
| Lc Chromic Luvisols | 32 | Sicily and Sardinia | Limestone | | 60-65% Chromic Luvisols 25-30% Eutric or Calcaric Lithosols Rock Outcrops |
| Lg Gleyic Luvisols | 63 | Italian rivers Sardinia | Glacio-fluvial and river-terrace deposits | Hydromorphic properties within 50 cm of the surface | 40% Plano Gleyic Luvisols 30% Albo Gleyic Luvisols (E horizon) 20% Orthic Luvisols |
| P1 Leptic Podzols | 84 | Italian Alps | Volcanic, crystalline or metamorphic rocks | Esodic B horizon coarse texture Albic E horizon | Leptic Podzols, Ferro humic Podzols 20% Spodo Dystric Cambisols Dystric Lythosols, Ranckers |
| Vp Pellic Vertisols | from 77 to 81 | Pontine Marshes Tavoliere Pugliese Southern Sicily Sardinia | Calcareous sediments alluvial deposits of marine or riverine | fine texture | Cambisols and Regosols |
| Je Eutric Fluvisols | 4,5 | Po river estuary Coastline of the Adriatic Sea | Alluvial deposits | Base saturation level 50% | 40% Gleyo-Eutric FLuvisols 30% Eutric-Gleysols 20% Eutric Regosols or 30% Gleyic Solonchacks |
| Rc Calcaric Regosols | 42 | Apennines zone | | CaCO ₃ between 20 to 50 cm from the surface | 35% Calcaric Regosols 30% Eutric Regosols 15% Eutric Cambisols, 10% Lithosols |
| Rc Calcaris Regosols | 43 | Sicily from Central Italy to Calabria | | CaCO ₃ between 20 to 50 cm from the surface | 35% Calcaric Regosols 25% Calcaro Eutric Cambisols 20% Vertic Cambisols, 15% Cromic and Pellic Vertisols |
| Id Dystric Lithosols | 53 | Alps | Acidic rocks eruptive or silicate metamorphic or sedimentary | Snow-covered areas small glaciers | 40-60% Dystric Lithosols 30-35% Rocks Outcrops |
| Eo Orthic Rendzinas | 67 | Alps, Southern and Central Apennines, Sicily | Hard or dolomitic limestone | A, CaCO ₃ 40% medium fine texture | 50-70% Rendzinas 10-20% Humic Cambisols or Eutric Cambisols 10-30% Lithosols |
| Be Eutric Cambisols | 14, 15 | Lower Alps Apennines, Sicily | Limestone and dolomite | Medium to fine texture | |
| Be Eutric Cambisols | 19 | Central and Southern Italy, Tuscany, Liguria Sicilia | Metamorphic and eruptive | Medium to fine texture | |
| Be Eutric Cambisols | 21 | Calabria, Sardinia | Limestone | Medium to fine texture | |
| Bec Calcaro-Eutric Cambisols | 31 | Central Italy and Sicily | Pliocene and Pleistocene marine sands, and Pleistocene calcareous fluvial deposits | Calcareous below 50 cm from the surface | |
| | 32 | Puglia (Murge) | | | |
| Bea Ando-Eutric Cambisols | 38 | Alban hills (Centr. Italy) Sicily, Sardinia | Volcanic areas | Amorphous material silt, sand, gravel | |

Table IV Physical characteristics

| PARAMETER | SOIL ISPRA 1 | SOIL ISPRA 2 | SAND |
|------------------|--------------|--------------|-----------|
| Particle density | 2.55 g/cm | 2.33 g/cm | 2.64 g/cm |
| Bulk density | 1.28 g/cm | 1.09 g/cm | 1.58 g/cm |
| Texture class | Sand | Sandy Loam | Sand |
| % Sand | 92 | 72 | 100 |
| Porosity | 0.49 | 0.53 | 0.40 |

Table V Physico-chemical characteristics

| PARAMETER | SOIL ISPRA 1 | SOIL ISPRA 2 |
|---------------------------|--------------|--------------|
| pH (H ₂ O) | 6.56 | 6.48 |
| pH (KCl, N) | 5.28 | 5.19 |
| EC' (mhos/an) | 58 | 60 |
| NT% | 0.21 | 0.28 |
| %o Ca CO ₃ act | 27 | 15 |
| % Organic Matter | 0.77 | 1.62 |
| C/N | 2.1 | 9.3 |

Table VI Elements in the mobile phase

| PARAMETER | SOIL ISPRA 1 | SOIL ISPRA 2 |
|-------------|-----------------|-----------------|
| Na, mg/100g | 2.66 (CV 0.0) | 2.53 (CV 0.29) |
| N, mg/100g | 3.10 (CV 0.0) | 8.23 (CV 0.45) |
| Ca, mg/100g | 35.00 (CV 0.0) | 78.00 (CV 0.1) |
| Mg, mg/100g | 1.63 (CV 0.0) | 3.92 (CV 0.54) |
| Mn, ppm | 0.25 (CV 0.47) | 7.33 (CV 0.38) |
| Fe, ppm | 10.13 (CV 0.11) | 67.12 (CV 0.22) |
| Cu, ppm | 1.08 (CV 0.110) | 3.92 (CV 0.38) |
| Pb, ppm | 2.82 (CV 0.6) | 29.60 (CV 0.5) |
| Cd, ppb | 121 (CV 0.7) | 193 (CV 0.6) |
| Cr, ppb | 19 (CV 0.7) | 94 (CV 0.7) |
| V, ppb | 63 (CV 0.7) | 261 (CV 0.4) |

$$CV = \frac{S}{X} = \frac{\text{Standard deviation}}{\text{Mean value}}$$

Absorption and desorption of 51-Cr chromate by sand have been also investigated and evaluated from column experiments. The method applied allows to determine the distribution coefficient under dynamic conditions according to Saas:

$$K_d = \frac{1}{V_d} (V_{1/2} - V_g) \text{ and}$$

$$\frac{u_e}{u_i} = 1 + \frac{K_d V_d}{V_g}$$

where

K_d = distribution coefficient

$V_{1/2}$ = saturation volume obtained from $C = 0.5 \cdot C_0$

C = pollutant concentration in the effluent

C_0 = initial pollutant concentration in the mobile phase

V_d = bulk density

V_g = pore volume

u_e = mobil phase velocity (H₂O)

u_i = pollutant velocity

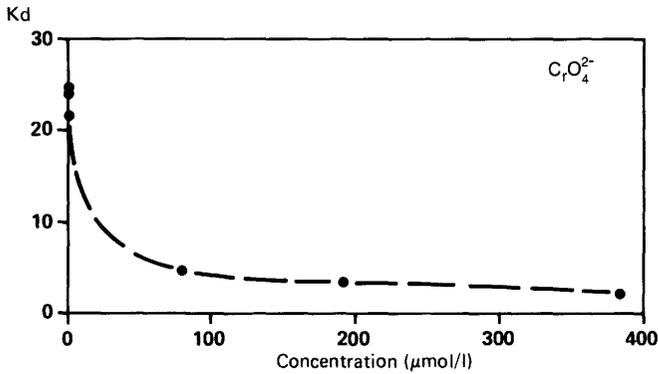


Fig. 22. Ispra 2 soil: K_d as a Function of Different Initial Concentrations of the Trace Element in the Solution

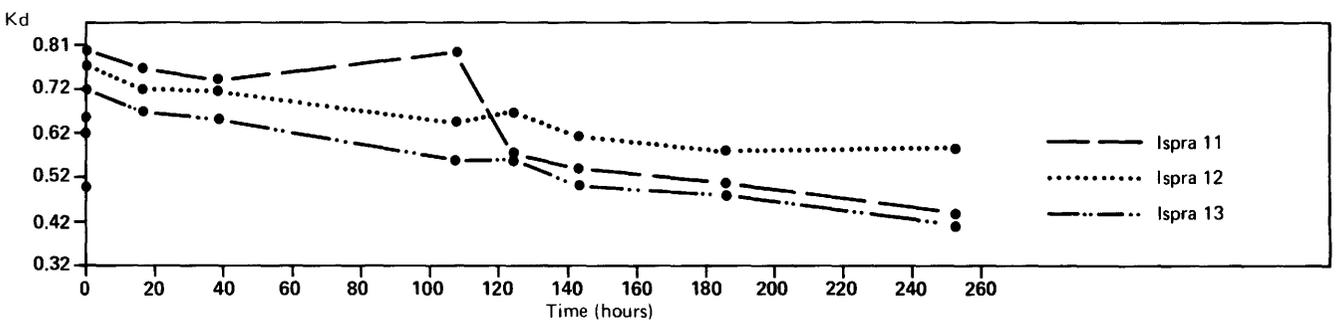


Fig. 23. Ispra 1 soil: Determination of Selenate-Soil Distribution Coefficient K_d by Batch Experiments

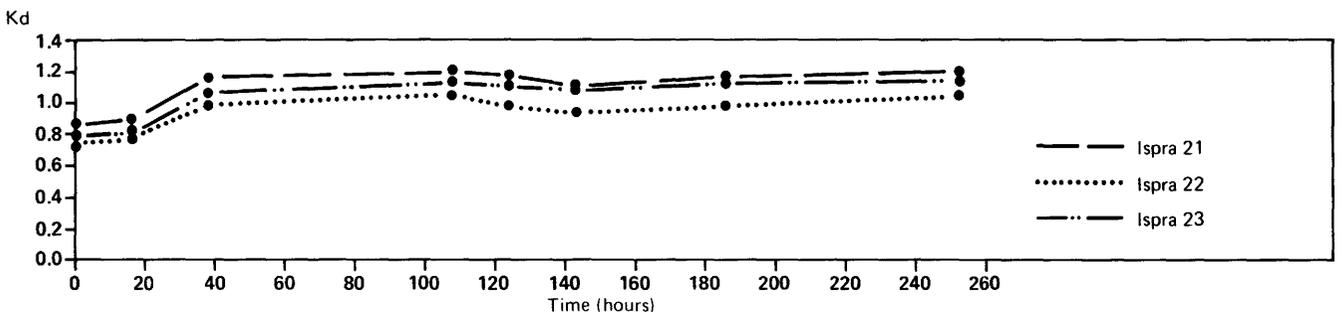


Fig. 24. Ispra 2 soil: Determination of Selenate-Soil Distribution Coefficient K_d by Batch Experiments

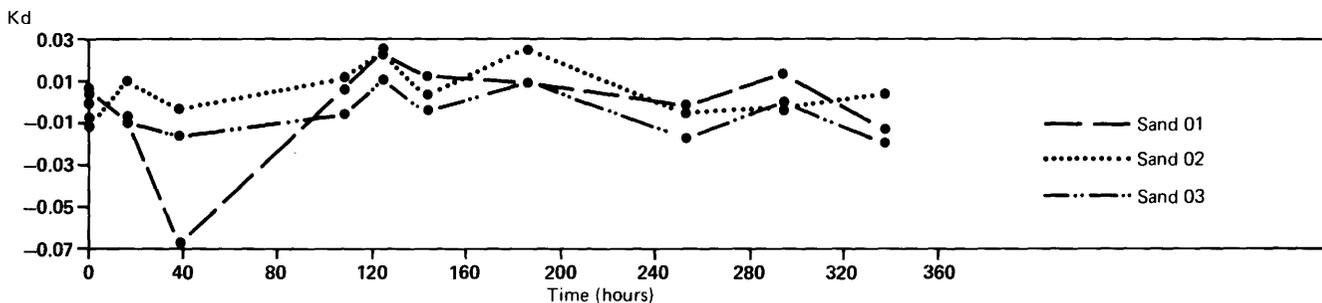


Fig. 25. Determination of Selenate-Sand Distribution Coefficient K_d by Batch Experiments

An initial chromium concentration of 5 mg/liter, the tolerable level for irrigation water recommended by EC-Directive has been used. Sand was packed into a glass columns of 10 cm length and 5 cm of inner diameter. Relative velocity u_i/u_0 of the chromate tracer can be measured if bulk density, porosity and mean saturation volume are known. The adsorption and desorption curves of ^{51}Cr chromate by sand are shown in Fig. 26. The porosity of the sand column had been previously determined by use of tritiated water, a non-reactive tracer (Fig. 27).

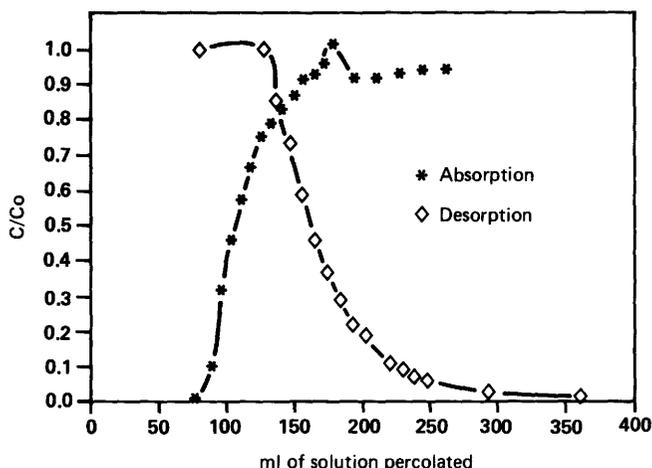


Fig. 26. Absorption - desorption of ^{51}Cr chromate on sand, as determined by column experiments

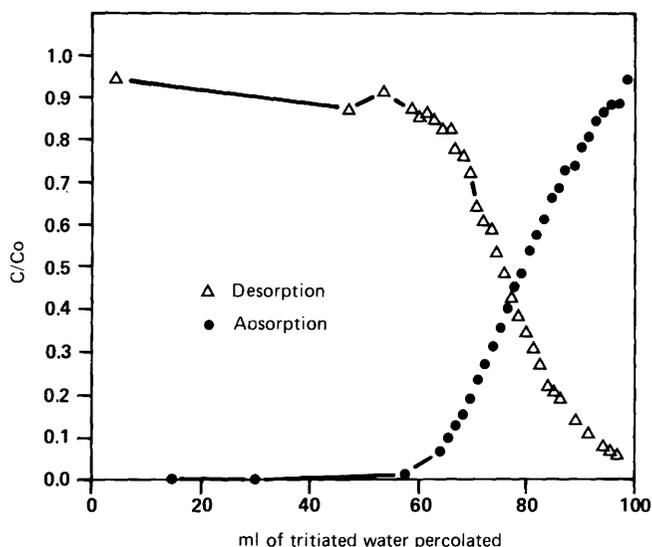


Fig. 27. Determination of porosity of a sand column by use of tritiated water

Environmental pathways and exposure by system analysis

During the last years chromium concentrations in human tissues in function of the distance to a fly ash repository have been calculated using a dynamic human dose model. It has also been shown, that chromium doses for human population living in a distance of 0 to 20 km from the source are higher than those due to the present normal exposure levels.

These first results necessitated the calculation of a probabilistic biological and sanitary risk for humans in order to obtain an idea of the importance of this potential trace metal pollution source for public health. Unfortunately no environmental epidemiological data of chronic chromium exposure exist. To overcome this gap calculation of the compared risk have been based on data found by biological monitoring of chromium exposed workers. These data permitted us to calculate the probability of mortality as consequence of acute chromium intoxication. The results (Table VII) expressed in percent of mortality due to various diseases and compared to other pollution sources as reported by IAEA represent the final goal of the present studies and conclude the first approach of calculating human dose commitment for chromium emissions from coal fly ash.

During these studies clearly emerged the importance of soil porous media and matrix for transportation and chemical transformation mechanisms and for the subsequent bioavailability of trace metals to the human food chain.

As soil is the major responsible of final dose commitment for human population there have been good reasons to continue our modelling studies on transportation mechanisms in soil porous media in order to arrive to a more realistic environmental model.

This improved model which is using finite element methodology will give us a more realistic assessment of the pollutant impact on fresh water resources.

- Finite element model

The transport of a dissolved constituent by groundwater is influenced by convective transport, hydrodynamic dispersion and chemical reactions. Mathematical analysis of the transport is further complicated by transient multidimensional flow of the carrier, which may occur under saturated and unsaturated conditions within the region or area of interest. Many authors have worked on this mathematical and physical approach to the dynamic fluid problem, but its complexity and the need to simulate realistically the long-term movement of toxic materials from a land-disposal site pose serious problems. For these reasons our attention was called to models which allowed us to arrive at a more complete computer code: Femwaste and Femwater from Oak Ridge National Laboratories. The transport mechanism treated by these two codes include: convection, hydrodynamic dispersion, chemical sorption and first order decay. The application of the finite element method by the model ensures that mass balance over the whole region considered is preserved and also a mixture-dependent retardation factor

Table VII Risk Assessment of Cr released from coal fly ash repository

| Type of exposure | Type of biological risk | Mortality per year and per million of persons due to the risk as in column 2 | Death-rate caused by exposure as in column 1 | Probabilistic risk (% of mortality) due to the death-rate as in column 4 referred to column 3 |
|-------------------------------------|----------------------------------|--|--|---|
| 1 | 2 | 3 | 4 | 5 |
| Natural environment | Cancer + Leukaemia | 1500 | 1 | 0.06 |
| Nuclear effluents (Dose = 5 mRem/y) | Cancer + Leukaemia | 1526 | 1 | 0.06 |
| Benzopyrene in atmosphere | Lung cancer and other diseases | 867 | 48 | 5.5 |
| Stack effluent from CFPP | Lung cancer and other diseases | 750 | 142 | 19.0 |
| General air pollution | Lung cancer and other diseases | 1050 | 425 | 41.9 0.5 ^b – 5 (1-5 km from source) |
| Chromium leached from fly ash | Cancer and other lethal diseases | 650 | 33 ^a | 0.12 0.06 (10 km from source) (20-30 km from source) |

a: Calculated from an average of 7 deaths in a group of 1550 exposed workers

b: taking into account of probabilistic dilution of food in the system

is employed in the definition of solute sorption in porous media of soil. The principal governing equations used in the model have been obtained from the law of mass balance. This can be written in the form:

$$\begin{aligned}
 L(c) = & \theta R_d \frac{\partial c}{\partial t} + \left(\frac{\partial V_x c}{\partial x} + \frac{\partial V_z c}{\partial z} \right) - \\
 & - \left[\frac{\partial}{\partial x} \left(\theta D_{xx} \frac{\partial c}{\partial x} + \theta D_{xz} \frac{c}{z} \right) + \right. \\
 & \left. + \frac{\partial}{\partial z} \left(\theta D_{zx} \frac{\partial c}{\partial x} + \theta D_{zz} \frac{\partial c}{\partial z} \right) \right] + \\
 & + \left(\frac{\partial \theta}{\partial t} + \alpha' \theta R_d \frac{\partial h}{\partial t} + \lambda \theta R_d \right) c - M = 0
 \end{aligned}$$

where θ is the moisture content, c is the concentration of trace metal in the water, p is the bulk density of the solid, S is the concentration of the constituent that is absorbed on the solid, α' is the modified compressibility coefficient of the medium, h is the pressure head of the water, D_{xx} , D_{xz} , D_{zx} and D_{zz} are the dispersion coefficient tensor components, V_x and V_z are the Darcian velocity components in the x and z -directions respectively, λ is the decay constant, M is the artificial source, x and y are the horizontal and vertical coordinates respectively, t is the time, L is an operator, $S = Kd \cdot c$ where Kd is the distribution

coefficient and $Rd = 1 + \frac{p Kd}{\theta}$ is the retardation factor, which

is a measurement of the delay of the breakthrough of the dissolved constituents.

It is easy to compare these above formulations with others representing the same phenomenon, to draw conclusions on the difficulty of solving this mathematical problem and also to consider the capacity of the model to represent environmental and dynamic structures.

- Application of the finite element model to a coal fly ash repository

A fly ash repository near a stream is assumed to be situated entirely in the unsaturated alluvial zone above the water table situated at a depth of 10 meters. The rainfall rate of 1 meter per year provides leaching of trace metals from the ash repository and water which drains into the aquifer (Fig. 28). To consider this problem, the first transformation of the original code was to introduce the results of our laboratory studies on leaching of chromium and arsenic not as a constant input to the environment considered but as a dynamic leaching as a function of time.

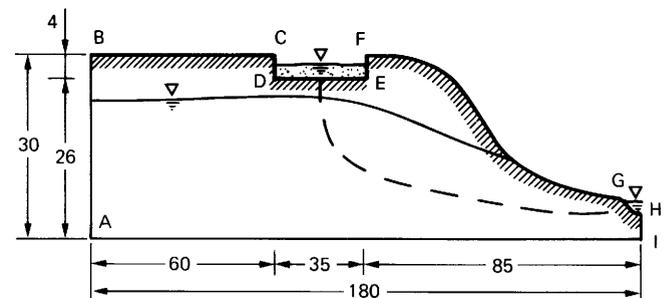


Fig. 28. Sketch of the region of interest for the seepage drainage problem (in meters)

The geohydrochemical parameters required for the simulation of the model are given in Table VIII where K_d values for leached Cr(VI) and As(V) are the average values for these elements in non specific alluvial soil.

Results obtained are described in the following. Because of its high mobility in the soil arsenic reaches saturated groundwater media (situated at 20 meter depth) after two years of continuous release (Fig. 29). It is interesting to note that there is a continuous movement of arsenic towards the surface water basin. Arsenic will reach this stream after seven years of con-

tinuous release (Fig. 30). Its average horizontal diffusion velocity is one third the calculated Darcy velocity (Fig. 31).

Fig. 32 shows that under a repository (20 m) arsenic concentration in groundwater persists for 60 years over the Maximum Permissible Concentration level (50 microgram As/liter) of EC 80/778 Directive on drinking water quality. Diffusion of chromium is similar. This element, however, will have an impact on the stream only after 10 years (Fig. 33) and its concentration will remain for much longer time over the MPC level (50 microgram Cr/liter) at the nodes considered (Fig. 34).

Table VIII The most important parameters used in the improved finite element model for Cr(VI) and As leached from fly ash repository to alluvial soil

| | |
|--|--|
| $K_{dCr} = 10 \text{ cm}^3 \text{ g}^{-1}$ (distribution coefficient) | $I = 0.95 \cdot 10^{-4} \text{ sec}^{-1}$ (water infiltration rate) dynam. viscosity of water = 0.013 |
| $K_{dAs} = 3.5 \text{ cm}^3 \text{ g}^{-1}$ (distribution coefficient) | XY contactivity direction = 0.58 E-7 |
| $\rho = 1.5 \text{ g cm}^{-3}$ (soil bulk density) | compressibility of soil and water = 0.0 |
| $a_L = 2130 \text{ cm}$ (longit. dispersivity) | pressure head = 800 to 0 and from 0 to 2000 cm |
| $a_t = 427 \text{ cm}$ (transverse dispersivity) | moisture content = 0.032 to 0.3 at 30 m depth |
| $\rho = 0.2$ (porosity) | relative permeability * viscosity / (density * gravity) = from 0.1 E-5 to 0.9 E-5 and from 0.1 E-4 to 0.13 E-4 |
| $a_m = 0.0$ (mol. diff. coeff.) | |
| $T = 0.0$ (tortuosity) | moisture content = from 0 to 0.3 E-2 and capacity from 0.2 E-2 to 0 |
| Water density = 1 g cm^{-3} | accel. of gravity = $980.6 \text{ cm sec}^{-2}$ |

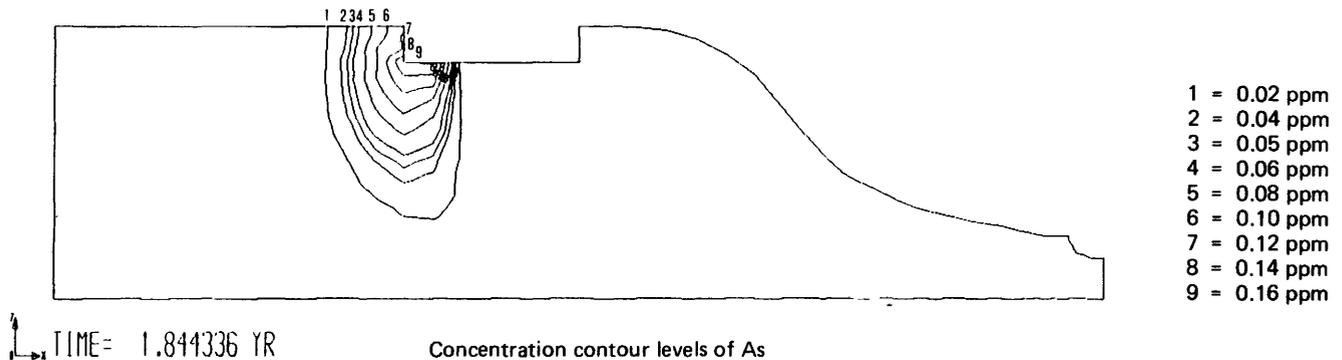


Fig. 29. Time dependent concentration contour levels of As after 1.84 years

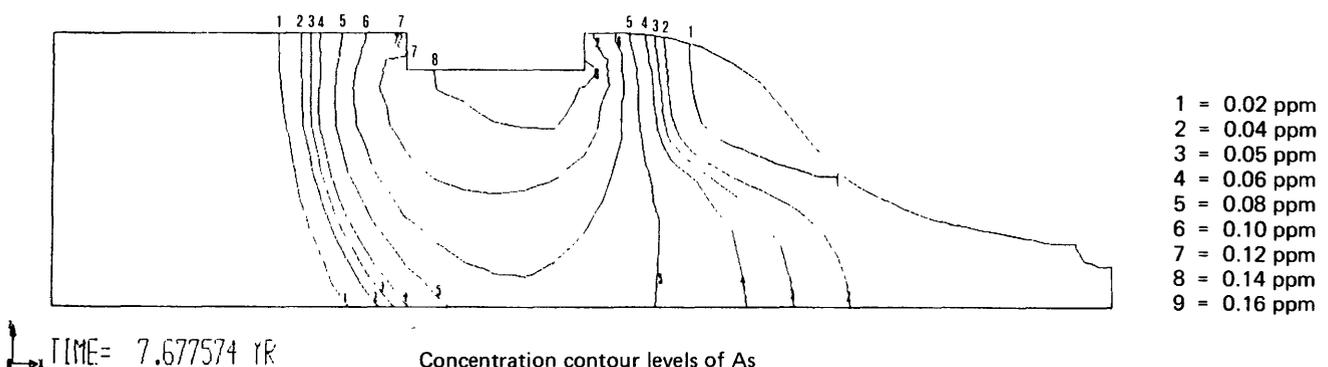


Fig. 30. Time dependent concentration contour levels of As after 7.68 years

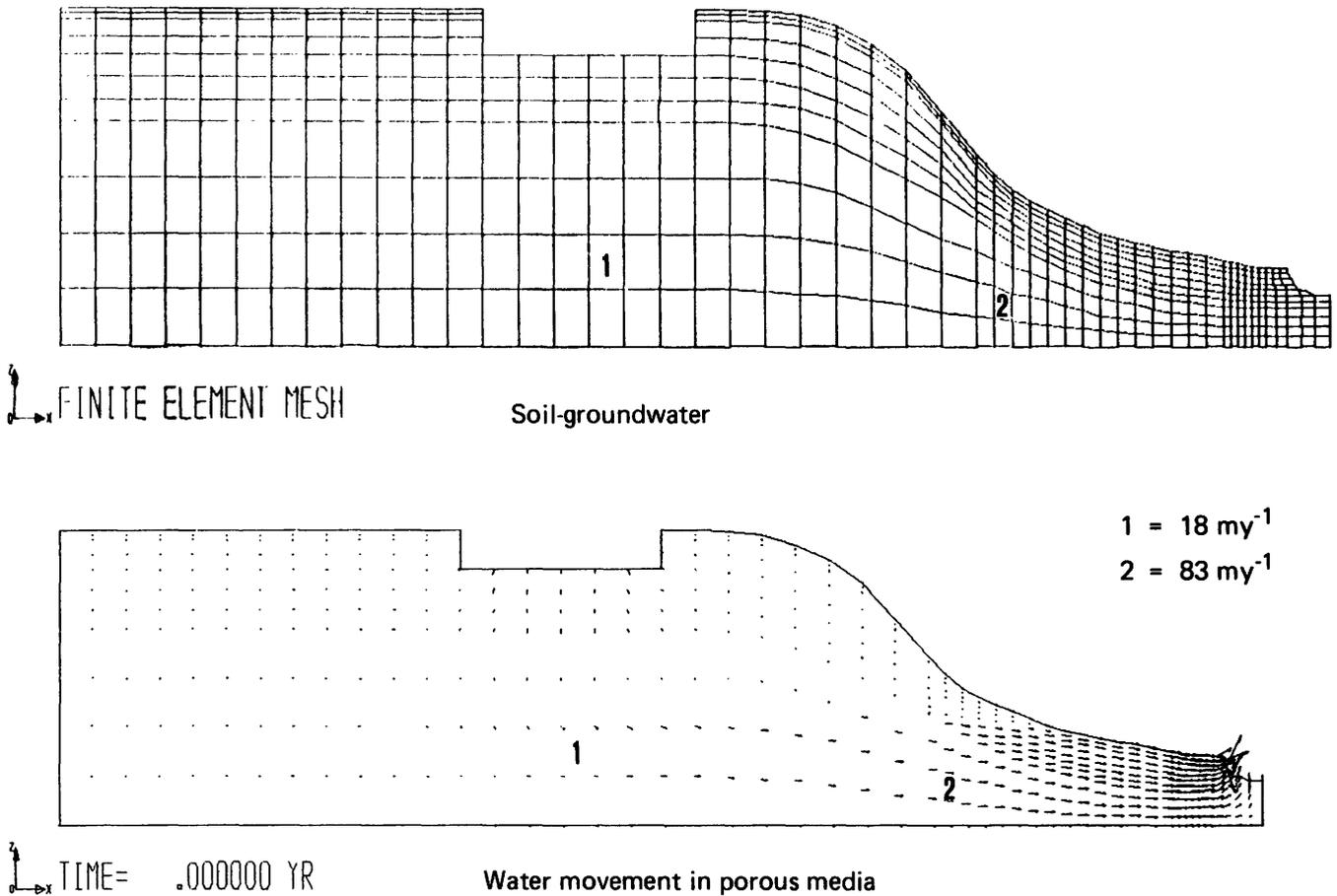


Fig. 31. Finite element discretization and associated water movement in soil porous media

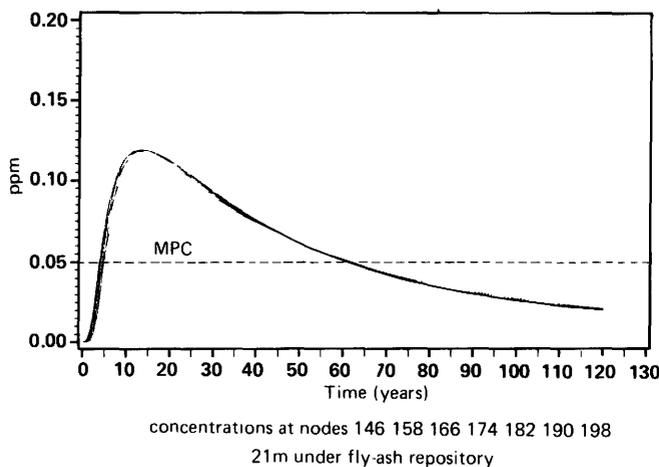


Fig. 32 Calculated increase of As concentration in groundwater using finite element model

Conclusions

Laboratory leaching studies

Data of the release of As, Cr, Mo, Sb, Se, V, W and Zn from fly ash of two power plants have been obtained. Concentrations in the leachates are similar to values obtained previously when investigating coal fly ashes of other provenances. Fly ash LH, however, shows minimum leachate concentrations of Cr, Mo, W and V in the range of 2-4 percolated porevolumes, never observed in other types of coal fly ashes studied until now. Time dependent filling up and leaching behaviour of a real fly ash repository has been simulated in the laboratory by stepwise

superposing of six single fly ash columns. The obtained results on time dependent trace metal concentrations will be introduced in the environmental migration model.

High performance ion chromatography combined with radiometric detection has been employed for chemical speciation of trace metals in fly ash leachates from neutron activated fly ash and in leachates equilibrated with radiotracers. This analytical technique has also been applied for quality control of the chemical form of radiotracers in solution. By this way it has been demonstrated that the chemical form of purchased radiotracers as originally indicated by the producer often represents only a part of the radioactive ions of the solution. Only after an adequate chemical treatment and a new control of the chemical form by the above method the radiotracer can be considered radiochemically pure.

Soil characterization and pollutant - soil interaction studies

This activity have been initiated in June. So a first objective has been the setting up of a laboratory for soil analysis and characterization. Two soils sampled in the Ispra Establishment area have been analysed and partly characterized. A series of experiments on the interactions of these soils with different trace metal species using radiotracers have been performed demonstrating the validity of the radiotracer method. In view of future soil sampling work, literature studies have been performed in order to find out the main European soils, their presence and geographic location in Italy and nearest the Ispra Establishment.

Assessment studies

Concerning the two models studied (compartment and finite element ones) we can draw the following conclusions: there are

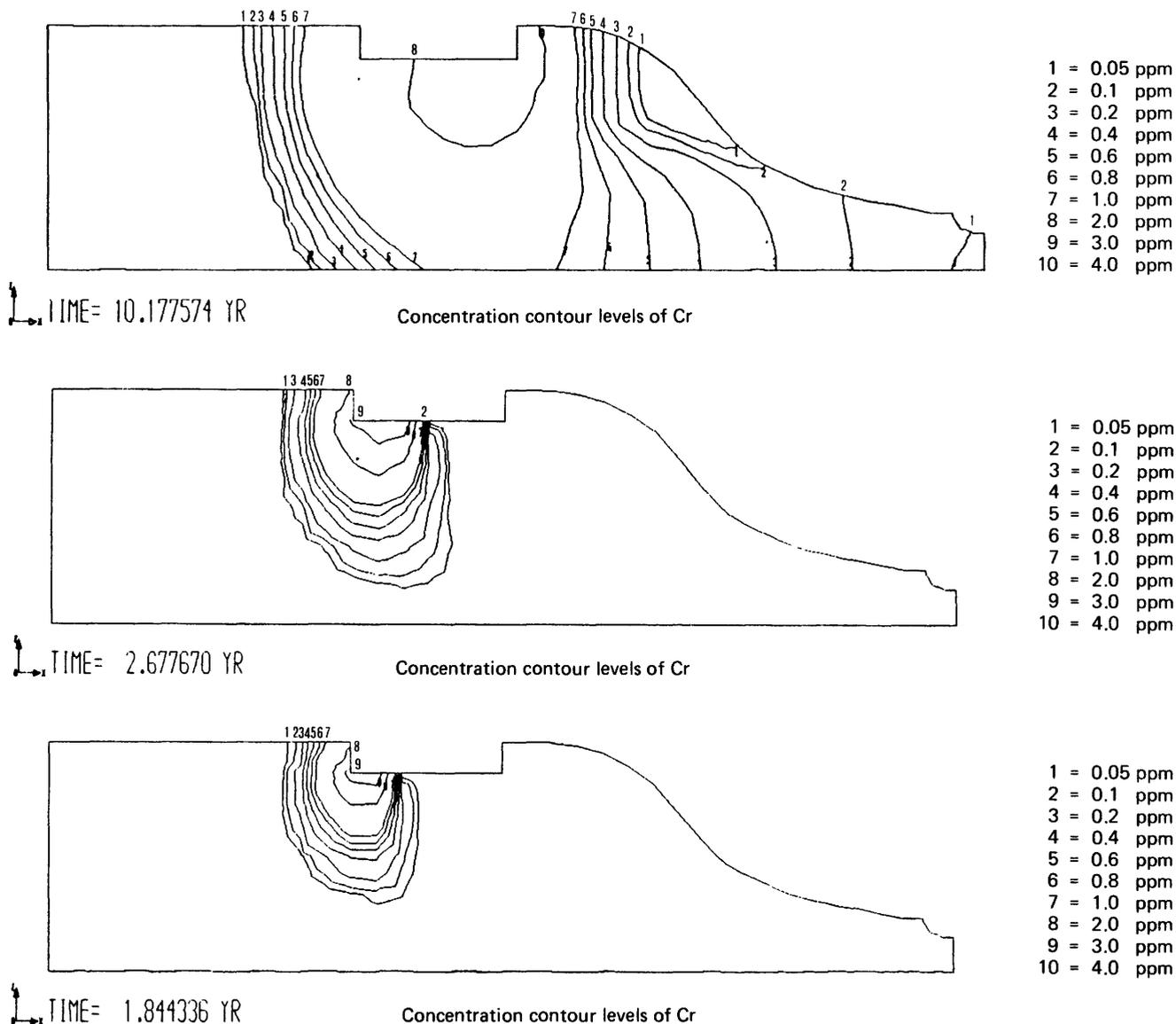


Fig. 33. Time dependent concentration contours of Cr

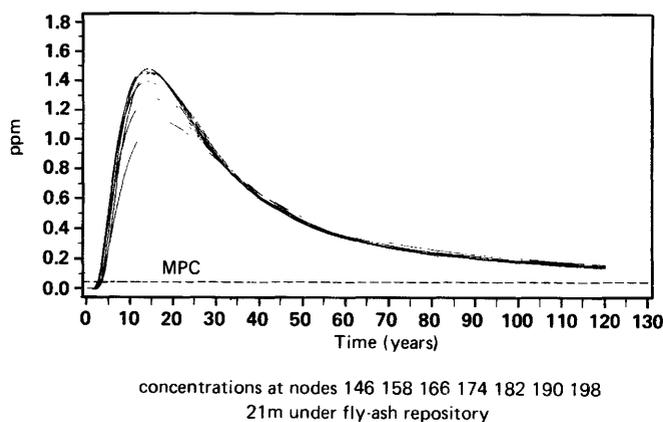


Fig. 34. Calculated increase of Cr(VI) concentration in groundwater using finite element model

many advantages associated with the use of dynamic compartmental models. They use a simpler mathematical approach, consequently they do not need a big computer and require few parameters. The disadvantage is that this type of model cannot consider the environmental variability and consequently will only be applied to the preliminary assessment studies.

On the other hand the finite element type model describes better the environmental variability also taking into account heterogeneity of natural soil porous media. Moreover it can represent graphically the analytical calculation of time dependent isoconcentration contour levels.

References

L. GOETZ, G. BIGNOLI and A. SPRINGER
Trace Metal Pollution by Coal-Fired Power Plants: Laboratory Studies of Trace Metal Leaching from Pulverized Fuel Ash. 7th International Symposium on Environmental Pollution, Toronto (Canada), June 11-12, 1987.

G. BIGNOLI and L. GOETZ
Environmental Impact Studies and Health Risk Estimation of Chromium Released from Stack and from Disposed Ash of a 2500 MW Coal-Fired Power Plant in Comparison with Other Potential Pollution Sources. 7th International Symposium on Environmental Pollution, Toronto (Canada), June 11-12, 1987.

S. KEPHALOPOULOS, G. BIGNOLI and L. GOETZ
Finite element methodology to assess the impact of trace metals released from a coal fly ash repository on groundwater quality. International Conference on Groundwater Contamination: Use of Models in Decision Making, Amsterdam (The Netherlands), October 26-29, 1987.

2. Atmospheric Pollution

The scientific understanding of atmospheric pollution is one of the major concerns of policy makers because only based on validated data, elucidated transformation processes and environmental pathways will it be possible to balance existing or projected pollution levels against adequate control measures. Of special concern are the continuing high emissions from fossil fuelled power stations and the high level of automobile traffic which ask for short term control strategies to avoid large scale irreversible ecological damage. With this in mind, JRC Ispra performs field experiments and simulation studies of chemical and photochemical reactions with special regard on processes forming acidic compounds; runs a Central Laboratory for Air Pollution Measurements and an EMEP-Monitoring stations; participates in national and european field experiments on the mass balance and transport of pollutants using ground based remote sensing techniques, tracers and micrometeorological measurements.

2.1 AIR QUALITY

INTRODUCTION

The project Air Quality consisted formerly of mainly two lines of research. One was dedicated to the study of the precursor photo-oxidant relationship in ambient air at relatively low concentrations. The major contributions to the appreciable photochemical ozone formation in the Ispra area should be identified and the connected summer haze checked for a characteristic pollutant of the visibility reducing aerosols. Through airborne measurements over several years it had been demonstrated that build-up of higher ozone concentrations during sunny summer periods effects the Po valley as a whole, which gives these types of studies a general importance. Therefore experiments under simulated atmospheric conditions for the study of chemical and photochemical reactions were continued. They gain importance with the presently discussed trend of tropospheric ozone increase and the modelling exercises for the development of abatement strategies. The experimental conditions are chosen as realistic as possible, for instance by using natural sunlight for irradiation and realistic precursor levels. The second line of research was centered around the analytic possibilities of Infrared Fourier Transform Spectroscopy. With this technique the role and the behaviour of nitrogen oxides in night-time air chemistry is investigated. The related processes are as important as the photochemical transformations during daytime with respect to the formation of acid compounds, like nitric acid.

To quantify the double importance of nitrogen oxides, namely its precursor role in photo-oxidant formation and its impact on acid deposition, is the long term goal of the project.

In line with this scope is the recently added third line of research, based on a hypothesis by which natural plant emissions, e.g. terpenes, enhance the formation of acidic pollutants if acid precursors and ozone are present simultaneously. The possibility for this process is probably limited to forested areas or crop plantations, but might constitute an important mechanism for the dry deposition of pollutant mixtures onto vegetation.

RESULTS

Chemical and photochemical reactions under simulated tropospheric conditions

The reactions of SO_2/O_3 with β -pinene and with the integral emission of a spruce branch (*picea abies*) were studied in teflon bags (see following Topical Report on «Reactivities of teflon bags in Photochemical Experiments»).

The reaction of β -pinene with ozone in the presence of sulphur dioxide leads to the formation of sulphur-containing particulate matter analyzed by flame photometry and as sulphate by ion chromatography (Fig. 1). At least 75% of the consumed 25 ppb of SO_2 was found as sulphate.

In addition, experiments were carried out using the emissions of a spruce branch (*picea abies*) reacting with ozone and sulphur dioxide in Teflon bags. Such an emission contains different terpenes (e.g. 30 ppb α -pinene, 53 ppb β -pinene, 5 ppb camphene, 7 ppb myrcene, 7 ppb limonene). We too found relatively rapid oxidation of the sulphur dioxide to sulphate within 1 h, which indicates the possible environmental significance of this process (Fig. 2).

Sunlight irradiation of a mixture of β -pinene, O_3 and SO_2 leads to the same products as by the reaction under dark conditions. With respect to the formation of sulphuric acid the measured amounts can be well compared to those of the dark reaction. Measurements on the seasonal variation of terpene concentrations in a pine forest (JRC-Ispra) indicate significant influence of climatic and other environmental conditions (Fig. 3).

Regarding the analysis of the terpene content of the needles from different coniferous trees, significant variations could be found only with respect to the different coniferous trees, significant variations could be found only with respect to the different tree species. Needles taken from several zones of the same tree (different height, shadow or sun site) did not show significant variations of their terpene depot.

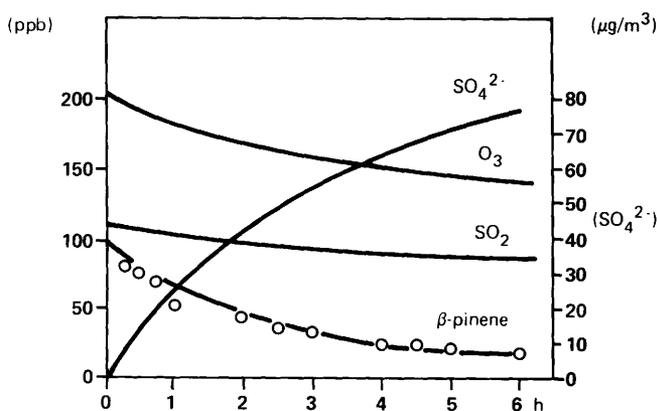


Fig. 1. Reaction of β -pinene with ozone and sulfur dioxide in a Teflon bag (filled with 800 l of purified air) in the dark (reaction time 6 h, rel. humidity in the bag \approx 6%, 22°C). The actual concentration of O_3 , SO_2 and sulfur containing particulate matter was measured continuously during reaction.

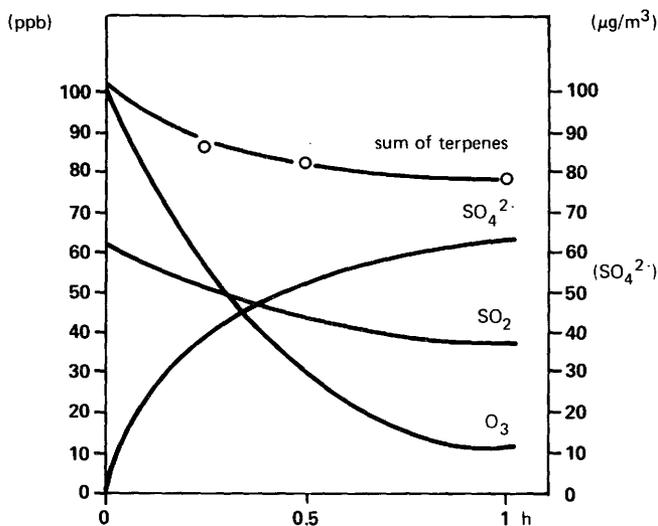


Fig. 2. Reaction of terpenes emitted from a spruce branch with sulfur dioxide and ozone in the dark. The spruce branch was put into a Teflon bag (filled with 800 l of purified air) for 2 h. The initial concentration of five selected terpenes (α -pinene, β -pinene, camphene, myrcene, and limonene) was measured immediately after removal of the branch (reaction time 60 min., rel. humidity in the bag \approx 50%, weight of the branch 272 g, 21°C). There was no change of SO₂ and O₃ of more than 6% in the absence of terpenes in the dark

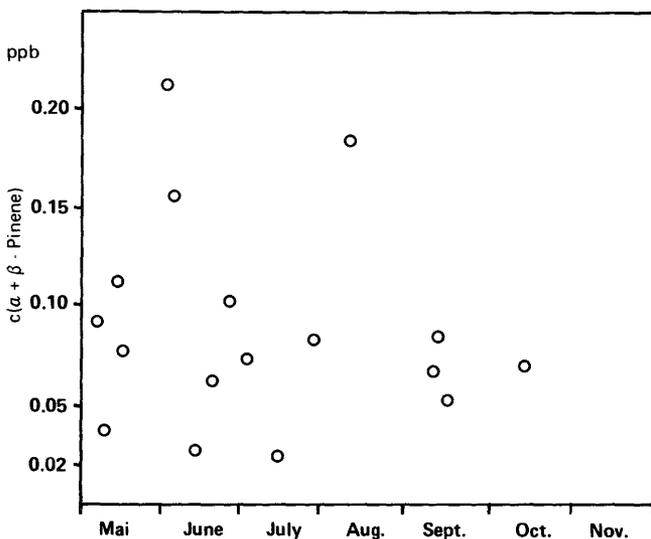


Fig. 3. Seasonal variation of the terpene concentration in forest air (pine forest, JRC-Ispira) Sum of α - and β -pinene (main components)

Publication

- H. STANGL, D. KOTZIAS and F. GEISS
How forest trees actively promote acid deposition.
The role of terpenes in the dry deposition of ozone and ozone/sulphur dioxide mixtures.
Naturwissenschaften 75, 42-43 (1988).

REACTIVITIES OF TEFLON BAGS IN PHOTOCHEMICAL EXPERIMENTS

C. Lohse, J. Hjorth, D. Kotzias, M. Duane, B. Nicollin, C.O. Nielsen and T. Schindler

Abstract

Experiments were carried out to characterize FEP (perfluorinated ethylene-propylene co-polymers) bags (Teflon bags) or reactors for studies of photochemical reactions of organic compounds in sunlight. Measurements of β -pinene loss, carbon monoxide oxidation, NO oxidation and O₃ formation in zero air and in ambient air made it possible to quantify the surplus reactivity due to the Teflon film material. This reactivity was equivalent to an OH radical concentration of (1,1 - 3,1) 10⁵ molecules cm⁻³ as compared to (7,6-19,2) 10⁵ molecules cm⁻³ found in ambient air. The OH source strength is kept up by photolysis of the film material. The teflon mass to volume ratio and not surface to volume ratio of the bags was shown to correlate with the surplus reactivity.

Introduction

Bags made of thin Teflon film are used by several laboratories for studies of chemical reactions in the gas phase. We have extensively used 2 m³ bags made of 0.05 mm thick FEP-Teflon film (Type 200A) for studies of atmospheric chemistry under simulated atmospheric conditions, using ambient air and natural sunlight.

The principal advantage of this approach is, in our opinion, the simplicity of the system and the relevance. The main disadvantages are the lack of control of all the parameters in the experiment and the effects of the Teflon film itself.

Several authors have demonstrated that Teflon bags cannot always be considered inert when used for photochemical experiment. Lonneman et al. (1) reported the release of large amounts of volatile compounds from a new Teflon bag. Kelly (2) pointed out, that FEP-bags, even after conditioning, exhibited some excess reactivity and were unsuitable for simulating photochemistry or precursor concentrations typical for rural or background conditions. Stangl et al. (3) have demonstrated the presence of OH radicals in Teflon bags with zero air in concentrations typical of ambient air. The wall loss of gaseous pollutants in outdoor Teflon bags has been discussed by Grosjean (4). The scope of the present work is to identify and quantify these sources for excess reactivity in Teflon bags.

Construction

Pillow-shaped bags with a volume of 2 m³ were constructed by careful heat-sealing of two pieces of 147 cm wide, 400 cm long and 0.05 mm thick Teflon film.

Great care was taken not to touch the interior surface of the bags, as this would cause contamination with organic compounds from the fingerprints. We found it necessary to seal the bags only on days with high air humidity as the bags otherwise would be contaminated by dust particles attracted by the electrostatic film material. The sealings were protected and the bags conditioned as previously described (3).

Gas-Permeability

Teflon bags are permeable to many compounds, especially small polar molecules.

We have previously reported some permeability data (3). However, as shown later, the key compounds responsible for surplus reactivity are, apart from the Teflon film itself, NO_x, H₂O and CO. We want to report some new findings on their origin. Water was found to have a permeability of 0,5% hour⁻¹. This is 10-20 times faster than other small molecules and corresponds to a diffusion of about 50 ppm of water each hour into a Teflon bag with dry air placed outside in typical ambient air (H₂O \sim 10.000 ppm). This high diffusion rate makes it impossible to con-

trol a low water content of the bags, and we found it easier to control the experiments when the water content of the bag air was adjusted close to that of ambient air.

NO₂ was found to have a very low permeability of about 0,2% in 24 hours. This means, that around 10 ppt of NO₂ will diffuse into a zero air bag during a one day experiment with the bag placed in ambient air (NO₂ ~ 10 ppb). Although this NO₂ quantity might cause some problems to the study of very sensitive reactions, we found the NO_x content of zero air to be a much more serious problem.

CO was found to have a permeability of 2% in 24 hours. This value is insignificant compared to the CO release from the Teflon material during sunlight irradiation.

We were not able to detect the diffusion of volatile hydrocarbons from ambient air into the bag. Similarly, the 24 hour decay of 4-100 ppb concentrations of β-pinene was found to be less than 5%.

Lifetime of Unstable Gases

The chemical inertness of the Teflon film is demonstrated by the long lifetime of ozone in Teflon bags. Half lives in the dark of about 160 hours at room temperature have been measured in our laboratory starting at O₃ concentrations of about 100 ppb in a 2 m³ bag. As expected, the half-life depends on the surface to volume ratio, getting shorter in a smaller bag. However, no proportionality was found.

Table I shows the first order decay rates for ozone degradation in three experiments, where the same 2000 l bag was filled with 2000 l, 1000 l and 500 l zero air with an ozone content of 100 ppb.

It is seen from the table, that the decay rate in the 2000 l bag is too high in comparison to the other two rates if the surface only was responsible for the ozone decay. The experimental rates can better be explained by assuming two decay processes. One depending on the surface area. The other, the decay rate of ozone in the absence of any surface. From the data in Table I, this «natural lifetime» of ozone could be calculated to be 350 hours.

Table I. Lifetime of ozone as a function of bag volume

| Volume | 2000 l | 1000 l | 500 l |
|--------------------|-----------------------|-----------------------|-----------------------|
| k, s ⁻¹ | 1.83·10 ⁻⁶ | 2.73·10 ⁻⁶ | 5.09·10 ⁻⁶ |

Impurities from Teflon Film Material

The main contaminant found in zero air samples in sun-irradiated bags is carbon monoxide, CO. Significant quantities, 4-10 ppm, of this compound are built up in the bags during irradiation of new Teflon bags. By subsequent irradiations the CO formation rapidly falls off, reaching a level of 200 ppb or less per day in sun. We consider this as an acceptable level as the CO content of ambient air is normally above this level.

The release of CO during one day experiments was found to be proportional to the integrated UV-flux, Fig. 1. However, by comparing the release rate in the same bag from one day to another, the ratio (release rate): (integrated UV-flux) could differ by more than a factor of 10. This demonstrates that only a narrow part of the UV-light (which we are unable to measure) causes the formation of CO. The release of CO in old bags is insignificant, 4 ppb per hour, on a hazy day. Much more CO is released under clear sky conditions.

It was demonstrated that CO is released by the Teflon film as such, and not by a precursor in the vapour phase. Moreover, the surface area of the film was found to be of no importance for the CO formation, whereas the mass of Teflon material was proportional to the CO release. We consider this an important

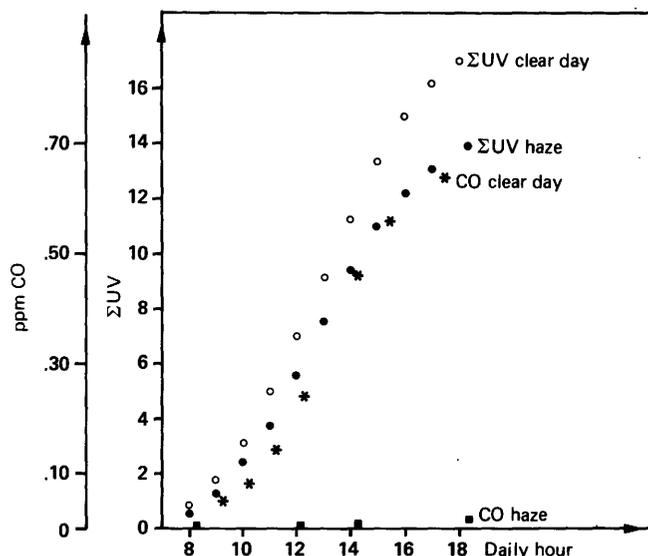


Fig. 1. CO formation from Teflon film on a clear day and on a hazy day

observation as it is experimentally much easier to construct a bag of a thinner material compared to increasing the size of the bag.

We looked for, but did not find, small fluorinated hydrocarbons. This is in accordance with previous publications (3), (5).

Impurities from Zero Air

Zero air was produced by an AADCO 737 clean air generator. This instrument has proved very efficient in removing traces of volatile organic compounds from ambient air. However, when zero air was analyzed for NO₂ by the Luminox chemiluminescence analyzer a 20 ppt content of NO₂ was found to be present.

Worse, when ozone, generated from the same zero air, was added to zero air prior to NO₂ analysis, as much as 0,4 ppb of NO₂ was found. This means, that the zero air contains ~0.4 ppb of NO. Fig. 2 demonstrates one of these experiments. Fig. 2 also demonstrates an apparent source of NO₂ from the ozone generator, or alternatively, interference of O₃ in the NO₂ measurements.

Irradiation of Teflon bags

Sunlight irradiation over a day of Teflon bags filled with zero air gives rise to varying amounts of ozone, typical 5-15 ppb. In the first 2-3 hours of irradiation, the ozone formation is followed by formation of ~0,4 ppb of NO₂ due to NO oxidation.

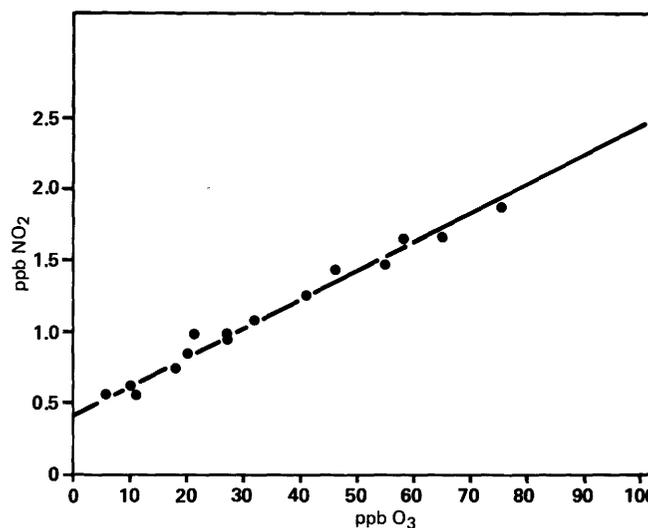


Fig. 2. Measured values at O₃ and NO₂ in zero air/O₃ mixtures

At a first glance this could look like normal smog photochemistry, however, in a number of ways the ozone formation in zero air in Teflon bags differs from that of polluted air.

The ozone production remains unaffected if some ppb of nitrogendioxide are added. This is an indication that usual ozone precursors like hydrocarbons are not involved, as ozone production then should be depending on the NO₂ concentration. Similarly, after the initial oxidation of NO to NO₂, the NO₂ concentration remains nearly constant during the rest of the experiments. Under bag irradiations of ambient air samples, NO₂ is normally used up.

We have carried out experiments which show still other effects most probably related to the film itself. A first set tries to elucidate the influence of the surface of the film and the mass of the film on ozone formation, a second set to estimate the source strength of the ozone forming process.

Experimental Procedures

The experiments in this study were carried out with bags conditioned by sunlight irradiations of zero air samples until the CO-release was less than 200 ppb per day. The irradiations were followed by treatment with zero air containing 1-2 ppm of ozone for 24 hours.

In the experiments where the effects of the film surface were separated from the effects of the mass of the film, the following three bags were used:

Bag No. 1: Made up of 2 pieces 147 cm wide, 400 cm long and 0,05 mm thick film.

Bag No. 2: Made up as No. 1, with the addition of a 147 cm wide, 400 cm long and 0,025 mm thick sheet of film inside.

Bag No. 3: Made up as No. 1, with the addition of a 147 cm wide, 200 cm long and 0,125 mm thick sheet of film inside.

Results and Discussion

Table II shows the ozone formation by one day irradiation of three 2 m³ Teflon bags where the surface to volume ratio and the Teflon mass to volume ratio were varied independently by the addition of extra Teflon film to two of the bags. The bags were constructed from 0,05 mm film. The extra added film was 0,025 mm or 0,125 mm. One of the bags served as a reference bag and contained only zero air. The other bags contained the same zero air + extra Teflon film.

It is clear from Table II, that addition of Teflon film enhances the ozone formation contrary to expected from the results from ozone life time measurements. It is furthermore demonstrated, that the surface of the film only plays a minor role, and the surplus ozone formation seems to follow the mass of the Teflon film involved. We find this observations surprising. It demonstrates however, as in the case with CO formation, that Teflon bags, constructed of as thin films material as possible, will offer the best choice for photochemical studies.

Fig. 3 shows the ozone formation and the integrated UV-flux during one day irradiation of zero air in a Teflon bag. The experiment demonstrates the close correlation between the two measured parameters. This is very different from ozone formation during smog episodes and from irradiations of ambient air samples in Teflon bags, where the ozone peak occurs around noon or in the early afternoon.

Table II.

| | Ratios | | | |
|-------|----------------------|-------------------------------------|-------------------------------|---------------------------------|
| | Added Film Thickness | Surface film bag Surface ref bag | Mass film bag Mass ref bag | Ozone film bag Ozone ref bag |
| Exp 1 | 0,125 mm | 1.5 | 2.25 | 2.13 |
| Exp 2 | 0,025 mm | 2.0 | 1.50 | 1.46 |

As in the case of CO formation, it could also be demonstrated that ozone does not come from a compound released prior to irradiation.

Fig. 4 shows the effect of water on the O₃ formation during irradiation of zero air. Fig. 5 shows the oxidation of NO to NO₂ in the same experiment. Both figures demonstrate a significant enhancement of the photochemical reactivity at high water concentrations.

Table III shows the calculated OH concentrations based on the decay of β-pinene during irradiations under various conditions. These concentrations are in very good agreement with the OH concentrations based on CO oxidation in Teflon bags as previously reported (3). We find it a very strong argument for the presence of OH in zero air during irradiation in Teflon bags. As seen from fig. 5, the initial oxidation of NO to NO₂ in zero air in Teflon bags is quite fast. The rate under these conditions is more or less the same as under smog episodes in ambient air. Nevertheless, no organic compound has been found by us, and the normal explanation for NO₂ formation via equation 1 seems to be invalid.



We are, of course, very much aware that the lack of detection of an organic compound as such is a poor evidence. However, additional support for the non-presence of organics in the air comes from the non enhanced ozone formation when more NO₂ is added to the bag. Ozone formation from bags in radiations of NO₂ - zero air mixtures constitutes in our experience

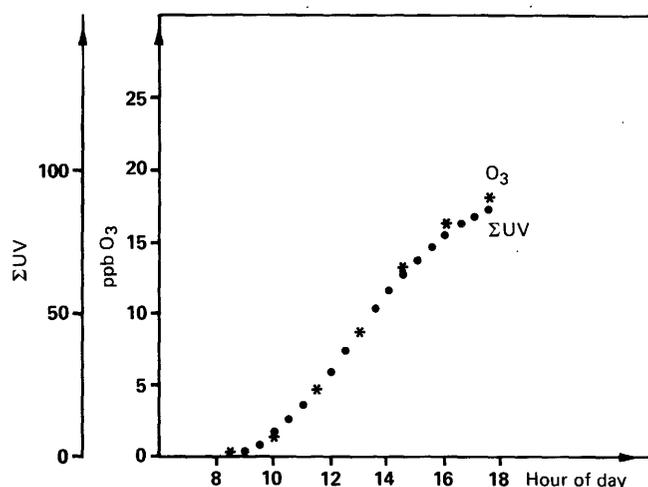


Fig. 3. O₃ formation and integrated UV flux by sun irradiation of Teflon bags

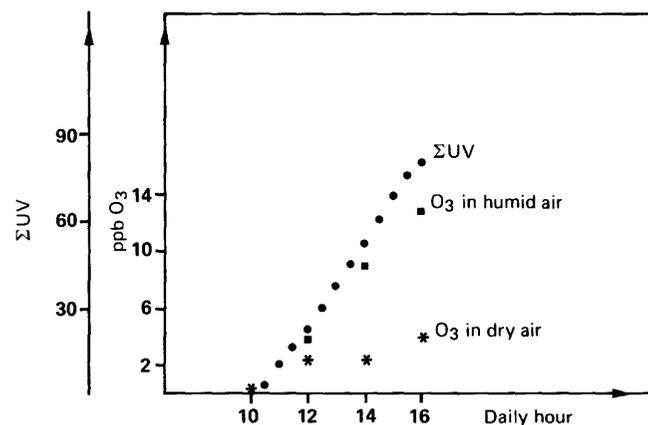


Fig. 4. Influence of water on O₃ formation by sun irradiation of zero air in Teflon bags. Humid air contains 11.7 g H₂O/m³ while dry air contains 1.0 g H₂O/m³

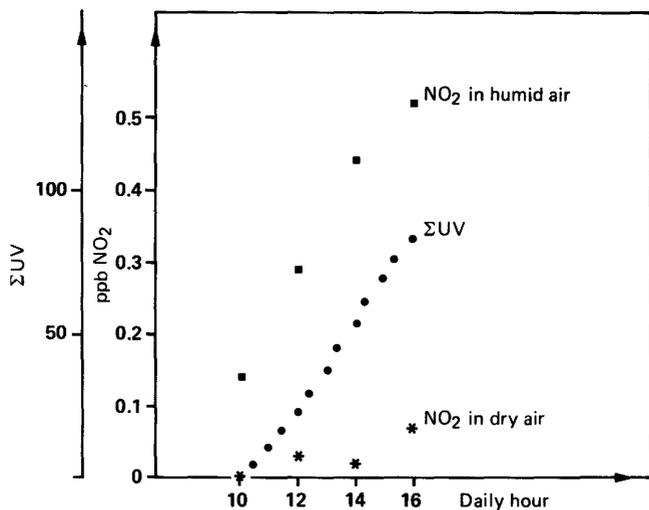


Fig. 5. Influence of water on NO_2 formation by sun irradiation of zero air in Teflon bags. Humid air contains $11.7 \text{ g H}_2\text{O/m}^3$ while dry air contains $1.0 \text{ g H}_2\text{O/m}^3$

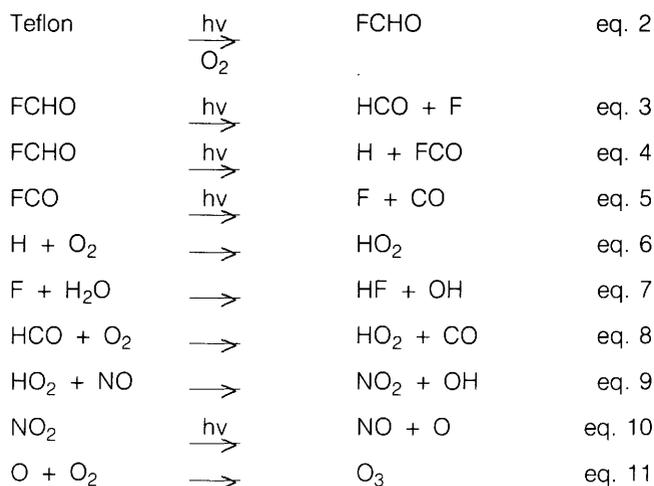
Table III.

| Date | Bag Content | Concentration of β -pinene, PPB | | [OH] molecular cm^{-3} |
|-----------|-------------|---------------------------------------|---------|---------------------------------|
| | | Morning | Evening | |
| 7.9.1987 | zero air | 83.7 | 75.0 | $1.12 \cdot 10^6$ |
| -- | zero air | 1.90 | 1.48 | $2.53 \cdot 10^6$ |
| -- | Ambient air | 4.01 | 1.59 | $9.41 \cdot 10^6$ |
| 30.9.1987 | zero air | 4.54 | 2.60 | $2.87 \cdot 10^6$ |
| -- | Ambient air | 4.51 | 1.09 | $7.58 \cdot 10^6$ |

the most sensitive and relevant test for organic impurities in the system.

The NO oxidation and ozone formation can be explained if the OH source can be identified. As seen in fig. 3, the ozone formation is strictly correlated to the UV flux. This suggests that the OH source is of photochemical origin. As possible explanation would be, that an OH precursor is released photochemically from the Teflon film, followed by further photolysis and reactions to produce OH.

We will propose formyl fluoride FCHO as an ozone precursor via equations 2-11:



Attempts to detect formyl fluoride have failed so far. However, substantial indirect evidence supports its presence.

- Formyl fluoride is photochemically decomposed followed by formation of HF (6).

Our sequence of processes are of photochemically origin.

- The reaction sequence would be promoted by water, eq. 7. This is observed.
- Fluorine ions would be formed in more or less the same amount as ozone. This is in fact observed (3).
- CO would be produced, which is not contrary to our observations and
- the reaction sequence would be unaffected of NO_2 addition, as observed.
- Finally, eq. 10 and eq. 11 constitutes the only known source of tropospheric ozone.

Conclusions

Irradiation of Teflon film material constitutes a source of OH radicals and results in ozone formation. The best way to minimize this process is to construct the bags of as thin film as possible as the mass of the film and not the surface area determines the surplus reactivity.

The amount of OH radicals provided by the Teflon in a 1 m^3 bag made up of 100 mill film is about 10% of the OH concentration in ambient air.

0,4 ppb NO was detected in zero air. This is a significant amount and this source should be taken into account in kinetic studies.

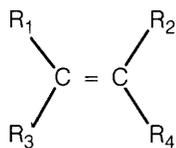
References

1. W.A. LONNEMAN, J. BUFALINI, R.L. KUNTZ and S.A. MEEKS (1981) «Contamination from fluorocarbon films», *Env. Sci. Technol.*, 15(1), p. 99.
2. N.A. KELLY (1982) «Characterization of fluorocarbon-film bags as smog chambers». *Env. Sci. Technol.* 16(11), p. 763.
3. H. STANGL, D. KOTZIAS, J. VAN EIJK, B. NICOLLIN, J. HJORTH, G. OTTOBRINI (1987) «On the use of Teflon bags for photochemical experiments» (*Chemosphere*, Vol. 16, No. 7, pp. 1405-1417 (1987)).
4. P. GROSJEAN (1985) «Wall loss of gaseous pollutants in outdoor Teflon chambers» *Env. Sci. Technol.*, 19(11), p. 1059.
5. N.A. KELLY (1985): «Test for fluorocarbons and other organic vapour by fluorocarbon film bags», *Env. Sci. Technol.* 19(4), p. 361.
6. H.W. MORGAN, P.A. STAATS and J.H. GOLDSTEIN (1956) «Vibrational spectra of formyl fluoride and d-formylfluoride», *J. Chem. Phys.* 25, p.337.

Laboratory studies. Nighttime Tropospheric Reactions

NO_3 has been found to react rapidly with many unsaturated organic compounds. The rates of the reactions between NO_3 and some biogenic hydrocarbons (isoprene and terpenes) have been found to be especially fast. These reactions may be of importance as sinks for organic compounds as well as for the nitrogen oxides. It seems however important also to establish which are the products of these reactions but until now only few (and contradictory) results have been reported concerning the products of reaction of one alkene (propylene) with NO_3 in the presence of NO_2 , N_2O_5 and air.

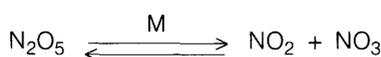
In our experimental investigations we have looked at the reactions between NO_3 radicals and two terpenes (α - and β -pinene); subsequently the study has been extended to some simple alkenes of the type.



where $\text{R}_1 - \text{R}_4$ are CH_3 or H .

The experiments were carried out in a 480 L Teflon covered glass cylinder with long path FTIR detection. In some runs product analysis was done also by bubbling the content of the reaction chambers through organic an solvent that was subsequently analyzed by GC-MS. In a typical experiment the hydrocarbons were added to a mixture of N_2O_5 and NO_2 in air.

NO_3 is formed in this mixture by the thermal dissociation of N_2O_5 .



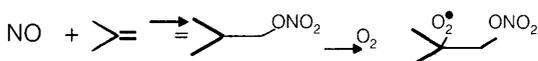
A series of IR spectra were then recorded to show the chemical changes with reaction time. The initial concentrations in a typical experiment were a few ppm for N_2O_5 and the hydrocarbons while N_2 was present at concentrations between a few and 70 ppm.

The functional groups present in the product compound as brought in evidence by the IR-spectra were $-\text{O}_2\text{NO}_2$, ONO_2 , $-\text{CO}-$ and $-\text{CHO}$.

In the beginning the main products of the reactions are nitrate and pernitrate compounds; later the amount of aldehydes and ketones increase while the pernitrate band slowly disappears. β -pinene seems to represent a special case as only nitrate bands are seen and a rapid formation of aerosols takes place.

The mechanism of the reactions can be tentatively described as follows, using isobutene as an example:

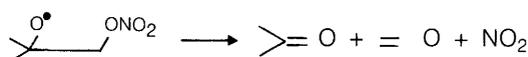
NO_3 adds to the double bond followed by addition of O_2



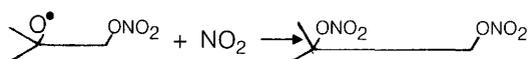
The peroxyradical may form a peroxyxynitrate with NO_2 or it may be reduced to an alkoxy radical by different mechanisms:



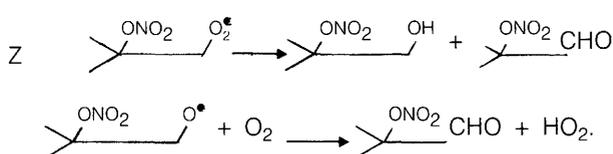
followed by either fragmentation



or addition of NO_2 :



We have good evidence for the presence of all of these products in the isobutene - N_2O_5 - NO_2 -air mixture (see fig. 1). Other types of reactions may however also occur when the alkylperoxy and alkoxy radicals are secondary or primary:



The GC-MS analysis of the products of the NO_3 - β -pinene reaction give support to the suggestion of such reactions.

Some chemical species of importance in the description of the chemistry of the gas system used to simulate tropospheric reactions, do not absorb in the infrared region in a way suitable for spectroscopic analysis at sufficiently low concentrations. This is the case of the NO_3 radical and other radical species (HO_2 , RO_2 etc.). Alternatively some species absorb in the IR but in spectral regions where strong interference by the absorption spectrum of atmospheric constituents (especially H_2O) occurs. Some of them however are characterized by specific absorptions in the UV-VIS part of the spectrum that can be used for identification and quantitative analysis.

To this scope a diode array UV-VIS spectrometer (optical multichannel analyzer) has been coupled to the photochemical reactor. In addition to the IR multipass a second White type three mirror system operated at 29 m total beam path has been installed in the chamber and a suitably filtered 75 W Xe lamp used to probe the gas mixture.

The diode array detector, attached to a 50 cm spectrograph, is controlled by a HP-97 computer: all the software for data acquisition and data treatment conceived according to the specific needs of this study has been developed in the Electronic Division.

Fig. 2 shows the spectrum recorded around 650 nm from synthetic air containing NO_3 (46 ppbv) generated by injecting NO_2 and O_3 in the reaction chamber. The two strong absorptions are due to the (1-0) at 623 nm and the (0-0) at 662 nm NO_3 bands.

Full operation of the UV-VIS spectrometer simultaneously with the IR spectrometer, is however presently slowed down because of the needs to fully elucidate the non coincidence of the probing volume in the reactor for the IR and UV-VIS analysis, which might affect the results of chemical modelling performed using both these data.

Derivative monitoring using tunable diode lasers

In order to match the operating conditions of a field monitor, the long path cell constructed in the laboratory was replaced with a special multipass cell developed at the IPM-Fraunhofer Institut-Freiburg FRG.

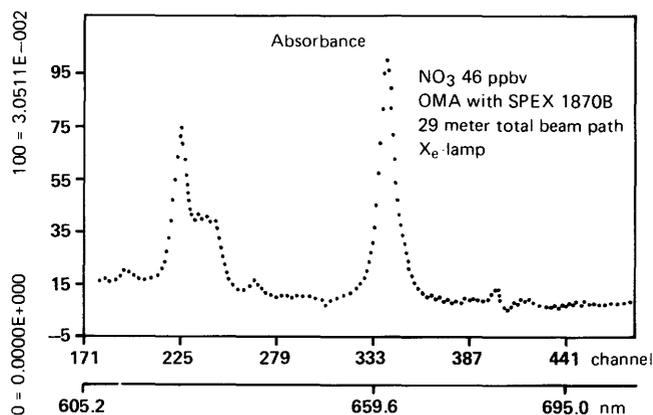


Fig. 2. VIS-spectrum of the NO_3 radical (46 ppbv) recorded in the same photochemical reactor used for the IR analysis. 29 m total beam path. 75 W Xe lamp filtered, Spex 1870 150 l/mm grating diode array (512 channels)

This device fulfils the requirements of a long beam path (up to 100 m) with correction for astigmatism in the optical scheme while keeping the cell volume sufficiently small (3 ℓ) to permit a short air residence time and then a high measurement rate. However the results have been unsatisfactory. The study focused on NH₃ measurements has not permitted to reach the sensitivities obtained three years ago in spite of the implementation of sophisticated signal handling techniques.

A careful analysis of the different parameters involved and comparison of the results with those obtained at IPM-Freiburg have shown that the responsibility of the poor results of the present set-up (around 2 ppbv NH₃ sensitivity) is to be ascribed to inadequate performances of the laser sources available in this last period.

EVALUATION OF SPECTRAL PARAMETERS

The study on CH₃D previously undertaken on the evaluation of broadening coefficients has been prosecuted with an analysis of line intensities in vibration rotation bands of this molecule. The absolute absorption intensities of 80 lines belonging to ν_3 , ν_5 and ν_6 fundamentals of ¹²CH₃D were measured in the range 1062-1480 cm⁻¹ using a dual beam tunable diode laser spectrometer. The data were analyzed at the Laboratoire d'Infrarouge - Orsay using energy and intensity formulations suitably developed for investigating all three bands within a triad model. The line strengths were reproduced with an overall standard deviation of 3.4% to be compared to an experimental uncertainty of 3%. The values derived for the band strengths of ν_3 , ν_5 and ν_6 are 40.1, 13.4 and 53.2 cm⁻² atm⁻¹ at 296 K.

In the frame of the study of the reaction of NO₃ with CH₂O, the absolute intensity of the ν_6 band of HCOOH has been measured. FT-spectroscopy and the 450-l gas cell were used to analyze the spectral absorption, calibrated by gas sampling followed by ion chromatographic analysis.

The measured value of the ν_6 absolute intensity could be compared with the only datum of the GEISA compilation showing a discrepancy by nearly a factor 2 /3/.

The same discrepancy appears with values reported in literature for the Q-branch (Table I).

TABLE I: HC¹²O¹⁸O: ν_6 band

| Q-Branch Intensity | |
|---|--|
| Ref. /1/ | 36 cm ⁻² atm ⁻¹ |
| Ref. /2/ | 20 cm ⁻² atm ⁻¹ |
| Ref. /3/ | 54 cm ⁻² atm ⁻¹ |
| This work (1102-1108 cm ⁻¹) | 110* cm ⁻² atm ⁻¹ |
| Total Band Intensity | |
| Ref. /3/ | 435.5 cm ⁻² atm ⁻¹ (296 K) |
| This work (1045-1150 cm ⁻¹) | 860* cm ⁻² atm ⁻¹ (296 K) |

References and J.R.C. Publications

- /1/ P. MAKER and H. NIKI
Unpublished, quoted in ref /2/.
- /2/ A. GOLDMAN, F.H. MURCRAY, D.G. MURCRAY and C.P. RINSLAND
Geophys. Res. Lett. 11 (1980) 307.

- /3/ A. CHEDIN, N. HUSSON, N.A. SCOTT, I. COHEN-HALLALEH and A. BERROIR
The GEISA Data Bank, revised 1986, Lab. de Météorologie Dynamique du CNRS - Palaiseau (France). For the Q-branch the integrated intensity has been calculated from the sum of the transitions given in the compilation for the specific wavenumber range.
- /4/ J. HJORTH, G. OTTOBRINI, F. CAPPELLANI and G. RESTELLI
J. Phys. Chem. 91 (1987) 1565.
A Fourier Transform IR Study of the Rate Constant of the Homogeneous Gas-Phase Reaction N₂O₅ + H₂O and determination of Absolute Infrared Band Intensities of N₂O₅ and HNO₃.
- /5/ N. LACOME, F. CAPPELLANI and G. RESTELLI
Appl. Opt.; 26 (1987) 766.
Tunable Diode Laser Measurements of Broadening Coefficients of Lines in the ν_6 Fundamental of ¹²CH₃D.
- /6/ J. HJORTH, G. OTTOBRINI and G. RESTELLI
J. Phys. Chem. accepted for publication.
Reaction Between NO₃ and CH₂O in Air: a Determination of the Rate Constant at 295 ± 2 K.

2.2 CENTRAL LABORATORY FOR AIR POLLUTION (CLAP)

BACKGROUND AND MEDIUM-TERM GOALS

For the implementation of the EC Directive N° 80/779, on the limit and guide values for sulphur dioxide and suspended particulates, JRC Ispra, on behalf of DG XI, acts as a Central Laboratory for measurements to be carried out by the Commission in collaboration with the Member States.

The programme for carrying out the responsibility assigned to the Commission was proposed by DG XI to the Member States in 1982. After discussions with government experts, the programme, finally accepted, started in 1983. JRC-CLAP contributes actively in the fulfilment of three well defined tasks until 1988:

Task 1: improvement of reference methods. Reference methods for SO₂, black smoke (BS) and total suspended particulates (TSP) as laid down in the Directive should be adapted to technical and scientific progress.

Task 2: harmonisation of analysis methods: SO₂, BS and TSP are measured by a variety of methods used in the Member States with uncertain comparability (applicability of the article 10.1 of the EC Directive).

Task 3: harmonisation of sampling methods. Different sets of limit values are laid down in the Directive (Annex 1 and IV) with unknown corresponding stringency (applicability of the article 10.3 of the Directive).

In general CLAP provides technical support for questions concerning measuring techniques, calibration methods and implements quality assurance programmes required to support the tasks 2 and 3 for the implementation of the Council Directive. In particular cases, CLAP collaborates in new analytical developments and measuring campaigns in the framework of other areas of atmospheric pollution research.

RESULTS

First quality assurance programme (task 2)

The ultimate evaluations of the first QAP are described in the topical report «Experience and Orientations of the EEC in the harmonisation of Measurement Methods for the control of Air Quality» at the end of this chapter.

Second quality assurance programme (task 3)

The quality control of the network instruments at selected stations of the Member States (article 5 of the Directive) started in June 87 and will be completed before July 1988.

The checks are performed according to the following procedures:

- a) The check of the Station Instrument (SI), without sampling line, by means of comparison standards transported in the mobile laboratory:
 - for SO₂ specific: check of the zero and span (50-70 ppb and 160-200 ppb) by means of 3 gas-cylinders;
 - for SO₂ measured by non specific manual methods (total acidity): check of standard solutions at 3 different SO₂ contents;
 - for black smoke: check of the sampler flowrate and the linearity of the reflectometer by means of the Kodak reflection density chart;
 - for TSP: check of the balances by means of calibrated weights.
- b) The check of the Station Instrument, used with its own sampling line, for 24 hours parallel measurements. In this test, the comparison (or reference) instrument (RI) of the CLAP is used with its own sampling line build up in parallel with the requested requirements of the Directive.
The tests are completed by asking the responsible of the station general information on the network, detailed information on the instruments and or calibration and maintenance procedures. When the intercomparison results are divergent, and if still time is available, complementary tests are undertaken. A final report including the detailed results and comments is sent to the responsible of the station for acceptance.

Some intercomparison results from Italy and Greece

a) Sulphur dioxide

In the 6 sites visited in Italy (fixed stations in Milano, Modena, Bologna, Marghera, Gela and mobile station in Caltanissetta) the SO₂ station instruments worked on the coulometric principle which is a quite updated method. The stations of Bologna and Milano showed by means of the cylinder test a negative bias of their instrument. This was consistent with the bias already noticed in the QAP/1 programme. Good correlation for cylinder crosschecks and 24 hours parallel measurements were noticed at Gela. At Marghera station the analyser, checked with the cylinders, was found in agreement (+7%) with the RI. On the contrary, no correlation was found in the 24 hour parallel test demonstrating the inefficiency of the sampling line (Fig. 1). It is likely that without

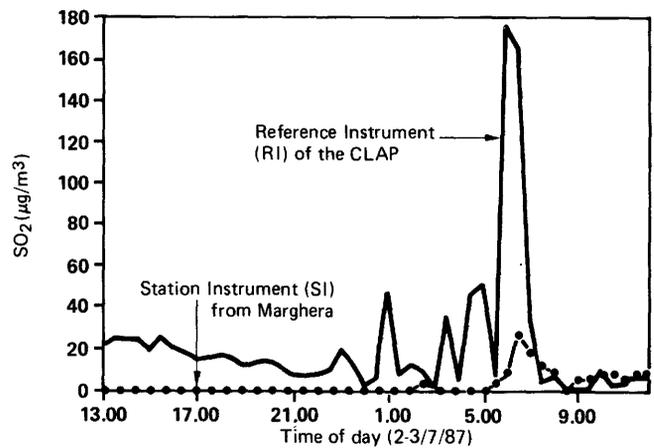


Fig. 1. Comparative measurements, for 23 hours at Marghera station, showing the inefficiency of the sampling line.

fan the large effective volume of the sample inlet (10 cm diameter, in comparison with the 8 mm diameter teflon tube used in parallel by the CLAP) may have caused the discrepancy and smoothed the concentrations.

Another consistent example on the inefficiency of the sampling line has been found in Greece where two stations (Patisision and Peireas) were visited. As shown in Table I, the concentration of the cylinders measured by the two instruments are consistent with those measured by the RI instrument. On the contrary, for the 24 hour parallel measurements carried out under routine condition, only the Patisision instrument showed a good correlation. With the Peireas instrument, the hourly relative differences versus the RI showed an important negative bias (-56%) which was certainly caused by absorption of SO₂ in a dirty sampling line.

b) Black Smoke (BS)

In Italy, black smoke was only measured at two stations: Modena and Bologna. The reference method of measurement was operated at both of these stations using the equipment (Environnement SA, SF8 sampler) supplied by the EC Commission for the execution of task 3. The results obtained during the comparison period agreed with the CLAP sampler within the expected precision of the method. The reference method procedure was followed at each station, as far as could be ascertained, except that at Modena, where the stain was collected on the rough side of the Whatman paper.

The flowrate of both samplers was well within the range prescribed by the Directive (2 m³/day ± 10%). The two reflectometers checked with the Kodak reflection density chart, showed both a greater degree of non linearity than might have been expected, likely caused by systematic reading errors by the operator.

In the 24 hour parallel measurements carried out in Athens the Station Instrument, SI₁ tested at Patisision station measured a much higher concentration of BS than the RI

TABLE I: Relative differences (% versus CLAP) measured at two stations in Greece by cylinder test (without station sampling line) and 24 hour parallel test (with station sampling line).

| Station | Cylinder test | | 24 hours parallel test | |
|------------|---------------------------------------|--|------------------------|---------------------------------------|
| | 54 ppb (from CLAP) (% vs. CLAP) | 172 ppb (from CLAP) (% vs. CLAP) | Linear correlation | Hourly differences (% vs. CLAP) |
| Patisision | +1 | +0.6 | 0.94 | 8 ± 11 |
| Peireas | +5.6 | +7.4 | 0.57 | -56 ± 4 |

instrument. The measurements, repeated 2 times at Patisson were compared with those carried out at Peireas station with SI₂. In both sites the samplers (SF8, Environnement SA) were identical to those used by the CLAP and their flowrates were in agreement within 5% tolerance limit. The only difference was in the material used for the sampling tube: Greece used PVC and the CLAP used PTFE.

In Table II, the intercomparison results in relative differences versus the RI (i.e.: $\frac{SI-RI}{RI} \cdot 100$) for the 2 station instru-

ments (SI₁, SI₂) used with original and new PVC tubes are given at the stages of the reflectance reading (RR) and surface concentrations (C).

The great differences observed were obviously caused by the smoke absorption in the RI sampling tube.

Although teflon is not prohibited by the Directive and has been used so far by the CLAP without any problem, we decided to clarify the problem, also in order to know with which material we should sample the black smoke in future.

To this end, some other intercomparisons were carried out at JRC-Ispira with two samplers: a sampler A used with a PVC sample tube and a sampler B used with a PTFE sample tube. The percent of smoke absorption in the sample

tube of B, calculated as $\frac{A-B}{A} \cdot 100$ was plotted versus

the black smoke concentration measured by A considered to be the true concentration in ambient air (Fig. 2).

At high BS concentrations (of the order of those measured in Athens) the absorption in the teflon tube was quite proportional to the concentration in the atmosphere. At decreasing concentration the BS losses in the tube B decreased and the difference of reflectance between the two stains, at Ispira concentrations, became indiscernible (± 1 reflectance unit is the precision of the reflectometer). In the light of this result, we decided to proceed the intercomparisons using a PVC sample tube and we proposed to add an amendment to the reference method of the Directive.

c) Total suspended particulates

In Italy two sites, Bologna and Modena used the Italian standard sampler (gravimetric) and at Caltanissetta, a commercial gravimetric sampler was used. At Milano, Marghera and Gela, β absorption samplers from different manufacturers were used. All of the above samplers agreed with the CLAP sampler to within $\pm 12\%$. However, at Modena, a β absorption sampler was operated in parallel with the gravimetric sampler and a larger deviation (-52% versus the CLAP sampler) was recorded. The instrument used in Greece (Hivol Sierra) sampled concentrations of the same order of magnitude as the RI instrument.

The results are reported in Table III.

TABLE II: Comparative measurements of black smoke between Greek station instruments (SI) and the reference instrument. Results given in relative difference versus CLAP for reflectance readings (RR) and smoke surface concentration (C).

| Station | SI ₁ (original PVC tubes) 14.9.87 | | SI ₁ (original PVC tubes) 15.9.87 | | SI ₁ (new PVC tubes) 16.9.87 | | SI ₂ (original PVC tubes) 17.9.87 | |
|----------|--|------|--|------|---|------|--|------|
| | RR(%) | C(%) | RR(%) | C(%) | RR(%) | C(%) | RR(%) | C(%) |
| Patisson | -25 | +269 | -18 | +176 | -21 | +193 | No measurement | |
| Peireas | - | - | No measurements | | - | - | -15 | +144 |

TABLE III: Intercomparison results of TSP samplers used in Italy and Greece and % difference versus CLAP.

| Station | Date | Type of SI (flow rate) | SP Concentrations ($\mu\text{g}/\text{m}^3$) | | % difference |
|-------------------|---------|---|--|-------|-----------------|
| | | | SI | RI | |
| Bologna (I) | 23/6/87 | Istisan (1.06 m ³ /h) | 61.0 | 62.0 | - 2 |
| Modena (I) | 25/6/87 | Istisan (1.2 m ³ /h) | 116.0 | 131.5 | - 12 |
| Modena (I) | 26/6/87 | Frieseke (bêta) (?) | 63.3 | 131.5 | - 52 |
| Milano (I) | 30/6/87 | Philips (bêta) (1.8 m ³ /h) | 187.6 | 169.5 | + 11 |
| Marghera (I) | 2/7/87 | Environ. SA (bêta) (1.56 m ³ /h) | 117.4 | 106.1 | + 11 |
| Gela (I) | 24/7/87 | Sap. Stil MPS (bêta) (1.5 m ³ /h) | 205 | 193.2 | + 6 |
| Athens (Patisson) | 14/9/87 | Sierra (84 m ³ /h) | 162 | 146 | + 12 |
| Athens (Patisson) | 15/9/87 | Sierra (84 m ³ /h) | 158 | 141 | + 12 |

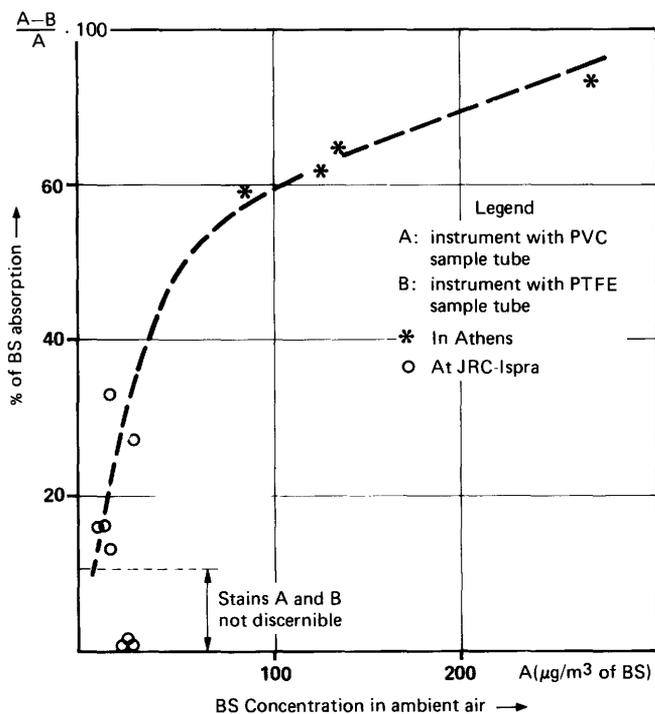


Fig. 2. Percent of black smoke absorption in a teflon sample tube versus concentration measured, in Athens and Ispra (one parallel sampling for each point)

EXPERIENCE AND ORIENTATIONS OF THE EEC IN THE HARMONIZATION OF MEASUREMENT METHODS FOR THE CONTROL OF AIR QUALITY

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1. INTRODUCTION

Efforts to combat pollution will not be successful unless environmental policy measures are taken at international level. The EEC Council Directive 80/779/EEC of 15 July 1980 on air quality limit values and guide values for sulphur dioxide and suspended particulates is just one stepping-stone, on the path towards an international clean air policy.

The EEC Council Directive 82/884/EEC of 3 December 1982 concerning a limit value for lead in the air is, after the Directive 80/779/EEC, the second Directive that lays down air quality standards.

Finally, the EEC Council Directive 85/203/EEC of 7 March 1985 on air quality standards for nitrogen dioxide is the third and, up to now, last of a series concerning ambient air quality limit values for EC Member States.

These Directives have to be considered as an additional element of the Commission's strategy to protect human health and the environment by a double approach which consists of:

the fixing of immission air quality standards which are in no case allowed to be exceeded all over the EEC and the laying down of emission standards for all major sources of these pollutants in accordance with the principles laid down in the environmental action programme.

The above Directives concern immission quality standards and require the harmonization of measurement methods of each concerned pollutant. This is a major aim for the European Commission.

This objective is being reached in cooperation with some specialized laboratories of the Member States and the Joint Research Center, Ispra, which acts as a Central Laboratory (CLAP) (1) for measurements to be carried out by the Commission in collaboration with the Member States.

The responsibility assigned to the Commission include:

- The working out of reference methods and sampling requirements. For each pollutant (NO_2 , Pb, SO_2 and suspended particulates) the Member States, in accordance with articles 10, 8 and 10 of the respective Directives, shall use either the EC reference method or any other method which the Commission has been shown is equivalent to the reference method. Taking as an example the NO_2 Directive, some requirements will be laid down in the present paper.
- The carrying out of performance tests for instruments and methods used in the Member States in order to verify the requirements of the Directives. The Lead Directive will be chosen, afterwards, for some pertinent examples.
- Intercomparison tests by the use of reference standards in order to determine the reproducibility of routine measurements and the need for a better definition of the reference methods. To this end, the Directive in SO_2 /suspended particulates will be considered.

2. HARMONIZATION OF MEASUREMENT METHODS IN THE FRAME OF THE IMPLEMENTATION OF THE EEC COUNCIL DIRECTIVE 85/203/EEC

The Council Directive 85/203/EEC fixes a limit value for NO_2 of $200 \mu\text{g}/\text{m}^3$ (2) for the 98th percentile calculated from the mean value per hour recorded throughout the year and lays down a reference method (Annexe IV of the Directive) which is the chemiluminescence method described in ISO Standard DIS 7996.

In using the measurement methods, the following points should be taken into consideration:

- The sampling head should be at a distance of at least 0,5 m from building in order to avoid a screening effect.
- The sampling line (pipes and connections) should be of inert materials (e.g. glass, PTFE, stainless steel) which do not alter the NO_2 concentration.
- The sampling line between the sampling head and the instrument should be as short as possible. The time taken for gas volume samples to pass through the sampling line should not exceed 10 seconds.
- The sampling head entry must be protected against rain and insects. If a pre-filter is used, it should be selected and maintained (regular cleaning) so as to minimize its influence on the NO_2 concentration.
- Condensation in the sampling line must be avoided.
- The sampling line should be cleaned regularly, taking local conditions into account.
- Sampling should not be influenced by gas discharges from the instrument or discharges from the calibration system.
- Sampling at the sampling head should not be influenced by adjoining installations (the air-conditioning or data transmission equipment).
- All the necessary precautions must be taken to prevent temperature variations from producing an excessive percentage of errors of measurement.

(1) CLAP: Central Laboratory for Air Pollution

(2) This figure is the same in the Italian legislation value (28.3.1983) but refers to the mean value per hour not to be exceeded more than once a day.

- The instruments should be calibrated regularly.
- The sampling line must be air-tight and the flow-rate must be inspected regularly.

Taking into account Article 10 provisions, Par. 1a, one would like to know what is the present situation in Member States. Some Member States mentioned in their official notifications to the Commission that they use, or will use, the reference method (Belgium, Italy, Portugal) or that the methods are comparable (F.R. Germany). The other countries did not give any official explanation how they intend to implement Article 10 provisions. The Commission will ask them to give these explanations as soon as possible.

Nevertheless, it is interesting to note that all the instruments set up by Member States for NO₂ monitoring use the principle of chemiluminescence and hence will almost certainly conform to the reference method of the Directive. The question of whether these instruments perform equally well cannot be assessed because they have not been tested as it is proposed for SO₂ according to harmonized test procedures. Such a procedure could be examined by the Commission in the coming months. In addition, as described in ISO 7996, the method of chemiluminescence needs a calibration by permeation tubes, which therefore becomes the reference calibration method. In order to comply with article 10, intercalibration exercises could be also examined by the Commission future.

3. HARMONIZATION OF MEASUREMENT METHODS IN THE FRAME OF THE IMPLEMENTATION OF THE EEC COUNCIL DIRECTIVE 82/884/EEC

The Council Directive 82/884/EEC concerning a limit value for lead in the air lays down characteristics to be complied with for choosing a sampling method and a reference method for analyzing the concentration of lead in the air.

The atmospheric particles shall be collected on the filter of a sample for subsequent determination of lead content.

3.1 The requirements of the Directive

Article 8 requires that the Member States shall comply with the characteristics mentioned hereafter for choosing the sampling method (a) and with the reference method (b), or any other method which has been proved to produce equivalent results, for analysing the samples.

a) Characteristics to be complied with for choosing the sampling method

- Filter: the filter shall have a collection efficiency at the face velocity used in the sampling of not less than 99% for all particles of a mean aerodynamic diameter of 0.3 μm.
- Sampler efficiency: the sampler efficiency is defined as the ratio of the mass concentration of the particles in the air, as collected on the filter, to the concentration in the atmosphere. The efficiency of a sampler may not be less than the values given in the following table and must be independent of wind direction.

Minimum acceptable efficiencies (%) for a sampler:

| Wind speed | Particle size (aerodynamic diameter) | |
|--------------------|---|-------|
| | 5 μm | 10 μm |
| 2 ms ⁻¹ | 95% | 65% |
| 4 ms ⁻¹ | 95% | 60% |
| 6 ms ⁻¹ | 85% | 40% |

- Aspiration flow rate of sampling: The aspiration flow rate of sampling must remain constant to within ±5% of the nominal value throughout a sampling period.

- As far as possible the sampling stations (or samplers) must be located in such a way as to be representative of the zones in which measurements must be made.
- Operation: Sampling must be continuous although breaks of a few minutes each day or week are permissible to enable filters to be changed. An annual mean value will not be considered valid unless sampling has occurred on a minimum of 10 working days per month, during the first five years after the notification of the Directive and on a minimum of 15 working days per month thereafter, as far as possible, evenly spread over the period under consideration. The mean annual value is calculated by dividing the sum of the valid daily values by the number of days on which valid values have been obtained.

b) Reference method of analysis

The reference method of analysis shall be atomic absorption spectrometry in which the analytical error for the determination of lead in the collected particles is less than a value corresponding to an atmospheric concentration of 0.1 μg m⁻³ of lead (5% of the 2 γg m⁻³ limit value (3)). This analytical error should be maintained within the specified range by an appropriate calibration frequency.

3.2 The current situation in the Member States

A quite comprehensive data base concerning the methods of sampling and analysis used by the Member States for the implementation of this Directive has been obtained by the Commission with the help of a questionnaire. Some Member States provided additional information in their official notifications; however, only F.R. Germany, Ireland and the United Kingdom officially state that the methods of sampling and analysis are equal or equivalent to the reference method. Other countries, e.g. France and Portugal, have incorporated the provisions of the Directive concerning sampling and analysis into the national legislation, but did not officially state that the methods which are actually used comply with Article 8.

a) Compliance with the sampling requirement

All Member States but Spain have at least one national method for sampling lead particles; two countries (F.R. Germany and the Netherlands) have two methods. Table I provides an overview of the methods used and their compliance with the Article 8 provisions.

The sampler used in Belgium, Luxembourg, France, Ireland and the United Kingdom have been shown to meet the requirements of the Directive.

This is also true for the German Kleinfltergerät. The Italian instrument failed in the tests to meet the requirements of the Directive. The German LIB-Filtergerät, the Danish sampler, and the two methods used in the Netherlands have not been tested in detail under wind tunnel-conditions with mono-dispersed aerosols.

There are indications that for higher wind speeds, the LIB-instrument samples significantly less particles (only 75 to 80% of the mass collected with the LIS/P). It is therefore difficult to assess whether or not the LIB-sampler meets the requirements of the Directive, in particular for higher wind speeds.

The design of the Danish sampler is quite similar to that of the LIB-sampler; KEMP ran the instrument under field conditions in parallel to the German Kelfiltergerät and, for the Danish instrument, obtained systematically higher readings for lead as well as for the total mass sampled.

LASKUS carried out similar experiments and found systematically lower readings with the Danish instrument.

(3) Identical to the Italian Legislation, expressed as the annual mean value of the 2 hours mean concentration.

TABLE I: Methods of sampling for the measurement of lead in ambient air used in Member States.

| Member States | Method(s) used | Equivalence with Art. 8 (requirements tested) | Test was successful/not successful | Not tested instrument complies most likely with Art. 8 as shown in Literat | Reference |
|---------------|--|---|------------------------------------|--|--|
| B | IHE-sampler | yes | successful | | BARRET et al. |
| D | Danish sampler | no | | yes | KEMP |
| F | PPA 60-sampler | yes | successful | | BARRET |
| FRG | LIB-Filterverfahren KleinfILTERGERÄT GS 0503 | no | | doubtful | VDI 2463, BL. 4 |
| GR | US-HiVol sampler | yes | successful | | VDI 2463, BL. 7 |
| | | no | | yes | US-FEDERAL REGISTER |
| IRE | M-type sampler | yes | successful | | BARRET et al. |
| I | method ISTISAN | yes | not successful | | ISTISAN |
| LUX | IHE-sampler | yes | successful | | BARRET et al. |
| NL | Medium Volume Sampler (10 m ³ /day) | no | | doubtful | VAN DER MÜLEN |
| | High Volume Sampler (3500 m ³ /day) | no | | yes | |
| P | US HiVol sampler | no | | yes | COMMISSION Doc. XI/477/87-EN and US-FEDERAL REGISTER |
| E | not communicated | | | | |
| UK | M-type sampler | yes | successful | | BARRET |

Thus, it remains to be proved under wind-tunnel conditions, whether or not the Danish sampler meets the requirements of the Directive. However, there are strong indications that the sampler would pass this test successfully.

The US-Hivol sampler is used for sampling lead in Greece and Portugal. The performance characteristics of this instrument are very well known, and there is no doubt that it meets the inlet-efficiency requirements of the Directive.

In the Netherlands, two samplers are used: a medium volume sampler with a flowrate of 10 m³/day and a high volume sampler which aspirates 3500 m³/day. Results obtained under wind-tunnel conditions are not available so that little can be said about the compliance with the requirements of the Directive. However, the Hivol sampler most likely meets them, but a question mark remains behind the medium volume sampler.

The requirement concerning the constancy of the aspiration flow has not been investigated systematically for all the samplers mentioned above. The German VDI-Richtlinien 2463, Bl. 4, Bl. 7, Bl. 8 which are relevant for the two German samplers listed above, also require that the flowrate should not decrease by more than 5% within the 24 hours sampling period. The US-Hivol should meet this requirement if it is used with a flowcontroller.

For Italian instruments, an allowed decrease in flow rate of 25% (from 20 L/min to 15 L/min) is laid down in the description of the method (ISTISAN). This, of course, is not in accordance with the Directive.

For the other instruments, no detailed description of the flow control devices has been submitted, so that no final assessment with regard to compliance or non-compliance with the provisions of the Directive can be made. However, unofficial information indicates that the Belgian, the French, the Danish and the Dutch Hivol sampler should have no difficulties in keeping the flow rate constant within $\pm 5\%$.

b) Compliance with the analytical requirements

The Directive allows the use of any other analytical method than Atomic Absorption Spectrometry if it produces equivalent results and precision; the evidence has to be submitted to the Commission before the method can be applied. Destructive and non-destructive analytical methods are in use for the determination of the lead content. Atomic Absorption Spectroscopy (AAS), which requires that the sample is first oxidized to destroy all organic matter, is an example of the former one; X-ray Fluorescence (XRFA), may serve as an example of the latter. However, a major obstacle to the application of XFRA is the profound matrix effect of the substances being analyzed. Non-destructive methods have therefore to be calibrated against a reference method, in most cases AAS.

In recent years, multi-element analysis techniques like X-ray Fluorescence Analysis (XRFA) and Proton Induced X-ray Emission Analysis (PIXE) are used widely. However, despite the fact that lead in filter samples is analyzed by several other methods than AAS within the monitoring programmes, for most of the laboratories AAS is still considered to be the routine reference method. It should be noted that only F.R. Germany and the United Kingdom have notified officially the Commission that they use an analytical method different from AAS.

Table II displays the information available to the Commission concerning the methods of analysis used in Member States. It should be noted that Belgium, Denmark, F.R. Germany, the Netherlands and the United Kingdom do not use the reference method. However, the methods used by these countries, if properly applied, performed in ringtests as well as AAS. Moreover, regular parallel checks against AAS are performed by the laboratories. There is therefore little reason to believe that the methods applied by Member States are not equivalent.

TABLE II: Analytical methods for the determination of lead in the sample used in Member States.

AAS = Atomic Absorption Spectroscopy
 XRFA = X-ray fluorescence
 PIXE = Proton-induced X-ray emission spectroscopy

| Country | Sample pretreatment | Method of analysis | Remarks |
|---------|---|--------------------|--|
| B | not necessary | XRFA | Regular parallel, check against AAS |
| DK | not necessary | PIXE | Comparison to AAS has been carried out |
| F | - wet decomposition in HNO ₃ -HCl | AAS | |
| FRG | - wet decomposition in HNO ₃ -HF-H ₂ O ₂ | AAS XRFA | see VDI 2267, Bl. 3 see VDI 2267, Bl. 2 |
| GR | ultrasonic extraction in HNO ₃ -HCl | AAS | |
| IRE | - wet decomposition in HNO ₃ -HCl | AAS | see AMERICAN PUBLIC HEALTH ASSOCIATION |
| I | not communicated | AAS | |
| LUX | not communicated | not communicated | |
| NL | - wet decomposition in HNO ₃ -HCl - not necessary | AAS XRFA | see NEDERLANDSE NORM regular parallel check against AAS |
| P | not communicated | AAS | |
| E | not communicated | not communicated | |
| UK | not necessary | XRFA | regular parallel check against AAS |

4. HARMONIZATION OF MEASUREMENT METHODS IN THE FRAME OF THE IMPLEMENTATION OF THE EC COUNCIL DIRECTIVE 80/779/EEC.

4.1. Definition of the problem

As related by ZIEROCK et Al., the harmonization tasks required by the implementation of this Directive are complicated because of the difference between the «type» of particulates measured in the Member States (black smoke or total suspended particulates) and the shortcomings of the reference methods. Four main points have been investigated.

- SO₂ is measured by non specific methods (France, Ireland, United Kingdom) and specific methods in the other Member States. Suspended particulates are measured with the black smoke method by Belgium, France, Ireland, Luxembourg, the Netherlands and United Kingdom which assess their results relative to the Annex I limit values. The other states (Denmark, F.R. Germany and Italy) use a gravimetric method incompatible with the black smoke method and assess their results relative to the Annex IV limit values, which are equivalent to the national air quality standards adopted in each of these three States (4). There is no evidence that the limit values of the two annexes show the same stringency (first point).
- The reference method of sampling for the determination of sulphur dioxide uses the equipment described in International Standard ISO 4219, first edition 1979/09/15. The reference method of analysis is based on draft International Standard ISO DP-6767 revised February 1979: «Determination of the Mass Concentration of Sulphur Dioxide in Ambient Air - Tetrachloromercurate (TCM)/Pararosaniline

method». This method of analysis, based on the principle of the colorimetric reaction with pararosaniline, was subsequently corrected (TC 146/SC3/WG7) but the improved version is not suitable for sampling over 24 hours. (2nd point).

- For the determination of **black smoke** and its conversion into gravimetric units, (expressed in µg/m³ as an equivalent index of standard smoke e.i.s.s./m³) the method standardized by the OECD working party on methods of measuring air pollution and survey techniques (1964) is considered to be the reference method. This method contains five different «proposals concerning international standard calibration measurements» based on studies in the early sixties giving rise to 5 arrangements (or configurations) between 2 types of Reflectometers (EEL-Diffusion Systems and Photovolt), 2 types of filter papers (Whatman n.1 and Schneider Poelman) with the use of 5 conversion curves! In the meantime, the emission situation and therefore the relationship of the various blackening indices to each other has changed considerably. It is likely that the various calibration curves no longer displayed the comparability needed for the current situation. Consequently it is obvious that the black smoke reference method needed more precise definitions. (3rd point).
- The description of the gravimetric measurement of suspended **particulates** set out in Annex IV to the Directive cannot be considered to be an unambiguous basis for a clearly defined reference measurement method. For example, Annexe IV, Item 3 states that: «The sampling system does not include a fractionating device». However, the sampling system itself constitutes a fractionating system because under atmospheric conditions only a fraction of the total suspended particulate matter can be captured. A second technical criterion for the measuring equipment as mentioned in Annexe IV, Item 7, is that the air velocity at the surface of the filter shall be between 33 and 55 cm/sec. inclusive, but this cannot guarantee comparable results if different equipment

(4) The medians of the daily mean values over the year are: 80 g/m³ for SO₂ and black smoke, 150 g/m³ for total suspended particulates.

geometries are used. Therefore it is likely that instruments complying with the provisions of Annexe IV could nevertheless yield incomparable results (4th point).

All the actions undertaken in order to study and solve the problems above-mentioned have been tackled in the frame of a «Common Measurement Programme» (CMP) which commenced in 1983.

In the light of the identified shortcomings of the reference methods, a «comparison method» was selected after a programme of performance test carried out by several investigators (CLAYTON, 1984, VAN DE WIEL et al. 1984, BARRET et al., MULLER). With the agreement of the Member States, the following devices were selected:

- SO₂: An UV-fluorescence (UVF) monitor;
- Black smoke: the French SF8 sampler with Whatman No. 1 filter and EEL 43 reflectometer;
- Gravimetric Suspended Particulates: small filter unit according to VDI 2463.

These methods «should be those that can be used in order to comply with article 10 until the reference methods will be reviewed» (ZIEROCK, 1984). These methods helped the Commission to study the problems above-mentioned for the carrying out of parallel measurements at selected stations of the Member States. From preliminary German, Danish and Italian investigations (BERTOLACCINI) concerning point a it seems that the Annex IV limit values for suspended particulates, have been shown more stringent than the corresponding black smoke limit values of Annex I. This is likely the consequence of the progressive substitution of coal fuels over the last 25 years, leading to a significant change in the constitution of fine particulate matter in the atmosphere.

4.2. Intercomparison programme required by article 10

Two Quality Assurance Programmes (QAP/1 and QAP/2) have been organized by the CLAP in cooperation with the Member States. QAP/1 (1984-86) was oriented towards intercomparisons in laboratories and QAP/2, still under way, towards network intercomparisons.

By checking the flowrates of the samplers, the calibration procedures, the reflectometers and balances, and by parallel monitoring in network conditions, these programmes aim to investigate if the instruments and methods comply with the requirements of the Directive.

The crosschecks have been performed by round robin tests of reference materials in QAP/2 (air-SO₂ mixtures at low concentrations of SO₂ contained in pre-treated cylinders, filters sampled at different darkness level and load, solutions of H₂O₂/SO₂ at known SO₂ content for the Total Acidity method) and by means of a mobile intercalibration unit in QAP/2. Some QAP/1 results are given hereafter.

a) **For sulphur dioxide**, the aim of the SO₂ cylinder test was to study the reproducibility between the calibration methods used in the Member States in relation with the reference method. In most Member States Reference Instruments (RI) calibrated with primary methods were selected. The RI instruments stand in reference laboratories and are normally used for the certification of secondary or transfer standards mixtures contained in gas cylinders.

A few Network Instruments (NI), as used for routine measurements, and hence calibrated with transfer standards, were also tested.

The instruments under test used 4 different principles of operation: UV-fluorescence, (UVF), flame photometry (FPD), conductivity and coulometry.

The UVF «comparison» instrument used by the CLAP to measure the cylinders was calibrated with the colorimetric TCM method, this latter having been improved (SEIFERT et al.; PAYRISSAT et al., 1984) for the requirements of the Direc-

tive (point 4.1a). The results of the intercomparisons, expressed in mean relative differences versus the CLAP are reported Table III. The following observations can be made:

- Under laboratory conditions most of the RI instruments (87% at both levels) produced comparable averaged results (within $\pm 6\%$). Reported to the total number of nosschecks (≈ 3 per instrument), 90% of them were within $\pm 12\%$.
- The quality of the measurements seemed not to be dependent of the measurement method. In fact, the 48 RI crosschecks with UVF, comparatively to the 22 crosschecks with all the other methods, did not cause an appreciable improvement of reproducibility ($\Delta\% = -0,5\% \pm 1$ instead of $-1,5\% \pm 2,8$). A similar conclusion can be drawn from the calibration methods.
- The lack of calibration or the use of instable transfer standards were assumed to be the main causes of deviations for network instruments.

It can be concluded that each laboratory or station contributes to the harmonization of the results since the deviations were more caused by the quality of the implementation of the chosen calibration method (TCM, permeation, static injection, etc.) than by a shortcoming of the measuring method itself. The good agreement between primary calibration methods confirms the TCM method as a valuable reference standard for SO₂ measurement. However also the TCM method's certainly not the most suitable for SO₂ calibrations, there is the need to include in the Directive «Laboratory reference methods» for the calibration of SO₂ instruments.

b) **For black smoke**, there were two aims to the ring tests of the black smoke stains.

Firstly, to investigate the reproducibility of the comparison method, as implemented in different Member States (quality test), and secondly to investigate deviations between the comparison method and other methods, (comparison test).

- In the quality test, 10 participating laboratories used the reflectometer of the «comparison method» (Par. 4.1c) in which the Reflectance Readings (RR) were converted in Surface Concentrations (SC) by means of the corresponding OECD conversion curve (1964). For black smoke concentrations over 80 $\mu\text{g e.i.s.s./m}^3$ (annual limit value) RR was read on the reflectometer with a precision «between labs» of ± 1 Reflectance unit. After conversion into e.i.s.s. concentrations, the reproducibility was about $\pm 5\%$ ($103 \pm 5 \mu\text{g/m}^3$ and $315 \pm 15 \mu\text{g/m}^3$ for the corresponding standard stains).

- In the comparison test, the stains were used to compare three actual configurations as used in United Kingdom (UK), France (F) and in the Netherlands (NL). The results versus the «comparison method» are discussed at the two stages of black smoke determination: RR and SC.

- At the stage of the reflectance reading, 4 reflectometers were tested: 2 models of Photovolt (575 and 670) as used in France, two models of EEL Diffusion System: EEL Mark III used in the Netherlands and EEL 43 used in the other Member States.

Compared to the «comparison» instrument, taken as reference (Fig. 1), the Photovolt 575 and the EEL Mark III showed similar readings.

The Photovolt 670 (old model, but still used in France) showed slight lower readings ($-9\% > \Delta\% > -2\%$).

- At the stage of the surface concentration obtained by means of the OECD conversion curves, recommended till now in the Directive, large differences were observed (Fig. 2).

With the use of the «Courbe parisienne», the French values were 33% higher than the reference. In conclu-

TABLE III: Mean relative differences of SO₂ measurements versus the CLAP for Reference Instruments and Network Instruments

| Member State | Laboratory | Measurement Method | Calibration Method | Nr. of cross-checks per conc. level | Relative difference versus CLAP (Δ%) | |
|------------------------------|--------------------|--------------------|--------------------|-------------------------------------|--------------------------------------|---------------------------|
| | | | | | Nominal concentr. 50 ppb | Nominal concentr. 190 ppb |
| REFERENCE INSTRUMENTS | | | | | | |
| UK | Warren Spring lab. | UVF | Hydrog. peroxide | 2 | -7.6 | - 1 |
| NL | RIVM | UVF | permeation | 3 | +2.6 | 0 |
| I | ISS | FPD | permeation | 3 | -5.6 | - 7.6 |
| D | UBA, Offenbach | UVF | static injection | 8 | -2.6 | + 0.5 |
| D | Essen | UVF | TCM | 3 | -2.6 | 0 |
| D | Hannover | FPD | static injection | 2 | -9.7 | - 5.7 |
| D | Hamburg | UVF | permeation + TCM | 2 | -2.8 | + 4.4 |
| D | Itzehoe | UVF | permeation + TCM | 2 | -1.3 | + 3.1 |
| D | Itzehoe | FPD | permeation + TCM | 2 | -5.6 | + 1.3 |
| D | Berlin, Senat | Conduct. | TCM | 2 | -0.7 | - 8.2 |
| D | Berlin, BGA | UVF | TCM | 2 | -2 | - 5.3 |
| D | Saarbrücken | UVF | permeation | 2 | -2 | - 1 |
| D | Oppenheim | FPD | permeation | 1 | +3.6 | - 4.8 |
| D | Karlsruhe | Conduct. | permeation + TCM | 2 | +1.1 | + 6.7 |
| D | München | UVF | permeation | 2 | -2.9 | + 4 |
| D | Wiesbaden | Conduct. | permeation + TCM | 2 | +2.7 | +18 |
| F | IRCHA | UVF | permeation | 8 | +0.2 | - 5 |
| F | Saint-Etienne | Coulom. | permeation | 8 | +4.4 | + 3.4 |
| F | Douai | UVF | permeation | 8 | -2.2 | + 1.3 |
| F | Marseille | UVF | permeation | 6 | -16 | -13 |
| NETWORK INSTRUMENTS | | | | | | |
| DK | Risø Lab. | UVF | Transfer standard | 2 | -2.8 | - 1.5 |
| GR | Athens | UVF | Transfer standard | 2 | -13 | - 0.6 |
| B | IHE | FPD | Transfer standard | 2 | -27 | - 8.4 |
| I | Roma | FPD | Transfer standard | 2 | +9.5 | +28 |
| I | Milano | Coulom. | Transfer standard | 2 | -9.5 | - 8.4 |
| I | Torino | Coulom. | Transfer standard | 2 | -43 | -24 |
| I | Bologna | Coulom. | Transfer standard | 2 | -28 | -18 |

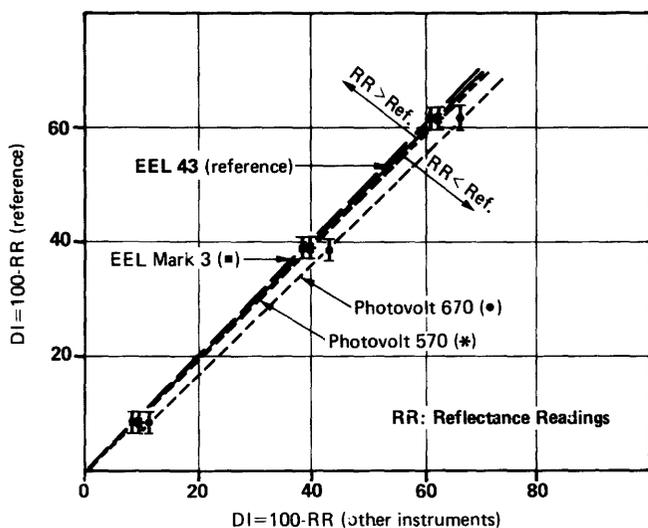


Fig. 1. Darkness index (DI) of 3 standard stains measured with 4 different types of reflectometers. Deviations versus the comparison instrument (reference)

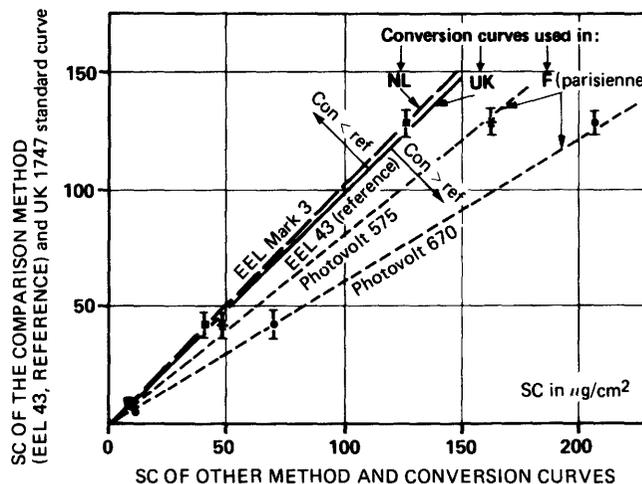


Fig. 2. Surface concentration (SC) of 3 standard stains measured with 4 different reflectometer/conversion curve configurations. Deviations versus the comparison method (reference)

sion, without an harmonized conversion curve, the limit values of e.i.s.s in g/m³ as laid down in the Directive, are more stringent for France than for the other Member States. On the other hands; the «comparison method», recently proposed to the Member States as a new ver-

sion of the reference method for black smoke, includes only one conversion curve and also more precise definitions for the sampling head, the sampling tube, etc. Hence this methods should lead to a harmonised measurement of black smoke throughout the community.

c) **For total suspended particulates**, a satisfactory EC reference method still has to be defined. Work on this is underway and should be completed in 1990. However the CLAP undertook a programme to investigate the effect of conditioning procedures of the filters currently in use in Member States.

A different set of 5 filters normally used in Denmark, Italy, Germany and Greece circulated twice between the participating laboratories, including the CLAP. In the first round the filters were unloaded; in a second round they circulated loaded after a 24 hour sampling by the laboratory starting the test. In order to know the influence of the conditioning procedure of the filters before weighing, Italy, which started two tests with the two types of filters, decided to keep the routine procedures used in its laboratory (ISS, Rome). The membrane and glassfiber filters before and after weighing, were held at 70°C for two hours and subsequently stored for 24 hours in dessicator with silica-gel. The conditioning procedures used by the other participants were decided to be those described in the Directive:

- Membrane filters are to be conditioned, before and after sampling, by holding them at a constant temperature between 90 and 100°C for two hours and subsequently storing them in a dessicator for two hours before weighing.
- Glass-fibre filters are to be conditioned, before and after sampling, by holding them for a period of 24 hours in an atmosphere at 20°C and 50% relative humidity before weighing.

BERTOLACCINI, ISS, Italy, tested the above mentioned procedure in view to propose some amendment to the Italian reference method. This modification should be able to reduce the losses of membrane material and volatile compounds by using a lower conditioning temperature. In comparison with the procedure of the Directive, this amendment would yield higher gravimetric values (Fig. 3), due to possible higher filter water content, specially if hygroscopic substances were sampled. In any case, this test showed that Member States need to use harmonized procedures in every detail of filter conditioning.

5. CONCLUSION

The harmonization of EC measurement methods is the main task for the control of air quality standards throughout the European Community. The commitment of the Commission with the definition and implementation of air quality Directives is, obviously, the first and indispensable step. There is no doubt that harmonization and hence the role of the Commission will not be achieved if the Directives are not respected. The approach

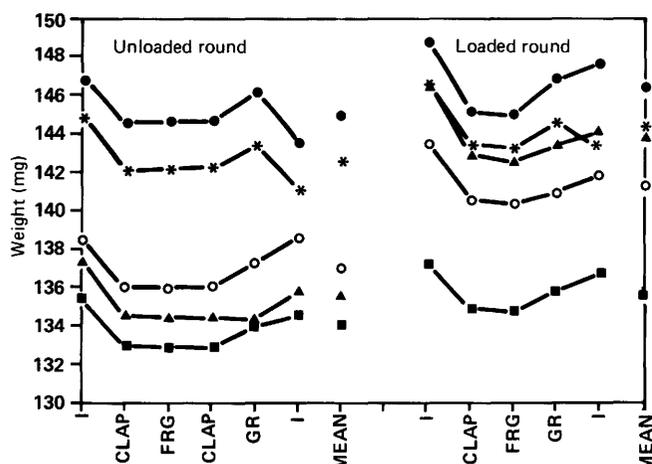


Fig. 3. Round robin test for 5 Italian filters used in medium volume samplers. Influence of the conditioning procedures of the filters (see text)

towards better defined reference methods must be followed by a constant effort towards greater respect of the legislation. As already proposed (STIEF TAUCH and BERTAIRE, 1987), the Commission and the Member States have a reciprocal responsibility to assure the quality of the measurement with respect to the Directive.

- The Member States should rationalize the implementation of their quality standards, possibly by:

- the creation or the improvement of reference (or pilot) Laboratory to support the quality of the measurements in each network; for example by preparation of secondary standard mixtures certified against primary methods;
- the development of mobile laboratories in order to check the routine measurements in network stations.

The Commission could propose regular intercalibration programmes between the reference and mobile laboratories.

- For harmonized implementation of the Directives in the Member States it is also important that the measuring stations are correctly placed. Network design studies should be implemented by Member States, possibly with the help of the Commission, to insure that the measuring stations are representative and comply with the Directive requirements

- It would also be useful to exchange experiences within and between Member States by means of exhibitions workshops and symposia.

The control of the air quality in the EEC is not only a long term job; it is a continuous endless task.

SHORT BIBLIOGRAPHY

- Commission of the European Communities (1985)
Council Directive of March 7, 1985 on air quality standards for nitrogen dioxide, 85/203/EEC, 0.5.287, 27.3.1985, pp.17.
- Commission of the European Communities (1982)
Council Directive of December 3, 1982 on a limit value for lead in the air, 82/884/EEC, 05.L378, 31.12.82, pp.15-18.
- Commission of the European Communities (1980)
Council Directive of July 15, 1980 on air quality limit values and guide values for sulphur dioxide and suspended particulates, 80/779/EEC, 0.5.L229, 30.08.1980 pp. 30-48.
- Gazzetta Ufficiale della Repubblica Italiana
Supplemento ordinario alla «Gazzetta Ufficiale» n. 145 del 23 maggio 1983.
- BARRET et al. (1985)
«A wind tunnel study and field comparison of three samples of suspended particulate matter».
Werren Spring Laboratory (UK), report LR 544 (AP M, ISBN O 85624 399X and EUR 9378 EN.
- Verein Deutscher Ingenieure (1982).
Messen von Partikeln. Messen des Massenkonzentration (Immission); Filterverfahren, Kleinfiltergerät, 050 VDI 2463, Blatt 7.
- ISTISAN (1981)
Metodi di prelievo e di analisi degli inquinanti dell'aria. Appendice 2. Determinazione del materiale particellare in sospensione nell'aria. Istituto Superiore di Sanità, Roma.
- L. LASKUS (1984).
«Measurements of suspended particulates using fractionating and non fractionating devices» in. Proceedings of the EC. Workshop on monitoring sulphur dioxide, black smoke, and total suspended particulates: Published by the National Institute of Public Healths and Environmental Hygiene (RIVM) of the Netherlands.
- K.U. ZIEROCK, J. SMEETS, P. STIEF TAUCH (1985)
«Harmonization problems in the implementation of the EEC Directive on air quality limit values and guide values for

sulphur dioxide and suspended particulates». *Env. Monitoring and Assessment* 5/255-269.

- P. CLAYTON (1984)
«Programme for testing and selecting a black smoke comparison apparatus - Final report», EUR 9377 EN.
- H.J. VAN DE WIEL (1984)
«Study to test and select one comparison apparatus for sulphur dioxide». Final report to Commission's study No. 6612/10/14.
- J. MULLER (1984)
«Field measurements of Suspended Particulate Matter (SPM) sampled with different instruments». Final report to CEC contract 6612/10/1 and 6612/10/5.
- M.A. BERTOLACCINI (1987)
«Programme for parallel measurements of black smoke and suspended particulates» 2nd Progress Report of July 1987.
- B. SEIFERT, L. ZHAO (1984)
«Comparative determination of sulphur dioxide in ambient air using TCM procedures with short term and long-term sampling». Final report to EC study contract B 483-654.
- M. PAYRISSAT et al. (1984)
«Improvement of the EC reference method for the determination of sulphur dioxide». in: *Proceeding of the EC-workshop on monitoring sulphur dioxide, black smoke and suspended particulate*. Published by the National Institute of Public Health and Environmental Hygiene (RIVM) of the Netherlands.
- ZIEROCK, 1987
«Preparation of a Report to the Council on the Implementation of articles 10(2) and 10(3) of Directive 80/779/EEC. Draft final report (August 1987).
- M.A. BERTOLACCINI (1987)
Comunicazione personale.
- P. STIEF TAUCH, J.G. BERTAIRE (1987)
«Rappel des Directives CEE concernant la qualité de l'air ambiant. Nécessité de la mise en oeuvre de certains programmes d'harmonisation en collaboration avec le CCR Ispra et les Etats Membres». *Accueil d'une delegation française au CCR Ispra. Journée d'étude du 5.3.87.*

2.3 EMEP MONITORING STATION

INTRODUCTION

The Programme on the Evaluation and Monitoring of European Pollution (EMEP) is carried out under the auspices of the Economic Commission of Europe (ECE) and the United Nations Environment Programme (UNEP), and its main objective is to provide governments with information on the deposition and concentrations of air pollutants and on the quantity and significance of pollutant fluxes across national boundaries. Actually 89 monitoring stations in 25 countries all over Europe are participating in the EMEP-programme in order to evaluate the long range transmission of air pollutants. According to the Council resolution No. 81/462/EEC, article 9, the Commission Services D.G. XI and J.R.C. proposed to participate actively in this programme by setting up at Ispra an EMEP monitoring station. Since November 1985, this station is working on a regular basis and data are transmitted to the Norwegian Institute for Air Research (NILU) for further statistical evaluation.

RESULTS

The activity of the JRC station has started, in November 1985 following the reduced EMEP measurements programme.

The geographic coordinates of this station, which is situated in a semirural region are: latitude: 45° 49', longitude: 8° 38', height above sea level 209 m. During 1987 the following parameters have been measured:

- hourly mean values and daily averages for sulphur dioxide, nitrogen dioxide and ozone contents in air.
- daily averages for sulphate, nitrate, ammonium, total suspended matter and acidity in atmospheric particulate.
- daily averages for sulphate, nitrate, chloride, ammonium, sodium, potassium, calcium, magnesium, pH, electrical conductivity and acidity contents in atmospheric precipitations when they occur.
- hourly mean values and daily averages for direction and speed of wind, temperature and relative humidity of air, atmospheric pressure, rainfall and solar radiation.
- Monthly values (obtained as mean values of the daily results) as well as the averages for the period from December 1986 till November 1987 of SO₂, NO₂, O₃ in air and SO₄²⁻, NO₃⁻, NH₄⁺, H⁺ and SPM in atmospheric particulate are reported in Table I and graphically in Fig. 1 and 2. It is interesting to show the highest values of SO₂ in air (Fig. 3) measured during February 2-5 (thermal atmospheric inversion). HCl, HNO₃, SO₂ and NH₃ in air have been sporadically measured after a daily sampling (24 m³/day) in the period March-June

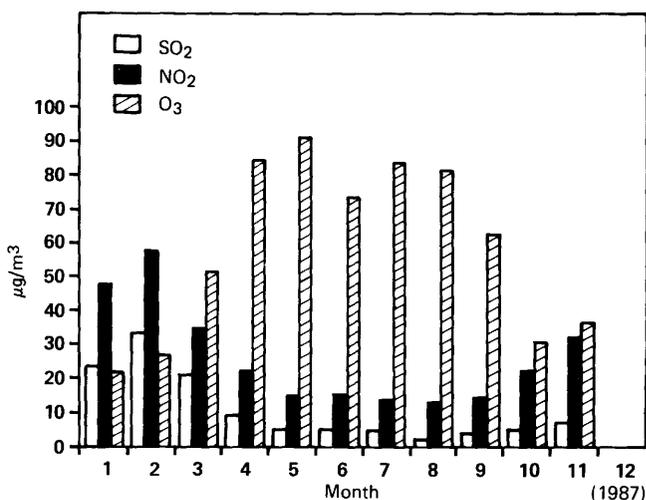


Fig. 1. Pollutants in air
EMEP Station JRC-Ispra

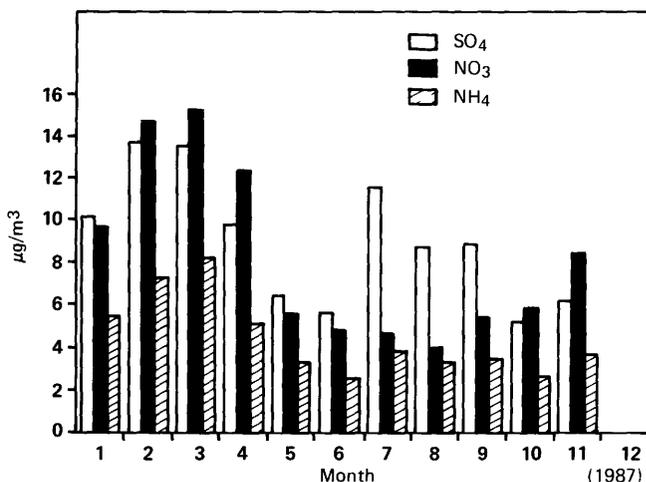


Fig. 2. Pollutants in atmospheric particulate
EMEP Station JRC-Ispra

TABLE I: Trace constituents in air and atmosph. particulate collected in JRC monthly values

| 1986/87 | GASES | | | AEROSOLS | | | | |
|---------|-------|--------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|-------------------------------------|
| | MONTH | SO ₂ μg/m ³ | NO ₂ μg/m ³ | O ₃ μg/m ³ | SO ₄ μg/m ³ | NO ₃ μg/m ³ | NO ₄ μg/m ³ | H ⁺ μg/m ³ |
| DEC | 11,7 | 30,4 | 17 | 6,9 | 8,0 | 4,8 | 23,4 | 62 |
| JAN | 23,4 | 47,8 | 22 | 10,1 | 9,7 | 5,5 | 26,8 | 71 |
| FEB | 33,2 | 57,5 | 27 | 13,7 | 14,7 | 7,3 | 51,3 | 77 |
| MAR | 20,7 | 34,5 | 51 | 13,6 | 15,2 | 8,2 | 31,2 | 97 |
| APR | 9,5 | 21,7 | 84 | 9,8 | 12,4 | 5,2 | 22,0 | 56 |
| MAY | 5,2 | 14,8 | 91 | 6,5 | 5,7 | 3,3 | 24,8 | 45 |
| JUN | 4,8 | 15,0 | 73 | 5,6 | 4,9 | 2,6 | 23,9 | 40 |
| JUL | 4,7 | 13,4 | 83 | 11,6 | 4,7 | 3,9 | 24,7 | 43 |
| AUG | 1,9 | 12,6 | 81 | 8,7 | 4,0 | 3,3 | 23,3 | 50 |
| SEP | 3,9 | 14,4 | 62 | 8,9 | 5,5 | 3,5 | 31,9 | 70 |
| OCT | 4,8 | 21,7 | 30 | 5,3 | 5,9 | 2,6 | 24,8 | 53 |
| NOV | 6,8 | 31,4 | 36 | 6,2 | 8,4 | 3,7 | 24,8 | 79 |
| AVERAGE | 10,9 | 26,3 | 55 | 8,9 | 8,3 | 4,5 | 27,7 | 61,9 |

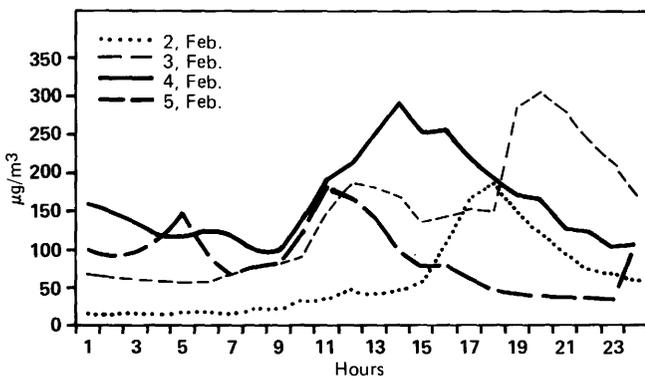


Fig. 3. SO₂ concentration in air Febr. 2-5, 1987
EMEP Station JRC-Ispra

by the annular denuder technique. The mean values of two consecutive days as well as their averages and ranges are reported in Table II. The mean values, based on 34 days of sampling, amount to 0.56, 2.06, 8.0 and 1.48 μg/g respectively for HCl, HNO₃, SO₂ and NH₃.

Some results on heavy metals (Pb, Zn, Fe, Cu, Mn, Cr and V) in the atmospheric particulate collected during the period October 1986 - September 1987 are reported in Table III. The volume of air analysed was about 12-13 m³/day; the reported values, expressed as μg/m³, are obtained after a collection of particulate during 1, 3 or 6 consecutive days. The mean contents of Pb and Zn are 0.18 μg/m³; the same values for Cu, Cr, Mn and V range from 0.015 to 0.025 μg/g.

Table IV reports the monthly values of SO₄²⁻, NO₃⁻, Cl⁻, H⁺, NH₄⁺, Na⁺, K⁺, Ca⁺⁺, Mg⁺⁺, pH, electrical conductivity and mm of precipitation, as well as the relative averages for the whole considered period (December 1986 to November 1987). These monthly values are obtained by analysis of the representative monthly wet deposition samples (bulk solution, of 10% of each daily precipitation sample). Figs. 4 and 5 represent the variation of the mean monthly value of pH of rain with its relative range and of the contents of SO₄²⁻, NO₃⁻ and NH₄⁺ respectively. It is interesting to point out the low value of pH and the high content of NO₃⁻ in some precipitations.

TABLE II: Trace constituents in air collected at JRC by annular denuders. All the results are expressed as μg/m³

| PERIOD | HCl | HNO ₃ | SO ₂ | NH ₃ | |
|---------|-------|------------------|-----------------|-----------------|---------|
| March | 9-11 | 0.8 | 2.0 | 23.2 | 1.6 |
| | 11-13 | 0.7 | 1.0 | 5.4 | 1.0 |
| | 16-18 | 1.1 | 1.0 | 4.8 | 1.3 |
| | 24-26 | 2.0 | 2.2 | 18.0 | 2.2 |
| | 29-31 | 0.4 | 1.8 | 4.6 | 0.7 |
| April | 1-2 | 0.2 | 1.2 | 19.6 | 1.3 |
| | 6-8 | 0.7 | 1.6 | 10.2 | 1.1 |
| May | 11-13 | 0.3 | 2.1 | 5.4 | 0.8 |
| | 13-14 | 0.3 | 1.2 | 2.4 | 1.5 |
| | 19-21 | 0.7 | 1.8 | 1.8 | 1.5 |
| | 25-27 | 0.4 | 4.0 | 9.6 | 2.2 |
| June | 1-3 | 0.3 | 3.4 | 7.2 | 2.2 |
| | 9-11 | 0.1 | 1.0 | 3.4 | 1.8 |
| | 16-18 | 0.3 | 1.8 | 2.2 | 2.0 |
| | 22-24 | 0.4 | 2.6 | 4.8 | 0.5 |
| | 24-26 | 0.2 | 3.2 | 9.8 | 0.8 |
| July | 29 | 0.6 | 3.2 | 3.6 | 2.7 |
| average | | 0.56 | 2.06 | 8.0 | 1.48 |
| range | | 0.1-2.0 | 1.0-4.0 | 1.8-23.2 | 0.5-2.7 |

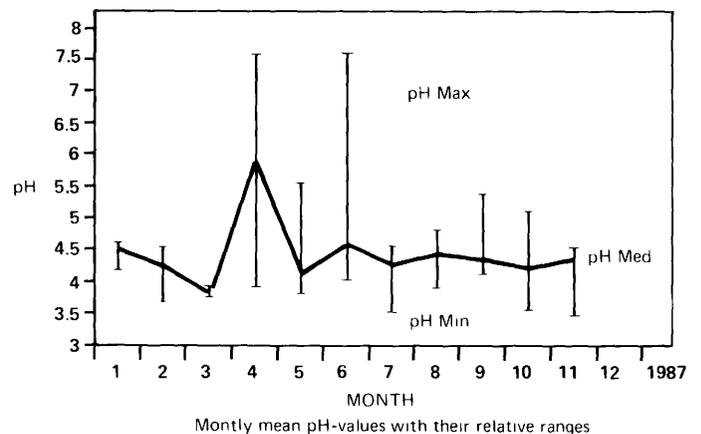


Fig. 4. pH-measurements in atmospheric precipitation
EMEP Station JRC-Ispra

TABLE III: Heavy metals in atmospheric particulate collected at JRC

| SAMPLING PERIOD | VOL. m ³ | Pb μg/m ³ | Zn μg/m ³ | Fe μg/m ³ | Cu μg/m ³ | Mn μg/m ³ | Cr μg/m ³ | V μg/m ³ |
|-----------------|---------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|---------------------|
| OCT. 86 | 12 | 0,18 | 0,25 | 0,58 | 0,02 | 0,02 | 0,02 | 0,02 |
| OCT. | 12 | 0,24 | 0,46 | 0,67 | 0,02 | 0,02 | 0,02 | 0,02 |
| NOV. | 36 | 0,47 | 0,46 | 0,87 | 0,04 | 0,04 | 0,09 | 0,02 |
| NOV. | 31 | 0,49 | 0,31 | 0,57 | 0,01 | 0,03 | 0,09 | 0,02 |
| DEC. | 34 | 0,29 | 0,19 | 0,49 | 0,04 | 0,03 | 0,09 | 0,03 |
| DEC. | 36 | 0,18 | 0,13 | 0,49 | 0,01 | 0,01 | 0,01 | 0,01 |
| DEC. | 36 | 0,18 | 0,07 | 0,26 | 0,02 | 0,01 | 0,01 | 0,01 |
| JAN. 87 | 34 | 0,11 | 0,20 | 0,17 | 0,01 | 0,01 | 0,01 | 0,01 |
| JAN. | 35 | 0,32 | 0,33 | 0,81 | 0,02 | 0,05 | 0,01 | 0,03 |
| JAN. | 34 | 0,25 | 0,20 | 0,48 | 0,01 | 0,01 | 0,01 | 0,01 |
| JAN. | 35 | 0,34 | 0,27 | 0,77 | 0,01 | 0,03 | 0,01 | 0,03 |
| FEB. | 35 | 1,05 | 1,03 | 2,55 | 0,06 | 0,16 | 0,10 | 0,15 |
| FEB. | 36 | 0,12 | 0,05 | 0,06 | 0,01 | 0,01 | 0,01 | 0,01 |
| FEB. | 35 | 0,12 | 0,01 | 0,02 | 0,01 | 0,01 | 0,01 | 0,01 |
| FEB. | 35 | 0,35 | 0,24 | 1,06 | 0,02 | 0,05 | 0,01 | 0,04 |
| MARCH | 36 | 0,38 | 0,39 | 1,20 | 0,01 | 0,06 | 0,01 | 0,05 |
| MARCH | 36 | 0,33 | 0,40 | 0,97 | 0,01 | 0,05 | 0,02 | 0,04 |
| MARCH | 34 | 0,19 | 0,07 | 0,74 | 0,01 | 0,02 | 0,05 | 0,03 |
| MARCH | 36 | 0,07 | 0,07 | 0,44 | 0,01 | 0,01 | 0,02 | 0,01 |
| APRIL | 37 | 0,08 | 0,09 | 0,15 | 0,01 | 0,01 | 0,05 | 0,01 |
| APRIL | 34 | 0,27 | 0,16 | 0,76 | 0,01 | 0,03 | 0,01 | 0,02 |
| APRIL | 36 | 0,15 | 0,13 | 0,86 | 0,01 | 0,03 | 0,06 | 0,01 |
| MAY | 37 | 0,01 | 0,04 | 0,24 | 0,01 | 0,01 | 0,01 | 0,01 |
| MAY | 36 | 0,01 | 0,09 | 0,38 | 0,01 | 0,01 | 0,01 | 0,01 |
| MAY | 36 | 0,01 | 0,04 | 0,21 | 0,01 | 0,01 | 0,01 | 0,01 |
| MAY | 35 | 0,02 | 0,07 | 0,52 | 0,01 | 0,02 | 0,01 | 0,01 |
| JUNE | 35 | 0,04 | 0,06 | 0,31 | 0,01 | 0,01 | 0,01 | 0,01 |
| JUNE | 35 | 0,11 | 0,23 | 0,84 | 0,01 | 0,04 | 0,01 | 0,01 |
| JUNE | 35 | 0,01 | 0,03 | 0,22 | 0,01 | 0,01 | 0,01 | 0,01 |
| JUNE | 35 | 0,07 | 0,09 | 0,44 | 0,01 | 0,01 | 0,03 | 0,01 |
| JULY | 34 | 0,06 | 0,13 | 0,98 | 0,01 | 0,03 | 0,01 | 0,02 |
| JULY | 34 | 0,04 | 0,17 | 0,62 | 0,01 | 0,02 | 0,01 | 0,01 |
| JULY | 35 | 0,03 | 0,16 | 0,35 | 0,02 | 0,02 | 0,01 | 0,01 |
| JULY | 35 | 0,06 | 0,09 | 0,30 | 0,01 | 0,01 | 0,01 | 0,01 |
| AUG. | 35 | 0,01 | 0,03 | 0,31 | 0,01 | 0,01 | 0,01 | 0,01 |
| AUG. | 79 | 0,11 | 0,08 | 0,62 | 0,02 | 0,01 | 0,01 | 0,01 |
| AUG. | 77 | 0,06 | 0,06 | 0,43 | 0,01 | 0,01 | 0,01 | 0,01 |
| AUG. | 79 | 0,11 | 0,15 | 0,30 | 0,01 | 0,01 | 0,01 | 0,01 |
| SEPT. | 79 | 0,09 | 0,10 | 0,50 | 0,01 | 0,02 | 0,01 | 0,01 |
| AVERAGE | | 0,180 | 0,183 | 0,578 | 0,015 | 0,025 | 0,023 | 0,020 |
| MIN. | | 0,01 | 0,01 | 0,02 | 0,01 | 0,01 | 0,01 | 0,01 |
| MAX. | | 1,05 | 1,03 | 2,55 | 0,06 | 0,16 | 0,10 | 0,15 |

TABLE IV: Composition of the rain collected at JRC monthly values

| 1986/1987 | | PRECIPITATION | | | | | | | | | | | | |
|-----------|-------------|---------------|------|----------------------|----------------------|----------------------|---------|---------|---------|---------|---------|--------|-------------|--|
| MONTH | No. OF DAYS | mm | ph | SO ₄ mg/l | NO ₃ mg/l | NH ₄ mg/l | Na mg/l | Mg mg/l | Ca mg/l | Cl mg/l | H+ mg/l | K μg/l | Cond. μS/cm | |
| DEC | 2 | 2,2 | 3,81 | 5,72 | 9,56 | 0,90 | 0,39 | 0,14 | 0,96 | 0,96 | 159 | 0,17 | 80 | |
| JAN | 4 | 78,5 | 4,50 | 0,87 | 1,68 | 0,17 | 0,10 | 0,02 | 0,07 | 0,19 | 32 | 0,10 | 16 | |
| FEB | 10 | 204,3 | 4,24 | 1,74 | 2,57 | 0,27 | 0,06 | 0,02 | 0,09 | 0,27 | 58 | 0,04 | 25 | |
| MAR | 2 | 15,4 | 3,80 | 9,98 | 16,42 | 4,03 | 1,42 | 0,19 | 1,47 | 1,30 | 158 | 0,65 | 95 | |
| APR | 7 | 146,2 | 5,91 | 6,89 | 4,43 | 1,52 | 0,81 | 0,28 | 4,54 | 1,37 | 1 | 0,91 | 40 | |
| MAY | 9 | 80,8 | 4,09 | 5,42 | 5,80 | 1,73 | 0,26 | 0,08 | 0,50 | 0,48 | 81 | 0,12 | 45 | |
| JUN. | 12 | 250,9 | 4,57 | 4,46 | 3,14 | 1,51 | 0,27 | 0,07 | 0,60 | 0,43 | 27 | 0,07 | 27 | |
| JUL | 14 | 130,6 | 4,24 | 5,69 | 5,09 | 1,61 | 0,35 | 0,10 | 0,59 | 0,61 | 58 | 0,12 | 42 | |
| AUG | 5 | 229,9 | 4,41 | 3,87 | 2,17 | 1,02 | 0,09 | 0,05 | 0,41 | 0,26 | 39 | 0,04 | 25 | |
| SEP | 2 | 95,7 | 4,33 | 2,94 | 4,16 | 0,88 | 0,17 | 0,06 | 0,42 | 0,27 | 47 | 0,07 | 28 | |
| OCT | 15 | 313,8 | 4,18 | 3,45 | 5,36 | 1,32 | 0,26 | 0,06 | 0,35 | 0,48 | 66 | 0,08 | 33 | |
| NOV | 6 | 110,2 | 4,36 | 1,17 | 2,13 | 0,36 | 0,08 | 0,02 | 0,09 | 0,21 | 44 | 0,05 | 17 | |
| AVERAGE | | | 4,37 | 4,35 | 5,21 | 1,28 | 0,36 | 0,09 | 0,84 | 0,57 | 064 | 0,20 | 39 | |
| Σ | 88 | 1658,5 | | | | | | | | | | | | |

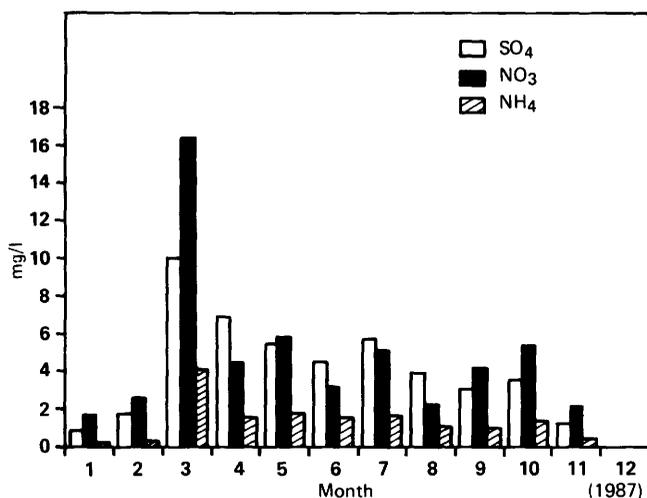


Fig. 5. Pollutants in wet deposition EMEP Station JRC-Ispra

- Correlation Spectroscopy (COSPEC) for total burden mapping and mass flow determination for SO₂ and NO₂;
- LIDAR for the tracking of plumes from conventional power plants;
- Micrometeorological Station equipped with a three dimensional anemometer/thermometer, microbarometer, radiometers and a three-dimensional Doppler acoustic radar (SODAR);
- Tracer techniques for the experimental validation of source-receptor relationships for pollution transport over complex terrain and different meteorological situations, using chemically inert substances like sulphur hexafluoride and perfluorocarbons which normally are not present in the environment.

Since 1975 the JRC participated in CEC-sponsored European Measuring Campaigns on the Remote Sensing of Atmospheric Pollution (1975 Lacq, France; 1976 Drax, UK; 1979 Turbigo, Italy; 1981, Ghent, Belgium, 1983 Fos-Berre, France). In 1985 the JRC gave a significant contribution to the German TULLA project (aiming at the pollutant mass-balance of the Land Baden-Württemberg) by direct participation with COSPEC and Tracer measurements and by coordinating and sponsoring of aircraft measurements. For the future an extended participation in the EUREKA/EUROTRAC proposals aiming at the study of pollution flow over complex terrain, is envisaged.

2.4 MASS BALANCE AND TRANSPORT OF POLLUTANTS

INTRODUCTION

In recent years the transboundary transport of atmospheric pollutants has become an important issue for the European environmental policy especially after widespread forest die back in Central Europe and lake acidification in Scandinavia have been related to the long range transport of acid forming pollutants like SO₂ and NO₂.

The JRC Ispra has developed instrumentation and methods for the remote sensing of atmospheric pollution and for the description of air-mass trajectories on the mesoscale (about 100 km), which are employed in mobile laboratories for measurements in European and national field experiments.

These are:

RESULTS

Air quality level in the Varese area

The Varese district, in which Ispra is situated, was considered low-polluted up to Autumn 1986 when occasionally pH values ranging from 3.8 to 3.5 were measured in rainwater samples by some environmentalists of the Centro Geofisico Prealpino. The consequent public concern emphasized by mass media was the motivation for a request of the local authorities to JRC to investigate the problem, particularly during the approaching cold season (Winter '86-'87).

Only the EMEP monitoring station at Ispra, 20 km SW from Varese was operating in the Varese district.

Three main questions were submitted: (1) was the air quality level within the legal limits, (2) were pollutants emitted from local sources or transported from distant area, particularly from the densely populated and industrialized Po valley, and (3) which initiatives could be undertaken by decision-makers to ameliorate the situation.

To approach the problem, the following steps were followed:

- evaluation of an emission inventory for the district. As only small or medium size factories existed, a large effort was concentrated on the two main sources, heating systems and traffic;
- analysis of the local climatology, in order to forecast days with pollution accumulation. If pollution level exceeded the legal limits during these episodes, the problem would have required a deeper investigation;
- some surveys during episodes by our mobile laboratory equipped with two Cospecs and monitors for ground-level concentration of SO₂, NO, NO₂, CO, Ozone and aerosols along the main traffic road. Similar investigations could help in localizing emission sources.

Basing on the meteorological forecast (in collaboration with the Aeronautica Militare, Milano), Meteosat images (available at the Centro Geofisico) and pollution data available at the EMEP station at Ispra some surveys have performed in the considered area. During one month (February 1987) two SO₂ sensors were installed at Varese (410 m) and at Campo dei Fiori (1226 m) to follow the day-and-night evolution; during one day (10 March) surveys have been repeated every two hours until 2.00 a.m. to monitor pollution evolution as traffic and heating systems were reducing.

Pollution episodes were particularly evident in presence of a weak wind circulation, associated with an anticyclonic area over continental Europe and Northern Italy and a levelled pressure field. Evident pollution sources were heating systems (an unsuspected amount of high S-content fuel is still used) and traffic (at one entrance of the town more than 23.000 cars are passing from 7.30 a.m. to 7.30 p.m.).

On beginning of April a conclusive report has been submitted to local authorities. Suggestions have been given for some legal control of fuel and for the localisation of three monitoring stations which are foreseen to be installed in near future. This study has been summarized in a paper presented at an international Symposium.

Monitoring Campaign in Greece: Athens and Thessaloniki

In February of this year the Greek Ministry for the Environment and the JRC agreed for a collaboration study on two large pollution problem cities in Greece: Athens and Thessaloniki. In September a two-weeks Campaign has been performed by our laboratory: the first week (14 to 20 September) in Athens, the second week (21 to 25 September) in Thessaloniki.

In Athens two monitoring stations (PERPA, Patision Str. and Pyreus) were calibrated by our colleagues of CLAP for sulphur dioxide, black smoke and total suspended particles. At the same time our mobile laboratory measured some pollutants along pre-selected roads inside the urban (Athens and Pyreus) and industrial (Elefsina) areas. On one measurement day (15 September) we met a «nephos» episode, a brown smog of unknown origin, which is considered to be responsible for extended human health problems. Table I summarizes average and maximum values for some trajectories, while Table II refers to the «nephos» day. At the same time at the Central Chemical State laboratory an analysis of methane and non-methane hydrocarbons has been performed.

A similar survey has been performed one week later in Thessaloniki, in the frame of a collaboration with the Ministry of Northern Greece. Particularly evident was the relatively high level of sulphur dioxide in the urban area (Table III) probably due to a transport from the industrial area.

As soon as meteorological data will be available from the Greek laboratories, a more detailed data analysis will be possible.

Atmospheric Tracers

a) Multi-Tracers Experiments

Multi-tracer experiments (SF₆, C₇F₁₄ and C₈F₁₆) have been carried out in the Ispra area.

The aim of these experiments was to check the reliability of

TABLE I. Some values from the Greece Campaign - September 1987

| Pollutant | SO ₂ (ug/m ³) | NO _x (ug/m ³) | NO (ug/m ³) | NO ₂ (ug/m ³) | CO (mg/m ³) | Ozone (mg/m ³) | Aerosols (mg/m ³) |
|----------------------------|---|---|----------------------------|---|----------------------------|-------------------------------|----------------------------------|
| Athens, central normal day | (20) | 400 | 350 | 138 | 10 | 60 | 0.09 |
| Athens, cent. nephos day | (35) | 1212 | 1085 | 280 | 25 | 20 | 0.30 |
| Athens, ind. normal day | --- | 606 | 550 | 140 | 4 | 50 | 0.20 |
| Athens, semi-rural area | --- | 300 | 260 | 80 | --- | 80 | 0.05 |
| Thessaloniki urban | 90 (50) | 170 (211) | 141 (172) | 46 (62) | --- | 44 (35) | 0.10 (0.06) |
| Thessaloniki industrial | 30 - 156 | 96 - 295 | 77 - 248 | 29 - 72 | --- | 67 - 42 | 0.05 - 0.09 |

TABLE II. Greater Athens Measurements - 15, September 1987 - Nephos Episode

| Pollutant | PERPA to | Glyfada | Glyfada to | Toll Post | Toll Post to | PERPA |
|-------------------------|----------|---------|------------|-----------|--------------|---------|
| | max | average | max | average | max | average |
| Ozone (ug/m3) | 138 | 32 | 104 | 55 | 106 | 66 |
| Dust (mg/m3) | 0.40 | 0.11 | 0.58 | 0.06 | 0.17 | 0.04 |
| NOx (ug/m3) | 1212 | 745 | 1051 | 352 | 603 | 257 |
| NO (ug/m3) | 1085 | 617 | 912 | 268 | 515 | 193 |
| NO ₂ (ug/m3) | --- | 196 | --- | 129 | --- | 98 |
| CO (mg/m3) | 32 | 11 | 18 | 2 | 13 | 2 |

TABLE III. Greater Thessaloniki Measurements - September 1987

| Pollutant | Ministry-Angialos | Ministry-Angialos | Industrial Area | Industrial Area | Urban Area night | Urban Area night | Industrial Area | Industrial Area |
|-------------------------|-------------------|-------------------|-----------------|-----------------|------------------|------------------|-----------------|-----------------|
| | max | average | max | average | max | average | max | average |
| Ozone (ug/m3) | 94 | 44 | 96 | 67 | 76 | 35 | 121 | 42 |
| Dust (mg/m3) | 0.75 | 0.10 | 0.21 | 0.05 | 0.13 | 0.06 | 0.28 | 0.09 |
| NOx (ug/m3) | 1228 | 171 | 588 | 96 | 792 | 212 | 1228 | 295 |
| NO (ug/m3) | 1139 | 141 | 510 | 77 | 640 | 172 | 1079 | 248 |
| NO ₂ (ug/m3) | --- | 46 | --- | 29 | --- | 62 | --- | 72 |
| SO ₂ (ug/m3) | 1050 | 90 | 532 | 28 | 325 | 57 | 1019 | 156 |

the perfluorocarbon tracer technique by comparing perfluorocarbon data with those obtained for SF₆, assuming the last one as a correct reference.

The comparison of the ratios between tracers at the release point with the ratios observed in the collected field samples was used for this purpose and is reported in Table IV.

If no error or systematic deviation would effect the data, the four values reported for each experiment and tracer combination i.e. the release, the linear correlation, the median and the mean should coincide. The fact that the ratios observed in the samples are different from those at the release point indicates the existence of random and/or systematic errors.

The following comments can be made.

There is no clear tendency for deviations in the three experiments. In the first and last experiment the smaller deviations are observed for the linear correlation slopes: mean and median ratios show higher for the mean. The linear correlation coefficients reported in parenthesis in Table IV show that the correlations are always highly significant and the correlation accounts by far for the greatest portion of the total variance of the data (in the last experiment 99.8%).

Considering this result, the technique for the dispersion and measurement of three independent tracers appears sufficiently advanced to carry out experiments up to ~ 100 km.

TABLE IV: Ratios between tracers

| | C_8F_{16}/SF_6 | C_7F_{14}/SF_6 | C_7F_{14}/C_8F_{16} |
|---|------------------|-------------------|-----------------------|
| 3 June 1985 | | | |
| release | 0.161 | 0.129 | 0.799 |
| samples | | | |
| a) linear correlation (correlation coeff.) | 0.160 (0.924) | 0.149* (0.974) | 0.981 (0.886) |
| b) median of single ratios | 0.181 | 0.193 | 1.064 |
| c) mean of single ratios | 0.238 | 0.248 | 1.072 |
| 3 July 1986 | | | |
| release | 0.138 | 0.138 | 1.000 |
| samples | | | |
| a) linear correlation (correlation coeff.) | 0.112 (0.957) | 0.101 (0.953) | 0.765 (0.862) |
| b) median of single ratios | 0.112 | 0.102 | 0.847 |
| c) mean of single ratios | 0.125 | 0.104 | 0.854 |
| 19 November 1986 | | | |
| release | 0.127 | 0.127 | 1.000 |
| samples | | | |
| a) linear correlation (correlation coeff.) | 0.131 (0.999) | 0.134 (0.999) | 1.021* (0.999) |
| b) median of single ratios | 0.169 | 0.156 | 0.877 |
| c) mean of single ratios | 0.175 | 0.155 | 0.868 |

Note: The values labeled «release» are derived from the weights effectively released.

The values labeled «linear correlation» are the slopes of the lines through the origin with two exceptions, where the slope of the least square line is reported because the intercept is significantly different from zero (values indicated with *). The number of data points available for the linear correlation calculations is between 22 and 29.

b) Dual-Trap Analyzer

A new instrument (Dual-Trap Analyzer) for the measurements of perfluorocarbon trace concentrations has been recently purchased.

Originally conceived and developed by Lovelock and modified by the Brookhaven Laboratory, the Dual-Trap Analyzer has been especially manufactured for the JRC-Ispra by the John Booker and Co. (Austin-Texas). This instrument can detect perfluorocarbon tracers in air samples at concentrations down to 10^{-2} ppt (10^{-14} v/v).

The Dual-Traps analyzer has two Amborsorb traps; while one is sampling, the other is thermally desorbed and analyzed on an *in situ* chromatograph column followed by an electron capture detector.

The time required for the measurements of the two perfluorocarbon (C_7F_{14} and C_8F_{16}) concentration in air at the ppt (10^{-12} v/v) level is about 2-3 minutes. For this reason this instrument can be used as a semi-continuous real time analyzer in a mobile van or aircraft. Fig. 1 shows a picture of the Dual-Trap Analyzer.



Fig. 1. The dual-trap analyzer

c) Mobile Unit for Trace Experiments

A mobile unit has been constructed with the aim to have the tracer release system and the tracer measuring equipment at the disposal without depending from any support of host laboratories.

A picture of this mobile unit composed of two independent cabins is shown in Fig. 2. One of these is fixed to the lorry and contains the equipment for the tracer release, while the other, equipped with tracer measuring instruments, can be displaced and fixed at the ground.

Micro-Meteorological Instrumentation

A three-dimensional Doppler acoustic radar (SODAR) has been purchased with the view to support other JRC teams during atmospheric tracers release campaigns, supplying vertical wind vector profiles. The SODAR works by sending periodically sound pulses of a given pure sine frequency into the atmosphere; the presence of turbulence causes the wave packet to be backscat-



Fig. 2. The mobile unit

tered, yielding a kind of echo which is detected by the instrument. The air motion makes the backscattered sound pulse frequency to be Doppler-shifted; the magnitude of that frequency shift is thus a measure of the velocity of the air motion along the sound propagation axis. Since the apparatus consists of three antennas whose axes form a trihedron, the whole wind vector can be reconstructed. Fig. 3 shows an external view of the SODAR, which has been for the time being placed behind the building 29 of the JRC for the first working tests.

The SODAR works on a routine basis, the output data being stored every 30 minutes (this averaging time is programmable, however) on a cassette. They are periodically transferred to the mainframe Amdahl computer of the JRC for further processing. Fig. 4 shows an example of vertical profiles of the horizontal wind components for a two days of continuous observations.

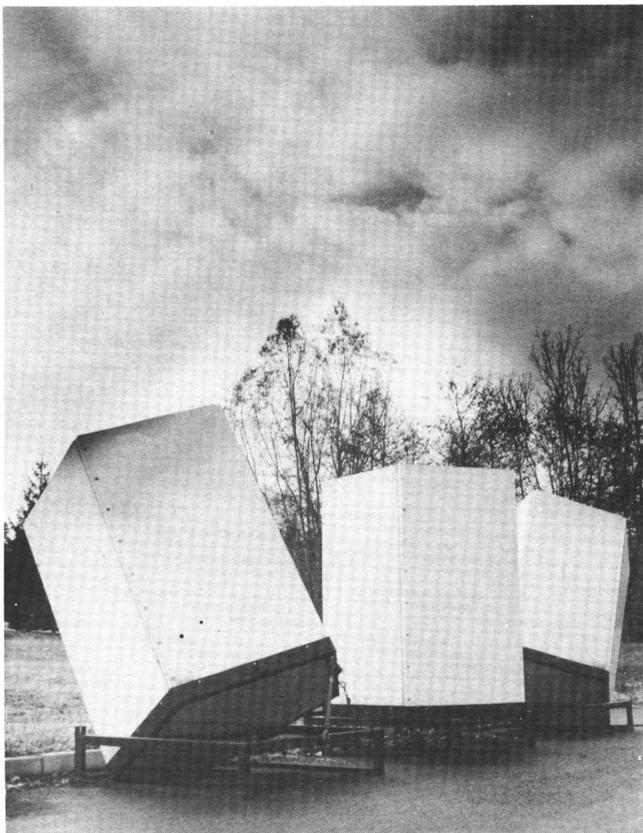


Fig. 3. External view of the Sodar

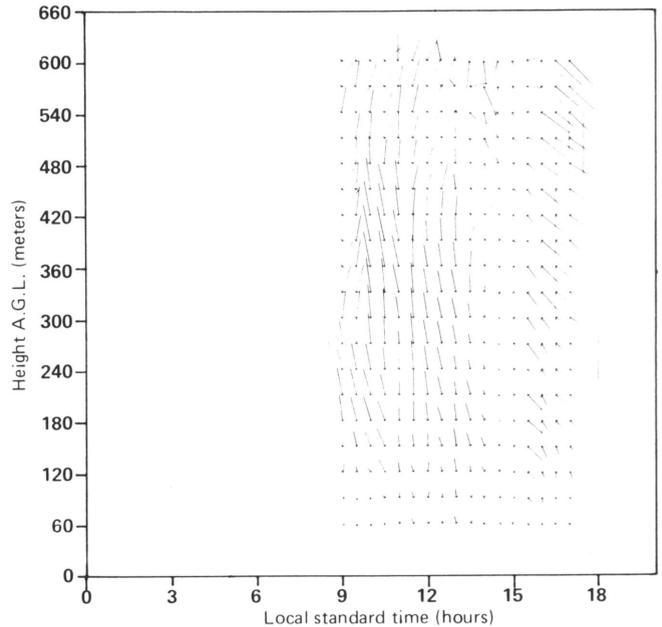


Fig. 4. Doppler sounder (Sodar) data for November, 1987. The arrow represent the horizontal component of the wind vectors; the vertical bars give the vertical extension of the inversion layer, if detected.

The SODAR is capable of detecting the heights of the inversion base and top as well. The standard deviations of the wind vector components are also recorded, but the physical meaning and validity of these data are still controversial. Such standard deviations are needed in a number of air pollution studies since they are a measure of atmospheric turbulence.

Also has been purchased a three-dimensional sonic thermoanemometer which measures the three wind-vector components and the temperature with a sampling frequency of 20 Hz at a fixed height, an automatic meteorological station consisting of a wind vane and anemometer, a temperature and humidity sensor, and a data logger; a chemiluminescent fast response NO₂ analyser and a telescopic 10 meter high mast have also been acquired.

The sonic anemometer and the NO₂ analyser have been used during a testing campaign which took place near Raisting, Bavarian plateau (FRG), in collaboration with the atmospheric chemistry group of the Fraunhofer-Institut für Atmosphärische Umweltforschung, Garmisch-Partenkirchen (FRG). The experimental set-up is shown on fig. 5a (general view), 5b (sonic anemometer) and 5c (NO₂ analyzer)

The main goal of that exercise was to test the performance of a dry deposition measuring system which works making use of the eddy-correlation principle, i.e. by deriving vertical fluxes of a trace atmospheric gas from the eddy-correlation, on covariance between the fluctuations of the trace gas concentration and the vertical wind vector component. The data acquisition system make use of a software developed by McMillen and Hicks and adapted by Nestlen (private communication) implemented on a standard PC.

The campaign took place during November 1987, the data will be available in early (1988).

References

- S. SANDRONI, C. CERUTTI
 «Evaluation of Air Quality Level in a urban area 4th Intern. Symp. on Environmental Pollution and its Impact on the Mediterranean Area, Kavala (Greece), September 1987.
- S. SANDRONI
 Editor, Regional and Long-Range Transport of Air Pollution, Elsevier 1987.

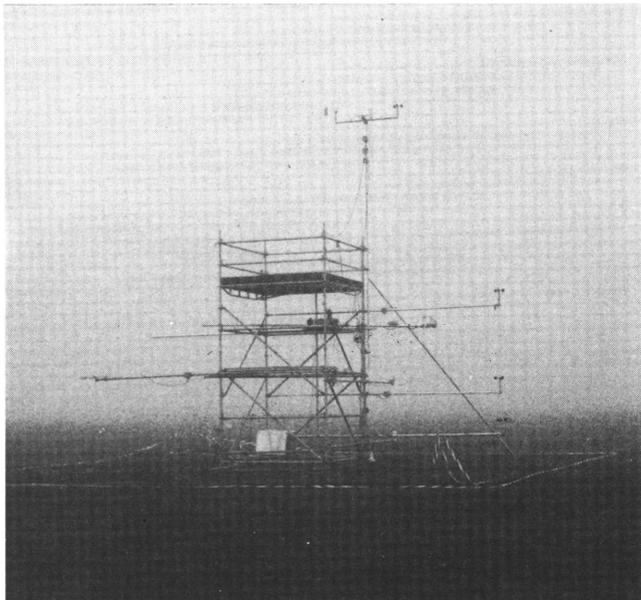


Fig. 5a. Tower installed at Raisting (FRG) for measuring dry deposition of NO_2

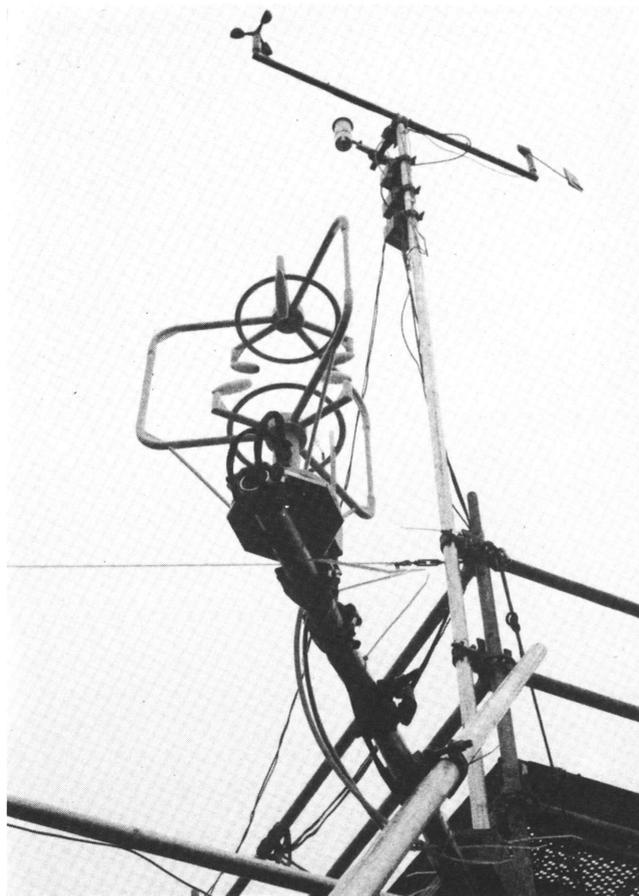


Fig. 5b. Sonic anemometer on the Raisting tower

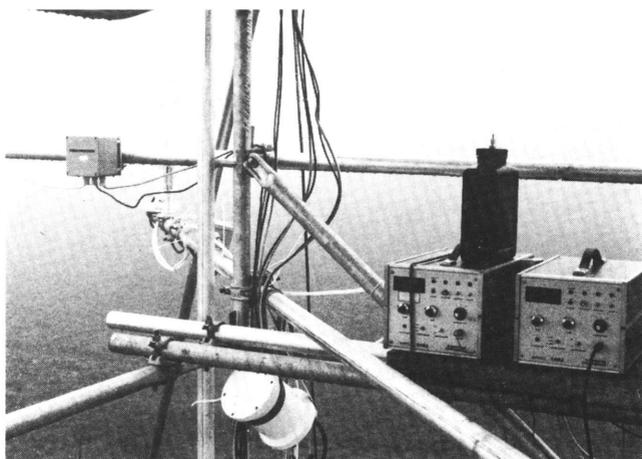


Fig. 5c. NO_2 analyzers on the Raisting tower

P. GAGLIONE

A description of the atmospheric tracer technology used at the J.R.C. - 4th Intern. Symp. of radioecology of Cadarache on the impact of nuclear origin accidents on Environment, Cadarache March 1987.

S. CIESLIK, G. SCHAYES

Modelisation of energy fluxes observed by a sonic anemometer during field experiments-paper presented at the Reunion Scientifique generale de la Société belge de Physique, Diepenbeek, Belgium, June 1987, and at the VIXth General Assembly of the Intern. Union of Geodesy and Geophysics, Vancouver, Canada, August 1987.

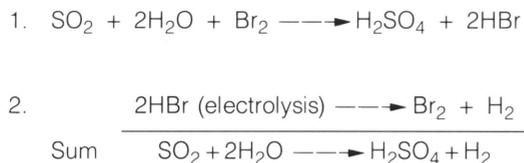
S. CIESLIK, H. BULTYNCK

A statistical method for deriving vertical temperature profiles from near-surface observations, J. Clim. Appl. Meteor. 25, 1315, 1986.

2.5 ISPRA MARK 13A PROCESS FOR FLUE GAS DESULPHURISATION

BACKGROUND

The ISPRA MARK 13A process is a new flue gas desulphurisation process producing, instead of gypsum like most of today's industrially applied processes, sulphuric acid and hydrogen. The process has been developed at Ispra as a spin-off from the former Hydrogen Programme and is based on the following reactions:



Potential advantages of this new process, which was tested for some years in bench-scale and laboratory plant operation conditions, are:

- the produced sulphuric acid and hydrogen are valuable chemicals which can be marketed or reutilised;
- all reactants are generated inside the process so that the disposal of solid products and waste water is not required;
- the reaction takes place in the liquid phase which allows high reaction rates and small equipment volumes leading probably to lower investment and operating costs.

At present the Commission supports the construction and operating of a pilot plant to desulphurise a flue gas throughput of 32.000 m^3/h in Sardegna (Italy).

Besides the abatement of sulphur dioxide, the removal of nitrogen oxides from flue gases is of primary importance for the protection of the Environment. Therefore, JRC conducts a research for extending the ISPRA MARK 13A process to a combined desulphurisation/denoxing process.

The basis ideas and preliminary laboratory experiments of this new approach are described in the following report.

THE CATHODIC ELECTROCHEMICAL REDUCTION OF NITROGEN OXIDES

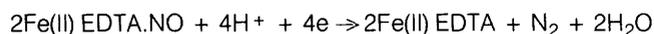
D. van Velzen and H. Langenkamp

1. INTRODUCTION

The work described in this report is directed towards the development and understanding of an electrochemical route for the removal of nitrogen oxides (NO_x) from flue gas. The method consists of the absorption of the nitrogen oxides in an aqueous solution containing a complexing agent and the subsequent electrochemical decomposition of the formed NO-complex.

It is known that nitrogen oxides form stable complexes in solution with a variety of reagents. Of particular interest are the complexes formed between ferrous iron (Fe(II)) and ethylenediamine tetra-acetic acid (EDTA).

It is reported [1] that these complexes may be reduced electrochemically to nitrogen and/or ammonia. The reduction reaction leading to nitrogen is shown below:



If this cathodic process could be developed to operate on a large scale, it would be of major interest. It could be used in conjunction with the Ispra Mark 13A [2] process for removing simultaneously nitrogen oxides (denoxing) and sulphur dioxide (desulphurisation) from a flue gas stream.

A single divided electrochemical cell would be required.

In the anodic compartment, bromine, to be used to oxidise sulphur dioxide to sulphuric acid, would be generated and at the same time a NO-containing complex would be reduced in the cathodic compartment.

The study of the electrochemical reduction of the Fe(II) EDTA.NO complex requires an understanding of the basic electrochemistry of the Fe(II) EDTA/Fe(III)EDTA redox couple.

II. ABSORPTION MEASUREMENTS

The absorption of NO on Fe(II)EDTA chelates is well known and has been extensively reported in the open and patent literature. However, it seemed interesting to study the stoichiometry of the complex Fe(II)EDTA.NO, i.e. the maximum solubility of NO in Fe(II)EDTA solutions. The experimental set up used for the absorption measurements is given in Fig. II.1.

A gas containing approximately 2000 ppm of NO is brought in contact at a controlled flow with a Fe(II)EDTA solution inside the reactor. The reactor liquid is circulated and the quantity of NO at the outlet of the reactor is measured by means of an analyser. In the course of the experiment, the quantity of gas entering the system is followed as a function of time. The outlet NO concentration can be plotted and the quantity of absorbed NO calculated.

II.1. Absorption of NO in Fe(II)EDTA solutions

Figure II.2 shows an absorption curve in 1 litre of a 0.07 M Fe(II)EDTA solution, at 20°C, i.e. the quantity of NO measured at the outlet of the reactor as a function of time. The gas mixture containing 2250 ppm of NO is entering the reactor at a constant flow (458 l/hr). The quantity of absorbed NO can be calculated from the absorption curves as follows:

NO_{out} = f(t) represents the mathematical equation of the absorption curve

NO₀ = the by-pass level (2250 ppm)

NO_{abs} = the quantity of absorbed NO and

F = the overall gas feed rate (l/h)

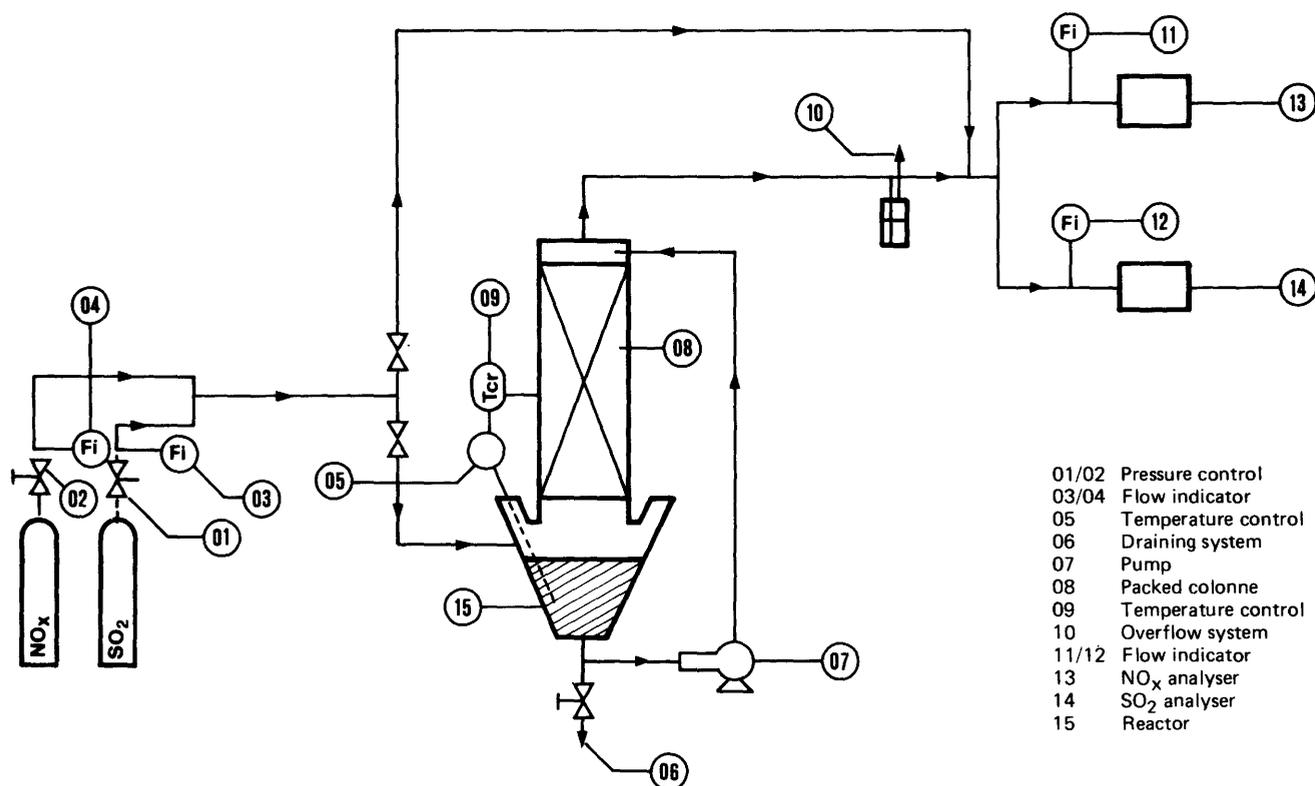


Fig. II.1 Experimental set-up for absorption measurements

$$NO_{abs} = \int_0^{\infty} F((NO_0 - f(t)) dt)$$

NO_{abs} is represented by the area under the curve of equation $g(t) = NO_0 - f(t)$.

To resolve the equation numerically, it can be assumed that:

$$NO_{abs} = \Sigma (NO_0 - f_a(t_i)) \Delta t_i$$

where Δt_i is a constant time interval (e.g. 1 min.) and $f_a(t_i)$ is the average value of $f(t)$ over that time interval. In the case of figure II.2, the bypass level is reached after 140 min (t_i).

The calculation of NO_{abs} in the case of figure II.2 gives:

$$NO_{abs} = 1.65 \text{ l, which means at } 20^\circ\text{C, } 0.068 \text{ mole of NO.}$$

This experiment has been repeated twice and the results are presented below:

| moles of complex Fe(II)EDTA in solution | moles of NO absorbed |
|---|----------------------|
| 0.049 | 0.046 |
| 0.035 | 0.030 |

These results indicate that at 20°C the absorption of NO on Fe(II)EDTA chaletes is stoichiometric. This is in agreement with the results of other workers [3].

II.2. Simultaneous absorption of NO and SO₂ in Fe(II) EDTA solutions

An absorption experiment has been carried out with a gas mixture containing 1400 ppm of NO and 520 ppm of SO₂ in 800 ml of a 0.07 M Fe(II)EDTA solution.

The absorption curve obtained is represented on figure II.3. This result tends to confirm the fact that SO₂, converted into sulfurous acid (SO₃²⁻) acts as a reductive agent with dissolved NO [3].

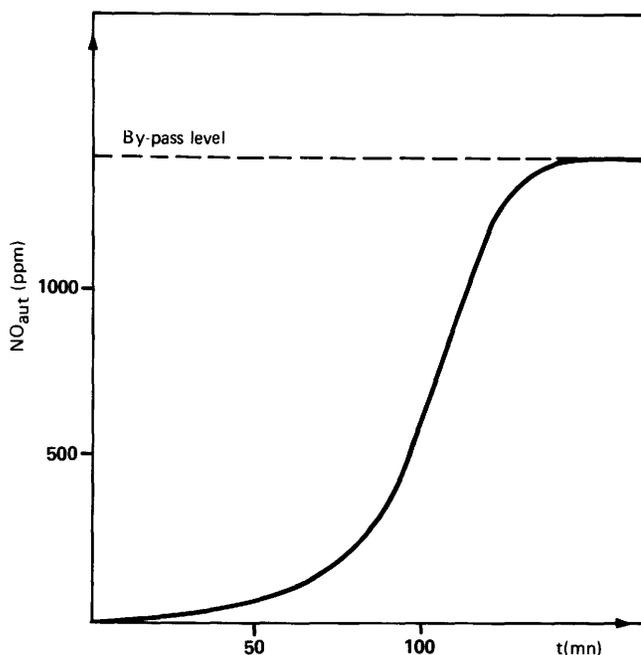


Fig. II.3. Absorption curve in 800 ml of a 0.07M Fe(II)EDTA solution. pH = 3; T = 20°C - Inlet gas composition: NO = 1400 ppm, SO₂ = 520 ppm

III. LINEAR SWEEP AND CYCLIC VOLTAMMETRY

Cyclic voltammetry has been extensively developed over the past decade, and a very detailed approach has been given in reference [5]. It is in the area of preliminary mechanistic investigations that this technique is probably most useful. An electrochemical spectrum, indicating the potentials at which processes occur can be rapidly obtained, while, from the sweep rate dependence, information about reaction kinetics can be derived. The experimental set-up is schematically shown in Fig. III.1.

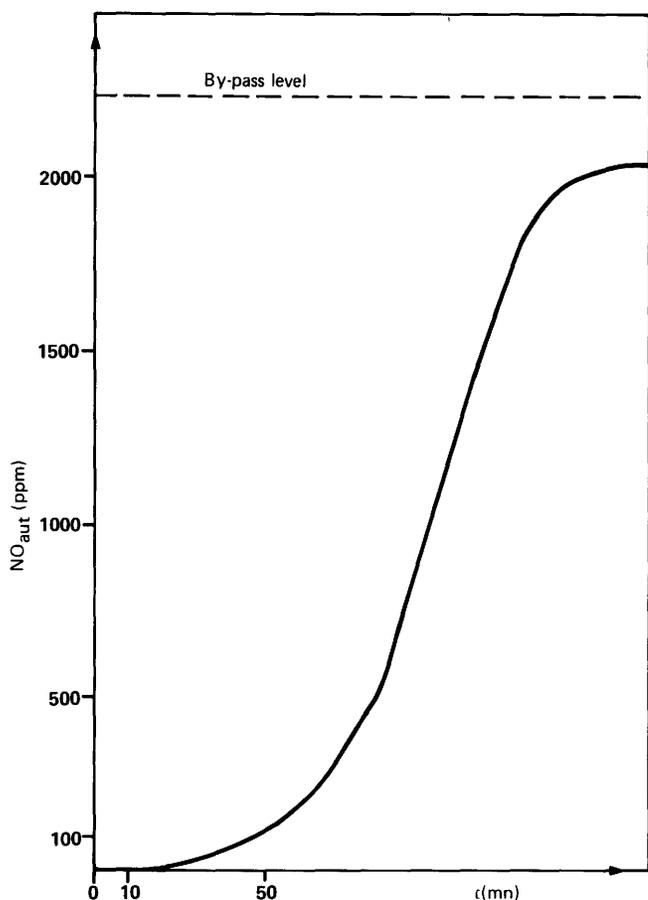


Fig. II.2. Absorption curve in 1 litre of a 0.07M Fe(II)EDTA solution pH = 3; T = 20°C - Inlet NO concentration = 2250 ppm

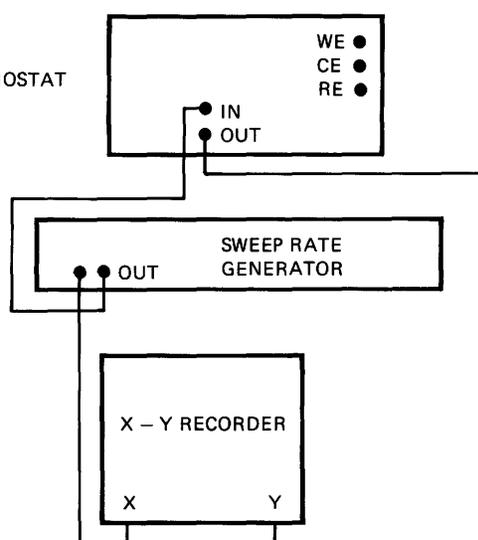


Fig. III.1. Experimental set up for cyclic voltammetry

The cyclic voltammetry experiments have been carried out in a standard three electrode cell described in Fig. III.2. The reference electrode is a commercial saturated calomel electrode (SCE), to which all potentials are referred. A large area platinum counter electrode (CE) is used. The potential between the working electrode (WE) and the reference electrode (RE) is monitored by using a Luggin capillary made from a glassware syringe. Two different working electrodes have been used for the cyclic voltammetry experiments:

- A Pt wire (0.64 cm²)
- A Hg pool (1.9 cm²)

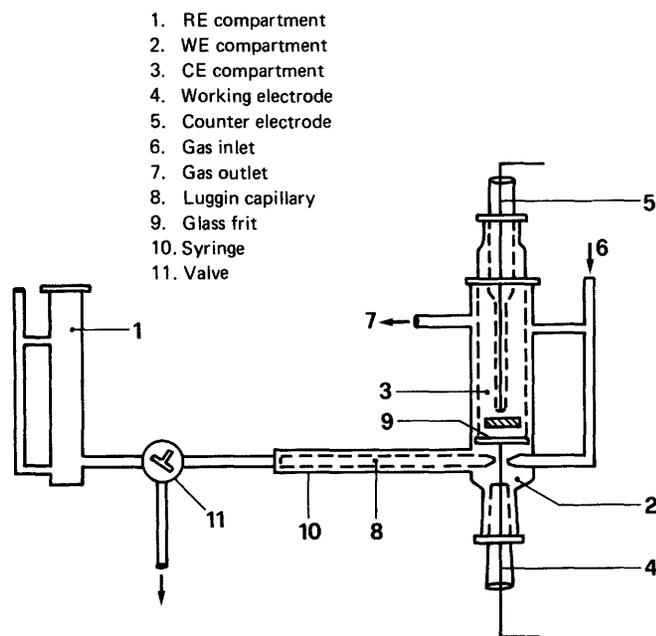


Fig. III.2. Standard three electrode cell

In order to check upon the complex reduction, preliminary electrolysis tests have also been carried out. In this case, a galvanostatic set up used to impose a constant current density to the WE (here the cathode). For this reason, the potentiostat was converted into a galvanostat, and only 2 electrodes were used, the working electrode (cathode) and the counter electrode (anode).

III.2. The Fe(II)EDTA/Fe(III)EDTA redox couple

Figure III.2 represents the cyclic voltammogram of a platinum wire working electrode (0.64 cm²), in a 0.075 M Fe(II)EDTA solution (pH = 2.8), starting at -1.0 V vs SCE, and scanning at 200 mV/s towards positive potentials (1.5 V vs SCE).

This cyclic voltammogram, carried out on a large potential range (-1.0; +1.5 V vs SCE) exhibits 3 distinctive peaks A, A' and B'. Peak B' is likely to correspond to the proton adsorption (H⁺ + e⁻ → H_{ads}), as some gas bubbles are visible at the electrode surface at this potential. Peak A corresponds to the oxidation (1), whereas peak A' characterizes the reduction (1'):



The stability potential range is limited by the decomposition of water, i.e. hydrogen evolution starting at -0.7 V vs SCE and oxygen evolution at 1.4 V vs SCE.

In order to check on the reversibility of the redox couple Fe(II)EDTA/Fe(III)EDTA, the sweep rate dependence of the cyclic voltammogram of Pt in a 0.075 Fe(II)EDTA solution has been studied in a narrower potential range (-0.5; +0.5 V vs SCE).

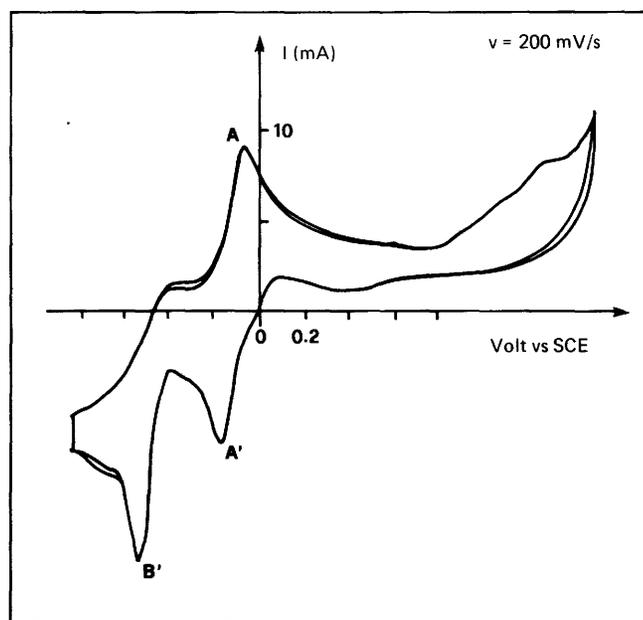


Fig. III.3. Cyclic voltammogram of platinum in a 0.075M Fe(II)EDTA solution

III.3. Reversibility of the Fe(II)EDTA/Fe(III)EDTA redox couple

The cyclic voltammograms obtained at different sweep rates, using a platinum electrode in the potential range (-0.5; +0.5 V vs SCE) are presented in figure III.4.

All these sweeps are started at -0.5 V vs SCE; the potential is scanned towards positive potentials at a sweep rate v(mV/s) and reversed at the same sweep rate.

Let us call:

I_p^a the height of the anodic peak A (mA)

I_p^c the height of the cathodic peak A' (mA)

E_p^c the cathodic peak potential (V vs SCE)

E_p^a the anodic peak potential

Table III.1 summarises the practical values of these different parameters, at various sweep rates. The following conclusions can be drawn from these results:

Table III.1 Cyclic voltammograms of the Fe(II)EDTA/Fe(III)EDTA system on Pt at different sweep rates

| v (mV/s) | v 1/2 | I_p^a | I_p^c | E_p^a | E_p^c |
|----------|-------|---------|---------|---------|---------|
| 100 | 10 | 6.25 | 6.25 | -0.02 | -0.19 |
| 200 | 14.14 | 7.7 | 7.50 | -0.01 | -0.2 |
| 300 | 17.32 | 9.25 | 9.10 | 0.00 | -0.21 |
| 400 | 20.00 | 10.20 | 10.00 | +0.01 | -0.216 |
| 500 | 22.36 | 11.12 | 11.00 | +0.02 | -0.226 |
| 600 | 24.50 | 12.00 | 12.00 | +0.03 | -0.230 |
| 700 | 26.46 | 12.75 | 12.50 | +0.04 | -0.230 |
| 800 | 28.28 | 13.00 | 13.25 | +0.04 | -0.240 |

$$|I_p^a| = |I_p^c| = |I_p|$$

I_p increases with $v^{1/2}$, but not proportionally.

$E_p^a - E_p^c$ is greater than 59 mV and increases with v.

E_p^c shifts negatively with increasing v.

These features are characteristics of a quasi reversible system.

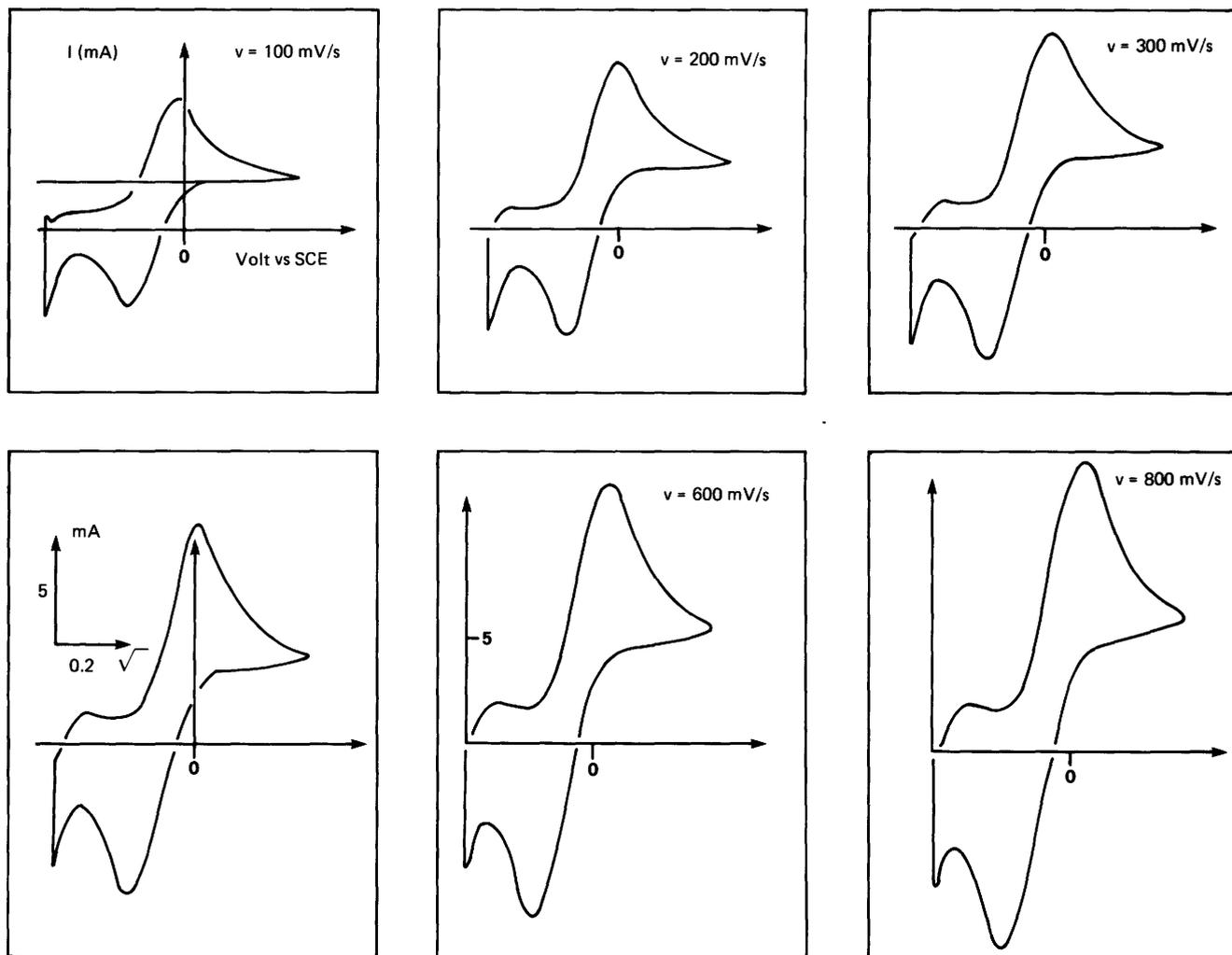


Fig. III.4. Cyclic voltammograms of Pt(0.64 cm²) in 0.075M Fe(II)EDTA solutions at different sweep rates

III.4. Behaviour of mercury in Fe(II)EDTA solutions

Figure III.5 presents the cyclic voltammograms of a Hg pool (1.9 cm²) in a 0.075 M Fe(II)EDTA solution, at different sweep rates. The sweep is started at -1.45 V vs SCE, at a sweep rate v , in the range of 100 - 400 mV/s, until reaching +0.2 V vs SCE.

Higher positive values of the potential could not be reached due to the formation of mercury oxides at the electrode. This formation starts at potentials very close to 0.2 V vs SCE, involves very high currents and changes the working electrode surface.

Peak A represents the oxidation of the complexed iron(II) to iron(III), whereas peak A' shows the corresponding reduction. Table III.2 summarises the values of E_p^a , E_p^c , I_p^a , obtained at different sweep rates on Hg. The sweep rate dependence analysis of the cyclic voltammograms leads to the same conclusions about the reversibility of the Fe(II)EDTA/Fe(III)EDTA system as with Pt-electrodes. However, hydrogen evolution on Hg starts about 500 mV more negative than on Pt (-1.4 V vs SCE), which also means a larger range of potential stability.

Table III.2. Practical values of the current and potential in cyclic voltammograms on Hg at different sweep rates.

| v (mV/s) | $v^{1/2}$ | E_p^a | E_p^c | I_p^c |
|------------|-----------|---------|---------|---------|
| 100 | 10 | 0.13 | -0.16 | 10.75 |
| 200 | 14.14 | 0.15 | -0.17 | 13.75 |
| 300 | 17.32 | 0.11 | -0.17 | 16.25 |
| 400 | 20.00 | 0.13 | -0.18 | 18.38 |

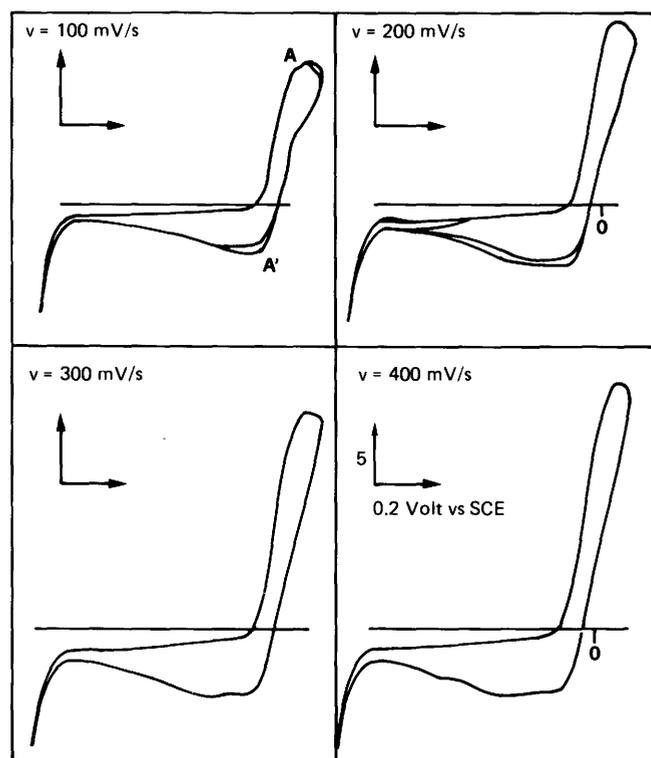


Fig. III.5. Behaviour of mercury in Fe(II)EDTA solutions - Electrode area: 1.9 cm²

IV. THE Fe(II)EDTA-NO COMPLEX

IV.1. Cyclic voltammetry of platinum in Fe(II)EDTA NO solutions

Figure IV.1a), b), c), and d) represent the cyclic voltammograms of a platinum electrode (0.64 cm²) in 0.075 Fe(II)EDTA solutions containing respectively:

- 0.011 mole/l of NO
- 0.016 mole/l of NO
- 0.046 mole/l of NO
- 0.070 mole/l of NO

The sweep is started at -0.8 V vs SCE, scanned at 200 mV/s towards positive potentials (1.5 V vs SCE), and reversed at the same sweep rate. The cyclic voltammograms exhibit three distinctive peaks A, A' and B', and an extra wave C appears at more positive potentials. When comparing figures IV.1 and III.4, it is clear that the presence of NO in solution, leading to the formation of Fe(II)EDTA NO complex is responsible for wave C, taking place about 1.0 V vs SCE. An oxidation of either the Fe(II)EDTA NO complex, or of the NO group is occurring; this reaction is strongly irreversible, as no reduction peak can be observed on the reverse sweep. A quantitative analysis of the charge Q_C and peak C demonstrates that Q_C increases with the NO concentration. It is interesting to notice that the charge corresponding to peaks A and A' decreases with increasing NO concentrations. This is easily understandable as the free Fe(II)EDTA in solution is being complexed. The charge under peak B' remains constant, independent on NO concentration, confirming the hypothesis of proton adsorption. The cyclic voltammograms do not exhibit any extra reduction wave related to the reduction of the Fe(II)EDTA NO complex, or of the NO group. In order to check upon any reducibility of the NO-containing complex, a cathode material with a high hydrogen overpotential is required. Therefore, experiments on mercury have been carried out in Fe(II)EDTA.NO solutions.

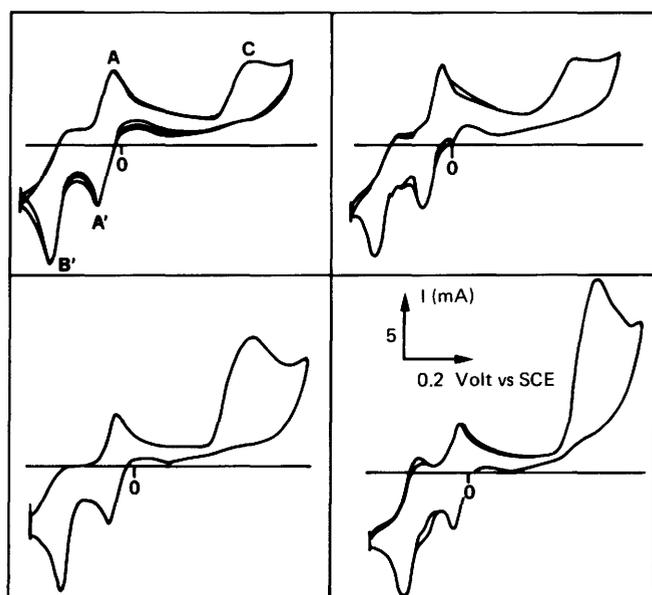


Fig. IV.1. Behaviour of platinum (0.64 cm²) in Fe(II)EDTA.NO solutions $v = 200$ mV/s

IV.2. Cyclic voltammetry of mercury in Fe(II)EDTA.NO solutions

Figures IV.2a), b) and c) give the cyclic voltammograms of an Hg electrode (1.9 cm²) in 0.075 M solutions containing respectively:

- C_{\max} mol/l of NO
- $1/2 C_{\max}$ mol/l of NO
- $1/3 C_{\max}$ mol/l of NO

68

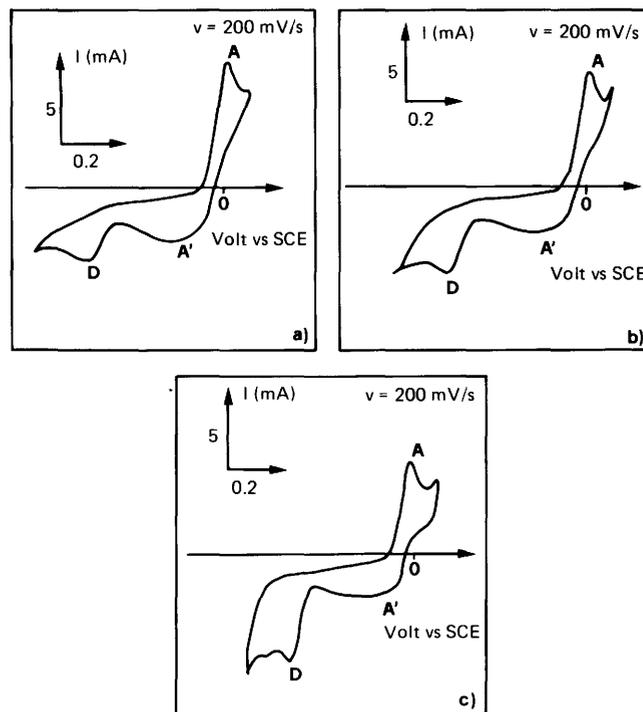


Fig. IV.2. Behaviour of mercury (1.9 cm²) in Fe(II)EDTA.NO solutions

The sweep is started at -1.4 V vs SCE, at 200 mV/s, towards more positive potentials (0.2 V vs SCE), and then reversed. The cyclic voltammograms exhibit the two peaks A and A', characteristic of the redox couple Fe(II)EDTA/Fe(III)EDTA, whereas a new reduction wave D, due to the presence of NO in solution, appears at -0.95 V vs SCE. As on Pt, the charge carried by peaks A and A' decreases with increasing NO concentration; conversely, the charge corresponding to wave D increases with the NO concentration although not proportionally. Table IV.1 summarises these results. It is worth noticing that the reduction corresponding to peak D is totally irreversible, as no oxidation peak can be observed on the forward sweep of the multicycle voltammogram.

Table IV.1 Influence of NO concentration on Q_D

| C_{NO} (mole/l) | Q_D (mC) |
|--------------------------|------------|
| C_{\max} | 5.6 |
| $1/2 C_{\max}$ | 4.9 |
| $1/3 C_{\max}$ | 3.5 |

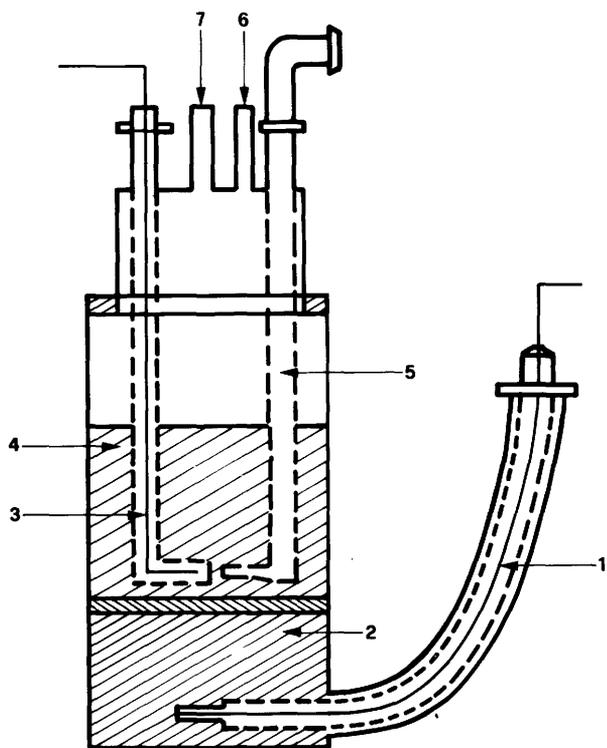
V. PRELIMINARY ELECTROLYSIS OF Fe(II)EDTA.NO SOLUTIONS

V.1 Qualitative results

Some preliminary electrolysis experiments have been carried out at low current density (100 A.m⁻²) in the set up described in figure V.1). The anodic compartment contains a 15 wt% HBr-15 wt% H₂SO₄ mixture, whereas the catholyte is a 0.05M Fe(II)EDTA.NO solution. Hydrogen evolution is occurring and qualitative analysis of the reaction products in the catholyte after electrolysis clearly showed a decrease in the reducible nitrogen concentration (NO), as well as the formation of ammonia NH₃.

Table V.1. Nitrogen balance of electrolysis experiment.

| Sample | Density g/ml | N _{Kjeldahl} mg/l | N _{reducible} mg/l | N _{NH₃} mg/l |
|--|--------------|----------------------------|-----------------------------|----------------------------------|
| A = 0.07M Fe(EDTA) | 1.051 | 1930 | — | — |
| B = 0.03 MFe(EDTA).NO + 0.04M Fe(EDTA) | 1.052 | 1930 | 395 | — |
| C = B after electrolysis | 1051 | 1920 | 310 | 39 |



- 1 1 cm² graphite anode
- 2 Anodic compartment
- 3 1 cm² graphite cathode
- 4 Cathodic compartment
- 5 Reference electrode compartment
- 6 Inlet
- 7 Outlet

Fig. V.1. Electrochemical cell used for electrolysis experiments

V.2. Influence of cesium ions in solution

This experiment has been carried out in the following conditions:

- catholyte: 50 ml of 0.035 M Fe(EDTA).NO + 0.035 M Fe(EDTA) + 0.5 M CsCl (pH = 3)
- anolyte: 35 ml of KBr + HBr (pH = 1.5)
- cathode: 0.64 cm² Pt wire
- anode: 1 cm² Pt flag
- current: 8 mA
- duration of the electrolysis: 4^{1/2} hour.

The charge Q passed during the electrolysis is equal to:

$$Q = 8 \times 4.5 \times 3600 \times 10^{-3} = 129.6 \text{ Coulomb}$$

At the end of the experiment, 1.1 meq of Br₂ have been formed in the 35 ml of anolyte, equivalent to 106.1 Coulomb, which means a current efficiency of 82%.

The results obtained for the cathodic compartment are summarized in Table V.1.

From the results of Table V.1 it can be deduced that the amount of NH₃ formed in 50 ml of catholyte during the experiment is equal to:

$$39 \times 50 \cdot 10^{-3} / 14 = 0.139 \text{ mmol.}$$

NH₃ is formed by a 5 electrons transfer, so that this formation is equivalent to:

$$0.139 \times 5 \times 96.5 = 67.1 \text{ Coulomb}$$

The amount of N₂ formed can be estimated as the difference between the decrease of NO and the formation of NH₃, i.e.:

$$(85 - 39) \times 50 \cdot 10^{-3} / 28 = 0.082 \text{ mmol}$$

this is a 2 electrons transfer, thus equivalent to 15.7 Coulomb. The remainder of the current consumption may be assumed to be used for hydrogen formation. This leads to the tentative product formation pattern presented in Table V.2.

Gas chromatographic gas analysis is necessary to check and complete this preliminary calculation.

Table V.2. Tentative product distribution of Cs-experiment.

| | Coulomb | % |
|---------------------------|---------|-----|
| NH ₃ formation | 67.1 | 52 |
| N ₂ formation | 15.7 | 12 |
| H ₂ formation | 23.3 | 18 |
| Losses | 23.5 | 18 |
| Total | 129.6 | 100 |

VI. SUMMARY AND CONCLUSIONS

VI.1. Formation of the Fe(II)EDTA.NO complex

The formation of the complex was studied by absorbing nitric oxide into a solution of Fe(II)EDTA reagent. At ambient temperature, the complex is made up of molar equivalents of Fe(II)EDTA and NO. This result is in good agreement with the conclusions of other workers [3].

VI.2. Electrochemistry of the FE EDTA complex

Measurements were made using the technique of cyclic voltammetry. Initially, the redox behaviour of the iron EDTA complex was studied on two electrode surfaces, platinum, which has a low H₂ overvoltage and mercury, with a high H₂ overpotential. The results indicate that the Fe(II)EDTA/Fe(III)EDTA couple is a quasi-reversible system. The interesting result from a point of view of a potential process is that the anodic peak current is equal to the cathodic peak current suggesting that the system will behave as a reversible couple.

The cyclic voltammograms recorded for mercury are less well defined than those for platinum, nevertheless, the conclusions are essentially the same. It must be noted that the range of potentials available for the reduction on the complex is larger.

VI.3. Electrochemistry of the Fe(II)EDTA.NO complex

The electrochemistry of the nitrous oxide complex was studied using cyclic voltammetry. No current due to the reduction of the complex was seen on platinum but an irreversible wave due to its oxidation was detected. This was not further investigated, as this process variant is of little interest. On mercury, which offers a wider cathodic overvoltage, a current due to the reduction of the complex was observed. The charge represented by this peak is roughly proportional to the concentration of the complex.

VI.4. Preliminary electrolysis

Some preliminary experiments were carried out. As no large Hg electrode system was available, it was decided to carry out the electrolysis on Pt. In this situation, (at a potential of -0.95 V vs SCE), the reduction of the complex will probably be masked by hydrogen evolution. Nevertheless, a significant amount of ammonia was detected in the product solution. Another experiment was performed to study the effect of metal ions (cesium). The results confirm the presence of a favourable effect. Ammonia was seen to be formed and also a decrease of the amount of nitrous oxide in the complex was observed.

VII. REFERENCES

- [1] D. VAN VELZEN and H. LANGENKAMP
Patent n°86407 (Luxembourg, April 1986)
- [2] D. VAN VELZEN and H. LANGENKAMP
U.K. patent n°7910315 (March 1979)
- [3] W. WEISWEILER, B. RETZLAFF and L. RAIBLE, Chem.
Eng. Process, 18, 85-92(1984)
- [4] J. MASEK and R. PRIBIL
Jr. Inorg. Chim. Acta, 4, 175 (1970).
- [5] SOUTHAMPTON ELECTROCHEMISTRY GROUP.
Instrumental methods in electrochemistry. Ellis Horwood,
Chichester (1985).

3. Water Quality

This activity is dealing with two research lines:

- **Ecological effects of Trace Metals**, with the principal aim to evaluate the effects produced by toxic trace metals (eg. Cu, Cd, Hg) on the development, vitality and composition of freshwater communities.

In the last years a field study on the shallow and eutrophic lake Comabbio near J.R.C. Ispra was performed making use of enclosures «which represent well characterized microecosystems» of controlled chemical composition but quasi-natural physical and biological conditions. Experiments showed that concentrations of the order of 100 ppb of Cu, Hg and Cd change drastically the community structure of phyto- and zooplankton with about 10 ppt of pollutant as ecotoxicological threshold limit. A recent result is that for testing the ecotoxicity of Nickel at relatively low concentrations (50 $\mu\text{g/l}$) the mortality and reproduction rate of **Daphnia Magna** proved to be a useful bioindicator.

In parallel the flow cytometry method was developed, which is expected to become a powerful tool for an objective, efficient and specific assessment of fresh and marine water quality.

(Recent developments and applications are described in the following report on Flow Cytometry).

- **Mass Balance of Trace Metals in a Freshwater Ecosystem**, with the main goal to understand the mechanisms leading to transport, transformation, deposition and remobilisation processes of trace metals and to predict pollution levels of an ecological significance by a mathematic model of a sufficient general character. As a test site the Monvalle bay of Lake Maggiore with three rivers carrying trace metal pollutants has been chosen. Field measurements on the spatial and temporal variability of metal concentration and nutrients in sediments, water and suspended matter are completed by laboratory investigations on metal mass transfer rates for the systems sediment-water and water-suspended matter. The trophic conditions of the test site have been determined for a full yearly cycle. The mathematical model MONVAL describing the time evolution of trace metal concentrations has been validated with the experimental data on trace metal speciation, physico-chemical lake parameters and the phytoplankton biomass. A topical report describes extensively the concepts and methods used in this approach.

3.1. FLOW CYTOMETRY

Introduction

In recent years flow cytometry (FCM) has started to provide a fast and quantitative alternative to conventional techniques (microscopic, colorimetric and turbidimetric) for studying characteristics of single cells. Measurements are carried out on a cell by cell basis at speeds of four to five orders of magnitude faster, than conventional techniques.

This means larger volumes may be studied and statistical significance of results is higher. Also, due to the high speed of analysis, sampling frequency may be increased, once again by orders of magnitude, allowing ecological processes to be studied with so far unknown time resolution. Thus, its application could be a valuable tool for the rapid acquisition of information on water quality parameters, as the composition,

abundance and distribution of algae in a water sample, which can be related directly to the level of inorganic and organic pollution in the sample (bioindicator approach).

During the last six years, a project to investigate optical properties of algae like light scattering and autofluorescence (chlorophyll fluorescence) has been carried out at the JRC-Ispra. This report provides the current status of the application of flow cytometry in water quality research at the J.R.C.

Development of the J.R.C. prototype flow cytometer

The capabilities and the main features of the J.R.C. prototype have been reported in the 1986 PPR. (Report available on request by J.R.C. Ispra).

Its main characteristic is to utilize multi-angle-light-scatter (M.A.L.S.) and fluorescence measurements to distinguish algae species from each other.

Some adaptations to the original system have been made in order to improve the performance of the instrument, and are described in the following sections.

Light scattering

The original photodiode array utilizes detectors having a sensitive area of 1 mm² at sixteen angles in the scattered field. These discrete photodiodes were mounted on a screen as illustrated in Fig. 1. The light scatter measurements made with this set-up were found to be of low intensity and high variation. A probable explanation for the latter effect was seen to be the very small angular acceptance window of the photodiodes. Any light scattered pattern with a high amount of fine structure would give rise to the effect, illustrated in Fig. 2, where any small change in the light scatter distribution such as would occur in the case where the algae measured were slightly different in size, shape or internal structure, or any small difference in the orientation of cells in flow would lead to very different intensities being measured for the diodes marked I, II and III for different members of the same species of alga. That these variations could be reduced by increasing the acceptance window of the detectors may be seen from Fig. 2b.

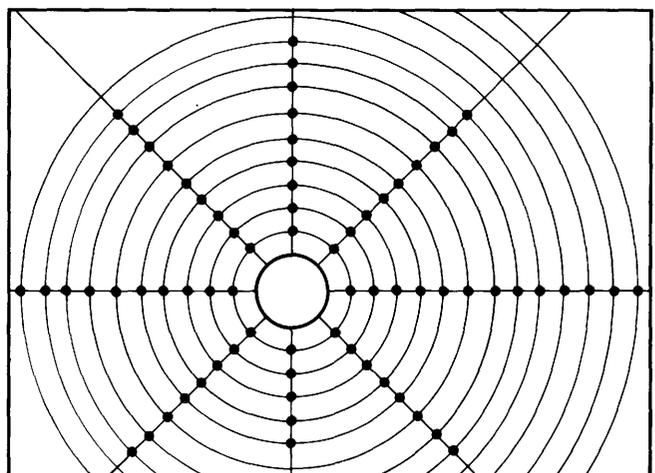


Fig. 1. Original photodiode mounting screen

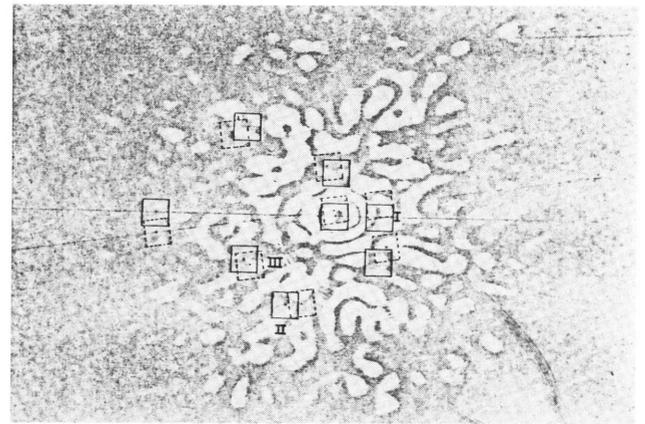
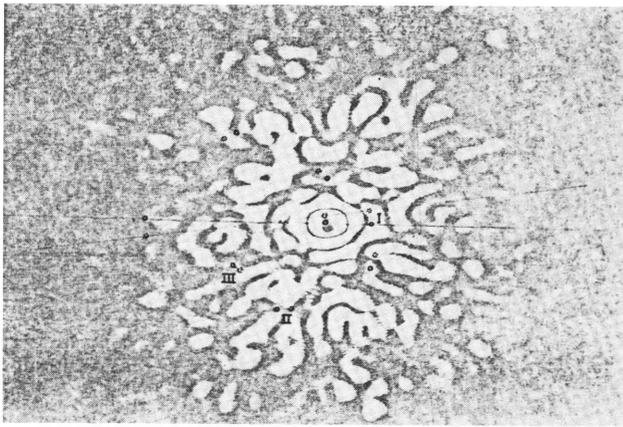


Fig. 2. Effect of cell orientation change on observed FLS intensities
a) Small area photodiodes
b) Large area photodiodes

Since much of the fine detail is not necessary for species distinction, it may be safely averaged out by the spatial intensity integration performed by the larger detectors and such small variations as described above would have a much lesser effect on the measured intensities.

While it would have been possible to increase the angular window of the detectors by moving them closer to the measurement point, this would have had the undesirable effect of moving them to larger polar angles.

Since most of the useful information in the light scatter distributions is contained within the first two diffraction minima, i.e. for 15 μm diameter sphere out to 2.2° , it was decided to use photodiodes having a larger sensitive area to achieve the desired reduction in variation.

Results obtained with *Selenastrum capricornutum* seem to confirm that the increase in intensity and reduction in coefficient of variation have been attained.

Fluorescence

For the purposes of flow cytometry we want to study the phytoplankton in vivo, thus since the accessory pigments transfer any absorbed energy to chlorophyll-a with a very high efficiency (close to 100%) the majority of phytoplankton emit fluorescence energy exclusively in the emission band of chlorophyll-a. The exceptions to this rule are the cyanobacteria, in which fluorescent emission by the phycobilins can be detected.

Discrimination between the major taxa of algae can be achieved by varying the excitation wavelength and observing the intensity of chlorophyll-a fluorescence emission, thereby identifying the major pigments present (Table I).

The addition of two photomultiplier tubes has allowed measurement of the intensity of fluorescent emission by the algae. This emission is collected at right-angles to the direction of propagation of the laser beam (polar angle 70° - 100°). It passes through

TABLE I: Excitation wavelength of argon laser and relative fluorescence emission of major phytoplankton pigments. †: positive fluorescence; =: no detectable fluorescence.

| Phytoplankton group/pigment | Argon laser lines | | | Fluorescence emission | | |
|-----------------------------|-------------------|-----------|-----|-----------------------|-----------|-----|
| | 457 | nm 488 | 514 | 530 | nm 590 | 680 |
| Cyanobacteria/phyco-bilius | • | • | • | = | = | = |
| | | | | = | † | = |
| | | | | = | † | = |
| Cryptomonas/phyco-bilius | • | • | • | = | † | † |
| | | | | = | † | † |
| | | | | = | † | † |
| Greens/chlorophyll-a | • | • | • | = | = | † |
| | | | | = | = | † |
| | | | | = | = | = |
| Diatoms/fucoxanthia | • | • | • | = | = | † |
| | | | | = | = | † |
| | | | | = | = | † |
| Dinoflagellates/peridinium | • | • | • | = | = | † |
| | | | | = | = | † |
| | | | | = | = | † |

a window in the flow chamber and is subsequently focussed by a lens onto the sensitive area of a photomultiplier tube. Scattered laser radiation is blocked by optical filters which are chosen to pass light in two wavebands: 550-600 nm to detect fluorescent emission by the phycobilins; 650-750 nm to detect fluorescent emission by chlorophyll-a.

The instrument is set up as in Fig. 3 with the photodiode array arranged as in Fig. 4.

The laser is operated at 100 mW with the EHT on both PMT's set at 700 V. Measurements are routinely made of fluorescence in two wavebands and of light scatter at 14 angles in the forward direction. Laser excitation is at 488 nm.

Triggering of a measurement is done by thresholding on chlorophyll-a fluorescence intensity in order to measure only on live cells. At least 5,000 measurements are made per sample.

Construction of a new flow cytometer (modular version)

(In collaboration with the Biophysics Research Group, University of Strathclyde)

This novel instrument differs from commercial ones in three main aspects:

- i It is specifically **designed for phytoplankton** analysis. Existing commercial instruments are constructed for biomedical applications and are not optimized for the wider range of optical and mechanical particle characteristics that may be encountered in natural water samples.
- ii It is designed to be **portable** so that it can be operated in mobile laboratories, or on board of a ship. Conventional laser-based cytometers are transportable only with difficulty and make considerable demands on their operating environment, including requirements for 3-phase power, cooling water, and compressed gas supplies.
- iii It is **modular** in the design of its optical and electronic subsystems, so that future developments in a rapidly expanding field of research can be easily incorporated. In particular, the design allows for the installation of more data acquisition channels than are available in any commercially available cytometer.

Basic configuration

The instrument is required to handle algal cells in the size range 1-200 microns. These particles are to be entrained in a fluid stream and presented to a focused illuminating beam of high intensity which will excite fluorescence from any photopigments that are present. The optical characteristics of the particles will be monitored by three photosensors, one measuring forward light scatter and the other two measuring fluorescence at two different wavelengths characteristic of the emission from the pigments phycoerythrin and chlorophyll-a. The analogue electrical pulses from the photosensors will be digitised and stored in a microcomputer for display and further analysis. The basic instrument configuration is illustrated in Fig. 5.

The excitation of chlorophyll and phycoerythrin fluorescence from microalgae is best achieved by stimulating the cells with intense illumination in the 400-500 nm region. In existing biomedical instruments this illumination is provided by either a water-cooled argon-ion laser or a mercury arc-lamp. Both sources have their disadvantages: the water-cooled laser is non-portable and expensive to purchase and maintain, while the arc-lamp is non-coherent and therefore does not provide a well-defined pattern of forward light scatter. As a compromise solution, we have taken advantage of recent advances in laser manufacturing technology and will use an air-cooled argon-ion laser manufactured by Cathodeon Ltd. Though less powerful than a water-cooled laser, this device is rated at 100 mW (all lines) and will deliver illuminating power densities to the sample particles well in excess of those achieved by the customary 100 W arc-lamp. The Cathodeon laser is comparatively portable and its plasma tube is user replaceable.

The distinguishing feature of flow cytometry as an analytical technique is the flow chamber, in which a particle-bearing core fluid is injected coaxially into a clean sheath fluid, and the two streams both passed through a constricting orifice. Conventional flow systems of the «stream in air» type present a cylindrical liquid surface to the laser beam.

This causes problems in shielding the photodetectors from the resulting annular diffraction pattern, and also introduces geometrical distortion into the scattered light pattern. It is possible to avoid these problems by using a square optical cell to

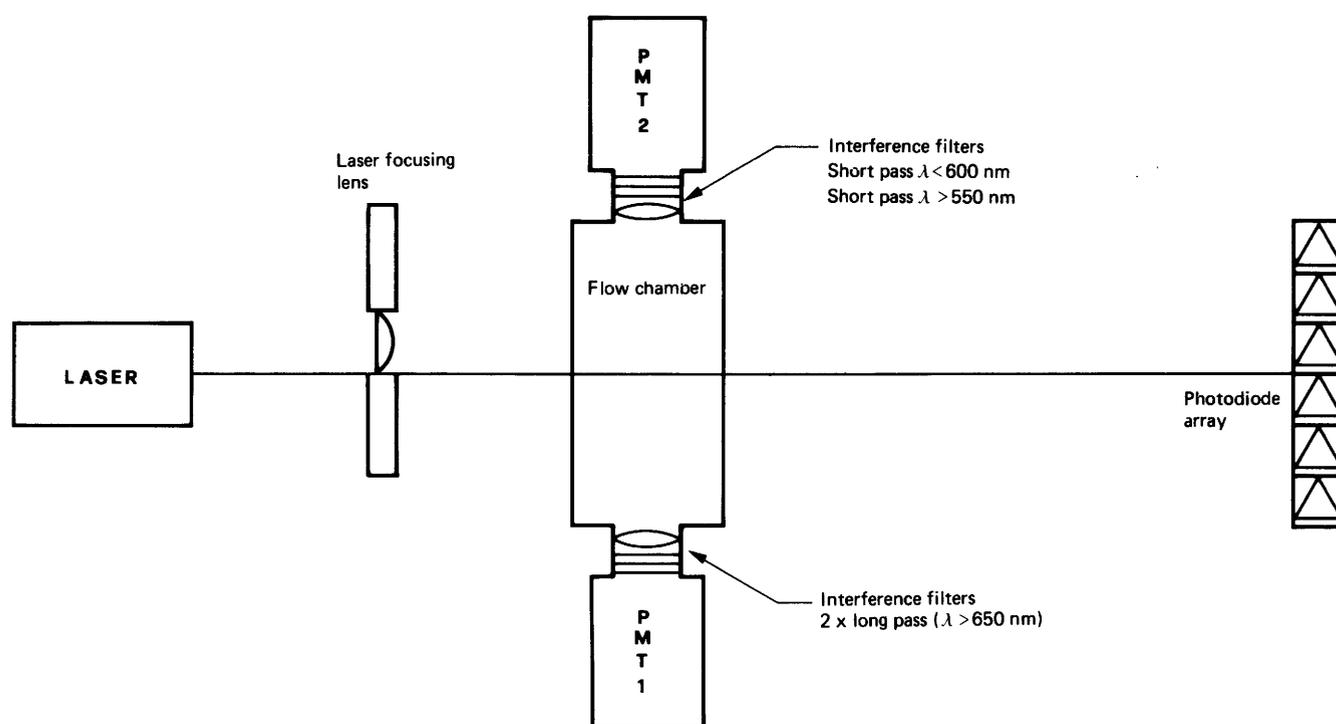


Fig. 3. Schematic of JRC flow cytometer configuration

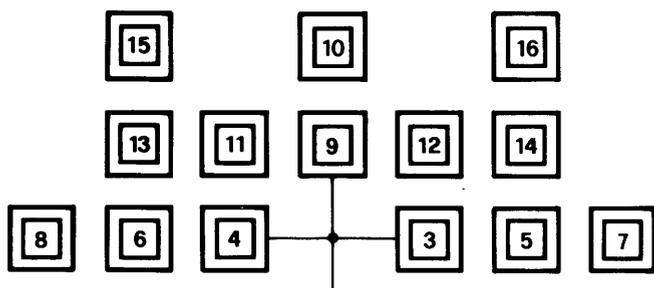


Fig. 4. Layout of photodiode array, showing channel number for data acquisition

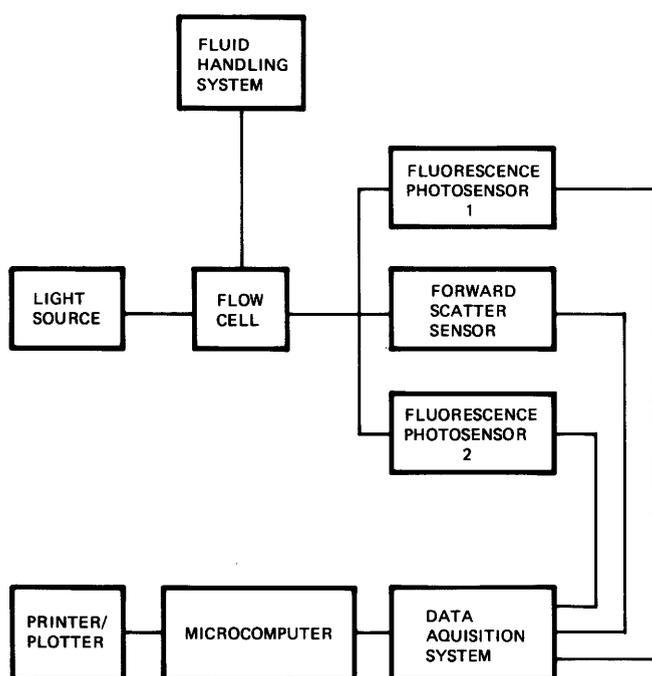


Fig. 5. Instrument configuration

enclose the particle-bearing stream in the sensing zone, but this in turn requires the introduction of a second sheath stream for optical matching purposes. The resulting flow cell layout is shown schematically in Fig. 6.

A second factor that has to be taken into account in ecological flow cytometry is the liability of the system to blockage by debris or clumps of algal cells. In commercial biomedical instruments, this problem is circumvented to a large extent by introducing a filter (typically of 100 microns pore size) into the sample injection line. Such severe prefiltration is obviously undesirable in phytoplankton analysis where the existence of larger particles may be of considerable scientific interest. Consequently, it is necessary to design a flow cell that will produce the required accuracy of hydrodynamic focusing without using the small orifice and injection pipe diameters that occur in commercial instruments. The penalty that must be paid for implementing such a wide-tube design is that the operating pressures in the flow system are much reduced, and the flow rates obtained become sensitive to the gravitational heads associated with the liquid levels in the fluid reservoirs. Nevertheless, we believe that this inconvenience is more than compensated for by the possibility of handling a wide range of particle sizes without having to change flow system components.

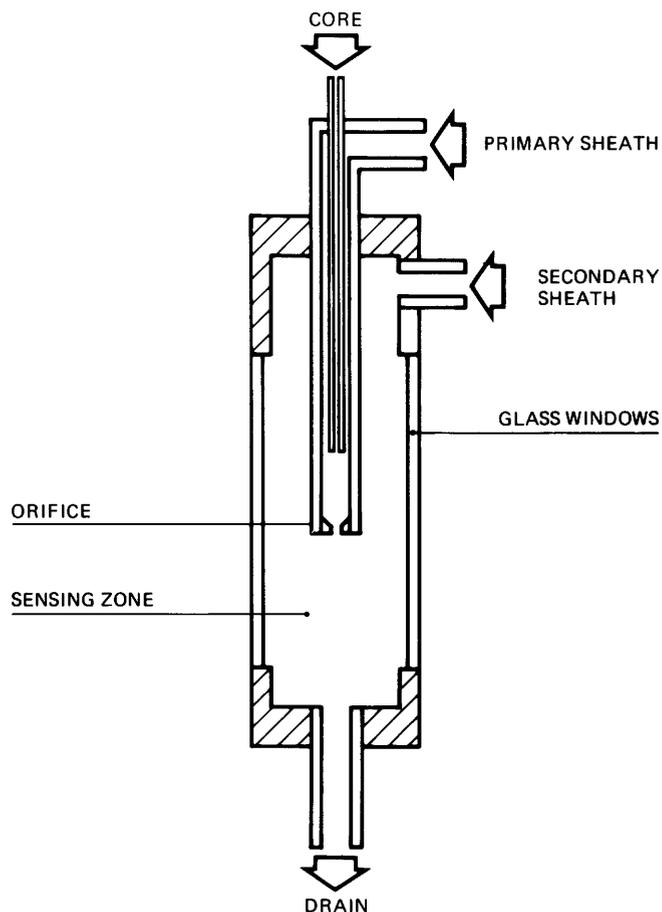


Fig. 6. Flow cell design

Computer and data acquisition system

Although the basic configuration of the cytometer requires only 3 data acquisition channels, it is important that this number should be easily expandable. The application of flow cytometry to water quality monitoring is likely to depend on the simultaneous measurement of as many particle optical characteristics as possible. Furthermore, it is intended that the basic instrument should be capable of accepting the multi-element scattered light detector array.

Consequently, a data acquisition system of a modular nature has been designed with the following features:

- i) an interface and control card which connects to the microcomputer expansion bus. This will handle address decoding, handshake routines and signal buffering and will accept inputs from the following modules;
- ii) analogue input modules, each with 8 channels of differential amplifiers with gain and bandwidth control, 8 sample and hold amplifiers; and 8 channel fast analogue to digital converter and 16 k of static RAM to allow at least 1,000 readings for each channel to be stored in the module;
- iii) event counting modules, each with up to six channels of input.

The system will accept up to 4 modules, and will be supplied initially with 2 analog modules and 1 counter module installed. Data will be logged on an R M Nimbus microcomputer, which combines small physical size with built in disk drivers, large random access memory (1 megabyte) and excellent graphics facilities. Hard copy output of tabulated data on graphs will be provided by dot-matrix printer.

Performances

Two series of experiments have been carried out to demonstrate the high degree of resolution that FCM is capable of. The first was on two very similar types of latex spheres and the second was on two similar types of marine algae.

In both experiments the FCM measured three parameters:

- Forward Angle Light Scatter (F.A.L.S.) at one angle (2.5 degrees in the forward direction)
- Green Fluorescence (GF)
- Red Fluorescence (RF)

The results of the experiments are displayed in two different ways: histograms and scatter plots. **Histograms** display intensity (arbitrary units) of measured parameters along the x-axis and number of events along the y-axis. **Scatter plots** show up any clustering of events in a two parameter «space» defined by the operator. In these the x- and y-axes are intensity of measured parameter. It is also possible to define areas on the scatter plots within which the number of events may be counted.

1. Latex experiments

Two batches of Coulter calibration latex spheres, of nominal size 10 μm and dyed with the same fluorescent dye, have been analysed. In fact there was a slight difference in the size specifications of these two types of latex sphere: type 1 (T1) were quoted as 9.83 μm and type 2 (T2) as 10.56 μm .

Analyses of 1024 events of T1 are presented in Fig. 7. The calibration run for T1 shows 954 single particle events in a tight cluster (Fig. 7b) and 19 double events in a cluster. Doublet events are caused by two latex spheres which are stuck together. These events show up best on a scatter plot of red fluorescence vs green fluorescence (Fig. 7c). The remaining 51 events out of the total of 1024 which are not accounted for in the clusters were due to misaligned particles.

The calibration run for T2 (Fig. 8) shows 987 single particle events in a tight cluster (Fig. 8b) and 14 doublet events in a cluster (Fig. 8c). The remaining 23 events out of the 1024 were misaligned particles.

The analyses of a mixture of T1 and T2 (Fig. 9) show complete discrimination of the two types of particles. The discrimination is achieved on the basis of FALS as can be seen in Fig. 9a where the light scatter distributions are completely separate. The cluster in Fig. 9b shows 407 events due to T1, the cluster in Fig. 9c shows 519 events due to T2 and the cluster in Fig. 9d shows 51 events due to doublets (of both T1 and T2). The other 47 events out of the 1024 events were misaligned particles. It is obvious that as the FCM can distinguish those particles which are very similar, then different algae should be easily discriminated.

2. Algae experiments

Two species of fairly similar marine algae have been analysed. These were *Dunaliella primolecta*, a green alga of dimensions 5-10 μm and *Pavlova lutheri* another green alga of dimensions 3-7 μm . These algae did not display any significant amount of green fluorescence. The calibration results for *Dunaliella* are presented in Fig. 10. The scatter plot (Fig. 10b) shows 998 events out of the 1024 in the count box. The calibration results for *Pavlova* are summarized in Fig. 11. The scatter plot (Fig. 11b) shows 1009 events out of 1024 in the count box.

Fig. 12 reports analyses of the mixture *Dunaliella* and *Pavlova*. Fig. 12a shows the histogram plots and it is easy to see that the two species of algae are completely discriminated on the basis of red fluorescence (dotted lines). Fig. 12b shows there were 554 out of 1024 events due to *Pavlova* in the mixture and Fig. 12c shows 464 out of 1024 events due to *Dunaliella*.

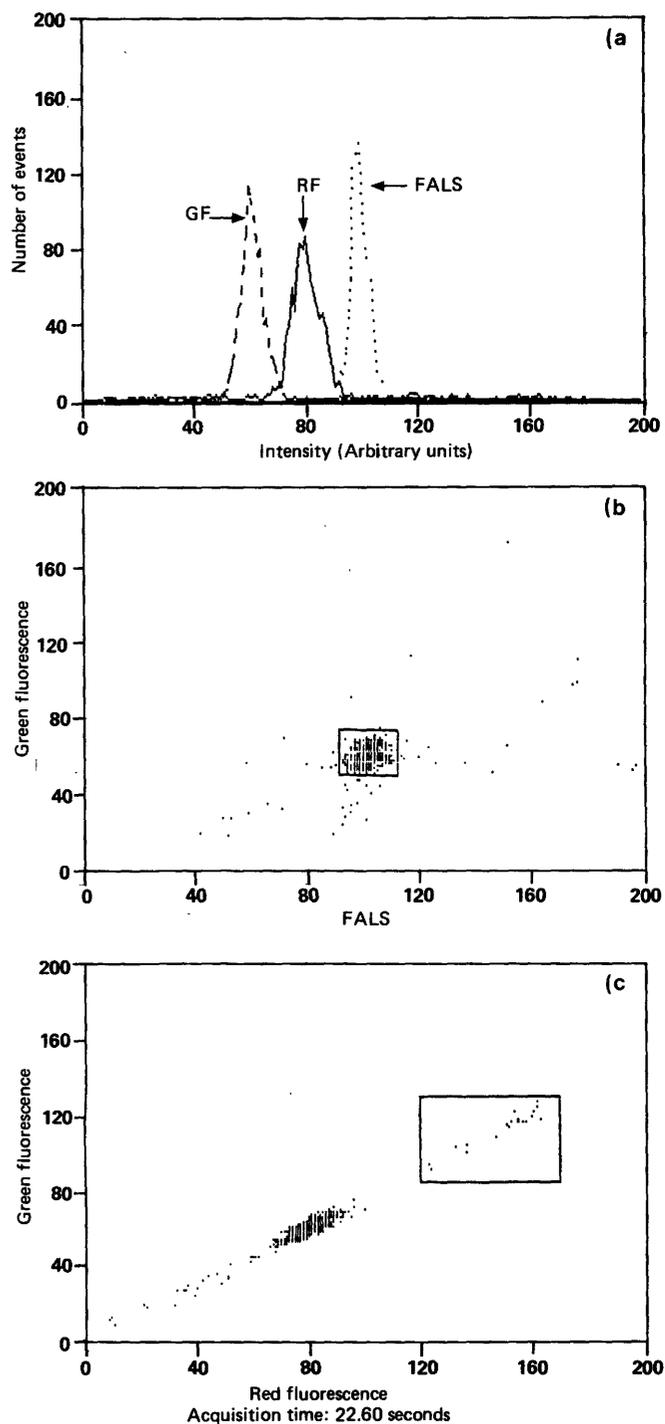


Fig. 7. Calibration data for latex spheres (9.83 μm).

- histograms;
- scatterplot counts in bounds: 954;
- scatterplot counts: 19

Note that this leaves only 6 out of 1024 events unclassified in the analysis of the mixture. Hence, these two similar algae are easily discriminated.

Results from these experiments clearly demonstrate the high degree of resolution the FCM is capable of.

Application in ecotoxicological research

These results represent to our knowledge the first cytometric analysis of freshwater algae populations in bioassays, carried out in Europe.

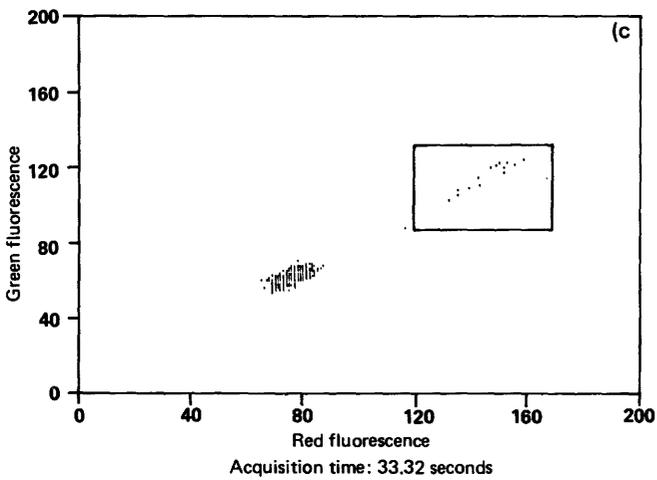
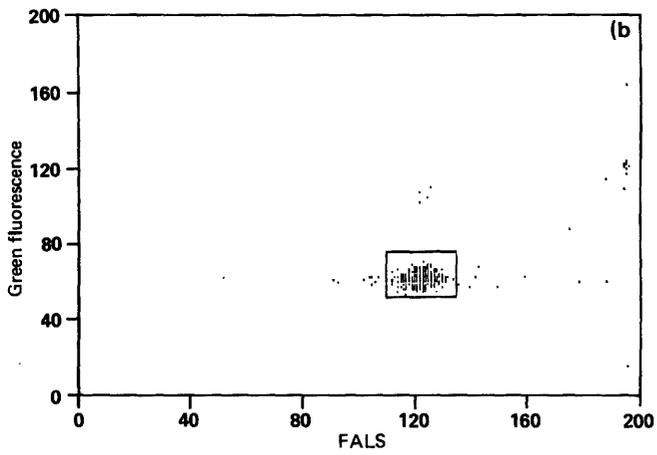
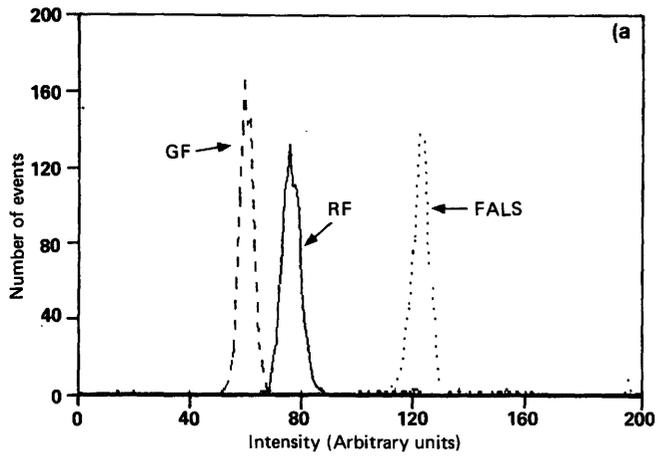


Fig. 8. Calibration data for latex spheres ($10.56 \mu\text{m}$).
 a) histograms;
 b) scatterplot counts in bounds: 987;
 c) scatterplot counts: 14.

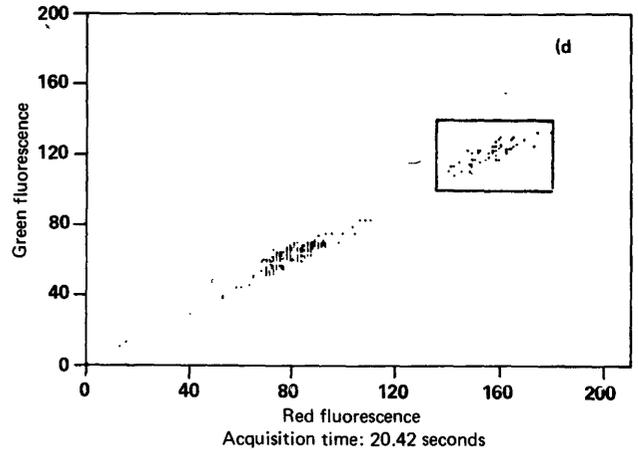
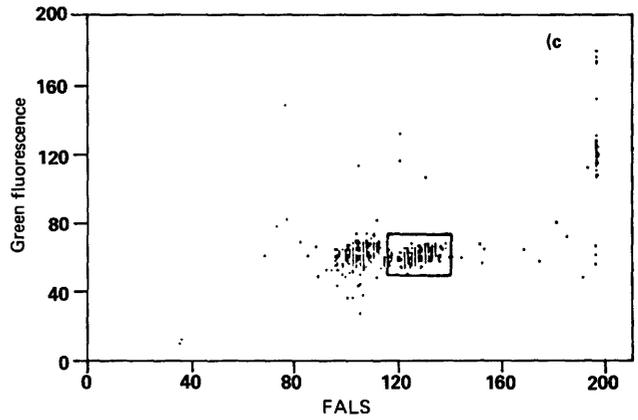
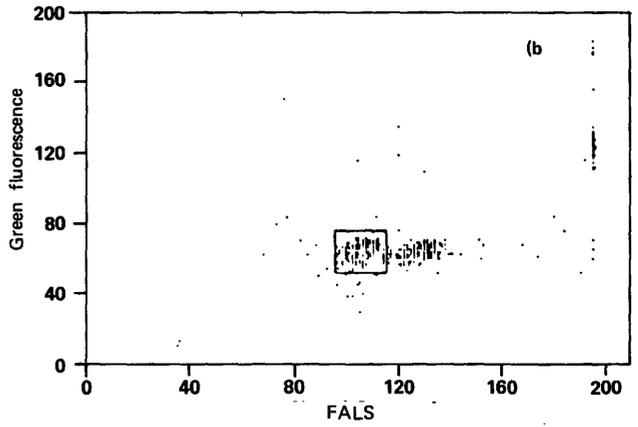
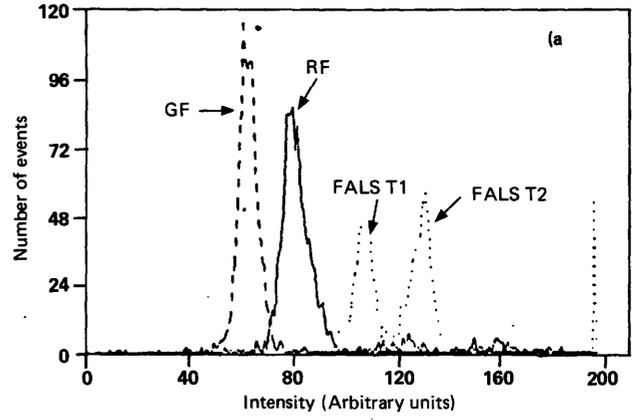


Fig. 9. Calibration data for the mixture of two latex spheres.
 a) histograms;
 b) cluster of $T1 = 407$
 c) cluster of $T2 = 519$
 d) cluster of both $T1$ and $T2 = 51$

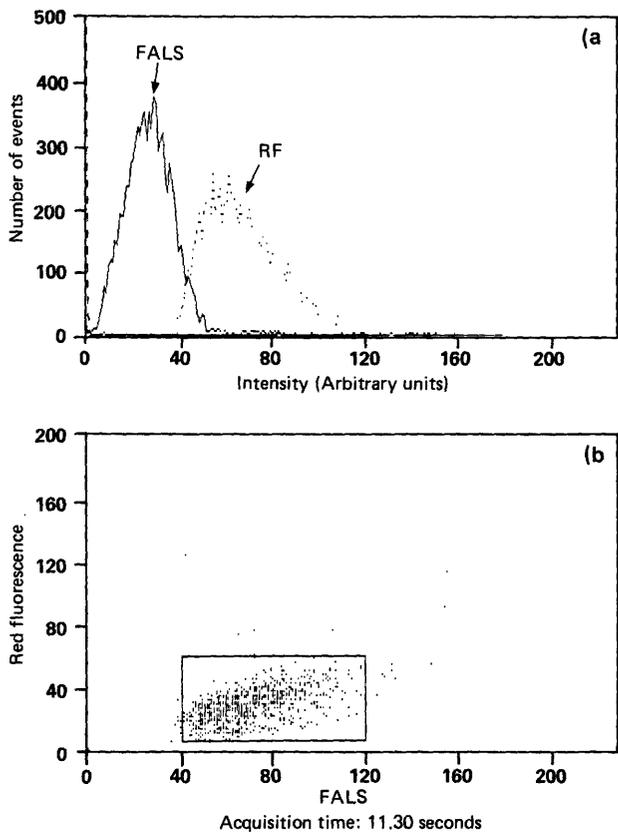


Fig. 10. Calibration data for *Dunaliella primolecta*.
 a) histograms;
 b) scatterplot counts in bounds: 998

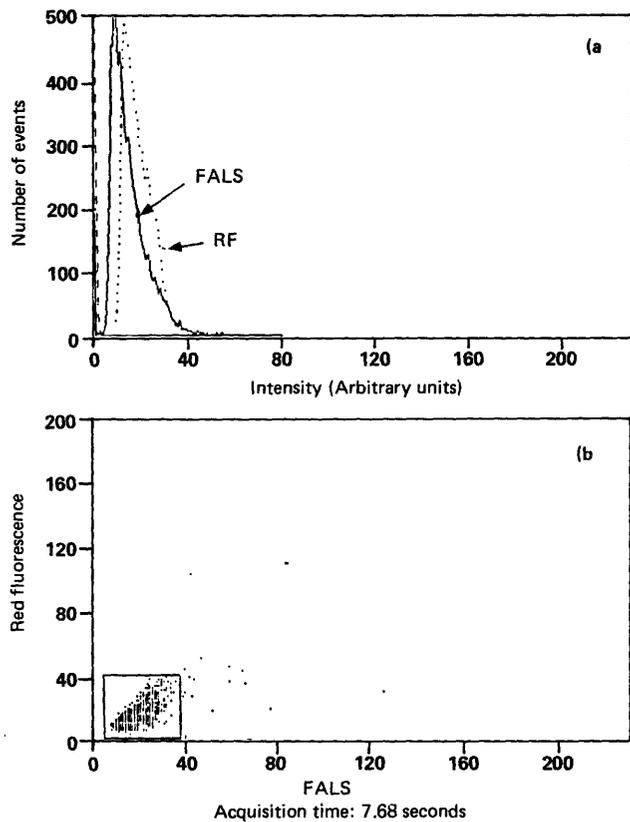


Fig. 11. Calibration data for *Pavlova lutheri*.
 a) histograms;
 b) scatterplot counts in bounds: 1009

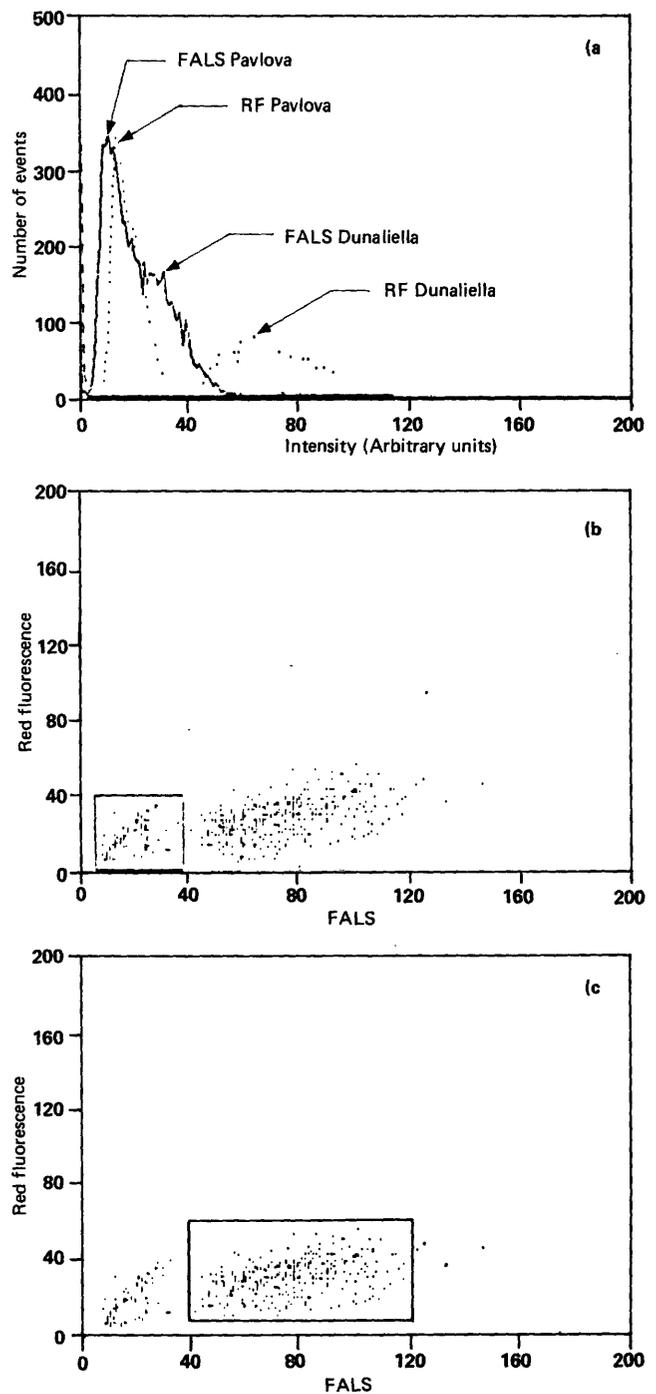


Fig. 12. Calibration results for a mixture of *Dunaliella* and *Pavlova*.
 a) histograms;
 b) cluster due to *Pavlova* = 554;
 c) cluster of *Dunaliella* = 464.

1. Trace metal experiments

The outline of the experiments to investigate the effects of environmental levels of trace metals (e.g. copper and cadmium) were reported in the 1986 PPR. These metals were chosen because of their well-known algistatic/algicidal properties, aiming to compare the responses of algae evaluated by traditional methods (i.e. Coulter or microscopic measurements). After devising a rigorous experimental protocol for routine operation of the flow cytometer that makes use of measurements on fluorescent microspheres between each run, to ensure that the alignment does not alter significantly during the time of an experiment (15 days), distributions of chlorophyll autofluorescence intensity from algae were obtained.

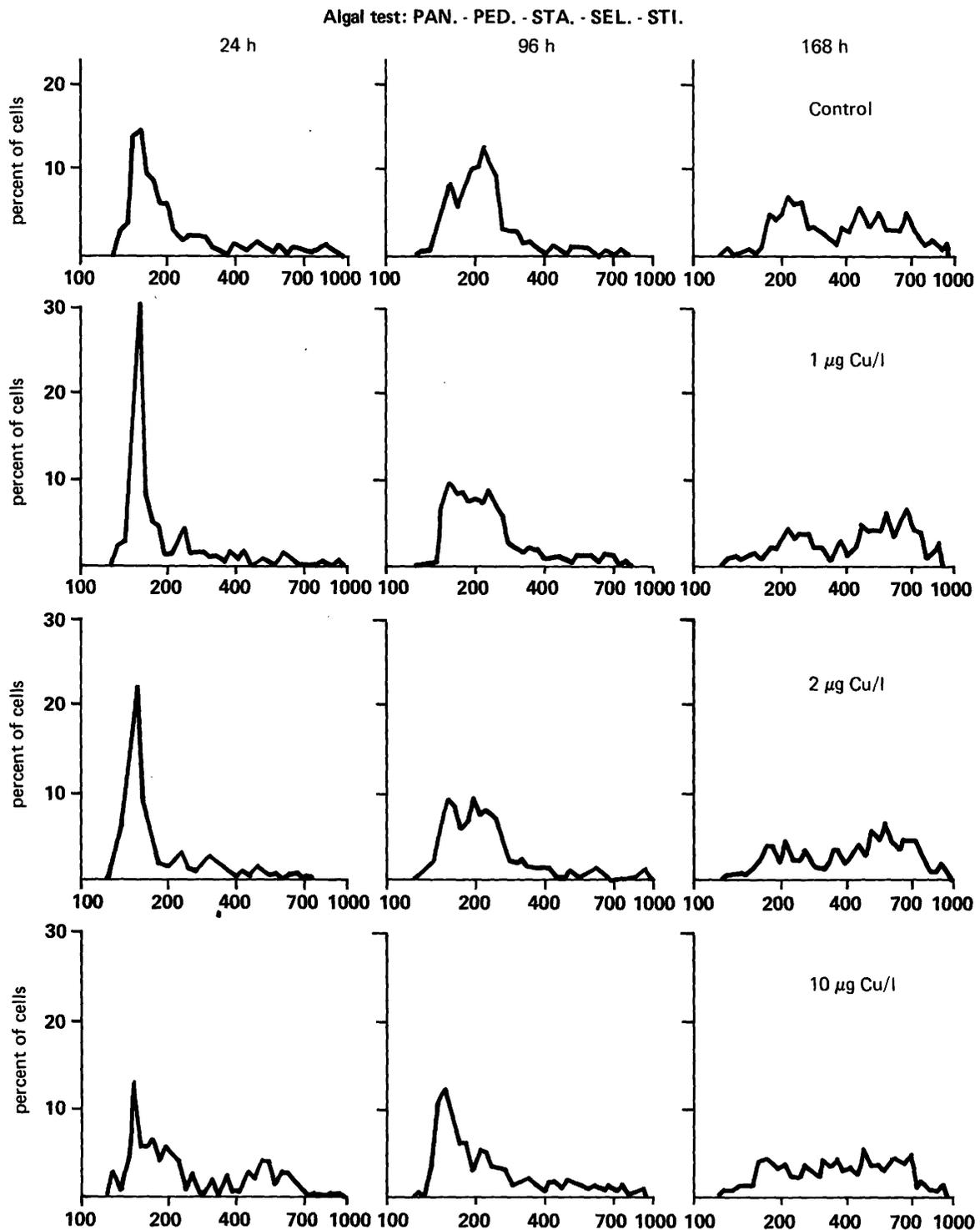


Fig. 13. Log red fluorescence intensity distributions (a.u.) ($\lambda > 650$ nm).

Measurements were made on monospecific algae populations consisting of *Pandorina morum*, *Pediastrum duplex*, *Selenastrum capricornutum*, *Staurastrum cingulum*, and *Stichococcus bacillaris*, and on mixed populations of all 5 species.

Example of the type of information produced are presented in Fig. 13. Interpretation of the data from the mixed sample is virtually impossible due to the spread and the irregularity of the distributions. The only species to show a characteristic intensity of chlorophyll autofluorescence was *Stichococcus* (Fig. 14), and the only effect evident from the mixed species data is that while there are a considerable number of events in this region early in the experiment, these seem to disappear after 7 days. This probably due to the disappearance of *Stichococcus* from

the mixed population.

The only distributions which were distinct enough to provide quantitative information through simple statistics were those of *Selenastrum* and *Stichococcus* (Table II) but no obvious trends were noted from these data which could be related to possible effects of either copper or cadmium.

However, an extra information provided by the fluorescence distributions, which was previously unattainable, was an estimate of the proportion of dead and damaged cells in a sample. This was utilised to modify the mortality rate induced by the toxicants as estimated using the EC 50, i.e. the concentration of metal required to reduce an algae population to 50% of the control. From Coulter measurements, the EC 50 was estimated at 96 hours after inoculation. Since the Coulter Counter cannot

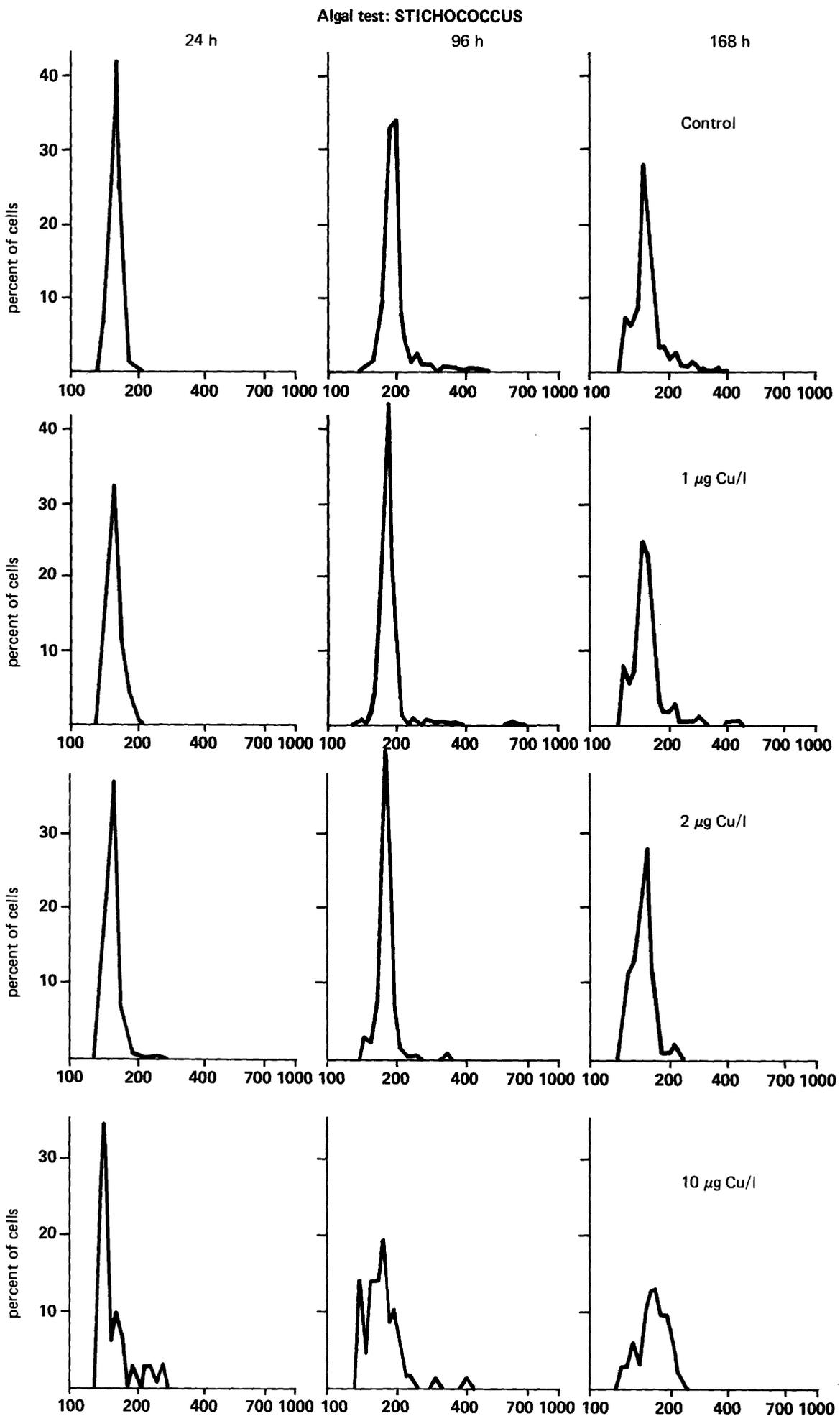


Fig. 14. Log red fluorescence intensity distributions (a.u.) ($\lambda > 650$ nm).

TABLE II: Statistic for copper/cadmium experiment (*Selenastrum* and *Stychooccus*)

| Species treated | | | Selenastrum | | Stychooccus | |
|------------------|--------|--------------------|-------------|----------------|-------------|----------------|
| | | | \bar{x} | S ¹ | \bar{x} | S ¹ |
| COPPER | Day 1 | Control | 557.28 | 16401 | 379.33 | 2428 |
| | | 1 $\mu\text{g/l}$ | 517.44 | 16065 | 384.28 | 4002 |
| | | 2 $\mu\text{g/l}$ | 537.38 | 18977 | 378.46 | 3415 |
| | | 10 $\mu\text{g/l}$ | 578.75 | 19600 | 325 | |
| COPPER | Day 2 | Control | 628.78 | 21326 | 432.49 | 5144 |
| | | 1 $\mu\text{g/l}$ | 611.47 | 18633 | 419.12 | 3675 |
| | | 2 $\mu\text{g/l}$ | 630.84 | 19960 | 406.23 | 2389 |
| | | 10 $\mu\text{g/l}$ | 595.81 | 16266 | | |
| COPPER | Day 4 | Control | 699.05 | 14989 | 507.00 | 2279 |
| | | 1 $\mu\text{g/l}$ | 625.90 | 10010 | 494.70 | 1873 |
| | | 2 $\mu\text{g/l}$ | 608.00 | 7831 | 497.12 | 1476 |
| | | 10 $\mu\text{g/l}$ | 661.92 | 19046 | 475 | |
| COPPER | Day 7 | Control | 686.46 | 23200 | 424.49 | 5632 |
| | | 1 $\mu\text{g/l}$ | 646.36 | 14515 | 431.42 | 5520 |
| | | 2 $\mu\text{g/l}$ | 655.24 | 17524 | 433.84 | 6005 |
| | | 10 $\mu\text{g/l}$ | 616.54 | 7081 | | |
| COPPER | Day 9 | Control | 543.82 | 7872 | 446.88 | 4230 |
| | | 1 $\mu\text{g/l}$ | 575.79 | 9676 | 454.10 | 3763 |
| | | 2 $\mu\text{g/l}$ | 562.28 | 9419 | 441.02 | 5256 |
| | | 10 $\mu\text{g/l}$ | 534.37 | 4181 | 373.32 | 3938 |
| COPPER | Day 10 | Control | | | | |
| | | 1 $\mu\text{g/l}$ | | | | |
| | | 2 $\mu\text{g/l}$ | | | | |
| | | 10 $\mu\text{g/l}$ | | | | |
| CADMIUM | Day 1 | Control | 1269.03 | 57593 | 972.33 | 8380 |
| | | 1 $\mu\text{g/l}$ | 1281.44 | 25875 | 972.06 | 8463 |
| | | 2 $\mu\text{g/l}$ | 1287.44 | 45011 | 980.14 | 7079 |
| | | 10 $\mu\text{g/l}$ | 1182.69 | 18254 | 985.30 | 9038 |
| CADMIUM | Day 4 | Control | 1149.35 | 28427 | 928.3 | 10687 |
| | | 1 $\mu\text{g/l}$ | 1143.32 | 27682 | 928.38 | 7001 |
| | | 2 $\mu\text{g/l}$ | 1129.97 | 26472 | 947.29 | 8464 |
| | | 10 $\mu\text{g/l}$ | 1118.32 | 18613 | 926.60 | 9071 |
| CADMIUM | Day 7 | Control | 1205.57 | 17246 | 1030.71 | 12849 |
| | | 1 $\mu\text{g/l}$ | 1246.74 | 11991 | 943.40 | 9898 |
| | | 2 $\mu\text{g/l}$ | 1283.98 | 13254 | 960.89 | 6181 |
| | | 10 $\mu\text{g/l}$ | 1212.04 | 18703 | 851.71 | 8204 |
| COPPER + CADMIUM | Day 7 | Control | 1303.79 | 19740 | 951.54 | 7585 |
| | | 1 $\mu\text{g/l}$ | 1264.95 | 20698 | 970.87 | 8770 |
| | | 2 $\mu\text{g/l}$ | 1244.76 | 19249 | 989.26 | 7545 |
| | | 10 $\mu\text{g/l}$ | 1160.84 | 19672 | 976.02 | 13763 |
| COPPER + CADMIUM | Day 4 | Control | | | | |
| | | 1 $\mu\text{g/l}$ | | | | |
| | | 2 $\mu\text{g/l}$ | | | | |
| | | 10 $\mu\text{g/l}$ | | | | |
| COPPER + CADMIUM | Day 7 | Control | 1227.42 | 13019 | 932.85 | 8843 |
| | | 1 $\mu\text{g/l}$ | 1157.86 | 14768 | 937.13 | 7091 |
| | | 2 $\mu\text{g/l}$ | 1168.37 | 16270 | 1008.98 | 8430 |
| | | 10 $\mu\text{g/l}$ | 1127.07 | 18164 | 988.42 | 28622 |

distinguish healthy cells from dead or unhealthy cells, this calculation probably overestimates the quantity of metal required to have the described effect. The fluorescence distributions were used to estimate the proportion of healthy cells in each sample and hence to modify the values of EC 50 obtained at 96 hours. Considering Fig. 15, it is clear that the fluorescence distribution is made up of several fractions. The low intensity fraction (peak at ~0.02 units) is at the level of the electronic noise, and is due to events caused by non fluorescent particles. There are also a number of events distributed at very low fluorescence intensities (below about 0.15 units). It may reasonably be argued that these are due to signals from dead algae. While it is true that dead algae no longer photosynthesise, it is probable that intracellular chlorophyll remains for a time. Since death in algae precludes the possibility of efficient photosynthesis, the light collected by the intact pigments in the light harvesting system of the algae will not be passed to chlorophyll via energy transfer between pigments as in photosynthesis, and any absorption will be done by the chlorophyll itself. Since absorption is decreasing, also chlorophyll emission will decrease but as long as the cell walls and the chlorophyll molecules remain intact, low intensity chlorophyll emission will be observed. This hypothesis cannot be tested without a cell-sorting capability, but it may prove possible to check for low intensity fluorescence emission by dead or dying cells under an epifluorescence microscope and may even be possible to estimate the proportion of such weakly fluorescent cells in a sample. The events at high intensities (2.0 units and above) are probably coincident events. The main part of the distribution illustrated is comprising healthy cells. Thus the modified values of EC 50 after 96 hours were estimated as follows.

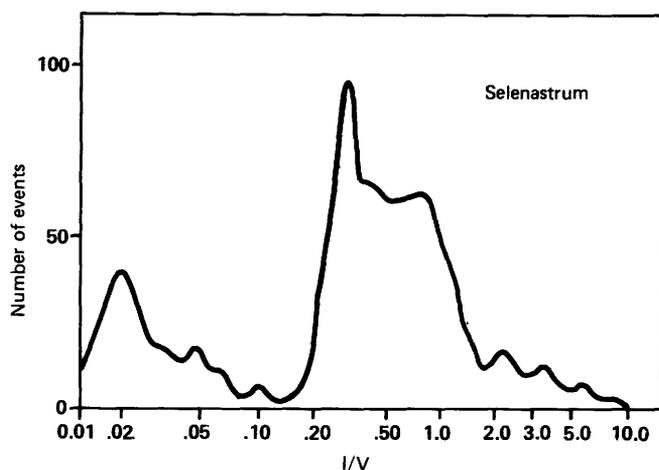


Fig. 15. Output intensity distribution for PMT1 (laser power = 350 mW, $\lambda > 650$ nm).

The low intensity region of the distribution was assumed to be composed of dead cells, unhealthy cells and other particles. The number of so-called «other particles» was estimated by counting the number of triggers obtained from light scatter in a measured volume of the liquid culture medium in which the cells were grown. Thus, the number of triggers obtained due to «other particles» was subtracted from the sample and the proportion of dead/damaged cells was estimated from the remainder of the fluorescence distribution.

These results are presented in Table III.

If should be mentioned that these represent only a rough estimate and that the difference in EC 50 values obtained for *Pandorina* are not significant, while considerable differences are noted for *Staurastrum* and *Pediastrum*.

2. NTA Experiment

This experiment was designed to investigate the effect of NTA (nitrotriacetic acid) on a mixed population of green and blue-green algae. It is based on a previous work in which it was observed that NTA may induce shifts in such populations. Analyses on these data do not allow any conclusions to be drawn on eventual ecological effects, however they do provide some information on the instrument performance.

Previously, to attain a reasonable discrimination percentage for *Oscillatoria* it had been necessary to utilise combinations of detectors and even discriminate function analysis. This was somewhat surprising, since from the static scattering photographs it was clear that almost 100% discrimination should have been possible using a single photodiode. In fact, as shown in Fig. 16, 95% discrimination of *Oscillatoria* from *Pandorina* was achieved in this experiment using only a single photodiode. In previous experiments it had also proved difficult to distinguish *Oscillatoria* (a blue-green alga) from green algae via its orange autofluorescence: in this case 90% classification of *Oscillatoria* from *Pandorina* was attained in this manner (Fig. 17).

Utilising these parameters it should therefore be possible to distinguish *Oscillatoria* from the other species with at least the 95% success attainable via light scatter on a single photodiode. This will allow us to deduce the proportion of a mixed population made up of *Oscillatoria* filaments. There is, however, a limitation to the instrument in its current state as the measurements on *Oscillatoria* do not allow as estimation of the biovolume.

Development of data analysis method

In order to exploit fully the ability of the FCM technique, it is felt necessary to develop sophisticated data analysis techniques, i.e. cluster analysis, pattern recognition of Fraunhofer diffraction patterns.

As a first approach a photographic library of light scatter pattern has been built up for all phytoplankton species cultured in our laboratory.

TABLE III: Values of EC 50 after 96 hours of exposure to test concentrations of copper, cadmium and a mixture of two

| | Copper | | Cadmium | | Copper + Cadmium | |
|---------------------|--------|--------|---------|--------|------------------|--------|
| | C.C. | L.F.C. | C.C. | L.F.C. | C.C. | L.F.C. |
| <i>Pandorina</i> | 1.5 | 1.3 | 6.2 | 6.3 | 4.6 | 4.5 |
| <i>Stichococcus</i> | 4.3 | 1.6 | 20.9 | 15.3 | 7.7 | 7.2 |
| <i>Selenastrum</i> | 1.9 | 1.9 | 19.0 | 10.8 | 4.6 | 4.3 |
| <i>Staurastrum</i> | 53 | 8.8 | 18.5 | 1.8 | 7.8 | 3.5 |
| <i>Pediastrum</i> | 190 | 100 | 6.8 | 5.9 | 45.5 | 26.0 |
| Mixed population | 28 | 27 | 12.0 | 11.2 | 30 | 10 |

C.C. = Coulter Evaluations

L.F.C. = Flow cytometry measurements

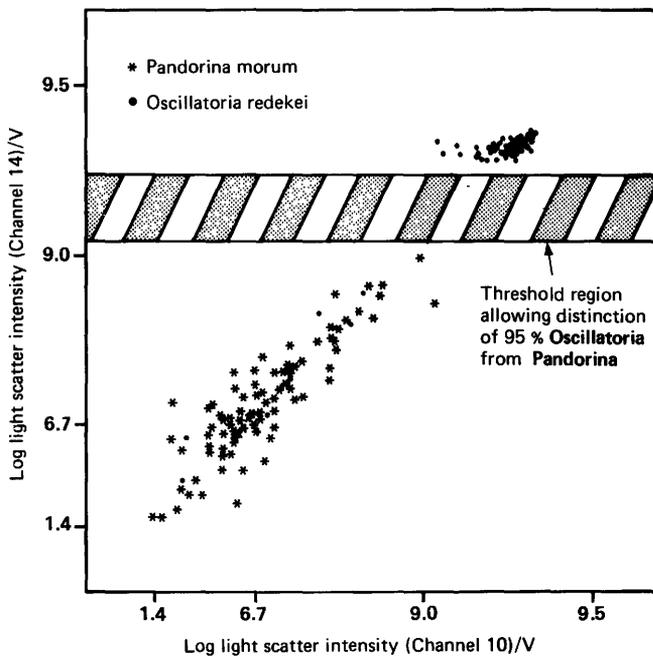


Fig. 16. Scatterplot of intensities measured at two different angles for two phytoplankton species.

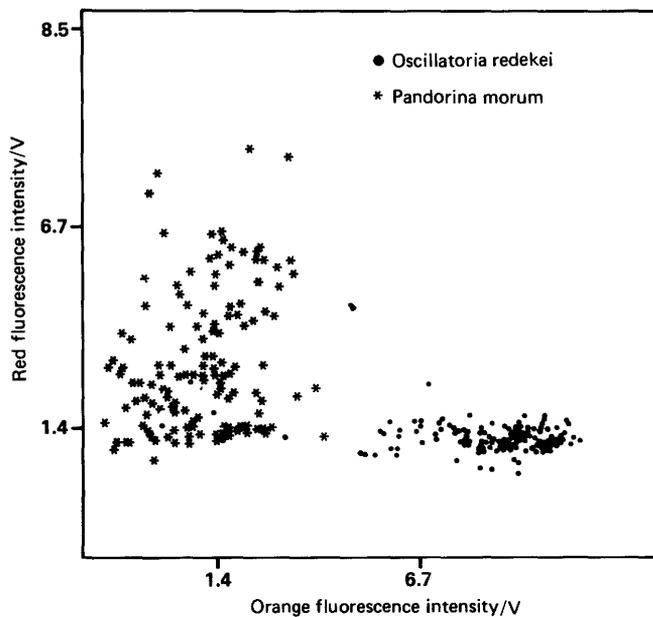


Fig. 17. Fluorescence scatterplot for two phytoplankton species.

These typical fingerprints have been used to predict the pattern of intensities which we would expect to observe on the photodiode array and they consequently allow selection of the best arrangement to achieve distinction between the species to be studied.

It has been demonstrated that in a mixture of three algae, consisting of *Oscillatoria* (rod shape) *Selenastrum* (croissant shape) and *Pandorina* (blackberry shape), the distinction between algae species is possible utilising the intensities measured on a correctly positioned single photodiode (94% success for rod shape algae). For the other two species a more complex analysis is required. To this end the following types of analysis have been developed:

- a) deterministic (discriminant functions, thresholding)
- b) probabilistic (combined probabilities).

a) Discriminant function analysis

A discriminant function, for classification purposes, is any function of a set of variables which results in a single value, representative of the variable set, which can then be used to subdivide the overall data set into classes of similar events.

The approach has been to attempt to identify combinations of the individual scatter intensities which reflect in some way the expected data patterns predicted from the photographs.

To illustrate the procedure used we consider a discriminant function designed to identify *Oscillatoria* using the photodiode arrangement illustrated in Fig. 18. From the form of the light scatter pattern of *Oscillatoria* we may predict that the intensities measured on the photodiodes numbered 9-16 should all be high relative to those measured for the other species. In a similar manner the intensities measured on photodiodes 3-8 should be lower than those measured for the other species. Thus we can define a discriminant function for *Oscillatoria* to be

$$\Sigma_H/\Sigma_V = \frac{\frac{1}{8} \sum_{i=9}^{16} I_i}{\frac{1}{6} \sum_{i=3}^8 I_i} \quad I_i = \text{intensity measured on diode } i.$$

For *Selenastrum* and *Pandorina* we would expect the value of this parameter to be close to 1.0, while for *Oscillatoria* it should be higher.

This has also been confirmed experimentally (see Fig. 19). Note that this discriminant function behaves as a form-factor for our measurements. Any filamentous alga will give very high values of Σ_H/Σ_V , and ellipsoidal or cylindrical species will give intermediate values.

However, for these latter forms misorientation in flow will greatly widen the distribution of the function and thus reduce the probability of correct classification.

b) Method of combined probabilities

Since deterministic methods of analysis are unlikely to provide a panacea for all discrimination problems, probabilistic and statistical methods of classification have been developed and tested.

These methods require that data be gathered using monospecies samples of all algae. If we make measurements on a sufficiently large number of cells, we may consider this

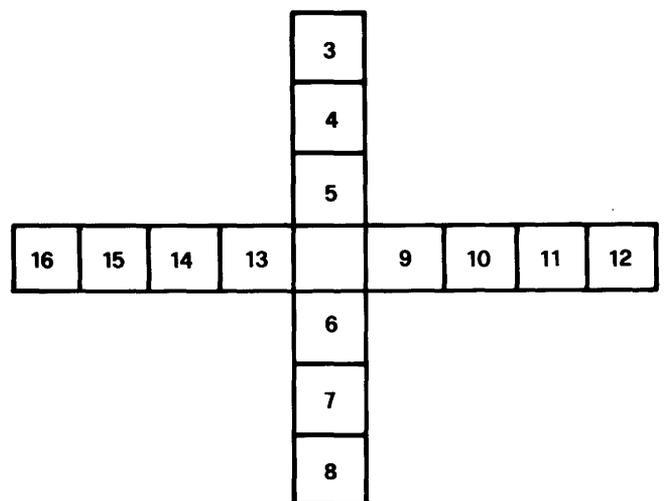


Fig. 18. Photodiode arrangement for the discriminant function on analysis.

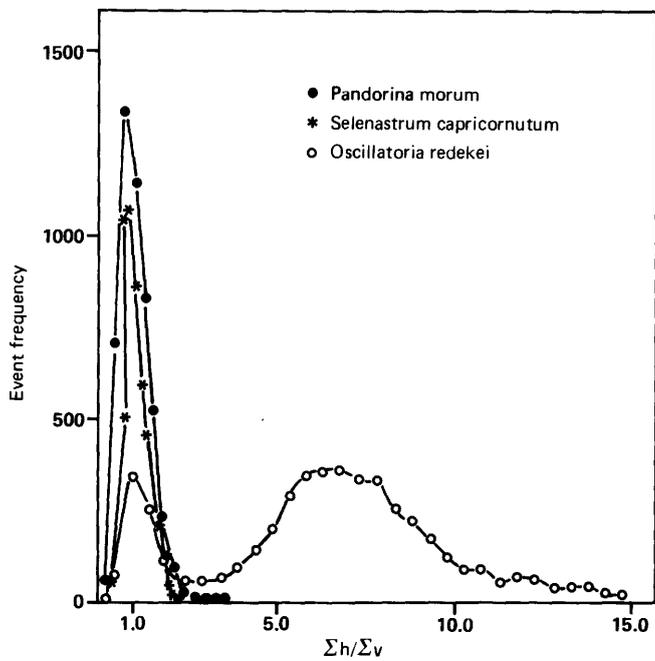


Fig. 19. Distributions of *Oscillatoria* discriminant function for three phytoplankton species (5,000 cells).

data to be characteristic of the species, and may expect the measurements to be reproducible under the same experimental conditions.

We may then choose or define a set of parameters which would allow us to characterise each cell type and to distinguish between different cell types. These parameters may simply be the intensities measured on each detector, or may be some arithmetic combination of these intensities.

Frequency distribution may be obtained for each of these parameters.

Normalising the frequency distributions we may therefore obtain probability density functions for these parameters. These may be combined using Bayes theorem to calculate the probability that an event \underline{x} was caused by an alga which is a member of the species represented by C_i :

$$P(C_i/\underline{x}) = \frac{P(\underline{x}/C_i) P(C_i)}{P(\underline{x})} = \frac{P(\underline{x}/C_i) P(C_i)}{\sum_{i=1}^N P(\underline{x}/C_i)}$$

i.e. we observe an event comprising a set of intensities x_j and the event

$$\underline{x} \equiv (x_j)$$

$$j = 1, m \text{ for } m \text{ parameters.}$$

The probability distributions provide us with the probability set

$$P(\underline{x}/C_i) \quad i = 1, N \text{ for } N \text{ species}$$

This is the probability of observing event \underline{x} given that it is measured on a sample of species i . $P(C_i)$ is the probability of observing an alga of species i . By default we set $P(C_i)$ to be equal for all species i .

Using this formula we can assign each event to the species considered most likely, to have given rise to such an event. Results obtained applying this analysis to monospecies samples are presented in Table IV.

Conclusions

The results obtained demonstrate that FCM is a powerful tool for aquatic ecology research.

Studies with 19 algal species of 5 different taxa have shown that it is possible:

- i) to distinguish autotrophic from heterotrophic cells;
- ii) to identify algal classes by photopigment autofluorescence within autotrophic taxa;
- iii) to quantify number and size of cells within populations.

The possibility to carry out daily measurements of scattering and autofluorescence on algal communities will allow to increase the accuracy of water quality assessment in an objective and comparable way.

Deterministic and probabilistic algorithms for the classification of algal species were developed.

In future more complex analyses like cluster analysis, will be used to develop more efficient classification methods and to extend the number of algal species which can be distinguished simultaneously.

References

- (1) G. PREMAZZI, G. BUONACCORSI, S. BINDA, A. BRAZZELLI and P. ZILIO (1987) «The application of flow cytometry to ecotoxicological research». *Basic and Applied Histochemistry* 31, 64.
- (2) G. PREMAZZI, P. ZILIO, G. ZANON and G. BUONACCORSI (1987) «Instrumentation and analyses for multi-angle light scatter measurements in flow cytometry». *Proceedings XII International Meeting of the Society for Analytical Cytology*, Cambridge (U.K.), August 9-15, 1987, 102.

TABLE IV: Results of application of probabilities analysis for calibration data

| | All | Fluor | Horiz | FL-Horiz | Square | FL-Square |
|---------------------|---------|---------|---------|----------|---------|-----------|
| Chlorella | | | | | | |
| Chlorella | 88.6049 | 54.1171 | 85.6784 | 85.8120 | 65.3081 | 69.6152 |
| Oscillatoria | 0.0021 | 9.1151 | 0.0128 | 0.0008 | 1.7741 | 0.6339 |
| Selenastrum | 11.3950 | 36.7680 | 14.3057 | 14.1879 | 32.8178 | 29.6512 |
| Oscillatoria | | | | | | |
| Chlorella | 10.4451 | 10.1992 | 9.5126 | 9.7004 | 6.7797 | 7.9371 |
| Oscillatoria | 60.0383 | 83.3385 | 83.3480 | 83.6996 | 64.0930 | 64.1742 |
| Selenastrum | 5.4166 | 6.4622 | 6.9895 | 6.5000 | 8.1273 | 6.8887 |
| Selenastrum | | | | | | |
| Chlorella | 27.3711 | 48.4057 | 30.3418 | 32.1579 | 22.9240 | 27.4351 |
| Oscillatoria | 0.1294 | 5.0180 | 0.0097 | 0.0086 | 5.1632 | 2.8649 |
| Selenastrum | 72.1160 | 46.5756 | 69.5985 | 67.8413 | 71.5127 | 69.3000 |

3.2. PATHWAYS OF TRACE METALS IN A FRESHWATER ECOSYSTEM - CONCEPTS AND METHODS

Topical Report by G. Rossi, H. Muntau, G. Marengo, J. Sangregorio

1. INTRODUCTION

Human activities lead to the dispersion of chemicals into the environment and inevitably, a major part of them reach the freshwater bodies, whose significance as drinking water reserves is most evident in the densely populated industrialized countries.

Freshwater bodies and lakes in particular, represent the first major sink in the global cycle of environmental contaminants of anthropogenic origin and a large number of chemical, physical and biochemical processes govern their dispersion, distribution and fate in the lakes (Figure 1).

Contaminant transport and reaction rates of processes such as chemical exchange at the sediment-water interface following deposition and resuspension, and the particulate matter-water interface, i.e., the dynamics of contaminant spread in lakes and forecasting of their fate by the use of mathematical models, are at the center of present-day studies.

Amongst the major groups of environmental contaminants - nutrients elements, trace metals, organic microconstituents and radioisotopes - trace metals were selected for a number of reasons. Trace metals are not degradable, they show an extraordinary reactivity with respect to biota and they are dispersed into the environment at rapidly growing rates.

Very little is known about their chemical exchange rates at solid matter-water interfaces, the reversibility of exchange reactions with allochthonous and autochthonous particles and in general about the rates at which the metals move between the chemical

pools represented by the many different geologic and biologic (living and dead) compartments of which the freshwater system consists.

The time and space scales of metal transfer processes range from microseconds to years and from micrometers to kilometers, and the complexity of the processes requires a multidisciplinary approach to their study.

The development and calibration of mathematical models for the forecast of the dispersion and transport of metals in lakes require the refinement of numerous experimental procedures ranging from the measurement of horizontal and vertical water mixing rates to the measurement of metal traces in micro size samples (suspended matter) and the differentiation of metal species concentrations in the dissolved and solid state.

It was, therefore, decided to allow a period of method and procedure development, test and refinement, dedicated to a smaller study area, such as a river-embayment system known to receive metals from both point and diffuse sources.

In general terms, the experimental study evolved as follows:

- establishment of a metal inventory in both the feeding rivers and the receiving lake embayment;
- identification of metal input sources and determination of average metal input rates from external sources;
- assessment of space and time variability in metal distribution on the basis of samples taken from a three-dimensional sampling network in the lake embayment and corresponding metal input rates from the rivers.

Measurements of vertical particle flux and particle-associated metal fluxes and metal input rates from in-lake metal remobilization processes yield further insight into the manyfold and complex mechanisms governing the fate of metals in lakes.

The mathematical model was intended as a tool to interpret

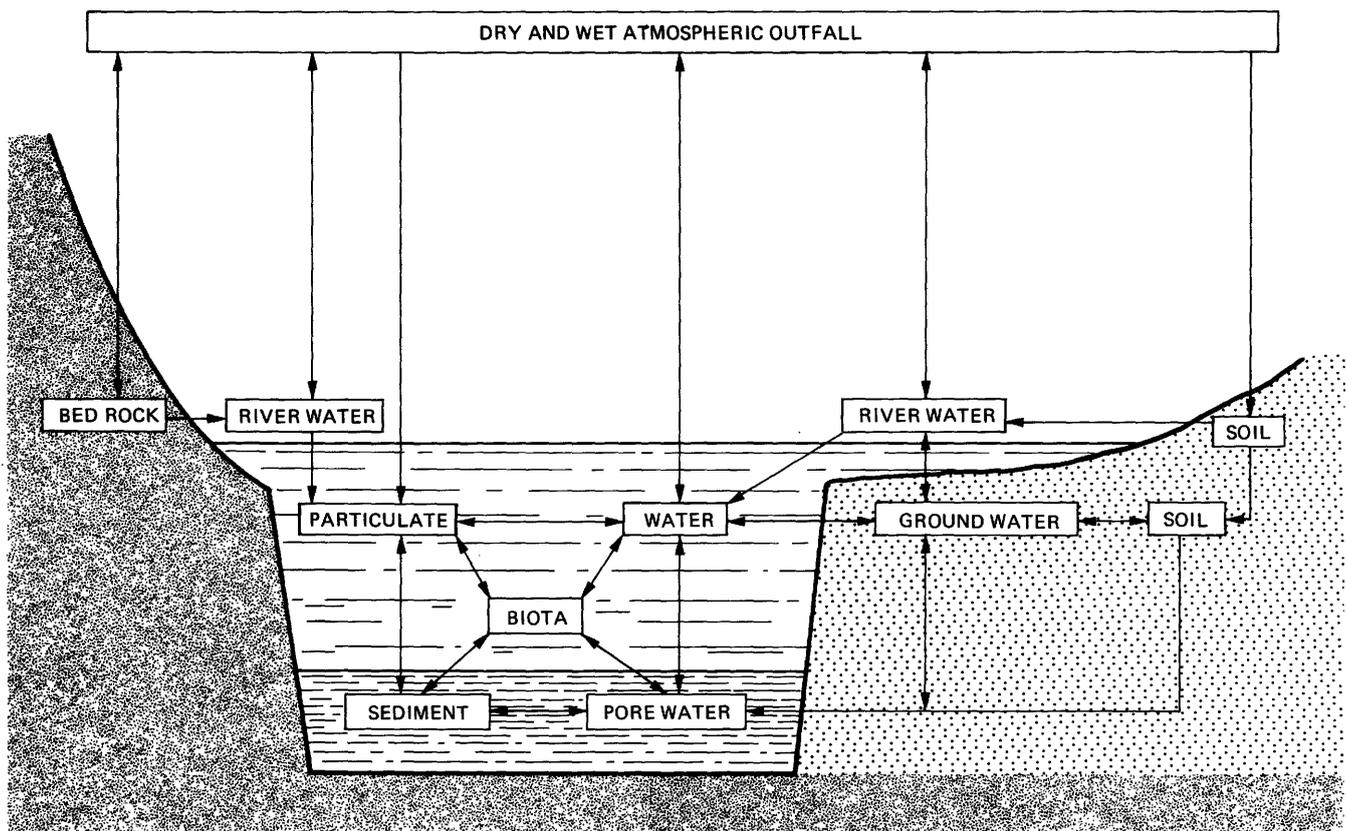


Fig. 1 Biogeochemical metal cycles in an aquatic ecosystem

the experimental data and to forecast the time evolution of the metal concentration in the different aquatic compartments. The model in its first version ignores speciation. It was conceived as applicable both to a bay and to a lake, in view of an eventual validation to be carried out in a lake where metal concentrations are undergoing an observable evolution and with the aim of predicting its recovery.

The application of the model to the considered water body proceeded along the following lines. The parameters entering the equation coefficients were evaluated on the basis of laboratory and field experiments.

Assuming constant values for the coefficients (based on yearly average values), the model equations were solved first of all analytically in order to assess the characteristic times of the transient terms and the asymptotic metal concentrations.

For the general (time-dependent) case a computer code was written in order to evaluate the coefficients as monthly average values and to solve the equations numerically.

Two types of model application could be envisaged: a) calculation referred to the past evolution of the metal concentration in the ecosystem in order to validate the model (based on «historical» experimental data); b) predictive calculations with the verified model in order to forecast the future evolution of the metal concentration in the ecosystem (based on experimental data describing the «present» situation).

2. SITE DESCRIPTION

The chosen test site (Fig. 2) is constituted by an embayment-river system on the Eastern shore of lake Maggiore. Three rivers - Monvallina, Bardello and Acquanegra - feed an embayment of about 3 km of length and 1.25 km of width with a maximum depth along the open boundary with the lake of about 130 m. The estimated volume of the waterbody studies was 0.27 l.km³, the surface 3.8 km² with an estimated sediment surface of about 4.5 km².

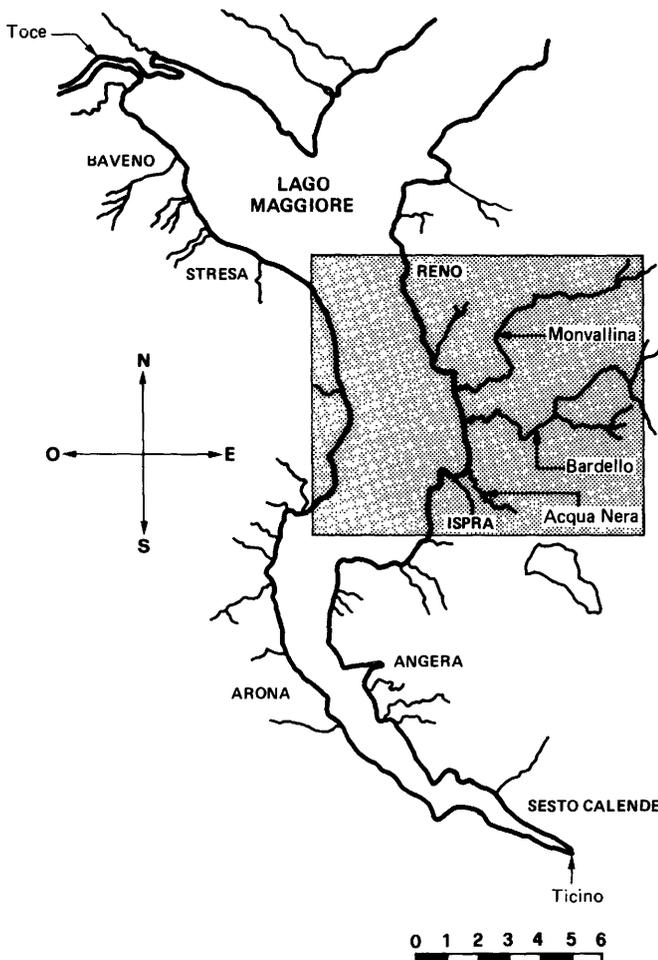


Fig. 2. Test site Monvalle bay - Lake Maggiore

The average flow rate of rivers Acquanegra and Monvallina is 0.75 and 0.85 m³/sec, respectively, while river Bardello, connected to lake Varese, shows an average flow rate of 4.5 m³/sec. The total watershed of the three rivers is estimated to be 300 km².

From earlier studies (Muntau, 1981 a,b) there are indications that the Monvalle embayment received metal immissions from various sources and, therefore, it offers an opportunity to study metal dispersion processes on a local scale.

3. GENERAL MODELLING CONCEPTS

The considered trace metal pollutant is present in the lake in a liquid (dissolved, ionic) form with concentration C_l and in a solid (particulate, adsorbed) form with concentration C_s (both mg·m⁻³). It is assumed that an instantaneous equilibrium is reached between the dissolved form and the adsorbed one. The concentration (referred to the mass of particulate matter) of the absorbed metal C_{sp} (mg·kg⁻¹) is determined by a «distribution constant» k_p (m³·kg⁻¹):

$$C_{sp} = k_p C_l.$$

A straightforward consequence of this assumption is that the metal concentrations in the liquid and in the solid forms can be evaluated from the total (liquid + solid) concentration C_t , provided that the suspended matter concentration C_p and the distribution constant k_p are known:

$$C_l = f_p C_t$$

$$C_s = (1 - f_p) C_t \quad f_p = 1/(1 + k_p C_p)$$

Then the balance equation for the metal in a lake region is referred to the total concentration C_t as to the only unknown function, which is associated to the factor f_p in the terms concerning the liquid form and to the factor $1 - f_p$ in the terms concerning the particulate form.

The balance equation for a single metal takes into account all processes except adsorption by suspended matter: inflow, outflow, advection, mixing, settling, chemical reactions (in particular complexation reactions), possible in situ production.

If we neglect the effects of trace metal pollution on phytoplankton, and we assume that production is a zero-order process (i.e. independent of metal concentration) and all other processes are first-order processes (characterized by time-constants resulting from experiments or submodels), any balance equations is a first-order linear differential equation, of the type:

$$d/dt C_t(t) = A(t) C_t(t) + B(t).$$

In a many box version of the model we have to solve a system of linear differential equations, each equation containing coupling terms where the metal concentration in an adjacent box appears. The number of equations is equal to the number of boxes. The metal distribution model utilized in the present study is referred to a «total» metal (Cd, Cu, Pb). The balance equations give the total (dissolved + particulate) concentration of the total metal; average value in a lake region as a function of time.

The general scheme of the model is presented in Figs. 3 and 4 (for all this matter, see Imboden and Schwarzenbach, 1984; Jorgensen, 1983). The reported analysis has been performed in the framework of a two-box scheme (shallow coastal zone and epilimnion of the «deep» region have been considered as a unique box).

4. EXPERIMENTAL

Chemical measurements were requested with regard to the establishment of the system contaminant inventory including both the rivers and the embayment as well as the major com-

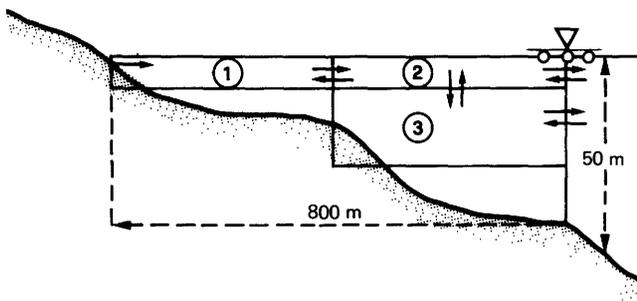
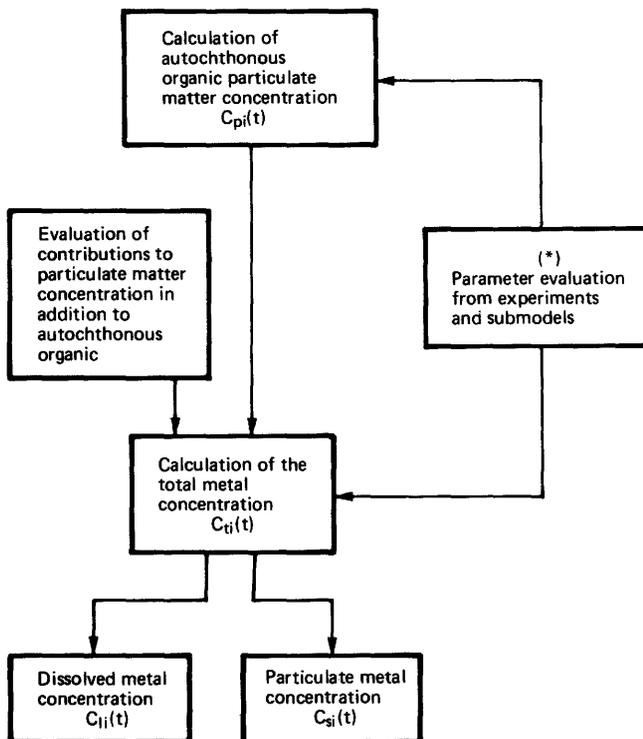


Fig. 3. Vertical section of the test site, etc.



$i = 1$ epilimnion
 $i = 2$ hypolimnion

(*) for the list of these parameters see the following page

Fig. 4. Layout of the model.

partments, i.e. sediments, suspended matter and water. Contaminant source identification and discrimination between anthropogenic and geochemical origin of the contaminants are important research issues in view of the later interpretation of data.

Spatial and temporal variability of the contaminants will determine the general reliability level of the entire study and, therefore, sampling station network density and sampling frequency need much consideration.

Contaminant input-output rate determination as well as intercompartment transfer rate assessment, for example with regard to the in-lake contaminant remobilization (internal metal loading), requires a number of physical measurements such as river flow-rates, current velocities and high-quality temperature measurements.

The determination of solid mass transfer rates is most important with regard to the contaminant-loaded suspended matter transported by the rivers into the embayment and the vertical transport of contaminants associated with settling solid matter. Resuspension, redistribution and resettling of sediments by undercurrents, lateral sediment sliding and similar processes,

which undoubtedly occur in river-embayment systems, will add to the contaminant circulation and a discriminating settling matter collecting system, operated over larger time intervals is, therefore, needed.

Solid matter contaminant speciation offers additional information about the system internal transport processes and its efficiency.

4.1. Chemical measurements

Metals and major constituents were determined in sediments according to a number of well established analytical procedures such as inductively-coupled plasma emission spectroscopy (ICP), neutron activation analysis (NAA), X-ray fluorescence spectroscopy (XRF), Wösthoff-oxygen combustion and others. The metal determination in a waterborn suspended matter required, due to the extremely small sample mass available, the development of special procedures and solid-sample-Zeeman atomic absorption spectroscopy was the method of choice. Later on, cumulative sampling procedures, followed by continuous centrifugation of the suspended matter, allowed also the application of ICP.

Metal speciation studies in sediment and suspended matter followed the recent method development by Salomons (1987) and Förstner and Kersten (1987) leading to highly diversified separation procedures.

Anions, such as sulphate, chloride and nitrate, were determined by ion-chromatography.

Metal determinations in water were performed by differential anodic stripping voltmetry (DPASV) and graphite furnace atomic absorption spectroscopy (GFAAS).

The use of reference materials was mandatory in order to obtain results of the requested quality and to minimize the influence of error sources. For methodological results the reader is referred to the specific papers (Gommes et al. 1981; Baudo et al. 1981; Muntau et al. 1981; Loch and Muntau, 1981).

4.2. Physical measurements

Existing information (Barbanti and Carollo, 1967) supported the conjecture that the considered embayment is weakly concerned by the main circulation of lake Maggiore. For this reason horizontal water exchanges inside the test site and between this and open lake were considered mainly of (eddy) diffusive type, in such a way that no systematic currentmetric measurement was foreseen.

Data on tributary inflow rates have been available through the courtesy of CNR Pallanza, which has monitored rivers Monvallina, Bardello and Acquanegra for the whole duration of the programme.

Information on thermal stratification and evaluation of vertical water exchange across the thermocline asked for temperature measurements along the water column, to be automatically performed and recorded.

In view of this an electronic apparatus was designed and assembled at J.R.C. and installed on a platform near the open boundary of the bay. Its data-logger is ready to accept data on 16 channels, this number being easily increasable to include meteorological data and physico-chemical parameters beside water temperature.

4.3. Results: Metal inventory

4.3.1. River sediments

The rivers were sampled for sediments and the encountered aquatic plants, which offer additional short-term contamination information (Gommes and Muntau, 1981).

The major rivers feeding the Monvalle bay, Bardello and Monvallina (Fig. 5) were sampled at regular intervals and the sediments analyzed for the most important trace elements such as Pb, Cd, Hg, Cu, Cr, Ni, Zn, As, Se and a number of

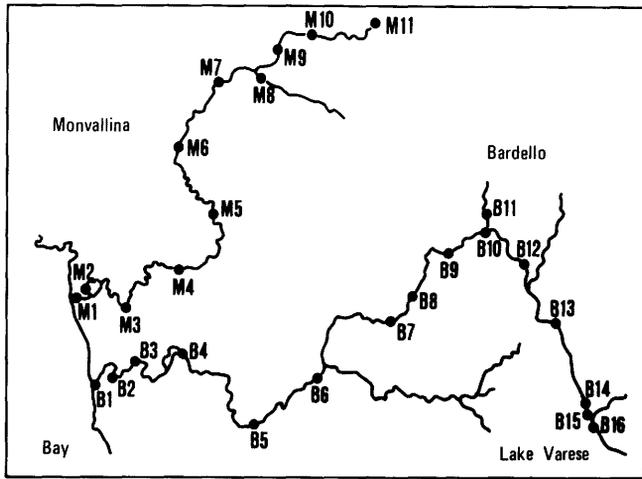


Fig. 5. Sampling station network of rivers Bardello and Monvallina

lithogeneous elements such as Ti, Rb, Cs, La and Ce in order to assess their anthropogenic and geochemical origin, respectively.

The distribution of some selected elements along the rivers courses is shown in Figs. 6 and 7.

Taking into consideration the uniform geological settings of both rivers, the distribution pattern of all three elements points to their relationship with human activities. The exception is obviously cadmium in river Monvallina, sediments exceeding not much the geochemical background values, thereby demonstrating that cadmium accumulations along the river Bardello are not necessarily connected to fertilizer dissemination.

Numerous point sources for a number of additional elements such as chromium, arsenic, antimony and zinc, have been identified, in many cases well supported by the corresponding analysis of the macrophytes (Muntau and Schramel, 1988).

4.3.2. Metals in lake sediments

Meaningful aquatic system analysis in view of future metal dispersion modellization attempts requires first of all extremely thorough investigation with respect to its sediment status.

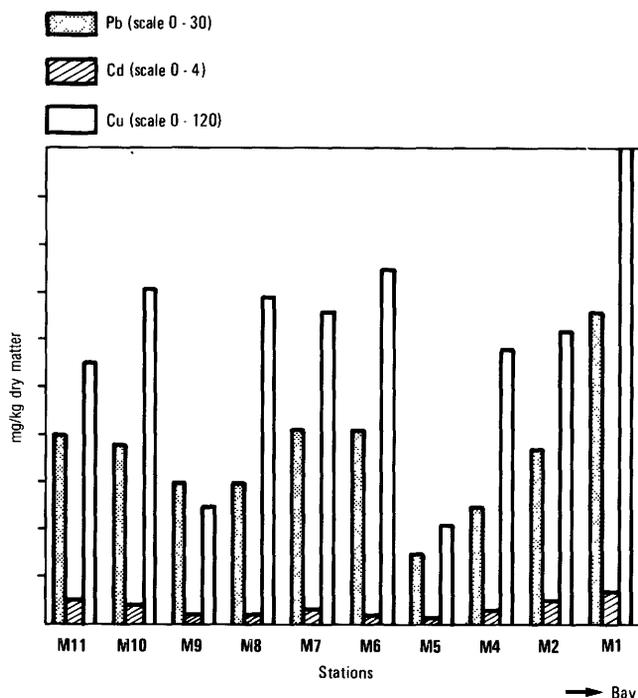


Fig. 6. Distribution of some selected trace metals (Pb, Cu, Cd) in the sediments of river Monvallina

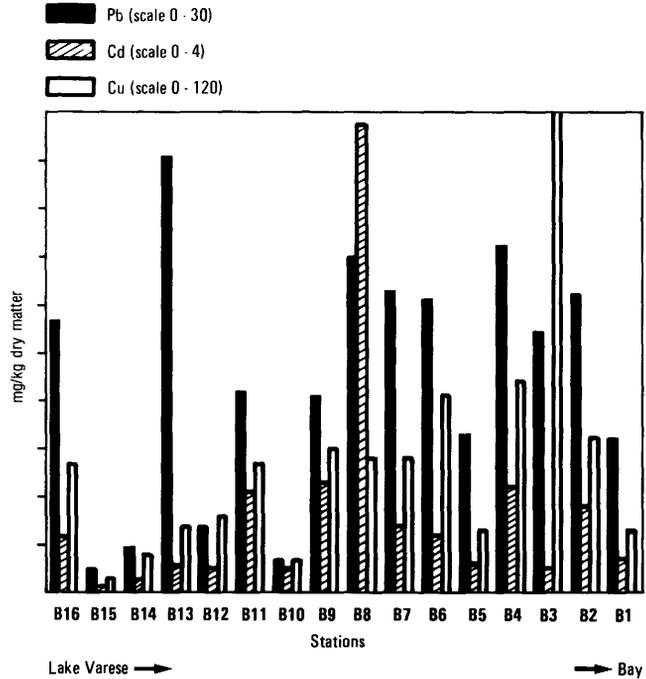


Fig. 7. Distribution of some selected trace metals (Pb, Cu, Cd) in the sediments of river Bardello

It is widely recognized that complexity of the aquatic system (feeding rivers with extremely varying solid discharges, complex current patterns and bottom morphology) and the heterogeneity of spatial element distribution are strongly correlated.

Earlier studies suggested high variability of most of the so-called anthropogenic elements in the bottom sediments of Monvalle bay and, consequently, an adequately dense sampling station network has been developed, following the lake depth contour lines (Fig. 8) leading to 115 sediment samples distributed over 3.8 km³.

Most of the environmentally interesting elements such as Pb, Cd, Hg, Cu, Zn, Cr, Ni, As, Se and Sb, as well as typical lithogeneous trace elements such as Ti, La, Ce and Sc, have been determined.

Not surprisingly, the element distribution patterns are highly complex and the influence of bottom morphology on sediment deposition and sorting is well documented by the distribution of organic carbon (Fig. 9). Two element distribution maps are shown here which demonstrate the specific metal input by the rivers Bardello (Zn) and Monvallina (Cu) (Figs. 10 and 11). The most evident separation between the copper «hot spots» is caused by rather steep underwater ridges which favour the lateral sliding of mobile, metal-rich sediments.

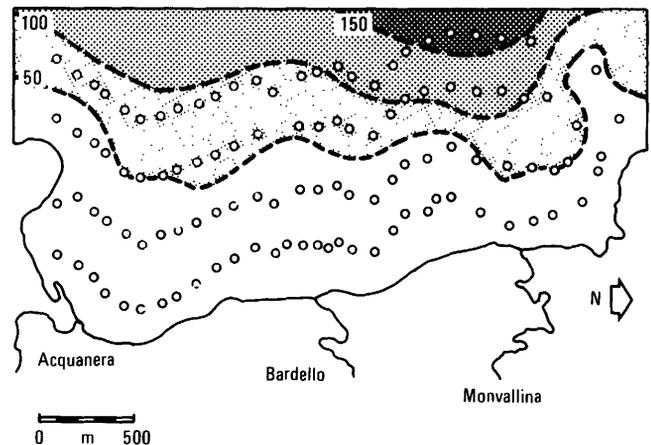


Fig. 8. Sediment sampling station network Monvalle Bay/Lake Maggiore.

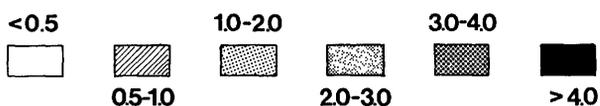
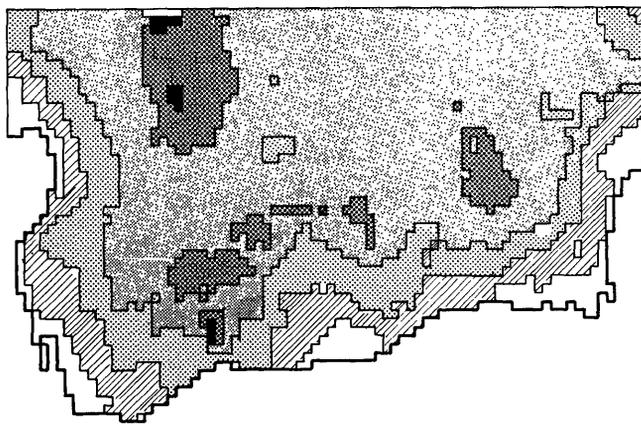


Fig. 9. Distribution of organic carbon in sediments of Monvalle Bay/Lake Maggiore

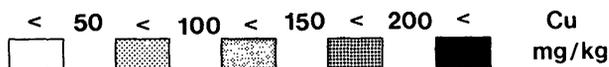
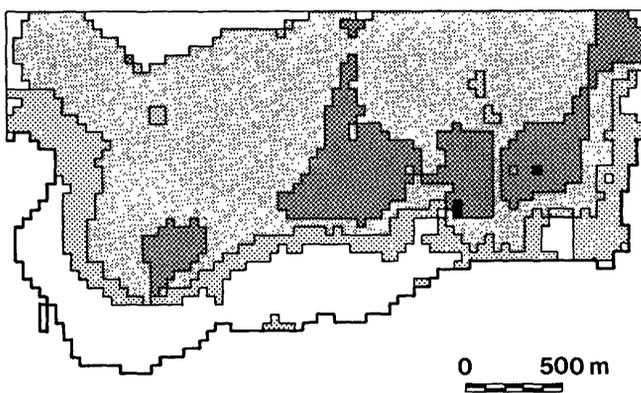


Fig. 10. Distribution of copper in sediments of Monvalle Bay/Lake Maggiore

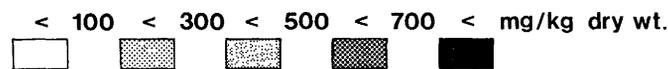
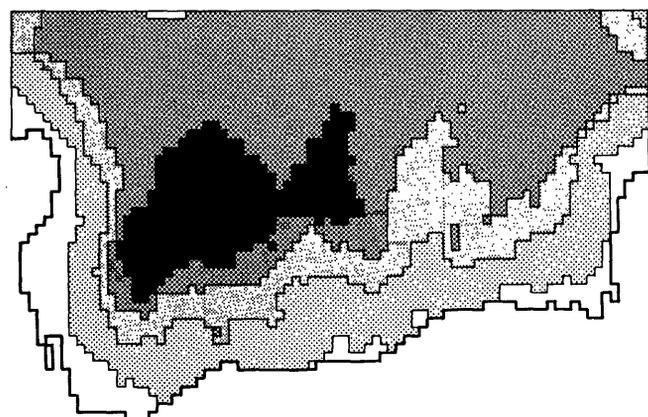


Fig. 11. Distribution of zinc in sediments of Monvalle Bay/Lake Maggiore

Table I shows the minimum and maximum concentrations of some selected elements of particular relevance to anthropogenic origin (Cd, Pb, Cu, Zn, Cr, Ni) and sediment structure (Ti, V, Mn). The sample frequency distribution (Fig. 12) reveals the importance of such studies in view of the correct sampling of complex aquatic systems.

Correlation analysis showed an extremely high correlated group of Cu-Zn-Cr-Ni-Cd, while Pb was correlated best with V.

Although the rivers do not indicate either mercury or selenium sources in their catchment area, there is a strong correlation of Hg-Se-As present in the embayment which might be ascribed to lake (north-south) transport.

The ratio of the lowest and highest concentrations of a single element has been used as an indicator of their either geochemical or anthropogenic origin. Monvalle bay sediment analysis would yield the following ranking with respect to geochemical origin:

$Hg < As < Pb < Cu < Cd < Mn < Cr < Zn < Ni < Ti < V$

Taking into consideration trace element concentrations of the typical bedrock types, forming the Bardello and Monvallina watershed, and hence, a somewhat more realistic picture of the geochemical background of the whole aquatic ecosystem, we obtain the following ranking:

$As < Cd < Pb < Hg < Zn < Cu < Mn < Ni < Cr < V < Ti$

An attempt to establish a quantitative estimate of geochemical and anthropogenic origin, respectively, of heavy metals present in sediments of Monvalle bay on the basis of the analysis of a long sediment core (2.5 m of length), taken near to the embayment-lake boundary, shows that As, Cd, Pb and Hg are most probably introduced into the bay by human activities, leaving just something in the order of 10% or less to be ascribed to lithogeneous origin (Fig. 13).

4.3.3. Metals in river water (dissolved and particulate)

Earlier investigations showed that high metal concentrations in sediments are very often accompanied by extremely high metal concentrations in the waterborne suspended matter (Grobecer and Muntau, 1985; Van Son and Muntau, 1987).

The highly variable discharge rates of the rivers, however, and the corresponding sediment mobilization requested the periodical record of total suspended matter concentration, suspended matter-associated and dissolved metal concentration by monthly sampling over one year.

TABLE I: Trace element minimum et maximum concentration as measured in Monvalle Bay sediments ($n = 115$)

| | Minimum concentration* | Maximum concentration* |
|----|------------------------|------------------------|
| As | 2.1 | 239 |
| Cd | 0.105 | 6.5 |
| Pb | 3.0 | 283 |
| Hg | 0.05 | 8.0 |
| Zn | 46 | 947 |
| Cu | 4.1 | 319 |
| Mn | 88 | 3900 |
| Ni | 10 | 133 |
| Cr | 14 | 366 |
| V | 12 | 89 |
| Ti | 270 | 2143 |

* Expressed as $mg \cdot kg^{-1}$

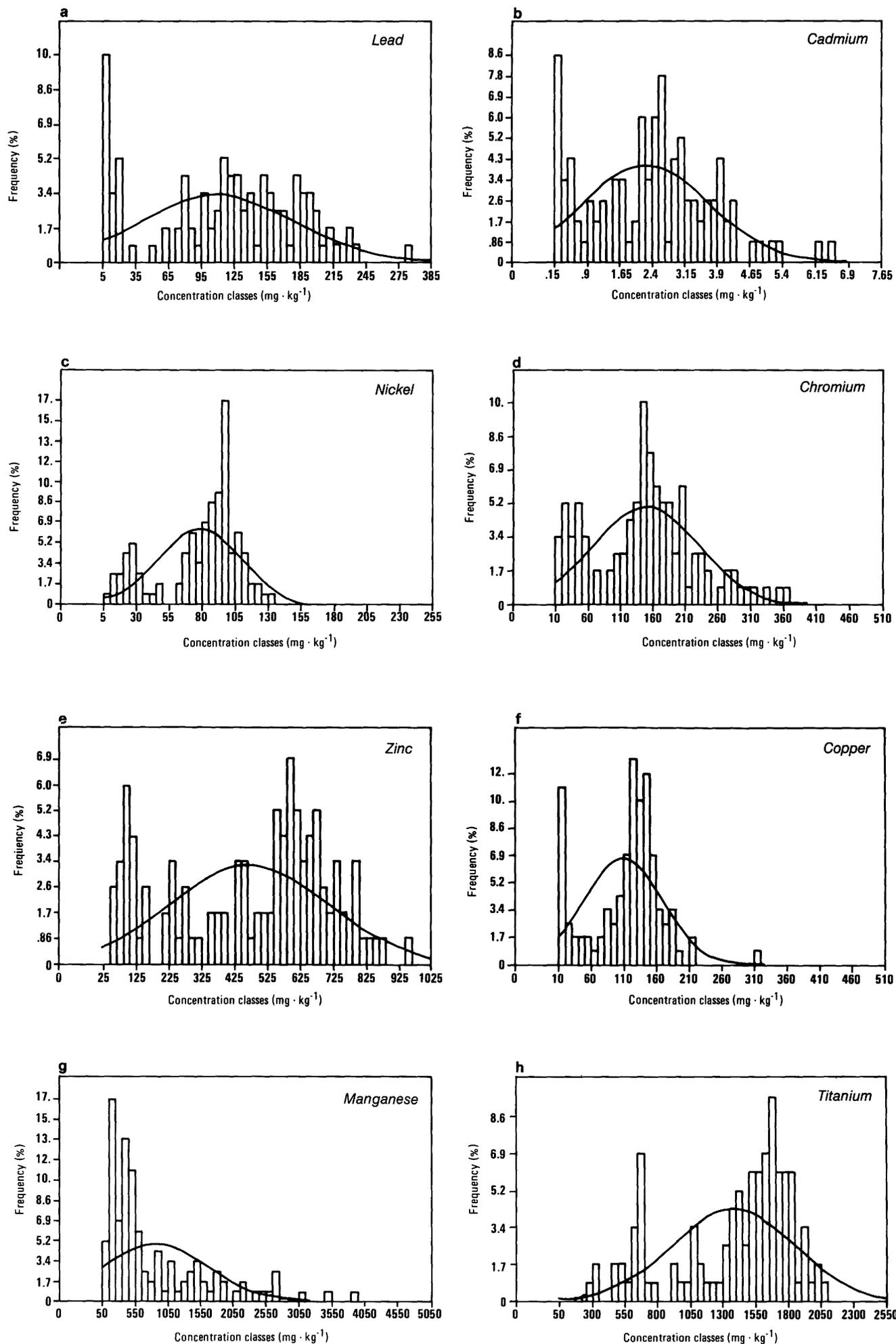


Fig. 12a-h. Element frequency distribution of trace elements in Monville Bay sediments

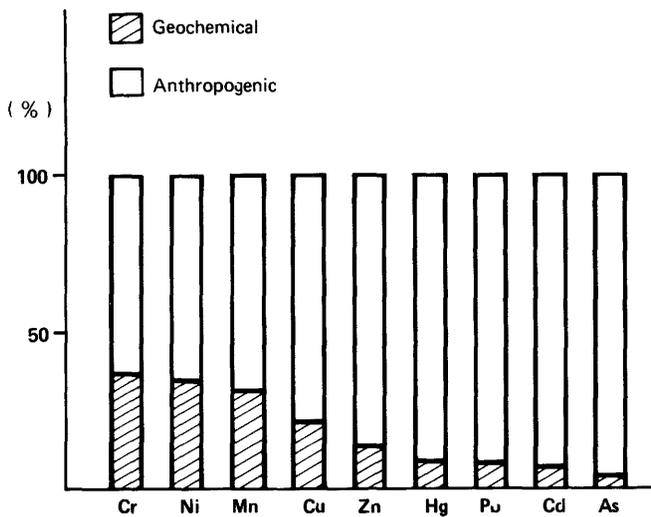


Fig. 13. Assumed origin of metals found in sediments of Monvalla Bay

Suspended matter concentration (Fig. 14) reached values as high as 98 mg/l and as low as 1.2 mg/l for the same river (Monvallina).

Metal concentrations, shown in Figs. 15-17 vary correspondingly. On the basis of the 1985 measurements riverine metal input, expressed as total annual loading, was 1032 kg of copper, 497 kg of lead and 354 kg of cadmium.

4.4. Spatial and temporal metal distribution in the lake

The spatial and temporal metal variability both in the dissolved and particulate form, has been assessed by repeated (n=4) sampling of a three-dimensional sampling station network in the embayment (Fig. 18). Data relating to this sampling are summarized in Table II.

The temporal evolution of the metals in the lake shows a peak for all stations in August 1985 (Fig. 19), which is most evident for the littoral stations 1 and 4 and which might be related to the high suspended matter input (Fig. 14) and the corresponding metal transport (Fig. 15-17).

Transport of the different - dissolved and particulate - forms of the metals has been evidence by plotting the concentration data of one single sampling campaign considering only the surface (- 1 m) stations (Fig. 20).

The metal in their respective forms show distinct input patterns which, most probably, are related to their sources.

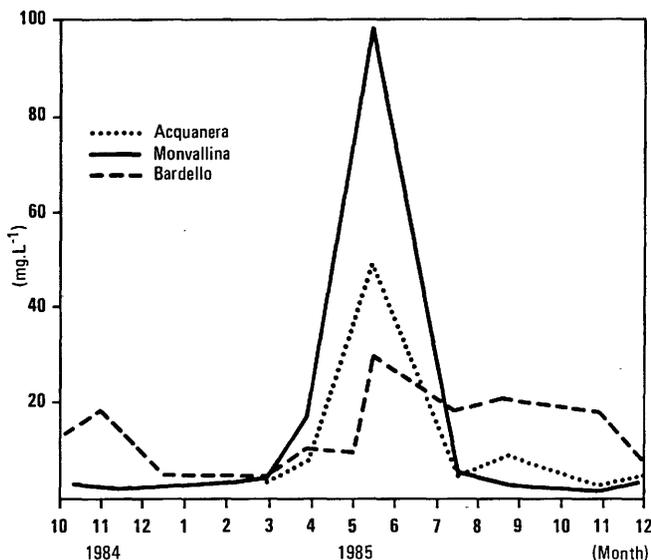


Fig. 14. Suspended matter concentration of river water

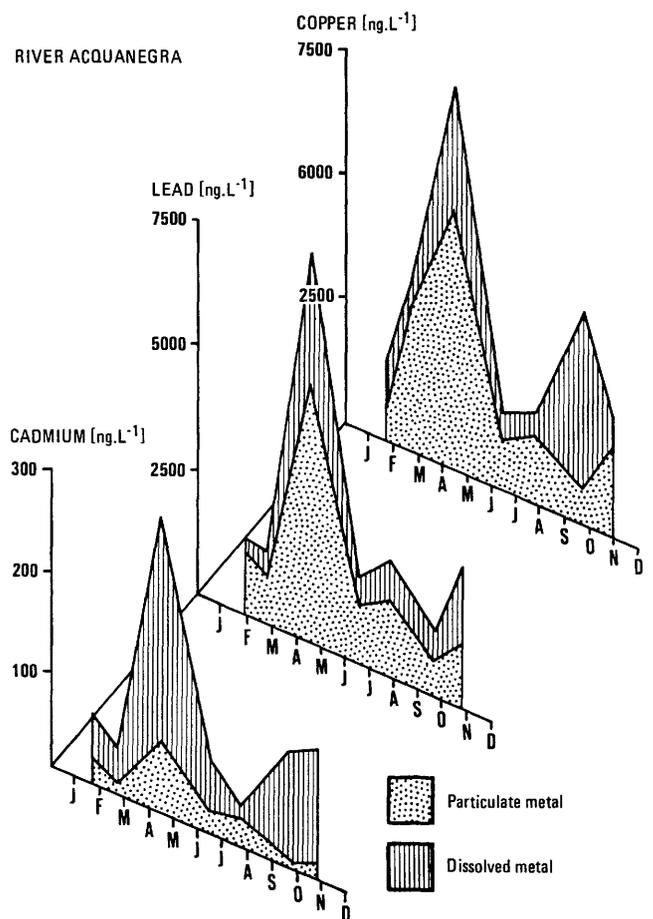


Fig. 15. Metal concentrations of river water (1985)

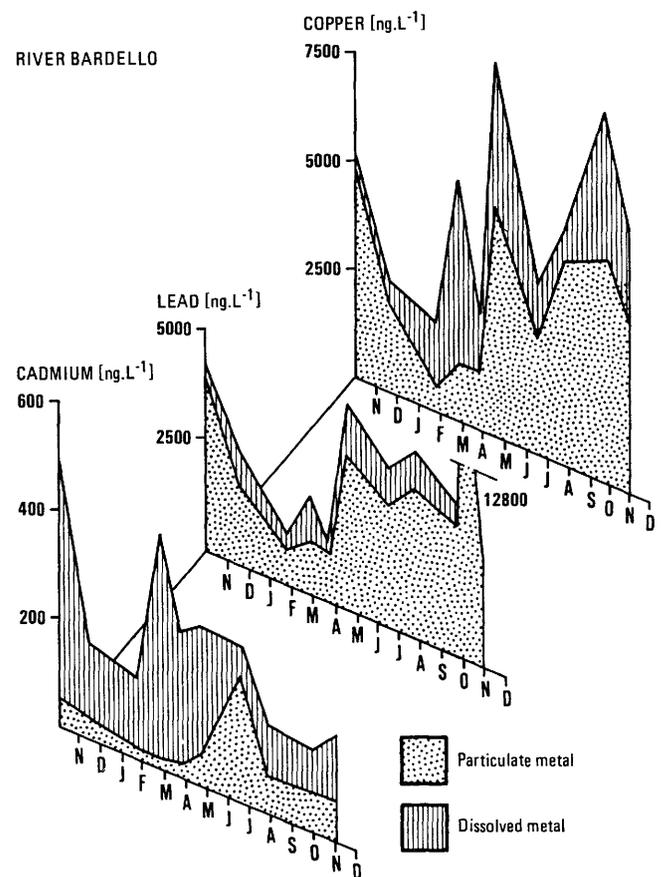


Fig. 16. Metal concentrations of river water (1985)

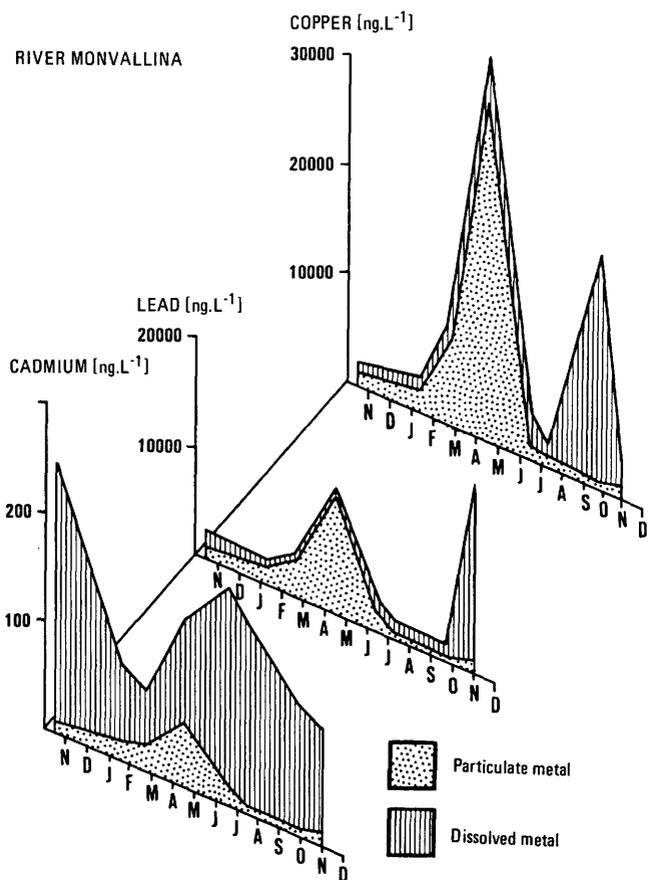


Fig. 17. Metal concentrations of river water (1985)

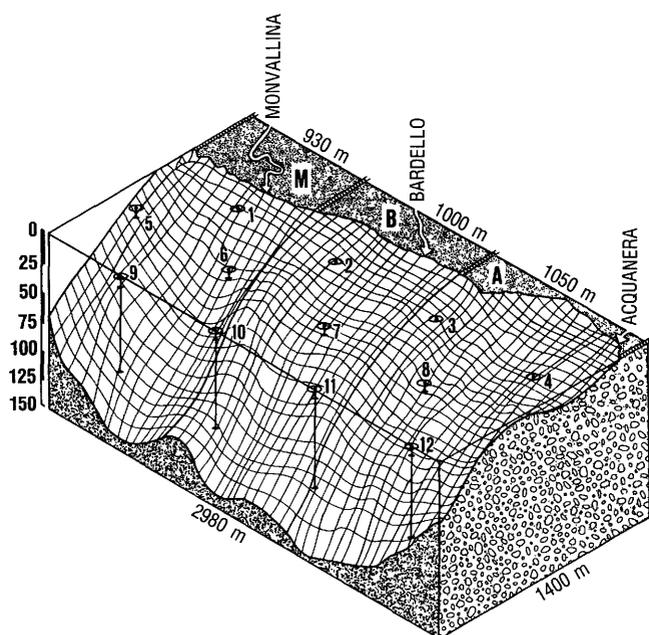


Fig. 18. River-bay sampling station network

Particulate lead and particulate cadmium, discharged mainly by the river Acquanegra, most probably originate from wharf operations (colour pigments), while dissolved (complexed?) copper is discharged preferentially by the river Monvallina. In order to improve the representativity of suspended matter sampling performed so far by filtering small water portions taken from many sampling stations, a procedure of cumulative sampl-

TABLE II: Metal concentrations in the water of Monville Bay (2/85 to 10/85)
Lake stations 5-12^a, all depths, all campaigns

| | | Mean (ng·l ⁻¹) | CV ^b (%) | Sample number | Range ^c (ng·l ⁻¹) |
|-------------|----|-------------------------------|------------------------|------------------|---|
| Particulate | Cd | 13 | 48.0 | 98 | 1-39 |
| | Pb | 223 | 46.2 | 98 | 50-1180 |
| | Cu | 79 | 40.5 | 97 | 35- 900 |
| Dissolved | Cd | 79 | 40.5 | 100 | 5-460 |
| | Pb | 695 | 75.4 | 100 | 38-6900 |
| | Cu | 1451 | 74.2 | 100 | 46-7400 |

^a The four shallow stations (1-4) have been omitted

^b Represents the spatial and temporal variability

^c Extreme single concentration values encountered in the lake

ing has been applied averaging large water masses both horizontally and vertically.

The bay was subdivided into three sectors according to their river inlets. From each sector (~1.25 km²) water was continuously collected between 1 and 10 m of depth, while the sampling boat was slowly moving in a meander-like way covering the whole sector at least twice.

The sample of about 100 l of water was centrifuged and metals were determined in both the water (dissolved) and the dried suspended matter (particulate metals).

Concentration figures for the metal concentrations in the suspended matter, the dissolved metal in the water and the related distribution coefficients are shown in Table III.

4.5. Trophic state assessment of the system

The total phosphorus values recorded in 1985 were averaged and compared with those of the whole lake (Calderoni et al., 1985). The distribution of the probability that the bay being examined may be in one or other trophic category is reported in Table IV and shown in Fig. 20a.

The total phosphorous concentrations (dissolved + particulate) for 1985 were [P] bay = 25 mg/m³ [P] lake = 18 mg/m³. It should be noted that in both cases one is dealing with values averaged not over a water column, but over the volumes.

Although the concentration of total phosphorus in the bay is only about 40% higher than that of the whole of Lake Maggiore, the productivity of the bay itself is clearly higher than this value. In fact the biomass which is generated disperses rapidly towards the open lake, as there is no physical barrier which can limit this phenomenon.

One should consider the short removal time of the rivers and those inside and outside the bay itself, which amounts on average to 45 days.

Because of this the P-particulate, particularly in the period of greatest primary production, is carried to the outside by surface waters, which contain hardly any reactive phosphorus, which is totally consumed to maintain algal production.

Account is finally taken of the phosphorus transported by the three inflowing streams, which in 1985 was about 50 tonnes (Marengo et al., 1986).

One can then say that, considering the amount of phosphorus involved, Monvallina bay is moving towards the eutrophic state.

The high productivity of the bay can also be seen from the quantity and quality of the material collected in a series of traps suspended underneath the floating platform, which is anchored in the middle of the bay itself. Using the same model of trap for some time, the material collected in our case is of the same order of magnitude as that collected in 1980 in the P. Tresa basin of Lake Lugano, which is an extremely eutrophic water body (G. Premazzi and G. Marengo, 1982). The total flux of trip-ton in both cases is around 2500 mg/m²/d.

METAL CONCENTRATIONS IN THE BAY: Particulate copper

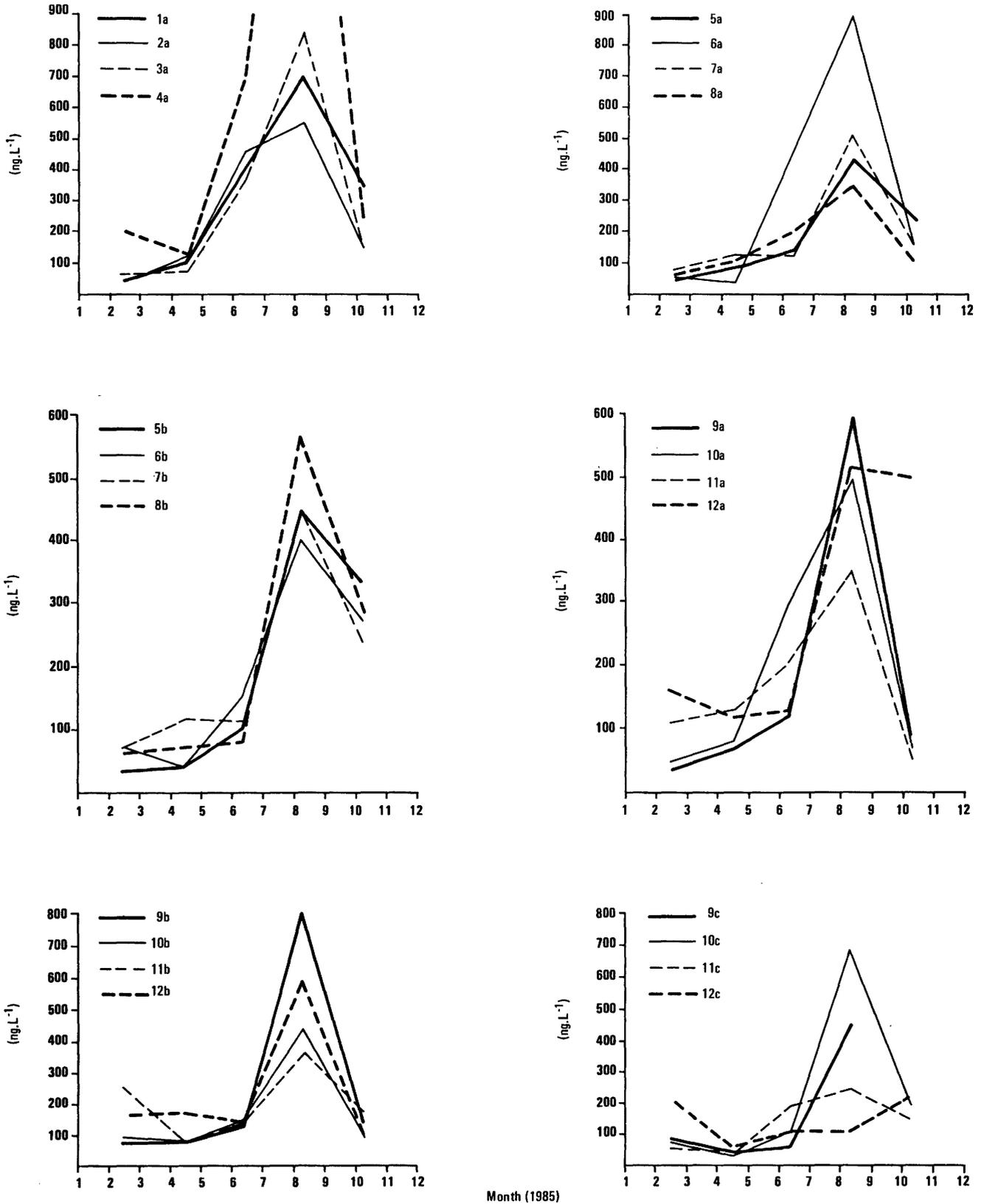


Fig. 19. Metal concentrations in the bay (1985): suspended matter associated copper

This shows the validity of the assumption made previously, i.e. most of the organic material produced rapidly leaves the bay, taking with it part of the trace metals adsorbed actively and/or passively.

In other words, if the allochthonous and autochthonous organic material were kept longer in the bay itself, i.e. if the removal time was similar to that of the entire lake, e.g. about 4 years, (IRSA, 1980), the probability of being in another trophic category

would be higher, presumably being similar to that of 1980 in the P. Tresa basin (G. Premazzi and G. Rossi, 1984).

A dedicated study on the distribution of phosphorous species in the Monvallina Bay and its feeding rivers Bardello, Monvallina and Acquanera has been carried out, aiming to describe transport, transformation and deposition mechanisms of phosphorus.

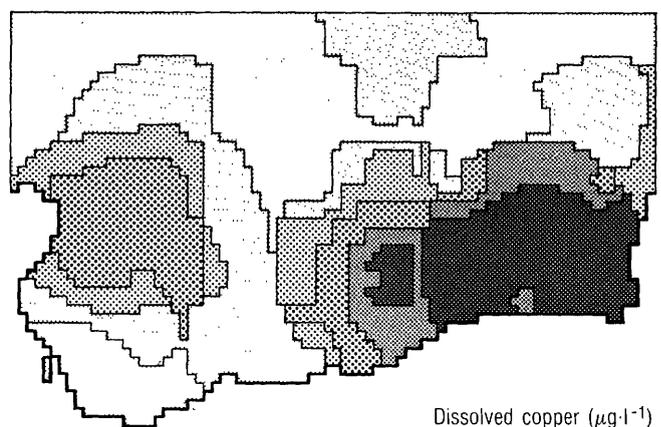
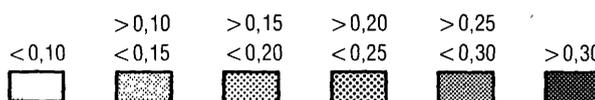
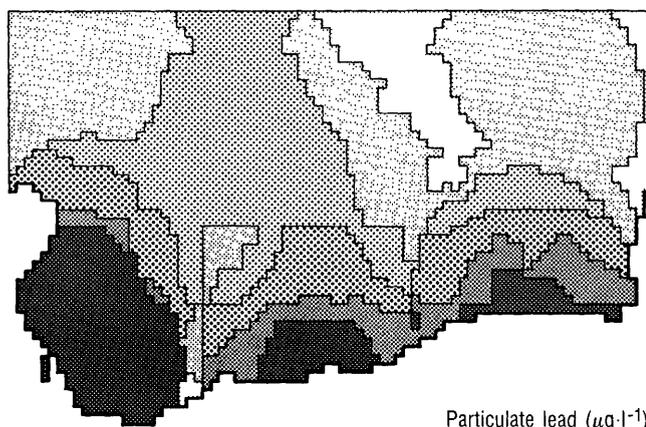
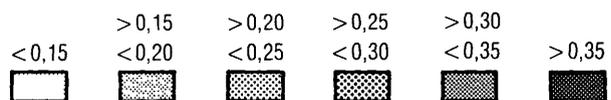
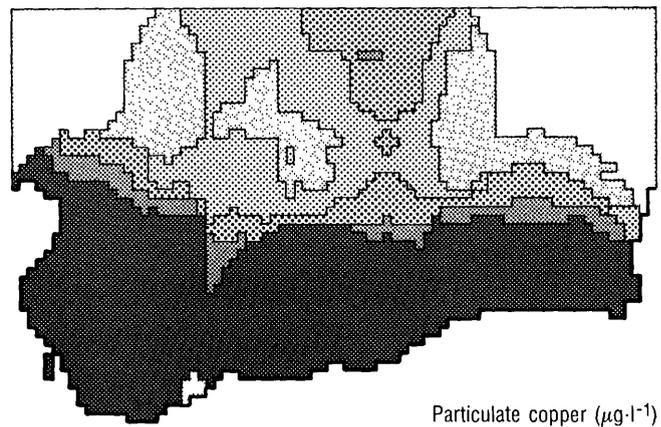
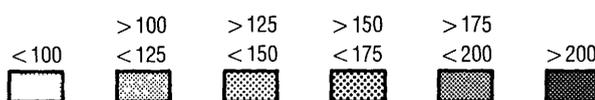
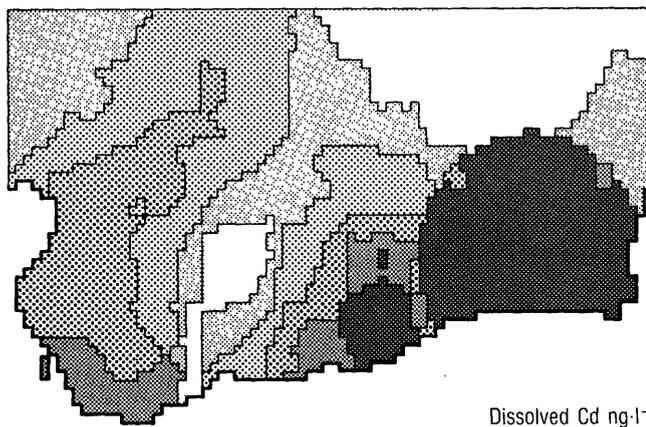
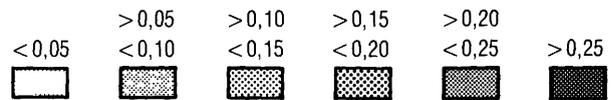
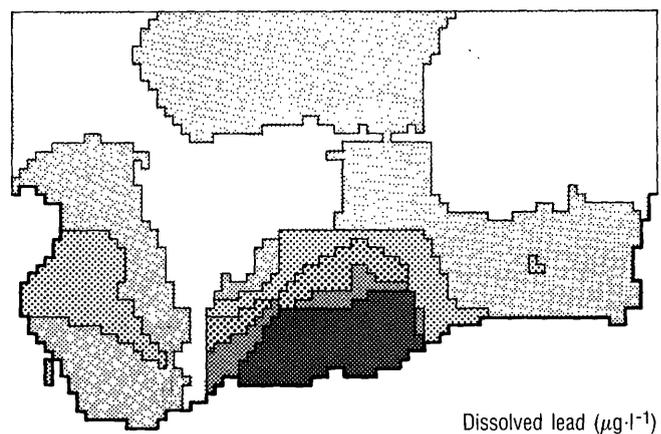
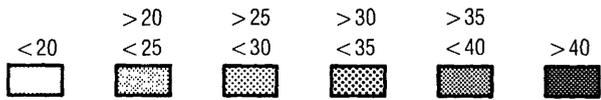
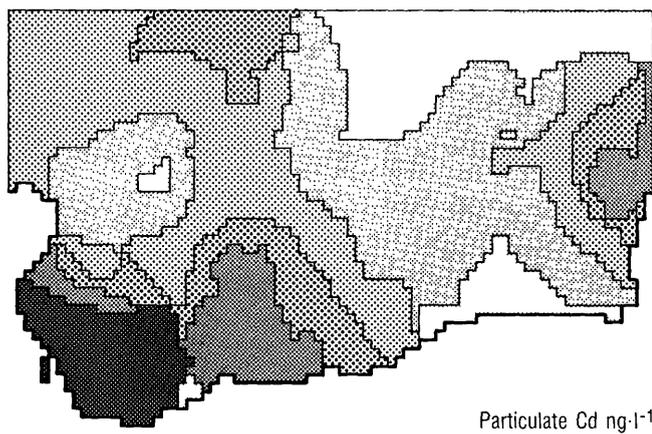


Fig. 20 Metal concentrations in the water of Monville Bay (Surface layer, 1 m of depth; August 1986)

TABLE III: Cumulative Suspended Matter Sampling: Subpelagic and pelagic zone (1-10 m depth)

| | Cu _{SM} ^a | Cu _{Diss} ^b | Kp ^c | Pb _{SM} ^a | Pb _{Diss} ^b | Kp ^c | Cd _{SM} ^a | Cd _{Diss} ^b | Kp ^c |
|----------|-------------------------------|---------------------------------|-----------------|-------------------------------|---------------------------------|-----------------|-------------------------------|---------------------------------|-----------------|
| Sector A | 138 | 0.85 | 162 | 137 | 0.30 | 457 | 6.6 | 0.05 | 132 |
| Sector B | 233 | 1.3 | 175 | 124 | 1.3 | 95 | 9.5 | 0.03 | 380 |
| Sector C | 145 | 0.78 | 186 | 105 | 0.93 | 113 | 8.9 | 0.06 | 148 |

a: metal in suspended matter (mg·kg⁻¹)

b metal in dissolved state (mg·m⁻³)

c distribution coefficient (m³·kg⁻¹)

TABLE IV: Probability distribution for Trophic Categories (%)

| | P. Tresa basin | Lake Maggiore | Monvallina Bay |
|--------------|----------------|---------------|----------------|
| Hypertrophic | 30 | 0 | 0 |
| Eutrophic | 60 | 7 | 17 |
| Mesotrophic | 10 | 57 | 66 |
| Oligotrophic | 0 | 36 | 17 |

TABLE V: Annual phosphorus load (kg·y⁻¹)

| River | P-PO ₄ ³⁻ | P-Sol. (minus P-PO ₄ ³⁻) | P-Part. | P-Tot. |
|------------|---------------------------------|---|---------|--------|
| Acquanera | 5 200 | 1 072 | 2 284 | 8 556 |
| Bardello | 25 218 | 3 709 | 7 597 | 36 524 |
| Monvallina | 4 008 | 665 | 508 | 5 181 |

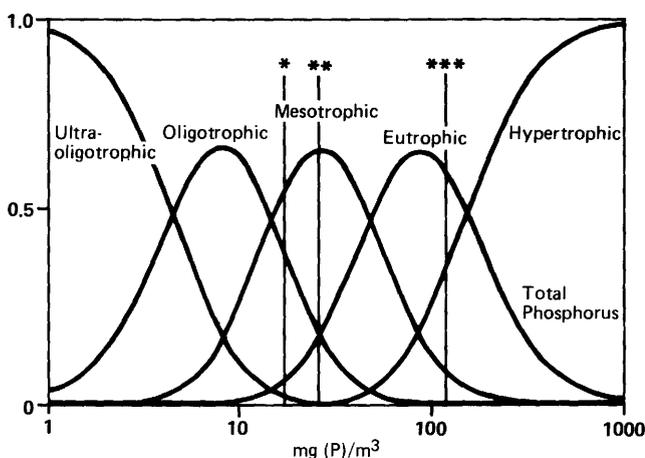


Fig. 20a Probability distribution of trophic categories

- * Lake Maggiore
- ** Monvallina bay
- *** P. Tresa basin

The three-dimensional sampling station network (Fig. 18) has been used to describe spatial variability inside the bay, and a bimonthly sampling provided the necessary information on temporal trends. The phosphorus major source is clearly represented by Bardello river, which accounts for 73% of the annual load; most of the supply (68%) is constituted by orthophosphate, but a significant fraction (21%) of the element is carried in particulate form or as other dissolved species (11%) (Table V).

The relative importance of the three phosphorous species is noticeably different in the bay; usually it varies with distance from the shore and depth. In summer, when a stable thermal stratification takes place, the orthophosphate fraction becomes negligible in the euphotic zone, as it is continuously taken up by phytoplankton.

Another important finding is the unusually high ratio total soluble P/orthophosphate, which means reduced mineralization and/or a high input of dissolved organic phosphorus species of hitherto unknown origin (Table VI).

4.6. Vertical metal transport

Particularization of metals and the subsequent deposition represent one of the first and certainly most important processes metals undergo during their cycles in freshwater bodies.

Vertical metal transport towards the lake bottom has been considered experimentally since summer 1986.

The presence of the research platform in the bay, positioned properly to meet the supposed drift currents in the bay, offered an opportunity to install a 6-level sedimentation trap system. Sediments traps of 10 l size were exposed to sedimentation and trapped material was collected by centrifugation (Table VII). The traps were positioned at -5, -7.5, -10, -12.5, -15 and -40 m depth, the lake bottom being at about -45 m depth. Samples were collected periodically over more than one year in order to assess the vertical metal fluxes towards the sediments.

Fig. 21 shows a selection of particle sedimentation rates (seasonally) versus depth. The varying influences of river input

TABLE VI: Total dissolved phosphorus/orthophosphate as found in subalpine lakes *

| Lake | P-Total soluble |
|----------------|------------------|
| | P-orthophosphate |
| Lugano | 1.11 |
| Maggiore | 1.15 |
| Como | 1.17 |
| Varese | 1.18 |
| Iseo | 1.32 |
| Monvallina Bay | 1.70 |

* Full circulation

TABLE VII: Composition of settling suspended matter

| Trap No | Depth (m) | Trapped matter (mg)* | Sedimentat. rate (mg·m ⁻² ·d ⁻¹) | Total carbon (%) | Organic carbon (%) | Total phosphorus (%) | Inorganic phosphorus (%) | Copper (mg·kg ⁻¹) | Cadmium (mg·kg ⁻¹) | Lead (mg·kg ⁻¹) |
|---------|-----------|----------------------|---|------------------|--------------------|----------------------|--------------------------|-------------------------------|--------------------------------|-----------------------------|
| T2A | 5.0 | 510 | 797 | 18.4 | 17.8 | 0.793 | 0.723 | 32 | 4.1 | 116 |
| T3A | 7.5 | 860 | 1344 | 12.6 | 11.4 | 0.221 | 0.169 | 90 | 4.4 | 165 |
| T4A | 10.0 | 1270 | 1985 | 10.5 | 9.8 | 0.264 | 0.197 | 80 | 3.5 | 89 |
| T5A | 12.5 | 1290 | 2016 | 8.4 | 7.6 | 0.171 | 0.128 | 73 | 2.9 | 71 |
| T6A | 15.0 | 1430 | 2235 | 7.8 | 7.0 | 0.163 | 0.122 | 54 | 2.9 | 92 |
| T7A | 40.0 | 2040 | 3188 | 7.7 | 6.8 | 0.237 | 0.193 | 38 | 2.7 | 119 |

during dry and wet season and the autochthonous production of particles are most evident.

Figs. 22-24 show the metal concentration versus total sedimentation rate measured at the -40 m trap. At least for cadmium and copper, the plotting suggests an influence of resuspension effects during the wet season, caused by cold bottom currents from the rivers.

Metal fluxes towards the lake bottom, calculated on the basis of 17 samplings (-40 m depth) are shown in Table VIII.

4.7. Intercompartment heavy metal mass transfer studies

Sedimentary processes in lakes differ from those in marine systems first of all by the unusually high sediment loadings and the heterogeneity of the sediment material ranging from the transport of clastic material associated with spring run-off over the sometimes highly intensive biological production to the formation of autochthonous inorganic phases such as carbonates and iron oxyhydrates following supersaturation.

Additionally, post-depositional physical processes, particularly near river deltas and coastal zones in general, promote the redistribution and resuspension of the sediments, thus enhan-

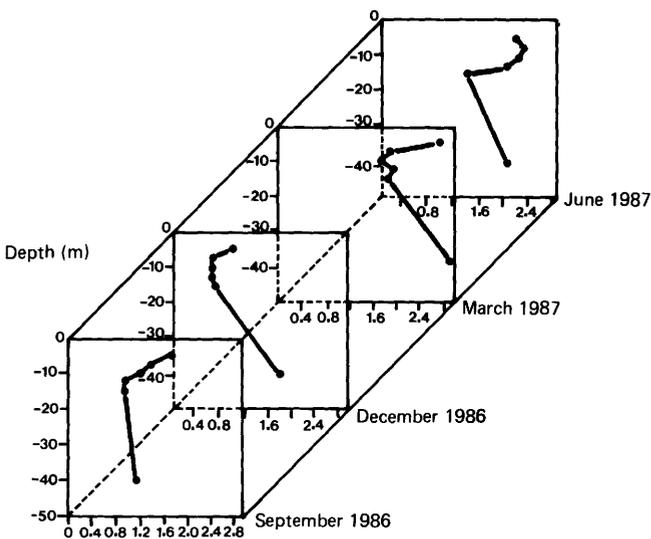


Fig. 21. Particle sedimentation rate (g/m²·day)

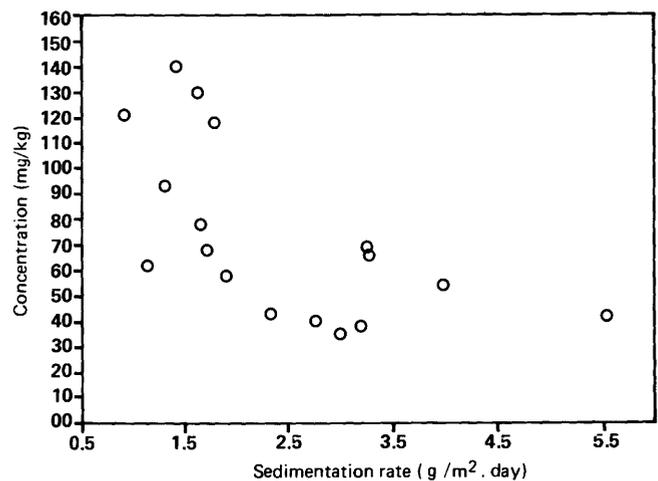


Fig. 23. COPPER - settling particle flux vs. metal concentration (40 m)

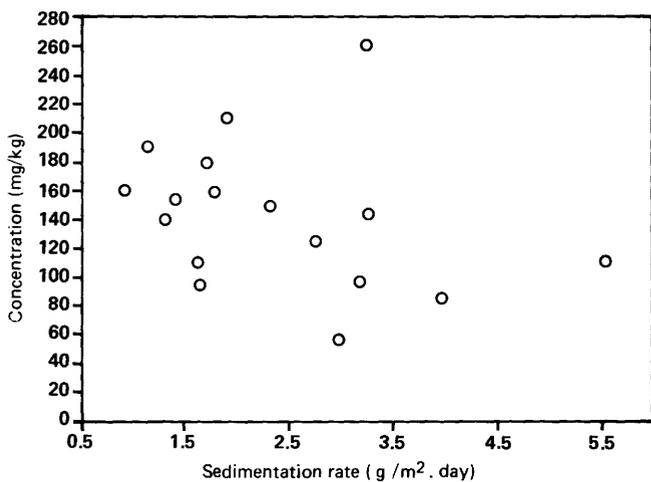


Fig. 22. LEAD - settling particle flux vs. metal concentration (40 m)

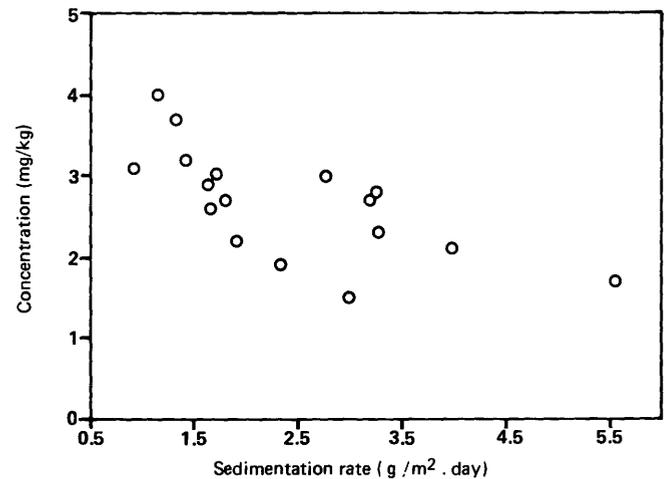


Fig. 24. CADMIUM - settling particle flux vs. metal concentration (40 m)

TABLE VIII: Sedimentation rate of settling suspended

| Sedimentation rate | | | | | |
|--------------------|--|---|---|--|--|
| | Average $\mu\text{g} \cdot \text{m}^{-2} (\text{d}^{-1})$ | SD $\mu\text{g} \cdot \text{m}^{-2} (\text{d}^{-1})$ | Highest rate $\mu\text{g} \cdot \text{m}^{-2} (\text{d}^{-2})$ | Lowest rate $\mu\text{g} \cdot \text{m}^{-2} (\text{d}^{-1})$ | Q * $\text{kg} \cdot \text{y}^{-1}$ |
| Cu | 152 | 55 | 232 | 71 | 211 |
| Cd | 5.6 | 2.1 | 9.4 | 2.8 | 7.8 |
| Pb | 325 | 132 | 844 | 155 | 451 |

Q * total embayment surface

cing the intensity of chemical, but also biological processes which convert the unstable muds into stable sediments. Main feature of these processes is the dynamic change of metals between water and many accumulative solid phases. The dynamics of these phase transfers via the dissolved state are hard to follow by in-situ experiments alone. Consequently, a series of laboratory-scale experiments have been performed:

- batch equilibria studies on stable sediments; variables are pH and complex former concentrations of both anthropogenic and natural origin;

- study of metal exchange dynamic of unstable (anoxic) sediments using the horizontal wave-movement simulation technique;

- in-situ studies at carefully selected sampling sites, identified on the basis of the 1985 spatial sediment variability study and timely distributed along the yearly water redox cycle.

Batch equilibria studies showed that rather low metal mobilities exist within the pH variability ranges observed in the Monvalle bay of 4.6 - 8.2, when completely oxidized sediments are used; cadmium and copper, however, show higher mobilities with respect to lead up to one order of magnitude. The slow oxidation of anoxic sediments, taken near to station No. 11 of the provisional sampling station network, carried out in the horizontal wave-movement simulator, revealed a highly complex metal (Cd, Cu, Pb) behaviour.

Generally speaking, all three elements show a rapid metal remobilization within the first 4-5 days, followed by a slow decrease of the dissolved metal species (Cd, Cu) obviously caused by adsorption processes on waterborne iron and manganese oxihydrates, while lead concentrations, surprisingly, remain relatively stable.

The elements cadmium and copper, the former earlier than the latter, appear increasingly after 28 d. This increase could be explained by the microbial oxidation of organic matter and the subsequent release of Cd and Cu associated with this kind of material.

Estimated remobilization rates derived from this exercise amount to $2.7 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (Cd), $93 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (Cu) and $50 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (Pb).

Many authors express serious doubt about the validity, i.e. the extrapolability of laboratory experiments such as the described ones, to real lake situations. Their limitation lies in the fact that they yield flash pictures only, with the necessity to carry out many of them during the yearly evolution of temporarily stratified lakes. A suitable compromise are enclosure experiments of adequate size, such as the MELIMEX exercise, which are, of course, expensive and require much man-power.

For the time being, in-situ experiments in view of the internal loading assessment of metals, careful samplings of sediment cores, their interstitial water, the contact water just above the sediment and the overlying water have been performed.

Sediment cores of 7 cm diameter have been taken at the 12 stations of the provisional sampling station network.

The overstanding (contact water) being removed for further analysis, the upper 10 cm of the sediment cores were removed and the pore (interstitial) water isolated with the aid of an especially developed full-TEFLON sediment squeezer. Elements analyzed were Cd, Cu and Pb.

Fig. 25 shows the analytical figures obtained for sediment, pore water, contact water and overlying hypolimnetic water for the element cadmium.

Most obviously, the mobilization of metals at pore water level is affected by a number of site-specific factors and studies on the solid-matter speciation, i.e. the effective binding sites in the sediment, yield more insight into these processes.

Sediment metal species were determined according to the procedure described by Foerstner and Kersten (1987). Five sediment cores were taken along the boundary of the embayment to the open lake. Figs. 26-28 show the results.

Surprisingly, copper appears less abundant in the exchangeable and carbonatitic phases; most of it is bound to the only moderately reducible iron-manganese phases and up to 20% is associated with the residual crystalline phases. Lead, on the contrary and against expectations, is more available than copper and its residual-associated fraction is lower.

Cadmium is the most mobile element. Up to 75% is available, a considerable part is associated with the reactive, easily reducible iron phases and only a very minor portion appears to be fixed in the residual fraction.

With respect to the total metal concentrations of the five sediment core samples examined we may conclude that the relative availability as deduced from the remobilization rates is confirmed and that an estimate around 20%-25% of the metals Cd, Pb and Cu would be potentially remobilizable during the yearly oxygenation of the surface sediment in winter time.

5. TOTAL METAL DISTRIBUTION IN THE TEST SITE IN THE TWO-BOX APPROXIMATION

A two-box analysis of the considered problem is necessary in the case of important hypolimnetic metal inputs (in particular release from bottom sediments) and/or marked inhomogeneity in particulate matter distribution, metal distribution coefficient and horizontal mixing coefficient.

Although this is probably not the case of our site, we present in this paragraph the results of a two-box analysis for the sake of generality.

Assuming constant coefficients, the mathematical framework is as follows:

$$d/dt C_{t1} = -a_{11}C_{t1} + a_{12}C_{t2} + a_{10}C_{t1}(0) = C_{t10} \quad (1)$$

$$d/dt C_{t2} = -a_{21}C_{t1} + a_{22}C_{t2} + a_{20}C_{t2}(0) = C_{t20}$$

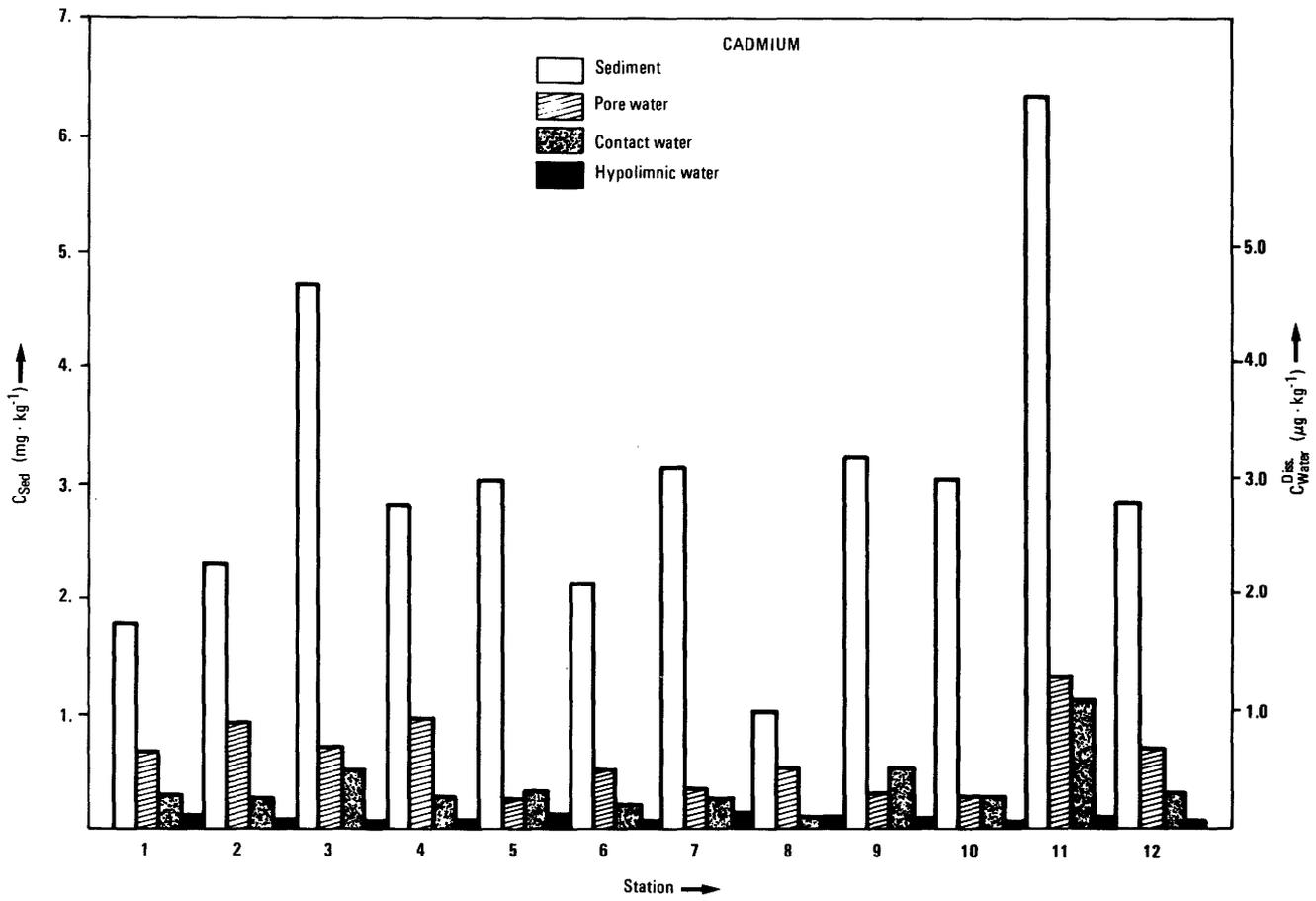


Fig. 25. Cadmium distribution at the sediment-water interphase

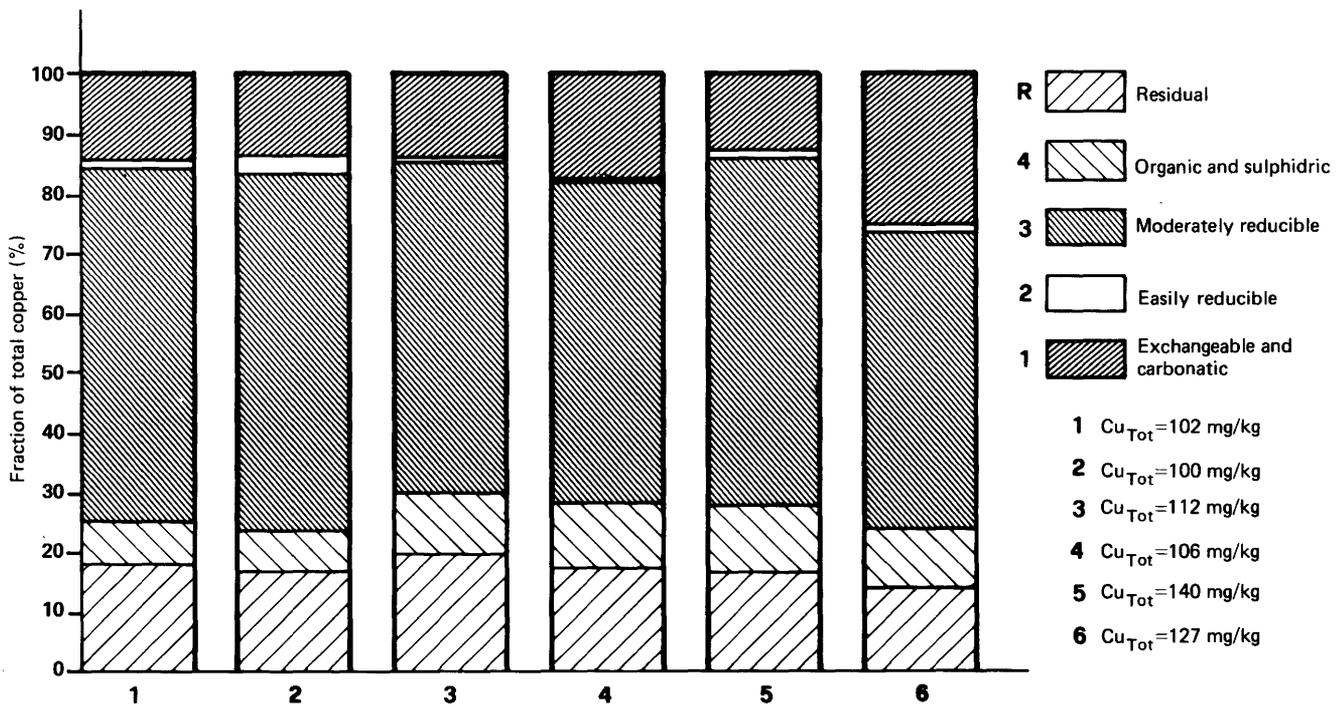


Fig. 26. Speciation of copper (Monvalle bay sediments)

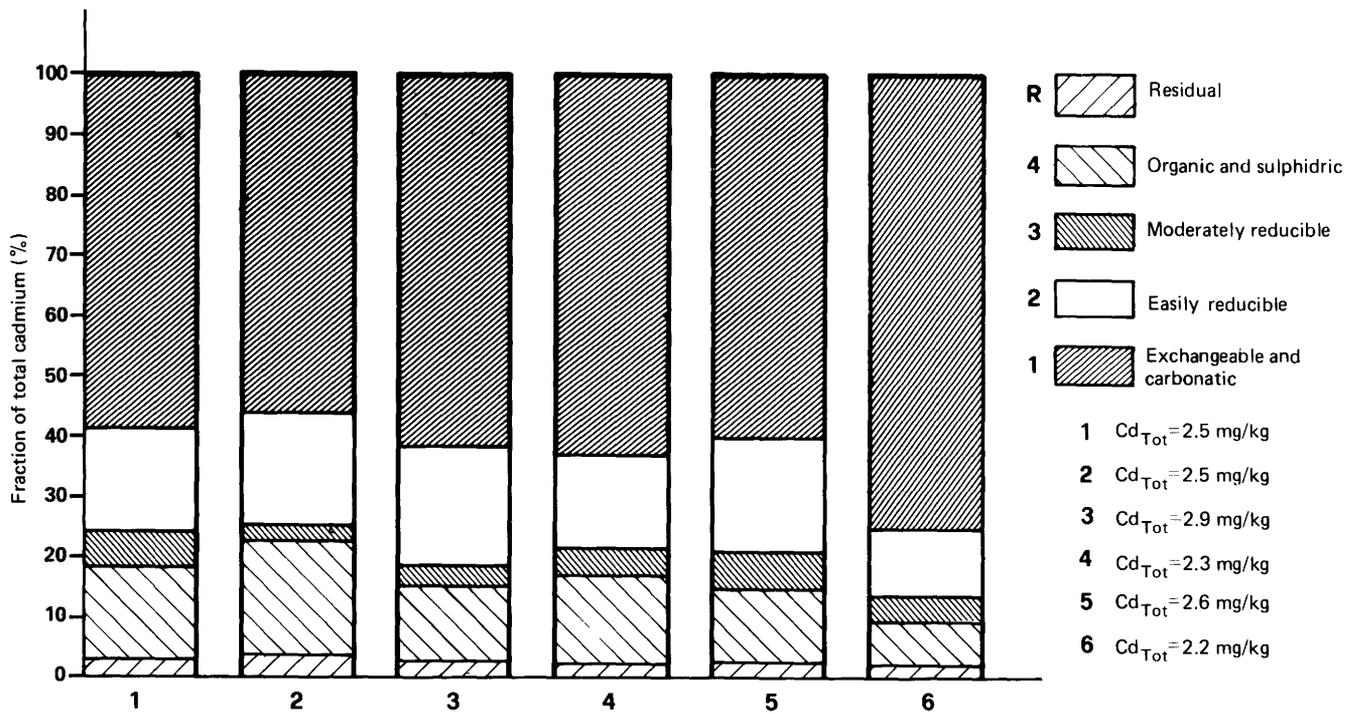


Fig. 27. Speciation of cadmium (Monvalle bay sediments)

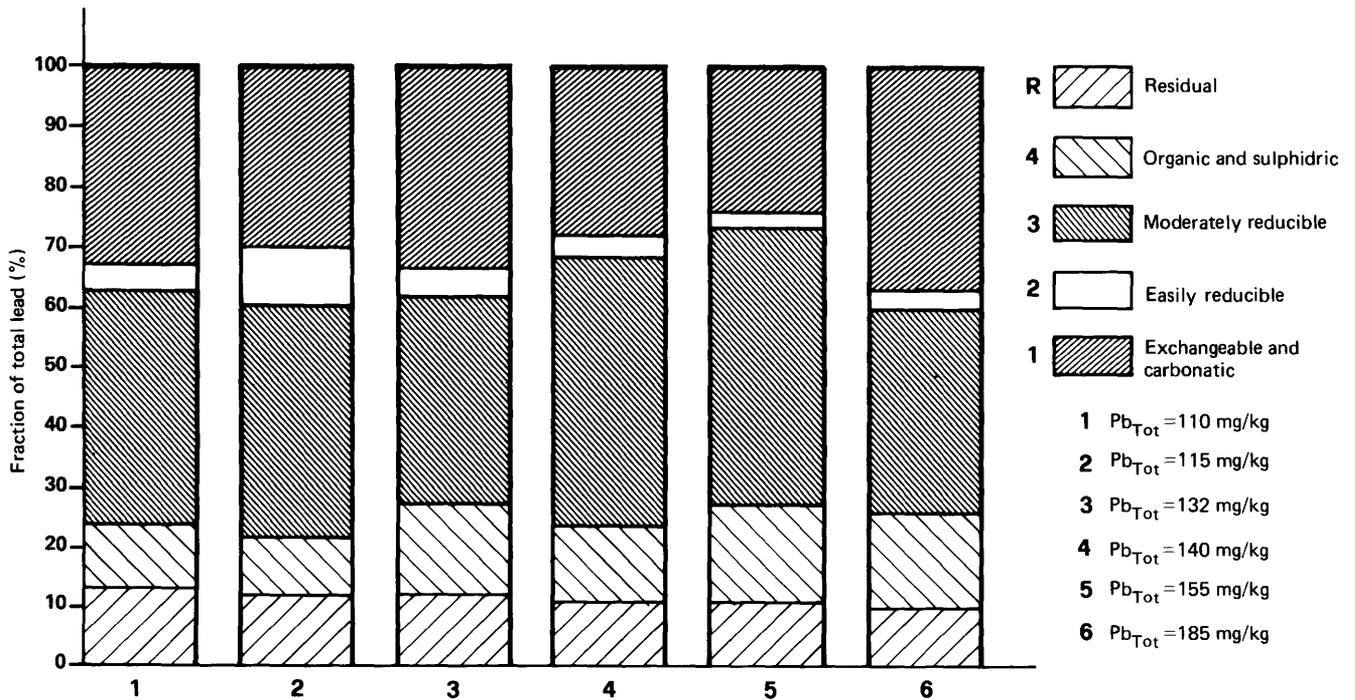


Fig. 28. Speciation of lead (Monvalle bay sediments)

where C_{t1} , C_{t2} are the total metal concentrations in epilimnion and hypolimnion, respectively, and

$$a_{11} = k_{ex, 1L} + k_{mix, 1} f_{p1} + k_{sed, 1} (1 - f_{p1})$$

$$a_{12} = k_{mix, 1} f_{p2}$$

$$a_{10} = k_{in, r} C_{t,r} + k_{in, L1} C_{t, L1} + \phi_1$$

$$a_{21} = k_{mix, 2} f_{p1} + k_{sed, 2} (1 - f_{p1})$$

$$a_{22} = k_{ex, 2L} k_{mix, 2} f_{p2} + k_{sed, 2} (1 - f_{p2})$$

$$a_{20} = k_{in, L2} C_{t, L2} + \phi_2$$

The symbols are defined in Table IX. The solution of system (1) has the form:

$$C_{ti} = A_i \exp(-\alpha_1 t) + B_i \exp(-\alpha_2 t) + C_i \quad (2)$$

(i = 1, 2)

where the time constants α_1 , α_2 of the transient terms, the coefficients A_i , B_i and the «asymptotic» concentrations C_i are given by rather cumbersome expressions containing the rates k_{ex} , k_{in} , k_{mix} , k_{sed} , the «external» concentrations $C_{t,r}$, $C_{t,L}$, the release flux ϕ and the «initial» concentrations $C_{ti}(0)$.

TABLE IX: Definition of symbols ($i = 1$ epilimnion; $i = 2$ hypolimnion)

| | |
|---|--|
| $f_{pi} \equiv \frac{1}{1 + k_p C_{pi}}$ | $C_{pi} \equiv$ concentration of suspended matter in region i |
| $k_{mix, i} \equiv \frac{m_{th} S_{th}}{V_i}$ | $\left. \begin{array}{l} m_{th} \equiv \text{mixing coefficient} \\ S_{th} \equiv \text{area of lake section} \\ V_i \equiv \text{volume of region } i \end{array} \right\}$ at depth of thermocline |
| $k_{sed, i} \equiv \frac{v_s S_{th}}{V_i}$ | $v_s \equiv$ settling velocity of suspended matter |
| $k_{in, r} \equiv \frac{q_{in}}{V_1}$ | $q_{in} \equiv$ inflow rate of tributary |
| $k_{in, Li} \equiv \frac{S_i v_{L \rightarrow i}}{V_i}$ | $S_i \equiv$ area of boundary surface region i - open lake $v_{L \rightarrow i} \equiv$ average value of water velocity orthogonal component to surface S_i |
| $k_{ex, iL} \equiv \frac{S_i v_{i \rightarrow L}}{V_i}$ | $S_L \equiv$ area of the bay surface |
| $\phi_1 \equiv \frac{(S_L - S_{th}) \varphi_1}{V_1}$ | $C_{t, r} \equiv$ total metal concentration in river $C_{t, Li} \equiv$ total metal concentration in open lake (region 1) |
| $\phi_2 \equiv \frac{S_{th} \varphi_2}{V_1}$ | $\varphi_1 \equiv$ mean release flux from bottom sediment in the shallow region of the bay $\varphi_2 \equiv$ mean release flux from bottom sediment in the stratified region of the bay |

Note that it must be on average:

$$V_1 k_{in, r} + \sum_i V_i k_{in, Li} = \sum_i V_i k_{ex, iL}$$

The time constants are given by:

$$\alpha = \frac{1}{2} (a_{11} + a_{22} \pm \sqrt{(a_{11} - a_{22})^2 + 4a_{12} a_{21}})$$

(α_1 with +, α_2 with -).

The asymptotic terms are given by:

$$C_1 = (a_{22} a_{10} + a_{12} a_{20}) / (a_{11} a_{22} - a_{12} a_{21})$$

$$C_2 = (a_{21} a_{10} + a_{11} a_{20}) / (a_{11} a_{22} - a_{12} a_{21})$$

The general integral of system (1) is given by:

$$C_{t1} = a_{12} / (a_{11} - \alpha_1) A_2 \exp(-\alpha_1 t) + a_{12} / (a_{11} - \alpha_2) B_2 \exp(-\alpha_2 t) + C_1$$

$$C_{t2} = A_2 \exp(-\alpha_1 t) + B_2 \exp(-\alpha_2 t) + C_2$$

the constant coefficients A_2, B_2 being determined by means of the initial conditions.

Neglecting the term connected to the shorter characteristic time, the structure for the time-dependent metal concentrations results as follows:

$$C_{t1} \sim (\alpha_1 - a_{11}) / \alpha_1 \cdot C_{t10} \exp(-\alpha_2 t) + (1 - (\alpha_1 - a_{11}) / \alpha_1 \cdot \exp(-\alpha_2 t)) C_1 + a_{12} / \alpha_1 \cdot (C_{t20} - C_2) \exp(-\alpha_2 t)$$

$$C_{t2} \sim (a_{11} - \alpha_2) / \alpha_1 \cdot C_{t20} \exp(-\alpha_2 t) + (\alpha_1 - a_{11}) / \alpha_1 \exp(-\alpha_2 t) C_2$$

$$(a_{11} - \alpha_2) (C_{t10} - C_1) \exp(-\alpha_2 t) + (1 - (\alpha_1 - a_{11}) / \alpha_1 \exp(-\alpha_2 t)) C_2$$

The characteristic times for the Bay of Monvalle have been evaluated on the basis of the process rates listed in Table X. The time constants of the transient terms in eq. (2) resulted as follows:

$$\alpha_1 = 2.72 \text{ month}^{-1}, \alpha_2 = 0.76 \text{ month}^{-1}$$

hence transient terms give rapidly vanishing contributions. The asymptotic total metal concentrations in epilimnion C_1 and in hypolimnion C_2 have been calculated on the basis of data for external and internal metal loading and metal distribution coefficients, listed in Table XI.

On the basis of model calculations on the seasonal evolution of the phytoplankton biomass in the bay and of river water sampl-

TABLE X: Process rates in the Monville Bay (month⁻¹)

| Process | Coefficient | Adopted value |
|----------------------|--------------|---|
| Horizontal transport | $k_{in, r}$ | 0.434 ($q_{in} = 4.85 \text{ m}^3 \text{ s}^{-1}$) |
| | $k_{ex, 1L}$ | 1.44 |
| | $k_{in, L1}$ | 1.00 |
| | $k_{ex, 2L}$ | 0.349 |
| | $k_{in, L2}$ | 0.349 |
| Vertical transport | $k_{mix, 1}$ | 0.823 |
| | $k_{mix, 2}$ | 0.753 |
| | $k_{sed, 1}$ | 1.65 ($v_s = 1 \text{ md}^{-1}$) |
| | $k_{sed, 2}$ | 1.35 |

TABLE XI: Parameters depending on the metal species (Monville Bay, 1985)

| | Cd | Cu | Pb |
|--|-------|------|-------|
| Distribution coefficient | | | |
| $k_{p1} \sim k_{p2}$ ($\text{m}^3 \text{ g}^{-1}$) | 0.06 | 0.06 | 0.16 |
| Metal concentration in the rivers (mg m^{-3}) | 0.23 | 6.7 | 3.3 |
| Metal concentration in the open lake (mg m^{-3}) | 0.006 | 0.4 | 0.032 |
| Release flux from the sediment ($\text{mg m}^{-2} \text{ month}^{-1}$) | 0.21 | 4.54 | 0.37 |

ing, the particulate matter concentration (organic + inorganic) has been assumed as 2.15 gm^{-3} in the epilimnion, 1.9 gm^{-3} in the hypolimnion

The results for Cu, Cd and Pb are presented in Table XII together with experimental average values (averages on space and time of experimental results obtained on 100 lake water samples).

6. REMARKS ON THE ESTIMATION OF THE COEFFICIENTS

A reliable estimation of the mixing coefficient bay - open lake, $k_{ex} = 1/\tau_w$ (τ_w = water mean residence time in the bay) should be based on hydrodynamic calculations and measurements.

TABLE XII: Space and Time Average Total Metal Concentrations in the Monville Bay (1985) (ng/l)

| | Cd_{diss} | Cd_{part} | Cu_{diss} | Cu_{part} | Pb_{diss} | Pb_{part} |
|--------------------------|-------------|-------------|-----------------|---------------|---------------|---------------|
| Rivers | | 230 | | 6700 | | 3300 |
| Open lake | 7 ± 4 | | 330 ± 120 | | 24 ± 25 | |
| Bay (measured) | 90 ± 44 | 14 ± 7 | 1703 ± 1304 | 230 ± 204 | 783 ± 654 | 251 ± 114 |
| Hypolimnion (measured) | 89 ± 22 | 9 ± 2 | 1776 ± 684 | 167 ± 40 | 673 ± 270 | 233 ± 91 |
| Epilimnion (measured) | 54 | 9 | 1681 | 216 | 610 | 210 |
| Hypolimnion (calculated) | 40 | 6 | 1302 | 159 | 443 | 144 |

In want of these, we have considered relationships involving k_{ex} between integral quantities, which are accessible to measurements, such as the relationship between steady state metal concentration and metal loading, and the relationship between metal concentration in the sediments and metal loading. The first relationship is the following:

$$C_{t, \infty} = \frac{k_{in, r} C_{t, r} + k_{in, L} C_{t, L} + \phi}{k_{ex} + k_{sed} (1 - f_p)} \quad (1)$$

which is derived from the one-box balance equation for a «total» metal. Assuming $\phi \sim 0$, and taking into account that

$$k_{in, r} + k_{in, L} = k_{ex}$$

eq. (1) becomes:

$$C_{t, \infty} = \frac{k_{in, r} C_{t, r} + (k_{ex} - k_{in, r}) C_{t, L}}{k_{ex} + k_{sed} (1 - f_p)} \quad (2)$$

where all quantities except k_{ex} are measured (see above). The values obtained during the 1985 campaign are as follows:

$$k_{in, r} = 0.194; \quad k_{sed} = 1.17 \text{ (month}^{-1}\text{)}$$

$$C_{t, r} = 6.8; \quad C_{t, L} = 0.33; \quad C_{t, \infty} = 1.9 \text{ (mg Cu m}^{-3}\text{)}$$

Furthermore, from the values adopted for k_p (Cu) and C_p (see above), we have:

$$f_p \text{ (Cu)} = 0.89$$

From eq. (2) we obtain:

$$k_{ex} = 0.65 \text{ month}^{-1}$$

Separate estimation of $k_{ex, 1}$, $k_{ex, 2}$ requires an additional information on the ratio between epilimnetic and hypolimnetic water velocity, which was assumed ~ 10 .

The second relationship is the following:

$$\bar{l} = \left(\frac{1}{k_p} + C_p \right) \left(\frac{1}{\tau_w} + \frac{1}{\tau_{sed}} \right) \bar{C}_s \quad (3)$$

where:

$$\bar{l} = \text{metal loading per year per unit volume (kg} \cdot \text{yr}^{-1} \cdot \text{m}^{-3}\text{)}$$

$$\bar{C}_s = \text{metal concentration in sediment (mg} \cdot \text{kg}^{-1}\text{)}$$

$$1/\tau_{sed} = k_{sed} (1 - f_p).$$

Eq. (3) is derived from the assumption that metal concentration in fresh sediments is the same as in settling material (Imboden et al. 1980). \bar{C}_s has to be taken as an average value in a given sediment layer. The other quantities, in particular \bar{I} , have to be taken as average values on the time interval to which the considered sediment layer is referred. From 115 samples taken in a ~ 15 cm thick layer at the sediment surface, an average value $\bar{C}_s = 108 \text{ mg Cu kg}^{-1}$ was obtained.

Assuming Cu loading as approximately constant during the last 11 years (time interval approximately corresponding to the 15 cm thick sediment layer), we have $\bar{I} = 15.9 \text{ mg} \cdot \text{yr}^{-1} \text{m}^{-3}$, and from eq. (3) $k_{ex} = 0.52 \text{ month}^{-1}$.

A not too large discrepancy between two independently obtained values of k_{ex} can be considered as a rather satisfactory consistency test for the experimental results.

For the determination of the distribution coefficient water-suspended matter, $k_p = C_{sp} (\text{mg} \cdot \text{kg}^{-1}) / C_l (\text{mg} \cdot \text{m}^{-3})$, specific laboratory research has been programmed at JRC. Preliminary adopted values as listed in Table XII have been obtained from measurements of C_{sp} , C_l on local samples. The values of k_p for Cu and Cd are in satisfactory agreement with the indications of Baccini et al. 1979.

The evaluation of the vertical mixing coefficient at the depth of the thermocline m_{th} was based on computer elaboration (code HEAT) of water temperature profiles, which have been automatically measured and recorded at the platform in the bay of Monvalle beginning with July 1986. (see Rossi et al. 1983). The interpretation of temperature data (see for instance Fig. 29 as for the interval 18-27 September 1986) resulted as particularly awkward, due to the presence both of internal waves and of advective thermal effects in the bottom layers.

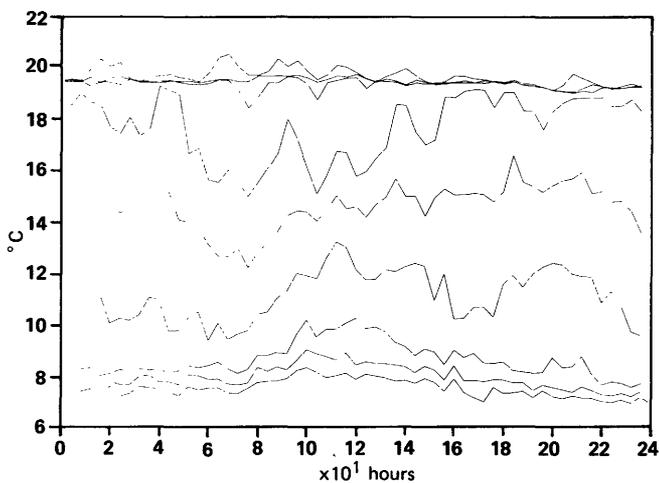


Fig. 29. Time variation of water temperature at fixed depths (Bay of Monvalle, 18-27th Sept. 1986)

7. EQUATIONS WITH TIME-DEPENDENT COEFFICIENTS: THE CODE «METALS»

The analytical solution of system (5.1) of linear balance equations with constant coefficients has the advantage of putting in evidence asymptotic values of metal concentration and characteristic time of transient terms explicitly. Interpretative or predictive calculations of the evolution of metal concentration in epilimnion and hypolimnion of a lake along a year asks for introducing time-dependent coefficients into the balance equations and solving the equations numerically.

Time dependence concerns physical quantities such as water temperature and vertical mixing coefficient, as well as chemical parameters such as pH and redox potential, which affect metal distribution between dissolved and particulate phase and

release flux from sediments. As for horizontal transport parameters, time dependence can only be introduced via inflow rate of tributaries.

The seasonal evolution of autochthonous organic suspended matter (i.e. phytoplankton biomass) concentration can be evaluated by means of a trophic model of the considered water body. As for allochthonous suspended matter, time dependence can be introduced via suspended matter concentration in the tributaries and overflow velocity. External metal loading can be evaluated by means of careful sampling of water and suspended matter in the tributaries.

The computer code METALS, which is described below, evaluates the coefficients and solves the equations numerically with time step = 1 month.

In the case of the Monvalle Bay, epilimnetic and hypolimnetic concentrations reach their asymptotic value rapidly in good agreement with the analytical solution of the equations with constant coefficients.

The code METALS gives a representation of the heavy metal cycle in a bay. It has been conceived as a vertical box interaction model with two regions: epilimnion and hypolimnion. The requirement of flexibility of the code has been taken into account and two versions are now available, corresponding each to different morphological characteristics. Version one describes the case of a bay which has a boundary surface with the rest of the lake, while version two considers the possibility of a closed bay or a whole lake.

Another feature of the code consists of the possibilities with regard to the particular input requirements of the mixing coefficient at the depth of the thermocline, and of the particulate matter concentration both in epilimnion and hypolimnion. These data can be supplied in the form of discrete values, either be calculated by the code BOX 2 describing the phytoplankton annual evolution, in which case the facility of a direct coupling of the two codes is provided. The seasonal evolution is described with a time step of one month.

To establish a complete picture of the input data, we supply the following outline:

- a) integration data for the STIFF routine, which solves the system of differential equations; the time step considered is one month;
- b) data defining the period to be treated, such as the start-date and the length of the period (number of months);
- c) data concerning the switch facilities:
 - switch parameter for the choice of one of the two versions, i.e. performing the simulation for a bay or a lake;
 - switch parameter for the coupling of the two codes METALS and BOX 2;
- d) initial conditions, i.e. the concentrations of the ecosystem constituents at the first month of the considered time interval;
- e) data concerning the morphological characteristics of the bay:
 - water volume of the epilimnion,
 - water volume of the hypolimnion,
 - area of the cross section of the waterbody at the depth of the thermocline,
 - area of the projected bottom surface of the epilimnion (including the shallow coastal zone),
 - area of the projected bottom surface of the hypolimnion,
 - surface area of the boundary between the epilimnion and the rest of the lake,
 - surface area of the boundary between the hypolimnion and the rest of the lake;
- f) physical and chemical data:
 1. settling velocity in the epilimnion,
 2. settling velocity in the hypolimnion,
 3. water-particulate matter distribution coefficient for the epilimnion,
 4. water-particulate matter distribution coefficient for the hypolimnion,

5. mixing coefficient at the depth of the thermocline.

All data described in points 3, 4 and 5 are provided as mean monthly values.

g) general data concerning the site:

1. mean inflow rate of the tributaries;
2. total metal concentration in the tributaries,
3. total metal concentration in the epilimnion of the rest of the lake, if the case in point is the bay version,
4. total metal concentration in the hypolimnion of the rest of the lake, if the case in point is the bay version,
5. particulate matter concentration in the epilimnion,
6. particulate matter concentration in the hypolimnion,
7. metal flux from the sediments to epilimnion (including the shallow coastal zone),
8. metal flux from the sediments to the hypolimnion,
9. mean velocity value of the water flowing from the epilimnion to the rest of the lake,
10. mean velocity value of the water flowing from the hypolimnion to the rest of the lake.

All data described in points 1-8 are provided as mean monthly values.

CONCLUDING REMARKS

The principal goal of the present study was the development and refinement of methods and procedures in the areas of trace element analytical chemistry and mathematical modelling of contaminant dispersion into large freshwater bodies.

The choice of an embayment system coupled to rivers, which emit trace metal pulses both in particulate and dissolved forms, allows a number of generalizations to similar situations in other European lakes.

Most important in this respect are the results on the spatial variability of metals in sediments. Foerstner and Salomons (1984) conjectured that trace metals are cycled in water systems according to complex physical (resuspension, redeposition, particle sorting, etc.) mechanisms, which result in an extremely inhomogeneous spatial distribution of metals and contaminants in general.

The reliability of contaminant mass balances and predictions of long term behaviour of contaminants in rivers and lakes, which is the final goal of our research activities, will suffer accordingly from this information gap and systematic sediment mapping with respect to their contaminant content is in our view a basic investigation for those freshwater bodies, which are likely to become drinking water sources in the future.

Earlier studies on lake Como, lake Maggiore, lake Varese and most recently lake Orta demonstrated the usefulness of such inventories for the correct evaluation of the contamination status of lakes (Muntau and Baudo, 1985 and 1986).

Similarly the distribution of metals in dissolved and particulate forms in the water body itself is essentially heterogeneous (Fig. 20), and erroneous results might easily be found by the point sampling approach, while cumulative sampling procedures will yield much more reliable results.

Summarizing, the extraordinary resolution obtained in the present study suggests that sampling strategies for contaminant analysis in aquatic system should be carefully considered and adapted to each specific case in order to avoid wrong conclusions.

While most authors agree that the process of sorption and settling is the major removal mechanism for contaminants in lakes and rivers, surprisingly little quantitative information is available for the vertical transport of contaminants and their subsequent transfer rates during diagenesis of the settled material.

Resuspension of settled particles by hydrological phenomena and bioperturbation are clearly coupled with the remobilization of contaminants and we need to know the remobilization rates for the evaluation of the quality of surface waters as drinking water sources.

Particle concentrations and fluxes towards the lake bottom are quite similar to those encountered in lake Constance and lake Zürich. Rivers Bardello, Monvallina and Aquanera discharge annually about 2700 t of solids, while about 3300 t/yr are settled in the area of the embayment (on the basis of the - 40 m sedimentation trap data).

Solid phase distribution measurements of contaminants in trapped settling matter allow the investigation on single processes such as autochthonous calcite precipitation and associated contaminant removal and mineralization of allochthonous and autochthonous organic substance and associated contamination freesetting. Much attention has still to be applied to the distinction of the «settling» and the «mobile», never-settling particulate matter.

Our studies on the differentiation of element-specific sedimentation fluxes and their correlation with external suspended matter loading and lake-internal particle generation evidenced the importance of particle resuspension from the lake bottom in the particle transport within the lake and associated contaminant transfer.

Clearly only a smaller part of the collected experimental data has been utilized for modellistic studies, whose final results couldn't be anything more detailed than average total metal concentrations as functions of time.

Relationships among metal concentrations in open lake, embayment (water and sediment) and tributaries have put in evidence the predominant influence of water exchange between bay and open lake, in such a way that occasional metal input pulses from tributaries produce rapidly vanishing effects on the average metal concentration in the bay.

We must obviously conclude that the considered coastal zone of lake Maggiore is presently in steady state conditions as for heavy metal pollution at levels which are below toxicity thresholds for biologic populations.

On the other hand modelling effort has succeeded in creating an interpretative and predictive scheme to be rather easily generalized to other water bodies, as well as in allowing a preliminary insight into the major problems of coefficient evaluation.

REFERENCES

- H. MUNTAU
Heavy metal distribution in the aquatic ecosystem «Southern Lake Maggiore»: I. Outlay of the project.
Mem. Ist. Ital. Idrobiol. 38 (1981), 1-18
- H. MUNTAU
Heavy metal distribution in the aquatic ecosystem «Southern Lake Maggiore»: II. Evaluation and trend analysis.
Mem. Ist. Ital. Idrobiol. 38 (1981), 505-529
- R. GOMMES, H. MUNTAU, R. CENCI, A. LATTANZIO and G. PIGOZZI
Characterisation du chimisme des eaux superficielles des Bassins Sud et de Pallanza du Lac Majeur.
Mem. Ist. Ital. Idrobiol. 38 (1981), 19-77.
- R. BAUDO, R. DE BERNARDI, E. SOLDVINI, B. LOCHT and H. MUNTAU
Spatial and temporal variations of metal concentrations in plankton of Lago Maggiore and Lago di Mergozzo.
Mem. Ist. Ital. Idrobiol. 38 (1981), 79-100
- H. MUNTAU, B. LOCHT, R. CENCI, A. LATTANZIO and G. PIGOZZI
Elementkomposition rezenter Schlämme und Sedimente im Littoral des Lago Maggiore.
Mem. Ist. Ital. Idrobiol. 38 (1981), 187-207
- B. LOCHT and H. MUNTAU
La composition chimique des sédiments profonds du Lac Majeur
Mem. Ist. Ital. Idrobiol. 38 (1981), 101-186

- R. BAUDO, R. DE BERNARDI, E. SOLDAVINI, B. LOCHT and H. MUNTAU
Spatial and temporal variations of metal concentrations in plankton of Lago Maggiore and Lago di Mergozzo.
Mem. Ist. Ital. Idrobiol. 38 (1981), 79-100
- H. MUNTAU, B. LOCHT, R. CENCI, A. LATTANZIO and G. PIGOZZI
Elementkomposition rezenter Schlämme und Sedimente im Littoral des Lago Maggiore.
Mem. Ist. Ital. Idrobiol. 38 (1981), 187-207
- B. LOCHT and H. MUNTAU
La composition chimique des sediments profonds du Lac Majeur
Mem. Ist. Ital. Idrobiol. 38 (1981), 101-186
- R. GOMMES et H. MUNTAU
La composition chimique des limnophytes du Lac Majeur
Mem. Ist. Ital. Idrobiol. 38 (1981), 237-307
- W. SALOMONS
Metal speciation in sediments and sludges
Contact Report (1987), BCR-CEE Brussels
- U. FÖRSTNER and KERSTEN
Metal species determination in sediments
Contract Report (1987), BCR-CEE Brussels
- H. MUNTAU and P. SCHRAMEL
Multielement analysis of trace metals in aquatic macrophytes
Unpublished results.
- K.H. GROBECKER and H. MUNTAU
Spurenelementbestimmung in Rückständen in und auf organischen Filtermaterialien und DZAAS
Fres. Z. Analyt. Chem. 322 (1985), 728-730.
- M. VAN SON and H. MUNTAU
Determination of cadmium, lead and copper in waterborne suspended matter by DZAAS
Fres. Z. Analyt. Chem. 328 (1987), 390-392.
- A. CALDERONI, R. MOSELLO, B. SULIS and G. TARTARI (1985) Caratteristiche chimiche e chimico-fisiche in: «Commissione Internazionale per la protezione delle acque italo-svizzere» Ricerche sull'evoluzione del Lago Maggiore» Campagna 1985: 47-49
- IRSA
Istituto di Ricerca sulle acque. 1980. Indagine sulla qualità delle acque lacustri italiane. Quaderni IRSA, N.43: 179-181.
- G. MARENCO, R. BAUDO and H. MUNTAU
Phosphorus speciation and its temporal and spatial variability in a bay
International Conference, Chemicals in the Environment, 30th June-3rd July 1986, Lisbon (Portugal).
- G. PREMAZZI and G. MARENCO
1982 «Sedimentation rates in a Swiss-Italian lake measured with sediment traps»
Hydrobiologia 92, 603-610 (1982).
- G. PREMAZZI and G. ROSSI
«Phosphorus Cycle in a Subalpine Lake»
Final Report - Directorate General for Science, Research and Development - EUR 9116 EN.
- D.M. IMBODEN and R.P. SCHWARZENBACH
Spatial and temporal distribution of chemical substances in lakes: modelling concepts - in «Chemical Processes in Lakes», ed. by W. Stumm, New York (1984), 1-30.
- S.E. JOERGENSEN
Modelling the distribution and effect of toxic substances in aquatic ecosystems - in «Application of Ecological Modelling in Environmental Management», ed. by S.E. Joergensen, Part A, 455-83 (1983).
- L. BARBANTI and A. CAROLLO
Analisi della diffusione turbolenta e dei processi circolatori nel Lago Maggiore - Mem. Ist. Ital. Idrobiol. 21, 37-87, 1967.
- D.M. IMBODEN, J. TSCHOPP and W. STUMM
Die Rekonstruktion frueherer Stoffrachten in einem See mittels Sedimentuntersuchungen - Schweiz. Z. Hydrol. 42, 1-14, 1980.
- P. BACCINI, J. RUCHTI, O. WANNER and E. GRIEDER
MELIMEX, an experimental heavy metal pollution study: Regulation of trace metal concentration in limno-corrals - Schweiz. Z. Hydrol. 41, 202-27 (1979).
- G. ROSSI, F. BEONIO-BROCCHERI and J. SANGREGORIO
On the evaluation of the vertical diffusion coefficient in lakes by means of measured temperature profiles - in «Analysis of Ecological Systems: State of the Art in Ecological Modelling», ed. by W.K. Lauenroth, G.V. Skogerboe and M. Flug, 615-21, 1983.

4. Chemical Waste

INTRODUCTION

In the past hazardous or toxic wastes have been regarded as an unavoidable consequence of industrial production. Now, due to the consequences of improper disposal, there is a general agreement that hazardous or toxic wastes are a matter of important concern and will be one of the major environmental and public health problems facing all industrialized countries in the 80's and 90's.

The field of hazardous waste management and disposal is so vast that a programme finding phase has to precede the start of experimental activities. During this phase experts of the chemical industry, regulator bodies and specialized institutions have been contacted. The activities emerging from this selection process have encountered a wide interest in the European Community and are strongly related to the present and future regulatory activities of the Commission (D.G. XI in particular). The activities of J.R.C. in the field of chemical waste, which are taking also in consideration its past experience in the field of nuclear waste and its acknowledged contributions to solve the SEVESO problems, are the following:

- fate, transformations and pathways of toxic chemicals released during waste management activities;
- estimation of human exposure to toxic residues originated from chemical waste;
- design and elaboration of a decision support system ChEM (Chemical Emergencies Manager) to give information on the management of toxic chemicals and wastes and to suggest strategies in the case of chemical accidents.

RESULTS

a) Fate and pathway of toxic compounds

For studies of safe disposal of toxic waste and on the fate of toxic compounds in the environment, new laboratory facilities have been installed and specialized personnel have been engaged. In particular, laboratories for the handling of toxic compounds at trace level were completed.

A mobile unit for «in field» studies arrived in the last quarter of 1987 and the installation of analytical instrumentation is under way.

The methodologies for studies on fate and pathways of chemicals in soils are under evaluation and experimental activities started.

A specific analytical procedure for the extraction and measurement of polyhalogenated aromatic compounds in environmental samples was developed. The method has been applied for the determination of polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofuranes (PCDFs) and polychlorinated biphenyl (PCBs) in fat containing samples. These compounds are strongly lipophilic and accumulate in a wide variety of matrices. Furthermore, they are very stable to environmental degradation contributing to food-chain contamination.

The method is based on liquid chromatography on different types of absorbent and was verified for application on fat containing samples by the use of ^{14}C radiolabelled TCDD and PCBs. The chlorinated compounds were extracted from spiked samples by methanol, ethylether and hexane. The extract was applied to a column of Bio-Beads for the separation of lipids (Fig. 1A). In a following column the solution was passed through

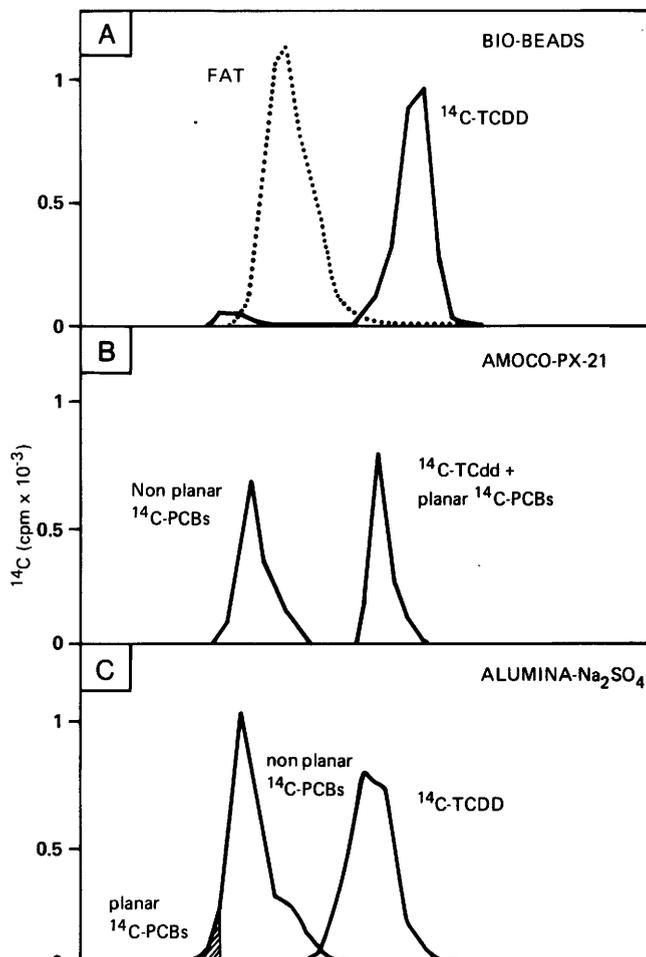


Fig. 1. Separation of radiolabelled (^{14}C) PCBs, TCDD from fat on different chromatographic columns

a layer of potassium silicate which completely hydrolysed remaining traces of lipids retaining polar fatty acids. Other interfering substances were eliminated by passing the solution through a layer of sulphuric acid on silica gel. The planar PCDDs, PCDFs and PCBs were then separated from non planar chlorinated compounds on a graphite carbon column (Amoco PX21, Fig. 1B). In this column planar molecules are adsorbed between layers of the graphite while non planar molecules, like ortho substituted PCBs are not retained. In a final column consisting of highly activated alumina, the dioxins and furans were separated from co-planar PCBs in order to avoid interferences in the mass spectrometry measurement (Fig. 1C).

By the procedure here described the over-all recovery of ^{14}C radiotracers was about 50 to 60%. Using High Resolution Chromatography / High Resolution Mass Spectrometry the detection limit should be in the order of 0.1 ppt.

The method was semi-automatized providing a meaningful tool for standard analysis. For application in studies on the migration of polyhalogenated aromatics in soils, the procedure has to be slightly modified by the substitution of the Bio-Beads column with a multilayer column consisting of sodium sulphate, acidic silica and activated silica.

b) Assessment of Human exposure

For the assessment of human exposure to polyhalogenated aromatic compounds, which may involve mixtures containing up to 75 different PCDD, 135 PCDF and 209 PCB isomers and congeners, various methods have been evaluated. To determine the risk associated with exposure to materials such as soot, incinerator fly ash, industrial wastes, and polluted soils, a reasonable estimation can be made by taking into account the distribution of different congeners or homologues and the likely relative toxicity of these compounds. The basis of this approach is the assignment of toxicity equivalent factors (TEFs) to each compound in relation to that of 2, 3, 7, 8, TCDD which is the most toxic and more studied congener. These assessment procedures varies according to different situations of exposure, depending on the ratio of congeners released from the source as well as on their bioavailability. Methodologies for wider applicability to situations of particular european importance are under development.

For the assessment of exposure to genotoxic compounds of potentially exposed individuals living in area surrounding disposal sites, studies devoted mainly to the identification of indicators of exposure are in progress. These methods are based on the measurement of adducts formed with cellular materials which may be used as chemical dosimeters.

c) Chemical Emergencies Management

The development of the Chemical Emergency Management (ChEM) decision support system for situations associated with halogenated aromatic compounds such as PCB, PCDD and PCDF, based on advanced Artificial Intelligence techniques, continued.

The research work has been evolving in the following areas:

- (a) Completion of the Threat Identification and Notification Expert System in a general purpose computing environment.
- (b) Development of the Knowledge Sources related to the various phases of the multidisciplinary complex problem of emergency management.
- (c) Development of an intelligent user interface based on the hypermap paradigm to coordinate and assist the decision making process.
- (d) Investigation and implementation of various knowledge acquisition and representation techniques.
- (e) Design of an intelligent information system which integrates the Knowledge Sources and Databases with the Hypermap and performs a coordinated, distributed, problem solving process.

In the following, a more detailed description of these points is given.

Threat Identification and Notification

The implementation of an expert system dealing with Threat Identification and Notification has been completed in a general purpose computer environment (IBM AT and VAX). The system developed, gathers information related to the context of the specific accident. The interaction with the user takes place through a menu-driven graphic interface. The output is an estimation of the level of the chemical threat related to general information about the incident, qualitative information about toxic levels, estimated damage to the environment, dynamics of the current accident state, suggestions about urgent actions to be taken etc.

The validation of the developed system has been achieved by verifying past accident histories in different dynamic phases. A small chemical substances database and simulators for the dispersion and migration in soil, water and atmosphere of these substances have been incorporated in the system. Also a «help»

utility has been integrated, containing a past accidents map system. Glossary, Tutorial and Handbook, related to the compounds involved, a guide for the knowledge base and technical data of the chemical progress.

Knowledge modules

In accordance with the strategy of creating an integrated system dealing with the various aspects of chemical emergency management, a knowledge acquisition and structuring exercise in various domains is under active development. The foreseen modules are as follows:

- (i) **CHEM1** estimates the current threat level, based on contextual information and any available data, as provided by analysis and observers at the site of the accident. The knowledge of this module is already contained in the expert system described above. At present, problems related with the integration of this module in the information system under design, and new knowledge representation techniques, related to the dedicated Knowledge Engineering environment and tools applied are considered.
- (ii) **CHEM2** designs a strategy for sampling of water, soil and air in the affected zone; it lists and organizes the human and material resources required for the sampling; it makes suggestions on the laboratory analyses to perform on the samples and finally it processes the analysis results. This module is under active development. It is subdivided in three sub-modules:
 - (a) The Inspection and Preliminary-sampling sub-module which supplies first indication of the extension of the damage and locates the affected zone, in which sampling should be performed.
 - (b) The main Sampling sub-module, which supplies the parameters and the plan necessary for sampling in the affected area.
 - (c) Analysis sub-module, which analyses the results of the sampling exercise and performs a diagnosis of the toxic dispersion, using mathematical models.Further, groups of experts and knowledge engineers are performing preliminary knowledge, organization and structuring for the following modules:
- (iii) **CHEM3**, which suggests countermeasures and actions to be undertaken in order to contain further distribution of toxic material, to protect the people (indication of the area to be evacuated and zones of resettlement, suggestions about evacuation routes, etc.) and the environment (barriers building, etc.) and to relieve the affected (suggestion for first aid, indication of the nearest hospitals, etc.).
- (iv) **CHEM4**, which draws up intermediate and final reports for those actively involved in the emergency (decision makers, experts, authorities, etc.); it estimates the costs and assesses the damage.
- (v) **CHEM5**, which is concerned with the postemergency services, designs the plans for decontamination and cleaning up of the affected zones and the final disposal of the remaining hazardous elements; it plans further medical and financial aid to people.
- (vi) **CHEM6**, which manages the available emergency services during and after the emergency; it optimizes their allocation according to the needs of the situation and their respective competences, by selecting the appropriate means for achieving the desired goals which are suggested by other KBs.
- (vii) **CHEM7**, which supplies advice on informing the public and the media, according to the gravity of the situation during the course of the emergency.

Hypermap interface

The Hypermap paradigm, which borrows many ideas from Hypertext systems, is a new approach to the design of chemical emergency systems interfaces. In the particular case of ChEM, the Hypermap User Interface exploits the spatial distribution of information and processes, which is an inherent characteristic of the situation, permitting an easy to use, fast and consistent interaction with all information available and the decision making tools.

The characteristics of the Hypermap Interface are:

- (i) the user interaction with the emergency system is supported by a set of linked maps, spanning from a very high level, like an overview map of the area under threat, down to a very low level, like detailed technical drawings of the machinery concerned;
- (ii) the user can navigate in a fast and easy manner through the hypermap structure, so that this standpoint during the problem solving operation determines the level of information-access and the control of exercises;
- (iii) it supplies the user with an easy to understand picture of the situation which is depicted via high quality graphic images;
- (iv) it supports information retrieval by relating spatially distributed information to its corresponding position.

A prototype of the hypermap model has been built, which is implemented for few chemical plants and locations in the North of Italy (Lombardy), underlaid by a rudimentary version of geographical database.

Knowledge acquisition techniques

Knowledge Acquisition has been achieved up to now, through a series of informal interviews with Experts in the various domains. Out of the interviews, the knowledge engineers have drawn the major concepts that served to create a formal structure, consisting of a semantic network and a rule base, representing the knowledge. At present, other techniques to perform this laborious task are investigated. One possibility is the induction of knowledge, under the form of rules, from a series of well documented chemical emergency situations, provided by literature and experts. To achieve this, a list of concepts, together with their attributes and possible values for these attributes has been created (protocol). For each well documented accident, this list is filled in with the values corresponding to the parameters of that accident. Out of all filled lists, interrelationships between the concepts are drawn by a so-called induction shell under the form of IF..THEN rules.

Another approach is to follow a strict methodology to formalize the knowledge, implicitly present in the interview protocols. An example of this is the KADS-methodology. Existing advanced software tools to support this formalization are under consideration.

Architecture of ChEM information System

The distributed nature of the problem solving process and the diversity of information required, lead us to the need for a design of an intelligent information system which contains the Hypermap User interface module, the independent Knowledges Sources and specialized Databases. These elements are controlled by a coordinating module, called **Accident Manager** which bases its action on the information contained in the **Accident Status Board** a memory-based global data base. This structure corresponds to the «blackboard model».

The data bases cover subjects like chemical engineering, toxicology, laws and norms, geology, watersystems, demography, medicine, etc. Information retrieval can be performed directly by the user or by the inference engines and model during their operation.

Various kinds of control information are made globally available

to the Accident Manager and the Knowledge Bases. This control information is used by the Accident Manager to determine the «focus of attention», which is the next KB to be activated. The problem-solving behaviour of the system is determined by the knowledge application strategy encoded in the Accident Manager. An appropriate strategy is based on a control theory perspective. According to this, first some system goals are established, which correspond to some global variables on the Accident Status Board. The system goals are achieved by satisfying some subgoals which are structured in a hierarchical way and expressed in the Accident Manager. The heuristics establishing the relationships between the system goals and the corresponding KBs, which should be activated, are also contained in the Accident Manager. The **Accident Status Board** contains information related to the current status of the emergency, encoded in a uniform data structure, such as attribute-value pairs organized in objects. Such standardization allows the definition of a unique protocol to access the data from any KB or other parts of the system, under the control of the Accident Manager.

The purpose of the Board is to hold computational and solution state data needed and produced by the KBs. Interaction among the KBs takes place solely through changes on the Board.

A commercially available knowledge system building environment which supports a diversity of tools like a frame representation language in combination with forward reasoning production-rule based tools like OPS5, backward reasoning tools like Prolog, is ideal for a complex knowledge engineering exercise like the creation of the emergency management information system. An integrated tool set with these characteristics is Knowledge Craft, which is used in this part of the project. This operates on both dedicated AI workstations and general purpose computer systems.

CONCLUSIONS

The quantitative assessment of impact on the environment and public health of a hazardous waste is a particularly complicated task. The complexity arises from the large number of physical, chemical and biological parameters which are potentially measurable. Therefore the first and necessary stage for any impact assessment is the selection of good quality, reliable data. The completion of laboratory facilities and the installation of new analytical instrumentation (HPLC/MS), as well as the use of radiolabelled tracers for the verification of clean-up procedures, have considerably improved the development of specific analytical methods for the identification and measurement of toxic compounds in environmental and biological samples. At present ChEM is capable of dealing with the most common types of accident involving PCB. The current implementation is still too biased towards the present state of the accident with a limited evaluation of the time evolution of the threat. Adaptations of the knowledge base, which will take into account the time dependent character of the threat, are in progress. These adaptation are based on the established concepts of migration routes and targets.

Refereces

- F. ARGENTESI, L. BOLLINI, S. FACCHETTI, G. NOBILE, W. TUMIATTI, G. BELLI, S. RATTI, S. CERLESI, G.U. FORTUNATI, V. LA PORTA
An Expert System for the Management of Chemical Accidents Involving Halogenated Aromatic Compounds. World Conference, Chemical Accidents, Rome, July 1987.

GLOSSARY

| | |
|----------|---|
| AAS | Atomic Absorption Spectroscopy |
| BS | Black Smoke |
| CAS | Chemical Abstracts Service |
| CFPP | Coal Fired Power Plant |
| ChEM | Chemical Emergencies Manager |
| CLAP | Central Laboratory for Air Pollution |
| CN | Condensation Nuclei |
| CNR | Comitato Nazionale delle Ricerche (Italian Research Board) |
| COSPEC | Correlation Spectrometer |
| COST | Cooperative Scientific Technique |
| ECDIN | Environmental Chemical Data Information Network |
| EINECS | European Inventory of Existing Chemical Substances |
| EMEP | Cooperative Programme for «Monitoring and evaluation of the long range transmission of air pollutants in Europe»; |
| ENEA | Italian Energy Agency (Ente Nazionale Energia Nucleare ed Energie Alternative) |
| ENEL | Italian Electricity Board (Ente Nazionale Energia Elettrica) |
| EPA | Environmental Protection Agency (U.S.A.) |
| EPCP | Environmental Polluton Control Project, Athens |
| EUROTRAC | Eureka Project on Transport and Transformation of Trace Constituents |
| EURONET | European Telecommunications Network |
| FCM | Flowcytometry |
| FID | Flame Ionization Detector |
| GC-MS | Gas Chromatography/Mass Spectrometry |
| GLC | Gas-liquid Chromatography |
| HPLC | High Pressure Liquid Chromatography |
| IAQ | Indoor Air Quality |
| ILE | Isotopic Lead Experiment |
| ILO | International Labor Office |
| INSIS | Integrated Interaction System of Community Services |
| IRPTC | International Registry of Potential Toxic Chemicals |
| KfK | Kernforschungszentrum Karlsruhe (German Nuclear Research Centre) |
| LIDAR | Light Detecting and Ranging |
| LLE | Low level/long term experiments in biochemistry |
| MALS | Multi-angle-light scatter |
| NAA | Neutron Activation Analysis |
| PPR | Programme Progress Report |
| QAP | Quality Assurance Programme |
| QSAR | Quantitative Structure Activity Relationships |
| SODAR | Sonic Detecting and Ranging |
| T.M. | Trace Metal |
| TEL | Tetraethyl Lead |
| TOSCA | Toxic Substances Control Act |
| TSP | Total Suspended Particles |
| TULLA | German Acronym for a regional pollutants mass-balance project (March 1985) in Baden-Württemberg |
| UNEP | United Nations Environmental Programme |
| WHO | World Health Organization |

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EN

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The research area **Environmental Chemicals** includes the data bank ECDIN, work on Indoor Air Pollution, Trace Metal Exposure and Health Effects and Environmental Pathways. The research area **Atmospheric Pollution** deals with field and simulation studies of photochemical reactions, a Central Laboratory for Air Pollution (in support to the implementation the Council Directive 80/779 on control of SO₂ and suspended matter), studies on pollution mass balance using ground based remote sensing techniques, tracers and micrometeorological measurements.

Water Quality deals with work on ecotoxicity of trace metals in freshwater communities and field work to determine the mass balance and pathway of trace metals in a freshwater ecosystem.

Chemical Waste includes environmental impact and risk assessment studies of toxic chemical wastes and supports the regulatory work of the Commission in this field.