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Multiannual programme of the Joint Research Centre 1980-83

# 1983 Annual Status Report

# Protection of the environment

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COMMISSION OF THE EUROPEAN COMMUNITIES



Multiannual programme of the Joint Research Centre 1980-83

# 1983 Annual Status Report

Protection of the environment

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#### PROTECTION OF THE ENVIRONMENT

#### 1983

Research Staff:

86 men-year

Budget:

11.061.000 ECU

#### Projects:

- ECDIN: Environmental Chemical Data Information Network
- Exposure to Chemicals:
  - Indoor Pollution
  - Chemical Products (Organics)
- Air Quality
- Central Laboratory of Air Pollution
- Water Quality
  - Nutrient Mass Balance in Aquatic Ecosystems
  - Ecological Effects of Chemical Pollution
- Heavy Metal Pollution
  - 1.L.E. (Pathway of Automotive Lead)
  - Exposure and Health Effects
- Environmental Impact of Conventional Power Plants

Programme Manager:

**B. VERSINO** 

Commission of the European Communities

Joint Research Centre Ispra Establishment

I-21020 Ispra (Varese), Italy

#### 1. INTRODUCTION

The 4 years programme (1980-1983) «Protection of the Environment» is the follow-up of the former programme «Environment and Resources» (1977-1980).

With a research staff of about 90 people working mainly at the Ispra and to a smaller extent at the Petten establishment, this programme represents about 8% of the total research effort of the Joint Research Centre.

The principal scope of the programme «Protection of the Environment» it to provide together with the related Indirect and Concerted Action Programme, scientific support to the Community's Programme of Action on the Environment (1982-1986). The following table gives a synoptic view of the major links of this action programme managed by D.G. XI (Direction: Protection and Improvement of the Environment) at Brussels with the above mentioned research programmes.

ECDIN, a pilot-data bank on environmental chemicals is by far the largest project in financial volume and already now acting as an internal consultant to other Commission services and has given proof of its use and competence especially in establishing the European core inventory EINECS in behalf of the D.G. XI.

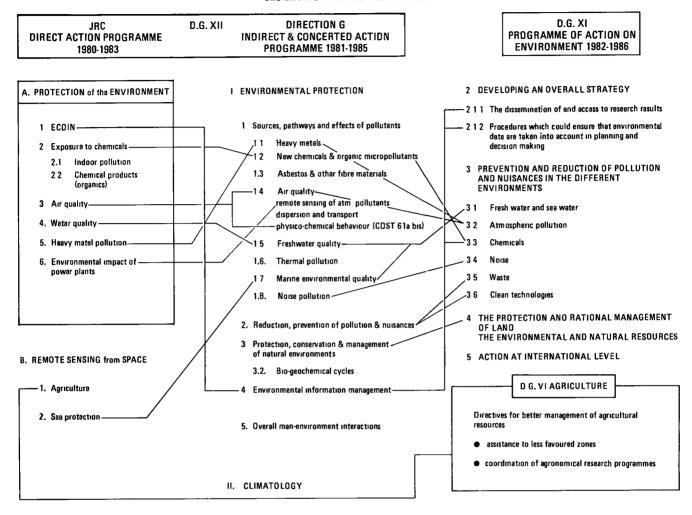
The longend survival of this project will depend, however, on the successful implementation of a «commercial» service justifying an ongoing research effort of a «scientific» ECDIN inside the Joint Research Centre.

Striking differences in air pollution levels inside and outside of private houses and public buildings led to the conception of the «Indoor Pollution» project. The study is focused on organic emissions in private houses, school rooms and department stores. The final goal is to reconsider the relevance of air quality standards.

The title «Chemical Products (Organics)» is related to the activities of a research group at the Petten establishment. This work is mainly concerned with analytical and synthesis aspects of organic chemicals related to environmental protection problems (e.g. carcinogenic and toxic substances).

The project «Air Quality» deals with the analysis of atmospheric pollutants with special regard to particle formation and photochemical reactions. It is fully integrated into the

#### **CEC ENVIRONMENTAL PROGRAMMES**



COST 61a-bis concerted action «Physico-chemical behaviour of atmospheric pollutants».

The project «Water Quality» focuses on the mass balance of nutrients in lakes, using a physico-chemical modelistic approach and the use of bio-indicators for the characterization of freshwater pollution.

The project on «Heavy Metal Pollution» comprises the conclusion of the ILE project (pathway of automotive lead using natural isotopic tracers) and extends the assessment studies around conventional fossil fuelled power plants to other heavy metal pollution sources like incinerators and fertilizers. Metallo-biochemistry is the key method to elucidate the pathway and health effects of these pollutants.

The «Environmental Impact of Power Plants» project deals with the diffusion and transport of emissions (gaseous and particulate) from conventional power plants. Special emphasis is put on micro-meteorological aspects of sites and the study of mesoscale transport by means of advanced tracer techniques. The input-output balance of pollutants in industrial or urban areas is related to these topics. The project is fully integrated in similar national and Community wide projects.

#### 2. RESULTS

# ECDIN (Environmental Chemicals Data and Information Network)

The experimental ECDIN service which started in spring 1982 ended on June 30, 1983. The users' reactions were monitored both by ASLIB (U.K.) and by BURICOM, (France). The main conclusions of the experimental service can be summarized as:

- 1. The interest for the ECDIN data bank is persisting, and the absence of similar data sources reconfirmed.
- 2. The present volume of loaded data is still considered as too low for an effective use.
- 3. The user dialog system is easily understandable but sometimes not rapid enough for skilled users.

At July 1st, 1983 the ECDIN marketing study was started by Datacentralen, Copenhagen. The first six months of this pilot project demonstrated an increasing interest and time of effective use.

In the meantime the data content has been considerably expanded, a new data file added, and many improvements were

inserted in the search system. The forecast for 1984 is so moderately optimistic.

In the meantime considerable effort was still devoted to the EINECS inventory completion. The submitted forms have been ca. 78.000, for ca. 135.000 substances, that is roughly the double than estimated, and consequently the work load considerably increased. Some problems of interpretation for the inclusion/exclusion criteria needed long discussions during the year, and some have not been solved at the end of 1983. As a consequence of this extra work load, only at the end of the year a first set of «problem letters» could be mailed to the Member States Contact Points.

For 1984 a solution of the «interpretation problems» are expected.

The contract with Datacentralen for the ECDIN marketing study will continue during 1984, supported by the ECDIN staff with ongoing data loading and system improvements.

#### **EXPOSURE TO CHEMICALS**

#### INDOOR POLLUTION

This activity is mainly aimed at promoting and supporting a European collaboration in the field of indoor air pollution and quality. It follows three major lines:

#### Preparation of a Concerted Action

A Concerted Action (CA) in the field of Indoor Air Quality (1AQ) is considered to be the most appropriate mean of sponsoring European research in this field. With the help of an ad hoc European Contact Group in 1982 a proposal for a CA had been prepared. In 1983 two further meetings of the contact group have been convened in order to practically prepare the action which was supposed to start in 1984. Work was concerned with establishing a list of priority issues to be tackled by CA working parties, and with updating an inventory of laboratories in the Community which are potential condidates for a participation in the action.

Practical collaboration was continued making a final revision of a measurement protocol and format for an inventory of detected indoor pollutant concentrations and indoor/outdoor concentration ratios. In addition two interlaboratory comparison experiments have been completed with the scope to assess the usefulness of passive samplers for organic indoor pollutant analysis and the agreement among laboratories on analysis of trace organic pollutants. While the latter appears satisfactory apparent inhomogeneities of sampler characteristics need further investigation.

#### Field Measurements

The revised proposal for an indoor pollutant inventory has been applied to «real life» measurements of indoor and outdoor concentrations of 33 volatile organic pollutants in 14 homes and one office building. The results of these measurements are summarized in Table 1. Mean indoor/outdoor concentration ratios range from 1.3 to 52 and confirm the predominant contribution of indoor air to human exposure to volatile organic pollutants.

A detailed analysis of volatile organics in the air of six indoor spaces resulted in the identification and quantification of between 47 and 118 compounds. Most of them, in particular hydrocarbons and chlorinated hydrocarbons, are typical solvent constituents and point to wide-use household products including points as major sources.

An analysis of 10 household samples yielded alpha-quartz as a major crystalline constituent (1.3 - 3.9% by weight). Alpha-quartz is the cause of silicosis (miners'lung disease), which has occasionally been detected in housewives apparently not exposed to industrial or occupational sources. Some household cleaning/scouring agents could be shown to contain up to 40% by weight of alpha-quartz and, hence, are potential sources.

#### Method development

Assessment of population exposure to indoor air pollution is an important goal which due to the large spatial variability of indoor pollution levels cannot be achieved by measurements alone, but needs a modeling approach. Models, however, besides other parameters, need information on pollutant source strengths and ventilation rates. With this scope in mind a method has been theoretically conceived and experimenally assessed which in appropriate conditions allows to determine simultaneously effective ventilation rates and pollutants source strengths by means of integrating real life measurements. The method uses a simple reference trace gas source (permeation device) which is placed in an indoor environment together with sampling devices which simultaneously collects the trace gas and pollutants, the source strength of which was to be determined.

#### **CHEMICAL PRODUCTS (ORGANICS)**

#### Environmental Carcinogens

Identification and testing of Cancer Suspect Environmental Chemicals.

The emphasis in 1983 was on the mutagenicity and cocarcinogenicity testing of a number of polycyclic and heterocyclic compounds which are released into the environment mainly as a result of coal combustion or conversion processes.

The results are summarized in table 2. The highest mutagenic effects were observed for aminoderivatives of PAH which occur primarily in coal liquefaction processes. In a complementary study the cocarcinogenic effects of selected heterocyclic PAH was investigated on rat liver microsomal chrysene oxidation. It was found that especially the benzonaphthothiopenes which have become ubiquitous in the environment are strong promoters of PAH metabolism in animals and, therefore, must be considered as potent cocarcinogens.

#### Atlas of Molecular Spectra

In 1983, the low temperature fluorescence and phosphorescence spectra were added to the collection of molecular spectra of PAH (taken at temperatures of approximately 15 K).

The advantage of this technique is its specific response which allows in many cases simultaneous analysis of PAH in complex

TABLE 1. Comparison of selected organic compounds in indoor and outdoor air

	Nr. of	Pollutant Concentrations (μg/m³)							Indoor/Outdoor Ratio				
	homes (a)	lowes	1 value	highest value		mean value (b)			lowest	highest			
		Indoor	outdoor	Indoor	onidoor	indo	or	outdo	ог	iowesi	nignesi	mean (c)	
RSP													
(respirable suspended particulate)	12	40	10	170	210		81		63	0.5	17		2.9
Total volatile organics (d)	14	240	130	8900	1900		3940		460	1.1	48		14
Formaldehvde	15	8	2	87	12		29		7.1	1.6	12		4.9
Acetaldehyde	15	1	<1	48	19		16		5.4	0.5	24		4.9
Butanal	3(15)	< 1	<1	34	10		15		8.0	0.5	5.7		2.3
Hexanal	3(15)	< 2	<2	20	< 2		12	(	e)	>2.7	>10	(>5)	
Nonanal	3(15)	< 2	<2	17	< 2		11		e)	>3	>8.5	(>5)	
Acetone	15	3	<2	157	17		40	(<71)	8.4	1.2	>28	(4)	6.4
Butanone - 2	9(15)	< 2	<2	38	12	(<8.6)	17	(<4.7)	8 3	0 4	7.5	(>2)	2.7
Trichlorofluoromethane (F-11)	9	13	2	230	39		45		11	0.7	58		10
Dichloromethane	7(9)	< 5	< 5	5000	100		1290		(<16)	5 9	>600	(>58)	
Chloroform	5(14)	< 1	<1	15	3	(< 2.6)	8.5		<11)	2	5	(>2)	
1.1.1-Trichloroethane	15	4	2	60	35	` ,	22	`	12	08	8 4	` ,	3.3
Carbon tetrachloride	15	2	2	12	22		69		74	0 1	3 3		13
Trichloroethylene	15	1	<1	86	24		19		86	0.8	>17	(18)	26
Tetrachloroethylene	15	3	1	47	48		17		14	0.3	4.3		18
1 4-Dichlorobenzene	9(15)	< 5	<2	230	4	(<62)	99	(<5)	3	7	(>115) 37	(>29)	22
n-Hexane	13	4	2	590	42		81		15	0.3	50		10
n-Heptane	13	3	1	76	17		19		6.0	07	40	(2.1)	6.0
n-Octane	12(13)	2	< 1	65	15		21		4.4	ì	34	(4.3)	7.9
n-Nonane	10(13)	< 1	<1	165	9		30		3.3	2	>33	(9.2)	12
n-Decane	13	2	<1	1100	10		25		3.3	0.7	> 220	(>5)	8.5
n-Undecane	10(13)	3	< 1	950	15	(93)	120	(< 3 4)	4.3	3	>190	(7.5)	9.0
n-Dodecane	10	< 1	< 1	220	5		11		2.0	3	>44	(>3)	4.5
Benzene	15	11	5	204	67		52		20	0.9	18		3.9
<b>Foluene</b>	15	17	7	378	156		127		38	0.9	25		6 2
Ethylbenzene	9	7	2	109	34		40		10	1	27		8.2
l 3-Xylene + 1 4-Xylene	13	11	3	390	111		92		26	0 9	40		7.9
1 2-Xylene	14	4	< 1	132	42		33	(<90)	10	07	40	(3.0)	8.2
1.3.5-Trimethylbenzene	9	3	<1	59	16		19	(<5.3)	66	06	13	(2.6)	3.5
1.2.4-Trimethylbenzene	9	7	1	150	44		46		13	1 3	51		10
α-Pinene	10	14	< i	605	3		122	(<2)	2.5	9.7	>605	(>21)	
Limonene	13	10	<1	480	11		126	(<3)	4.5	1.1	>480	(40)	52
Naphtalene	8(9)	<1	<1	70	11		15	(<3)	4.0	1.2	16	(>4)	5.6

 <sup>(</sup>a) Values in parenthesis include also cases with indoor concentrations below the
detection limit (in all these cases also the outdoor value was below the detection limit)

mixtures without the need for prior separation which is necessary with conventional analytic methods.

Of the 42 compounds included in the series, only 16 exhibit also phosphorescence spectra, consisting of a few narrow, characteristic emission lines.

The Atlas was completed by adding data on the occurrence of PAH in the various environmental compartments, on biological activity (mutagenicity, carcinogenicity and toxicity) and other relevant data.

In addition, the UV-, fluorescence, mass- and NMR-spectra of a number of mostly heterocyclic compunds (benz- and dibenzacridines) were determined (see fig. 1) as well.

#### Occupational carcinogens/Toxic chemicals

In this year, the fourth and final phase of the collaborative study on analytical methodology for specific migration tests, involving the diffusion of potentially toxic plastic additives into packed foods, was completed and evaluated.

As a final conclusion of the four collaborative studies on the methodology in specific migration tests, sources of error are not so much related to the migration test proper, but more to the analytical procedure for determining the migrant in an unequivocal, accurate and sensitive way. Quantitative determination of migrants by a conventional analytical technique is liable to produce significant scatter in the results. The use of labelled additives in this study allowed simple detection methods with repeatable migration results.

Reproducibility of the values is, in general, better for long tests at 40°C than for the accelerated tests at 70°C. But neither labelling nor the rigorous control of storage conditions gave highly reproducible migration values for the poorly migrating selected antioxidant.

<sup>(</sup>b) Values in parenthesis are the mean of all values, including those below the detection limit. Values without parenthesis are the mean of values above the detection limit only.

<sup>(</sup>c) Values in paranthesis are median values; values without parenthesis are mean of those cases only where indoor and outdoor values above the detection limit have been found.

<sup>(</sup>d) Hydrocarbon equivalent of the total integrated F1D signal.

<sup>(</sup>e) All values are below the detection limit.

TABLE II. Mutagenic effects as determined from the slope of dose/response curves

	T.	A 98	TA 100		
Compound	rev/μg	rev/nmol	rev/μg	rev/nmol	
Benzo(a)pyrene	9.5	2.43	57	15	
Benzo(2,3)phenanthro-					
(4,5-bcd)thiophene	35	9	200	50	
Benz(a)acridine	1 7	0.4	8	18	
Benz(c)acridine	16	0.5	3	1	
Dibenz(a,c)acridine	06	0.16	61	17	
Dibenz(a,h)acridine	0 5	0 14	21 5	6 4	
Dibenz(a,j)acridine	5 0	14	21	6	
Dibenz(c,h)acridine	0.4	0 1	34	8.6	
Benzo(a)fluoranthene	1	0 4	20 5	5 2	
Benzo(ghi)fluoranthene	1 7	0 4	48	11	
Dibenzo(a,e)fluoranthene	20	6.1	22	6.8	
Dibenzo(a,l)pyrene	8 5	2.6	20	6	
Benzo(b)chrysene	_	_	3	0 8	
Benzo(c)chrysene	_	_	20	5.6	
1-aminoanthracene	48	9.3	62	12	
2-aminoanthracene	475	92	1401	270.5	
3-aminofluoranthene	380	82	60	13	
2-aminobenzo(c)phenanthrene	$435 \pm 15$	$106 \pm 4$	$480 \pm 60$	$117 \pm 15$	
3-aminobenzo(c)phenanthrene	$2130 \pm 70$	$520 \pm 20$	$800 \pm 40$	$194 \pm 10$	
4-aminobenzo(c)phenanthrene	$200 \pm 80$	$49 \pm 20$	140	34	
Benzo(a)carbazole	0.6	0.1	4.5	1	
Benzo(c)carbazole	10	2 2	14 5	3 2	
10-azabenzo-	4.5	1 1( + S9)	8 4	2 1	
(a)pyrene		(—S9)	1	0 2	

#### Central Laboratory of air pollution (CLAP)

This new activity started end of 1982 at DG XI's request in order to provide a technical support to the Commission for the implementation of the EC Directive n° 80/779 of 15 July 1980: Control of sulphur dioxide and particulates in air in the Member States. For this purpose, DG XI proposed to government experts a programme for the period 1983-88 (improvement of the reference methods, check of measuring instruments, verification of the corresponding stringency between the limit values for 1/2 hour and 24 hours as reported in the Directive) and charged JRC 1spra to set up a laboratory for the measurement of Sulfur dioxide, black smoke and total suspended particulates (TSP). The work carried out in 1983, aimed at the improvement of the reference methods for TSP and SO<sub>2</sub> as described in annexes IV and V of the above mentioned Council Directive.

Gravimetric measurements of TSP were carried out by means of two instruments (Metal Work samplers) supplied by DG XI. An exchange of filters for comparative weighing evaluation began with the «Pilot Station des Umweltbundesamtes» in Frankfurt.

Preliminary results indicated that the conditioning and weighing procedures of glass fiber filter (only used in this exercise) as mentioned in annex IV, require some precisions. For instance, regarding only the weighing of unloaded filters (ca 4 g), a relative standard deviation of 0.03% can be obtained provided that the weighing are performed inside an air conditioned room ( $20^{\circ}$ C  $\pm 0.5\%$  and 50%  $\pm 5\%$  relative humidity).

The revision of the reference method for sulfur dioxide was the main task of the CLAP. The method, as described in annex V of the Directive does not mention the sampling procedure for

24 hours and, therefore, the Annexes I and II giving daily limit and guide values for SO<sub>2</sub>, cannot be applied by the Member States.

In this method, determination of the  $SO_2$  in air by tetrachlormercuratepararosaniline (TCM method), sulfur dioxide is absorbed from the air in a solution of sodium tetrachloromercurate and EDTA by formation of the dichlorosulphitomercurate complex. Reactives are added to the sample solution to neautralize the interference of trace elements.

The reaction with added acid-bleached pararosaniline and SO<sub>2</sub>, as bisulfite anion, produces an intensely coloured acid which behaves as a two-color indicator. The SO<sub>2</sub> concentration is deduced from a calibration curve obtained with sodium bisulfite solutions of known composition, calibration gas mixtures or permeation device.

The preliminary results of the revised SO<sub>2</sub> reference method were presented to the government experts at the end of 1983. It was decided to verify the method and the proposed amendments in urban polluted air. At this end a contract has been forewarded to the Bundesgesundheitsamt, Berlin.

#### **AIR QUALITY**

This project comprises two lines of activities.

The first one is rather advanced and aims at a description of the processes leading to ozone and particle formation in the troposphere. The experimental approach involves field measurements of different nature (comparative monitoring of pollutants, air borne measurements) and experiments under simulated atmospheric conditions for the study of chemical and photochemical reactions. These conditions are chosen as realistic as possible, for instance by using natural sunlight for irradiation and often ambient air samples. The activity is completed by developments for the analysis of important organic trace gases.

The second line of activity is centered around the analytical possibilities of Infra-red Fourier Transform Spectroscopy. Besides an analytical support to the above activity it should provide in the long term an orientation versus the study of Environmental Chemicals in the atmosphere, which are of increasing importance to the environment. Their behaviour and degradation under photo-oxidation conditions is of major concern.

#### **Analytical Development**

A gas-chromatographic procedure for the determination of  $C_1$ - $C_6$  hydrocarbons has been set up. Together with the high pressure liquid chromatography for the determination of carbonyl compounds and the gas chromatography/mass spectrometry for  $C_5$ - $C_{20}$  hydrocarbons, it is now possible to scan the whole range for eventual precursors which lead to the relatively high photo-chemical ozone formation found at Ispra. The separation of a test mixture of 16 hydrocarbons is shown in Fig. 2.

Fig. 3 shows an example of a typical outside air sample at 1spra taken in the morning during a sunny summer period.

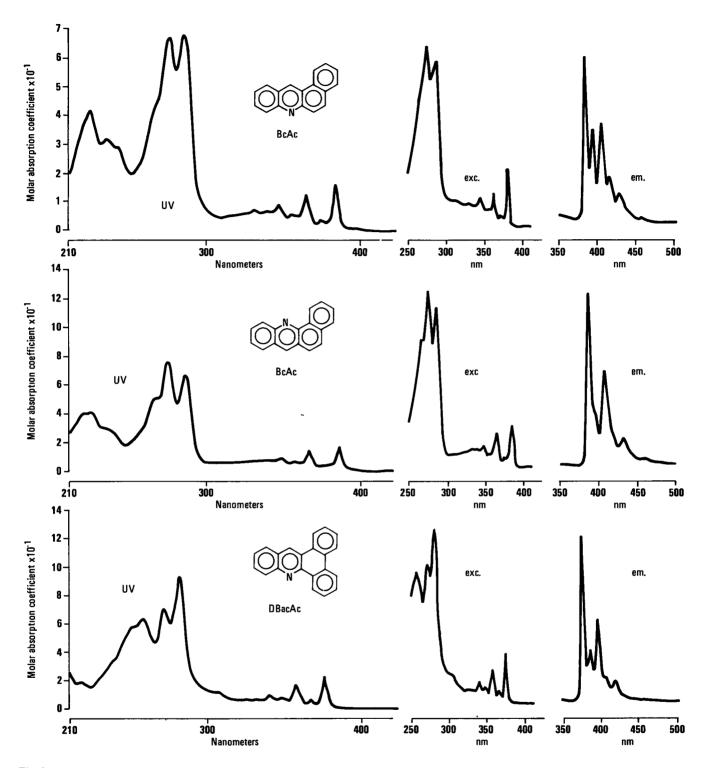


Fig. 1.

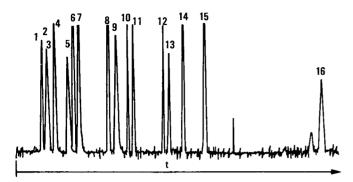


Fig. 2. Gas-chromatogram of a test mixture of 16 hydrocarbons (C<sub>1</sub>-C<sub>6</sub>) 1 methane, 2 ethane, 3 ethylene, 4 propane, 5 propylen, 6 i-butane, 7 n-butane, 8 dimethyl-propane, 9 buten-1, 10 2 methylbutane, 11 n-pentane, 12 2,2-dimethyl-butane, 13 penten-1, 14 2-methyl-pentane + 3-methyl-pentane, 15 n-hexane, 16 hexene-1, concentrations are 15 ppb each HC. Fused silica column coated with Al<sub>2</sub>O<sub>3</sub> temperature 60°C, He flow 3 cc/min. 30 cc P L.O.T., i.e. 0,32 mm, FID detector.

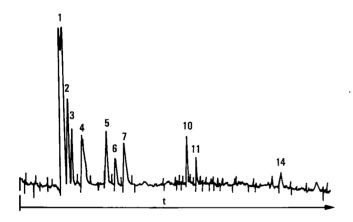


Fig. 3. C<sub>1</sub>-C<sub>5</sub> hydrocarbons in ambient air in Ispra (11.8.83, 9.52). Numbering as in fig. 2 Concentrations 1 1.5 ppm, 2 8 ppb, 3 5 ppb, 4 6 ppb, 5 5 ppb, 6 1 ppb, 7 3 ppb, 10 3 ppb, 11 2 ppb, 14 2 ppb.

#### Field Measurements

The collaboration contract with the «Deutsche Forschungsund Versuchsanstalt fur Luft- und Raumfahrt» (DFVLR) for airborne measurements of air pollutants in the Po Valley has been prolonged till end of 1983. Very successful measuring flights were performed during the following periods:

> 18.8.1983 - 20.8.1983 6.9.1983 - 9.9.1983 26.9.1983 - 30.9.1983

This includes summer and early fall meteorological conditions. In addition to the usual flight programme of vertical profiles at Ispra and east or west of the greater Milan area and of horizontal tracks along a large circle around the Milan area, the eastern part of the Po Valley was especially investigated. Horizontal flights were extended all along the valley and well over the

Adriatic Sea and vertical profiles were taken there. High altitude (> 3.000 m) crossings from Bavaria to the Po Valley were flown to identify differences in background ozone levels. Horizontal flights inside the ozone reservoir, a few hundred meters below the inversion layer, concluded this programme. The final report by DFVLR will be available by June 1984. A method for the continuous measurement of sulfate in air, based on a modified flame photometer, has found wide acknowledgement. Some technical improvements and long periods of testing have led to a better base line stability and a through understanding of disturbing factors, like humidity. The detection limit is at the moment  $\sim 4 \,\mu \mathrm{g} \, \mathrm{SO_4/m^3}$ , corresponding to 1 ppb SO<sub>2</sub>. The JRC participated with this instrumentation in the 4th CEC Measuring Campaign at Fos-Berre (Marseille), France, in June 1983.

A comparison of the data from this industrial site with the 1982 measurements at 1spra revealed drastic differences, especially with respect to SO<sub>4</sub> concentrations in connection with higher local SO<sub>2</sub> emissions. A correlation of this kind has never been found for 1spra and one must consider a rather fast oxidation process for SO<sub>2</sub> close to the emission source or even direct emission of particulate sulfur. Slow photo-oxidation processes, giving rise to the typical day-night trend found at 1spra, play only a minor role for a certain background sulfate concentration in this area.

# Photo-chemical experiments under simulated atmospheric conditions

Experiments, using ambient air in large Teflon bags and sun irradiation, were carried out to clarify the role of carbon monoxide as precursor of part of the ozone formed in the troposhpere. At the same time it was also tried to get an estimation of the average OH radical concentration in ambient air at Ispra through these experiments. Two types of experiments were designed. In the first set additional CO was added to ambient air to give a 2-4 fold higher concentration and the effect on ozone formation over one day was compared to a sample with the "natural" level ony. The results showed quite clearly no measurable influence on ozone production, which was around 60 ppb in these experiments. In the second set <sup>13</sup>CO was added to ambient air in its decrease, caused by the reaction with OH radical was followed. The 13CO was analyzed simultaneously with 12CO, CH<sub>4</sub> and CF<sub>2</sub>Cl<sub>2</sub>, added as inert tracer, by long path infrared absorption spectroscopy. The <sup>13</sup>CO decrease was close to the detection limit of the technique; however, the statistical analysis of the results of 13 experiments performed in sunny days in the period May-July allowed to estimate an average OH radical concentration equal to 2x106 cm<sup>-3</sup> with an upper limit of 4x10<sup>6</sup> cm<sup>-3</sup>. This value would permit only a very limited O<sub>3</sub> production from the ambient carbon monoxide concentrations found at Ispra.

#### **Application of Infrared Spectroscopy Techniques**

Periodical monitoring of CH<sub>4</sub> and CO was performed all over the year by infrared absorption spectroscopy to the scope of achieving a better characterization of the area from a photochemical point of view. Computer simulation was used to evaluate the best operating conditions for monitoring of gaseous ammonia in air at ppb level using infrared diode lasers. Spectral regions have been identified and compared for ambient pressure and low pressure monitoring (in closed multiple reflection cells, in flux). Special attention was given to the problem of calibration. Preliminary measurements performed at the end of the year show a sensitivity of about 1 ppb for 128 meter total beam path in air at 20 torr.

#### WATER QUALITY

#### Nutrient Mass Balance in Aquatic Ecosystems

The problem of the influence of phosphorous release from sediments (P internal loading) on phytoplankton growth has acquired a paramount importance after that depuration plants sharply reduced external phosphorus sources.

The previous experimental and modellistic analysis of the phosphorus mass balance in the Ponte Tresa basin of Lake Lugano has lead to the conclusion that in a lake with a mean depth of 33 m, which cannot be classified as a shallow lake in a strict sense, the sediment-water system plays a key role in controlling the water quality of the whole lake.

To reach more general conclusions the study has been extended to a deeper basin (Agno bay, mean depth 58 m), whose morphometric and hydrologic characteristics and input conditions are more complex.

During 1983 the main effort has been devoted to the concluding interpretation of the data collected in the Agno basin during the past years (1980-1982). This was based on a correlation between experiments and an eutrophication model. The results of the modellistic analysis can be summarized in the following way:

- phosphate (P-PO<sub>4</sub>) release flux from the bottom sediments is less intense than in the Ponte Tresa bay. Its average value during the summer stagnation was evaluated to be between 10 and 20 mg P m<sup>-2</sup> d<sup>-1</sup>. Due to dilution effects and to the heavy external P loading the influence of this flux on the algal growth in the basin is negligible. The last statement cannot be generalized to the other south-western basins of the lake.
- The epilimnetic (metabolic) P cycle in the Agno basin is characterized by the important role of the dissolved organic phosphorus forms. Following two extreme assumptions as for this role, the total P turnover time compatible with the experimental data resulted between 5 and 18 days.

The biological availability of phosphorus associated with suspended sediments has been investigated using the algal assay technique and **Selenastrum capricornutum** as test organism. A significant fraction (30%) of the particulate from the main tributary of the Agno basin resulted to support algal growth. Assuming the phosphate-P fraction of the total P load as completely available, and neglecting the availability of the soluble organic P fraction, we concluded that 60% of the external P loading from the catchment area of the Agno basin is potentially available for algal growth.

Aiming at a better understanding of the phytoplankton dynamics during bloom periods, an application of the laser light scattering technique to natural samples of Lake Lugano has been carried out. The first exercise was to study the composition (in terms of genus type) of a fixed sample.

Three main types of algae have become evident during the sampling period, these being Oscillatoria rubescens, Cryptomonas ovata, and Peridinium cinctum. Primary results are very encouraging: the sample analysis using a microscope demonstrated a 95% success rate of the technique.

At the same time algal growth models have been written and tested in order to interprete batch culture and dual culture diffusion experiments.

In the framework of the preparatory studies for the 1984-1987 Water Quality project on the pathways of trace metals in a freshwater ecosystem, sediments, water, particulate matter and aquatic plants were taken at 23 stations along the rivers Bardello and Monvallina: the samples are undergoing analysis with various techniques. During the summer stagnation water temperature profiles have been extensively measured in the test coastal zone of Lake Maggiore, in order to investigate the stratification characteristics of the water body.

#### **Ecological Effects of Chemical Pollution**

The aim of this research is to evaluate the effects produced by trace metals (e.g. Cd, Cu, Hg, Al) on freshwater communities under semi-natural conditions («enclosure» or «microecosystems» method). With this method, adopted to evaluate the effects of nutrients and toxic substances in freshwater and marine communities, more realistic results may be obtained in comparison with those from laboratory experiments. Experiments were carried out in Lake Comabbio (Varese, Italy) to measure the fate of low concentration (100 ppb) of Cu, Cd and Hg inside of the enclosures, and the effects of the metals on phyto- and zooplankton.

The most evident results obtained were the following:

- At the beginning of the experiment the greatest part of the metal (Cd, Cu and Hg) was in filtered water, after few days almost all the metal was adsorbed by the sestonic particles and sediment.
- Population density of zoo- and phytoplankton decreased to a very low level during the first 4-5 days. The importance of this decrease varied with the species.
- The physical and chemical parameters controlled by the biota (e.g. water transparency, oxygen concentration, pH) varied in relation with the population density of the plankton.
- The influence of the season on the biological effects was evident.

#### **HEAVY METAL POLLUTION**

#### Isotopic Lead Experiment (I.L.E.)

ILE (Isotopic Lead Experiment) is a large scale, non radioactive tracer experiment, using as antiknock compound added to

petrols, a lead from the Australian Broken Hill mine of an isotopic composition (Pb206/Pb-207 = 1.04) significantly different from the lead encountered in the environment of the test area (Pb206/Pb207 = 1.18) at the beginning of the project.

The primary goal of the ILE study is to determine the fraction of petrol lead in human blood.

Other objectives are the determinations of the pathways of petrol lead through air, vegetation, soil, food and, possibly, its distribution in the human body. The test area is the Region of Piedmont in Northwest Italy.

During 1983 petrol, airborne particulate and blood samples have been analysed in order to update the curve showing the change of Pb206/Pb207 ratios with time.

Figure 4 illustrates the last findigs. The average annual values for petrol and airborne particulate are:

Sample	Year	Pb206/Pb207		
Petrol	1982	$1.125 \pm 0.017$		
Petrol	1983 (1st semester)	$1.129 \pm 0.010$		
Airborne particulate	1982	$1.130 \pm 0.008$		
Countryside	1982	$1.129 \pm 0.005$		
Airborne particulate				
Turin	1983 (1st semester)	$1.122 \pm 0.002$		
Airborne particulate				
countryside	1983 (1st semester)	$1.121 \pm 0.001$		

The blood lead results for Pb206/Pb207 ratio on five new follow-up subjects confirm those previously found. They are shown in Fig. 5.

The dynamical evolution of the blood isotopic ratio of the following-up subjects reported in the ILE Status Report (EUR 8352 EN) has been mathematically modelled and recently published under separate cover (EUR 8760 EN, Isotopic Lead Experiment, A dynamic analysis of the ILE results).

This report tries to ascertain whether an analysis of all experimental blood lead isotopic ratio data covering the 1975-1979 ILE period could support the fraction of petrol lead impacting on blood estimated in the ILE Report.

According to the model the percentages of lead of local petrol origin impacting on blood during the ILE experiment were 26%, 17% and 14% for Turin, near and far countryside respectively. These values compare with the corresponding figures given in the ILE Report which were 24%, 13% and 11%, the difference being probably due to the not yet reached (but assumed) equilibrium conditions adopted in the ILE Report calculations.

#### **Exposure and Health Effects**

This activity continued along three main lines: sources and environmental pathways (assessment studies); analytical quality assurance studies (parameters and factors affecting the microdetermination of HM in environmental and biological samples); environmental biochemical toxicology (metabolism and biochemical mechanisms of HM at present environmental levels and studies on tissues of human origin).

#### - Assessment studies

An assessment of the environmental pathway of arsenic

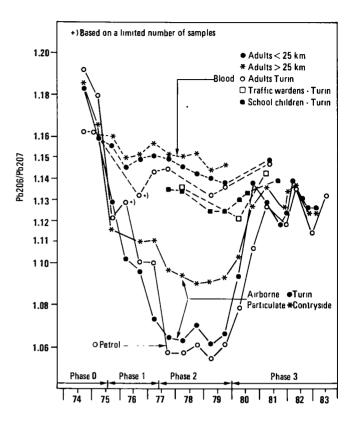


Fig 4. Change in Pb-206/Pb-207 ratios in petrol, airborne particulate and blood from 1974 to 1983

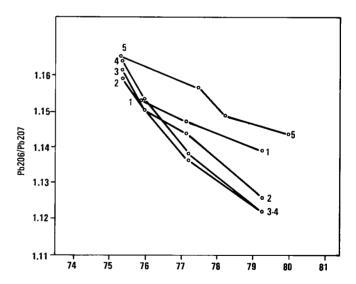


Fig. 5. Individual values of blood Pb-206/Pb-207 ratio for subjects follow up in Turin (4 new subjects) (numbers 1-4) and Castagneto Po (1 new subject) (number 5)

released from two potential pollution sources, a coal fired power plant (CFPP) and phosphatic fertilizer has been carried out using a dynamic model.

The results show that a 40 years operation of a 2500 MW CFPP as well as the application of phosphatic fertilizers to agricultural soil, do not substantially increase the arsenic background levels. The determined degree of mobilization

of arsenic in the soil matrix suggests that this element has a greater migration ability compared to Cr and Cd. This high mobility of arsenic through soil layers is responsible for the low bioavailability of this element to plants and explains the low predicted degree of accumulation.

It should further influence the groundwater quality, whose concentration should not exceed the Maximum Permissible Concentration level of 50  $\mu$ g/l in the European Communities however.

— The research on water leaching of trace metals from waste materials such as precipitator fly ashes of CFPP and municipal incinerator proceeded with speciation experiments on Chromium. Since in the inner part of big fly ash stock piles probably anoxic conditions prevail preventing oxidation of certain elements such as Cr the study was carried out under oxic (in air) and anoxic (in nitrogen box) conditions. The experiments involved the elution of <sup>51</sup>Cr (III) radiotracer applied to the top of columns of a coal fly ash and performed both in air and in the nitrogen box. The influence of oxygen on the rate of elution of chromium through the column is evident (Fig. 6). The higher rate of elution of Cr in the experiments under air is explained by the oxidation of the cationic Cr³+ to the Cr₂O₄²- anion which has higher mobility.

#### **Analytical Quality Control**

Radioanalytical techniques and atomic absorption spectrometry have been used for the microdetermination of vanadium in biological specimens such as human tissues and body fluids (Figure 7).

The use of <sup>48</sup>V radiotracer permitted investigations on the vaporization and retention mechanisms of vanadium. Higher vanadium oxides are probably converted to lower oxides decomposing to VO in gaseous form followed by the dissociation to «free vanadium» and oxygen. It was found that about 20% of <sup>48</sup>V radioactivity was consistently retained, probably in the form of carbide, does not vaporize under the conditions used for the analysis. Determinations of vanadium at ppb level in 10 urine samples by neutron activation analysis and by graphite furnace atomic absorption show agreement which can be considered satisfactory for practical purposes. The method allowed the study of vanadium in blood and urine of power plant workers.

#### **Environmental biochemical toxicology**

Work concerning the metabolism of environmental levels of As, Tl and Cr. Of particular interest are the findings from:

— comparative metabolic studies on environmental organic forms of arsenic in different animal species (in collaboration with the Swedish National Institute of Environmental Medicine): the tissue distribution and retention of arsenic in rats, mice and rabbits of other arsenic compounds. Unlike arsenobetaine, arsenocholine is incorporated into phospholipids, which is probably the reason for the different distribution pattern and the lower rate of clearance from tissues. Although the toxicological significance of the

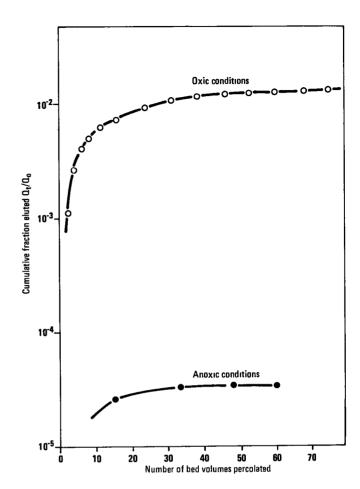


Fig. 6. Percolation of <sup>51</sup>Cr<sup>3+</sup> through a column of fly ash colum under oxic and anoxic conditions

accumulation of arsenic in form of arsenolipids in tissues seems difficult to evaluate at present, it may explain the high levels of arsenic found in the lipid fraction of some animal species and the higher concentration of arsenic found in the cerebral cortex than in the gray matter of human brain. Thus, altough the concentration of arsenocholine in seafood seems to be much lower than that of arsenobetaine it may be, however, of greater toxicological concern.

— Metabolism and toxicity of thallium (I) in the developing rat (in collaboration with the Institute of Pharmacology, University of Pavia, Italy): since clinical reports indicate that human fetus may suffer from the transplacentally acquired thallium intoxication the toxicity potential of thallium on pre-implantation embryos has been investigated by culturing in vitro mouse embryos from the 2 cell stage to the blastocyst stage. Concentration of the order of I μM of Tl resulted in a great blockade of the embryonal development suggesting the possibility for thallium to accumulate in the fetus under circumstances involving the environmental thallium exposure during pregnancy as well as a decreased fertility potential of females exposed to low level of thallium ions.

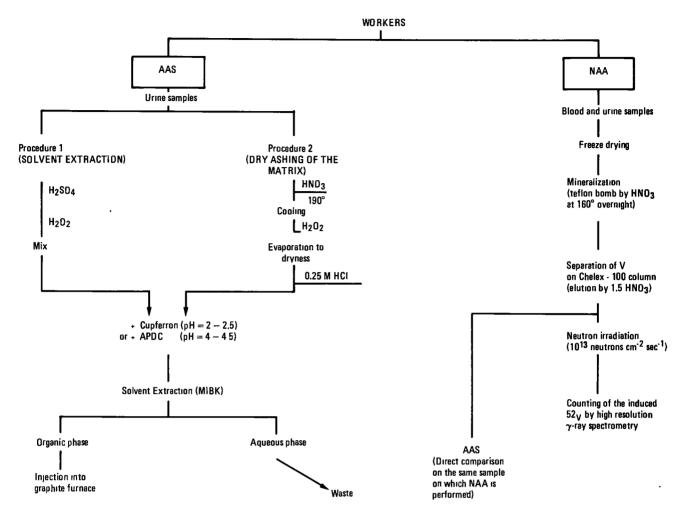


Fig. 7. Procedures developed for the microdetermination of vanadium in blood and urine of human subjects

Metabolism of different chemical forms of chromium: the metabolic pathways of low doses of inorganic chromium ions are depending on their chemical forms. Chromium in the blood administered as trivalent specie is present nearly totally in the plasma mainly bound to transferrin whereas when administered as hexavalent ions more than 80% enters the red blood cells and is transformed to a form different from the original one. The elimination of chromium is also dependent on the chemical forms and the route of administration, e.g. the biliary excretion of Cr(III) is nearly 50 times lower than that of Cr (VI), the urinary excretion of this latter form being significantly higher than that of Cr (III). More research is needed to re-evaluate the biochemical mechanisms which are involved in the essential and toxic properties of chromium.

# ENVIRONMENTAL IMPACT OF CONVENTIONAL POWER PLANTS

This project represents the follow-up of studies which were undertaken in recent years and progressively unified under the general theme «Remote Sensing of Pollution Phenomena around intense localised sources».

Techniques and methods developed in this frame constitute a proven structure for applications in field, as shown by joint participation of JRC teams in national or European campaigns. Four laboratories with different measuring techniques are contributing, namely:

Micrometeorology; Correlation Spectrometry (COSPEC and TELETEC); L1DAR; Tracers.

The activities of these groups for 1982 can be summarized as follows:

VIth CEC Campaign at Fos-Berre. In June 1983 three of our teams (Micrometeorology, Correlation Spectrometry and Lidar) participated among other teams of CEC Member States, Sweden, Spain and Canada. This Campaign was held in the industrial area of Fos-Berre, close to Marseile, France, under the sponsorship of the French Ministry of Industry and of DG XII-G. This Campaign was the follow-up of previous field exercises held in France (Lacq, 1975; Cordemais, 1977), England (Drax, 1976), Italy (Turbigo, 1979) and Belgium (Ghent, 1981). The goals of this exercise were the study of the logical meteorology (associated with a complex orography, sea, ponds, hills and valleys) and the evaluation of pollutant emission and

dispersion of a large variety of industrial plants (power plants, refineries, chemical factories).

The JRC groups participated with:

- a mobile laboratory equipped with a Cospec, an SO<sub>2</sub> and sulphates;
- a fixed apparatus for continous monitoring of SO<sub>2</sub> and sulphates;
- a Lidar;
- a Sodar:
- a micrometeorological station equipped with an ultrasonic anemometer-thermometer.

At this Campaign the Lidar unit was employed for systematic observation of vertical burden stratification and investigation of mixing layer or inversion layer topography.

- Data elaboration of the Turbigo exercise. The analysis of experimental data gathered by Lidar, Cospec, Tracer and Micrometeorological instruments for the characterisation of plume dispersion in a breeze regime around the Turbigo power station has been completed. It is shown that by an appropriate extrapolation of aerosol data from Lidar and wind data a correlation with Cospec and tracer data at larger distances is possible.
- Pollutant Transport Models. SO<sub>2</sub>-measurements gathered at the CEC Campaign held at Ghent in 1981 have been validated by a bigaussian and an analytical model, in collaboration with A.R.S., Milano. The data have been interpreted in terms of pollutant transport.

Furthermore, a three-dimensional wind-field model has been set up and applied to the Milano area, already studied by the previous two models.

#### Tracer experiments in the Karlsruhe area.

In collaboration with KfK (Karlsruhe) an atmospheric dispersion experiment using both tracer (SF<sub>6</sub>) and tetroon techniques was performed on April 1983 over a distance of about 50 km in the South-West Germany.

In Fig. 8 the experimental area with the sampling network, the tracer release point and the sectors interested by the SF<sub>6</sub> plume are shown.

With regard to results from tracer data only a summary of the average lateral  $(\sigma_x)$  and vertical  $(\sigma_x)$  dispersion parameters by evaluation of the experimental data are shown in the following table.

	R = 11	,8 km	R = 24	1,6 km	R = 44,5 km		
	σ <sub>y</sub> (m)	σ. (m)	σ <sub>y</sub> (m)	σ, (m)	σ <sub>y</sub> (m)	σ,	
$\sigma = \frac{\sum_{i=1}^{\infty} \sigma_i}{N}$	1049	1133	1783	1946	2685	1865	
S.D <sub>2</sub> (σ)	146	353	373	292	573	307	

where R is the distance from the release point

o, is the value of the ith measurement period

N is the number of the measuring periods

To our knowledge this is the first successfull experiment performed in continental Europe on a 50 km distance.

In the frame of a collaboration with ENEA-DISP tracer experiments have been carried out on June 1983 at Montalto di Castro (Italy), a seacoast site where a nuclear power station will be in operation during next years.

Further tracer experiments will be performed at the same site during 1984 for the validation of a local sea breeze atmospheric dispersion model.

The JRC tracer analytical laboratory partecipated in a European interlaboratory comparison (9 laboratories) on the  $SF_6$  determination in air, which was organized by the Direction of DG XII, in cooperation with the Belgian centre in Mol. The results of this comparison are now available and they will be published soon.

Efforts have been devoted to the implementation of the perfluorocarbons ( $C_7F_{14}$  and  $C_8F_{16}$ ) tracer technique, with particular concern to the analytical determination and the new designed release system. A first experiment using both SF<sub>6</sub> and  $C_8F_{16}$  tracers, is planned for Spring 1984 in South-West Germany.

#### Micrometeorological measurements

The instruments and the programmes developed for micrometeorological measurements in the past years had been previously tested in a few days field experiment at the Turbigo power station. In fact at the Fos-Berre campaign this was the only station which did the rather delicate heat and momentum flux measurements continuously during all the campaign. About 1 million of data became available on computer compatible tape.

The goal of creating a computerized station for field measurement of turbulent atmospheric parameters relevant to modellers being achieved with this successful operation, the activity of the coming years is intended to involve theoricians for an appropriate data interpretation and application in the validation of atmospheric models.

#### 3. CONCLUSIONS

The performance of the Experimental ECDIN Service, with partly encouraging results, and the starting of the semioperational commercial ECDIN operation may be considered as important milestones achieved in setting up a data bank interesting enough for European users and hopefully self-sustaining in financial terms for the medium future.

A more balanced staffing and additional resources, as planned for the 1984/87 programme, should allow to meet the major criticisms, that is lack of data and insufficient updating. Another strong improvement is expected by the implementation of the new search language ADACCL, planned for mid

A deeper and more frequent contact with the Commission DGs potentially interested in ECDIN should permit to support the Commission needs in a more opportune and effective way.

The sponsoring of European collaboration and the preparation

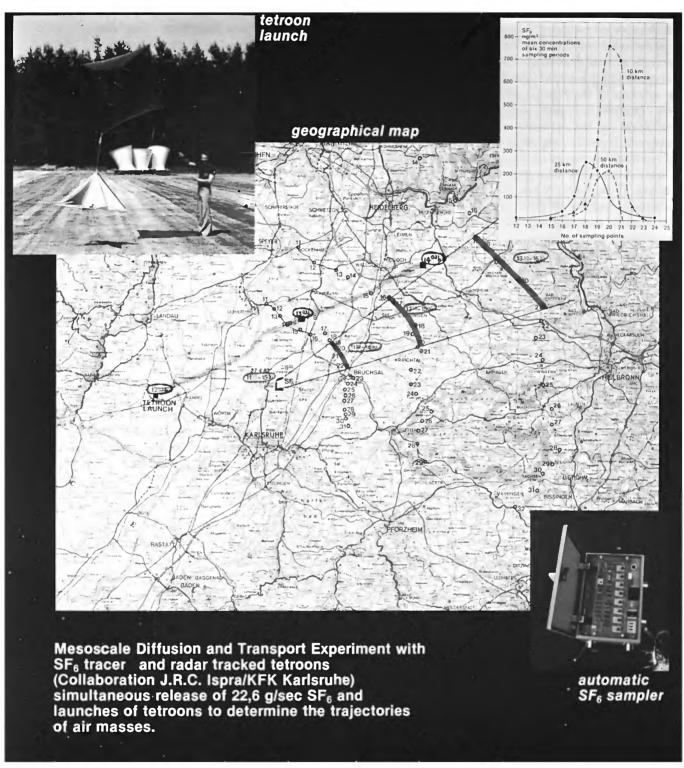


Fig. 8 Geographical map (South - West Germany)

of a Concerted Action in the field of IAQ remains the central point of the JRC's activity in the **Indoor Air Pollution** project. The Community Contact Group has been a valuable help in this preparatory work.

The JRC's experimental activity is essentially aimed at supporting European collaboration. This is obvious for the interlaboratory comparison of passive samplers. Results obtained in this field indicate that the applicability of passive samplers will be limited to a fairly rough assessment of indoor concentrations of major unpolar pollutants. The time between exposure and analysis should be kept as short as possible. Further work including also polar compounds in under way.

First data on the comparison of organic indoor and outdoor pollution and on the (detailed) survey analysis of organic indoor pollutants have been reported. Indoor/Outdoor concentration ratios are consistently higher than 1 and highest for a few chlorinated hydrocarbons which do not occur outdoors. The study of household dust samples suggests to avoid alphaquartz containing household products.

The activities of the Petten Establishment on Chemical Products - Organics were continued successfully.

New results on the mutagenic activities of polycyclic and heterocyclic aromatic compounds occuring in coal combustion and conversion processes are available and will be included in the final edition of the Atlas of Molecular Spectra of Polycyclic Aromatic Compounds. Work on testing and validation of analytical procedures for the determination of contamination risks to plastic packaged food by toxic packaging components (antioxidants) was continued.

A model study for reducing food contamination risks by using a newly synthesized bi-functional antioxidant with strongly reduced migration tendency was successfully concluded.

Laboratory activities of the Project Air Quality continued with the successfull implementation of chromatographic methods (GC, GC-MS, HPLC) for application in photochemical bag experiments. The airborne measurements in collaboration with DFVLR have been concluded in August/September and the evaluation of data is in progress.

The air quality project participated with two flame photometric sulphur analyzers for SO<sub>2</sub> and particulate sulphur in the 6th CEC Campaign at Fos-Berre (France). For the continuously mesuring sulphate instrument other laboratories have expressed interest in the meantime.

The Infrared-Spectroscopy group has now conclusive results from bag experiments that carbon monoxide plays no important role as precursor for photochemical ozone formation in the Ispra ambient air. Continuous trace gas monitoring by IRFTS was focussed on methane.

For the implementation of the EC Directive N° 80/779 JRC lspra acts in behalf of DG XI as a Central Laboratory for measurements to be carried out by the Commission in collaboration with Member States.

The first task to improve the tetrachloromercurate (TCM) pararosaniline (PRA) reference method for SO<sub>2</sub> determination in ambient air has been accomplished.

Work on total suspended particulates (TSP) has started with tests on loaded and unloaded fiber-glass filters. For the first quality assurance programme to be executed by Member States under the supervision of the Commission a draft proposal has been prepared.

The project Water Quality continued along the two research lines «Ecological Effects of Chemical Pollution» with new

results on the ecotoxicity of cadmium and «Nutrient Mass Balance in Aquatic Ecosystems» with work on model validation for the P-PO<sub>4</sub> flux at the sediment/water interface.

A laser light scattering technique has been developed for algal population counting. This method when becoming routine could open new spheres in limnology for the study of the dynamics of algal populations, intractable by classical microscopy.

In preparation of the future project on «Mass Balance of Heavy Metals in a River-bay Ecosystem» trace metal screening started at the Lago Maggiore test site.

In the frame of the Isotopic Lead Experiment (I.L.E.) the dynamic evolution of the blood isotopic ratio of the follow-up subjects has been modelled and published as an addendum to the ILE Status Report. A joint experiment JRC/Greek Ministry of Physical Planning, Housing and Environment on impact of automotive lead on population has been decided.

This experiment, using the sharp decrease from 0.4 to 0.15 g Pb/l in the great Athens area and the response in lead blood concentrations of about 130 individuals, is expected to support the findings of the ILE project.

#### Exposure and Health Effects from Trace Metal Pollution

The project Exposure and Health Effects from Trace Metal Pollution continued along the research line «environmental impact assessment of fossil fuelled power plants, municipal incinerators, fertilizer practices and similar anthropogenic activities» (assessment studies) and the study of the «metabolic behaviour of trace metals in tissues and cellular components of laboratory animals and man» (environmental biochemical toxicology).

A model describes the dynamic transformation of chromium ions released from different pollution sources. Experimental activities were concentrating on water leaching of trace metals from precipitator fly ash landfills (column experiments) and biochemical experiments on cadmium, mercury, arsenic and chromium.

In the frame of the project Environmental Impact of Power Plants three teams from JRC lspra (Correlation Spectroscopy, LIDAR and Micrometeorology) participated successfully in the 6th CEC Campaign on Remote Sensing of Air Pollution at Fos-Berre (France).

Data evaluation of the Fos and the previous Ghent (1981) campaign continued. The results of the first meso-scale JRC/KfK tracer/tetroon atmospheric diffusion and transport experiment (Karlsruhe, April 1983) were evaluated and displayed at the poster session of the EC/KfK Symposium on Acid Deposition.

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