منظمة الأغذية والزراعة للأمم المتحدة
联合国粮食及农业组织
FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
ORGANISATION DES NATIONS UNIES POUR L'ALIMENTATION ET L'AGRICULTURE
ORGANIZACION DE LAS NACIONES UNIDAS PARA LA AGRICULTURA Y LA ALIMENTACION

FIR/MEDPOL/HERB/2

21 April 1992

# REPORT OF THE FAO/IAEA/UNEP REVIEW MEETING ON THE HERBICIDES PILOT SURVEY

## Athens, 7-9 April 1992

Organized in the framework of the Long-term Programme
for Pollution Monitoring and Research in the
Mediterranean (MED POL - Phase II)

Convened jointly with:

IAEA

UNEP

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ADMINISTRATIVE REPORT

1. The IAEA/FAO/UNEP Workshop on the assessment of pollution by herbicides and fungicides (Monaco, 30 October - 1 November 1990) recommended that a pilot survey be initiated to establish the levels of herbicides in selected Mediterranean areas. Given the large number of active ingredients used, a short list of compounds of potential concern to the marine environment was prepared by balancing the available information on usage and persistence of the compounds. For the purposes of the pilot survey, this list was further reduced on the basis of the analytical methodology used.

2. The present meeting was organised to review the results of the pilot survey which was undertaken during 1991 in areas of France, Spain, Greece, Italy and Egypt, to draft a consolidated report on the data and make recommendations for future action. It was jointly convened by FAO, IAEA and UNEP in the framework of the MED POL activities and took place in Athens at the seat of the Co-ordinating Unit for the Mediterranean Action Plan, from 7-9 April 1992. It was attended by the principal investigators of the pilot survey and by representatives of IAEA and FAO. A list of participants appears as Annex I.

3. The meeting was opened by Mr. Salvino Busuttil, Co-ordinator of the Mediterranean Action Plan, who welcomed the participants and wished them every success in their deliberations. Mr. G.P. Gabrielides, Senior Fishery Officer (Marine Pollution), welcomed the participants on behalf of FAO and explained the background and scope of the meeting. Mr. J.W. Readman welcomed the participants on behalf of IAEA.

4. The meeting unanimously elected Ms. Silvana Galassi, Senior Research Scientist at the Water Research Institute in Milan, as Chairperson, and Mr. Jacek Tronczynski, Research Scientist at IFREMER, Nantes, as Rapporteur. Mr. G.P. Gabrielides acted as Technical Secretary.

5. The provisional agenda prepared by the Secretariat was unanimously adopted and appears as Annex II. Furthermore it was agreed that no rigid timetable would be followed and that discussion and writing sessions would be decided by the Chairperson as necessary.

6. Each principal investigator presented the results of the survey in the area of his responsibility. Mr. D. Barceló also presented the data from the Nile delta since he participated in the sampling and analysed the samples in his own laboratory. In general, the methodology used was that agreed by the IAEA/FAO/UNEP Workshop in Monaco, but no intercalibration exercise was possible. However, a spiked freeze-dried water sample is now available and it was agreed that all participating laboratories should analyse it. Results will be sent to IAEA-MEL where the data will be interpreted.

7. On the basis of the individual reports presented, the Group prepared a consolidated report, which appears as Annex III, using the data generated through the pilot survey .

8. As a result of the deliberations, the meeting made the following recommendations:

a) additional information should be compiled on herbicide use in the Mediterranean region

b) information on levels should be collected from Mediterranean regions other than those examined in the present study

c) the compounds detected in this survey are to a certain extent, a function of the selected analytical techniques. Research should be encouraged to develop suitable methods for the analysis of additional compounds of interest and importance such as paraquat, diquat, TCA, glyphosate, etc.

d) laboratories involved in the monitoring of herbicides should participate in an intercalibration exercise involving a spiked freeze-dried water sample which has recently become available

e) relevant research work should be encouraged to obtain additional information required for assessing the behaviour of herbicides in the marine environment and their potential ecological impact.

9. This report was adopted by the participants of the meeting on Thursday, 9 April 1992.

10. The meeting was closed by the Chairperson who thanked the participants for their active participation. In his closing remarks the Technical Secretary expressed, on behalf of the collaborating UN Agencies, his appreciation for the excellent work performed by the participating laboratories and especially by C.I.D. (Department of Environmental Chemistry) which also undertook the analysis of samples from Egypt.

# ANNEX I

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## ANNEX II

## AGENDA

1. Opening of the meeting
2. Background and scope
3. Election of officers
4. Adoption of the agenda
5. Organization of the work
6. Analytical methodology
7. Review of the results
8. Preparation of a consolidated report
9. Recommendations for future action
10. Adoption of the report
11. Closure of the meeting

**ANNEX III**

FAO/IAEA/UNEP PILOT SURVEY OF HERBICIDES
IN SELECTED MEDITERRANEAN AREAS

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## 1. INTRODUCTION

Herbicides are a large group of chemicals used for weed control in agriculture and as total herbicides for more general applications such as railways, roadside verges, airports etc.

Herbicide usage in agriculture has increased greatly during the last twenty years primarily due to convertion to intensive agriculture and changes in agricultural practices. For example, the annual application of herbicides in Italy increased from 9602 tonnes of active ingredient in 1971 to 24810 in 1982 and 33000 in 1987. In the Northern Mediterranean, France uses the largest amount of herbicides: 36000 tonnes in 1988 representing 36% of the total pesticides used in the country. In Spain and Greece the proportional usage of herbicides is less; in 1989 it was 3000 tonnes of active ingredient in each country (Fielding et al., 1992). No data are currently available for the southern Mediterranean coast.

Herbicides can be subdivided into groups according to their chemical structure (i.e. triazines, urea derivatives, phenoxyacids, thiocarbamates, dipyridinium salts). Differences in structure influence their modes of action and their environmental fates. Persistence and toxicity, the most relevant properties needed for a risk evaluation are not known for many herbicides used in the Mediterranean countries (IAEA/FAO/UNEP, 1990). However, since plants are the target organisms for herbicides, algae and aquatic plants should be the most sensitive organisms for herbicide pollution. In fact, a toxicity of 34 $\mu g\ l^{-1}$ is reported for algae (Trotter et al., 1990) while fish acute toxicity is 10 $mg\ l^{-1}$. In addition, changes in number and composition of stressed primary producers might influence community structures.

Herbicides have been frequently detected in many rivers flowing into the Mediterranean sea: river Pô (Galassi and Leoni, 1987; Baraldi et al., 1991; Galassi et al., 1992), river Rhône (Tronczynski et al., in press), river Llobregat, Spain (Rivera et al., 1987), Axios and Aliakmon rivers, Greece (Albanis, 1992). In contrast, only very limited data are available for estuarine locations (Baldi et al., 1991) and no data are available for coastal and sea water.

This pilot project represents the first systematic approach to detect herbicide contamination within the Mediterranean basin.

## 2. SELECTED AREAS

The selected areas are shown in Fig. 1. These are the Ebro delta in Spain, the Rhône delta in France, the river Pô and Adriatic sea in Italy, the river estuaries of Axios, Loudias, Aliakmon in Thermaikos bay (Greece) and of Arachthos and Louros in Amvrakikos gulf (Greece) as well as the Nile delta in Egypt.

### 2.1 The Ebro delta, Tarragona, Spain

The survey in this area was conducted by the Department of Environmental Chemistry, CID-CSIC, Barcelona (principal investigator: D. Barceló, co-workers: Gaël Durand and Véronique Bouvot).

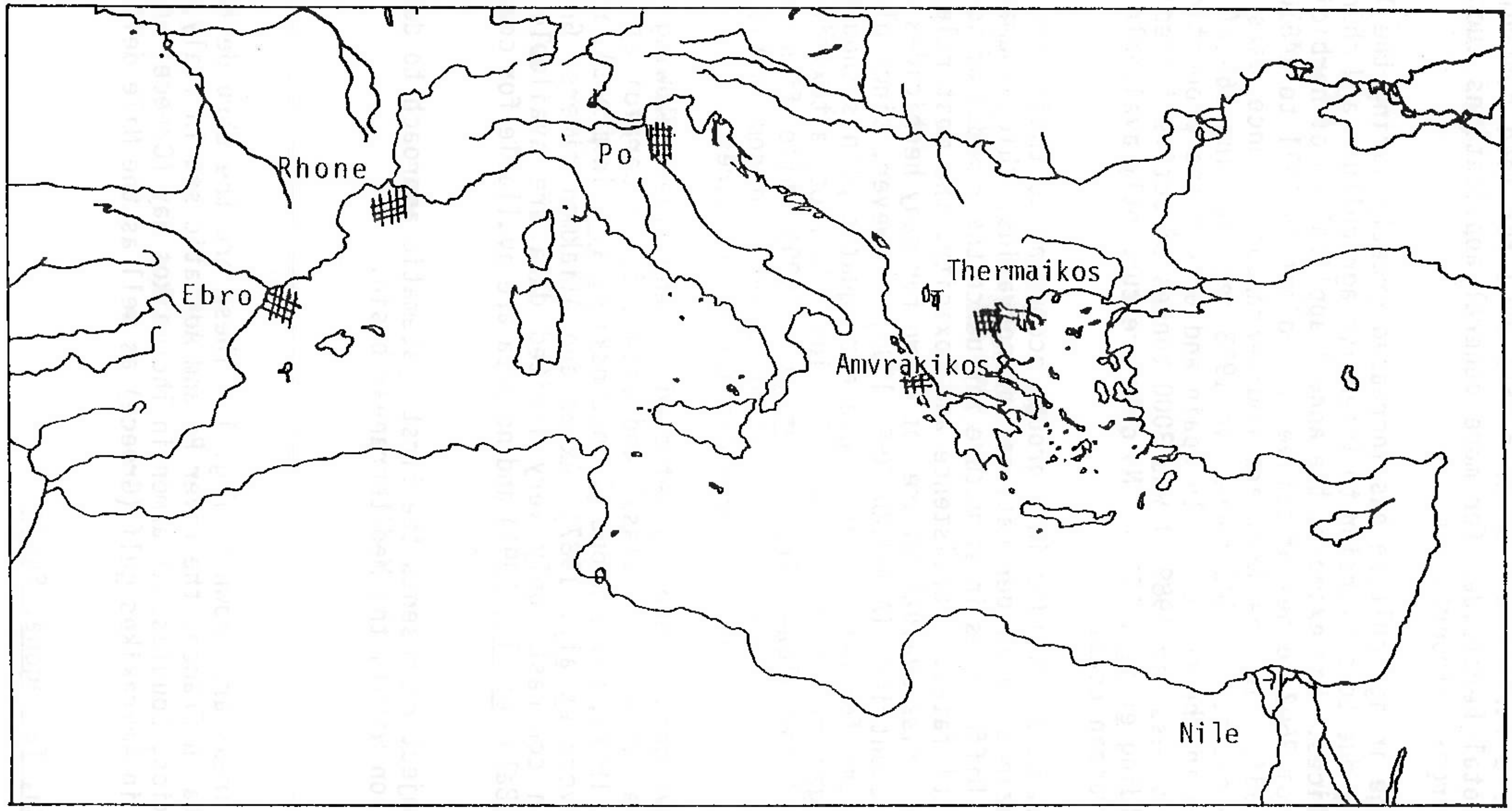



Fig. 1 The selected Mediterranean areas for the herbicides pilot survey

Description of the area

The Ebro delta is an alluvial plain of about 35 $km^2$, situated on the Western Mediterranean coast. About 20% of its surface consists of lagoons, drainage canals and marshes. The rest is devoted to intensive agriculture, principally rice culture. The area is considerably developed from the agricultural and industrial point of view, with an extensive use of pesticides and herbicides and industrial activities at the lower course of Ebro, as well as in the coastal area. The main cultivation is rice and 40-50 tonnes/year of active ingredient of molinate and bentazone used. Other herbicides used are alachlor, metolachlor, atrazine and simazine, about 1 tonnes/year of active ingredient.

Sampling

Samples were collected from seven locations (two for sediments and five for water samples) as shown in Fig. 2. Soil samples were collected from stations 1 and 2. Samples of water were collected at stations 3 to 7 with the following names: Ebro river (station 3), Carreté drainage canal (station 4), Encañizada lagoon (station 5), Encañizada lagoon for fishery (station 6) and Tancada lagoon (station 7).

Soil samples were sampled monthly from December 1990 to June 1991. Water samples were sampled monthly from April to June 1991.

2.2 The Rhône delta, France

The survey in this area was conducted by IFREMER, Nantes (principal investigator: J. Tronczynski, co-workers: C. Munschy and D. Pont)

Description of the area

The Rhône river is the largest river entering the Mediterranean Sea since the damming of the Nile river (Martin and Thomas, 1990). Situated on the Southern French coast, the alluvial plain of the Rhône river enters the Gulf of Lyon of the Mediterranean Sea. With a mean flow of 1650 $m^3$ $sec^{-1}$ and a mean annual solid discharge of 4-5x$10^6$ metric tonnes. The Rhône represents the major source of chemicals arriving to the Gulf of Lyon from its highly populated drainage basin which includes about 15% of the cultivated surfaces in France and a lot of its industries. The lower course of Rhône, occupied by its 750 $km^2$ delta, is devoted to intensive agriculture, principally rice culture. These activities employ massive usage of biocide agrochemicals in this area, introducing potential exposures and risks from these compounds to the marine environment within the Mediterranean. The herbicides used are a highly diverse form of agrochemicals and are propably the most used pesticides today. The estimated annual use of atrazine and simazine in the Rhône basin is ca. 700 tonnes for two main cultivations: corn (atrazine) and vineyard (simazine). The amount of herbidices used in the Rhône basin represent 7% of the total amount of herbicides used in France.

Sampling

The survey was carried out monthly at three sampling sites of the Rhône delta (Fig. 3), namely: (a) riverine fresh water, station - RFM, (b) great canal drainage waters outflow of rice culture (la Camargue) discharged

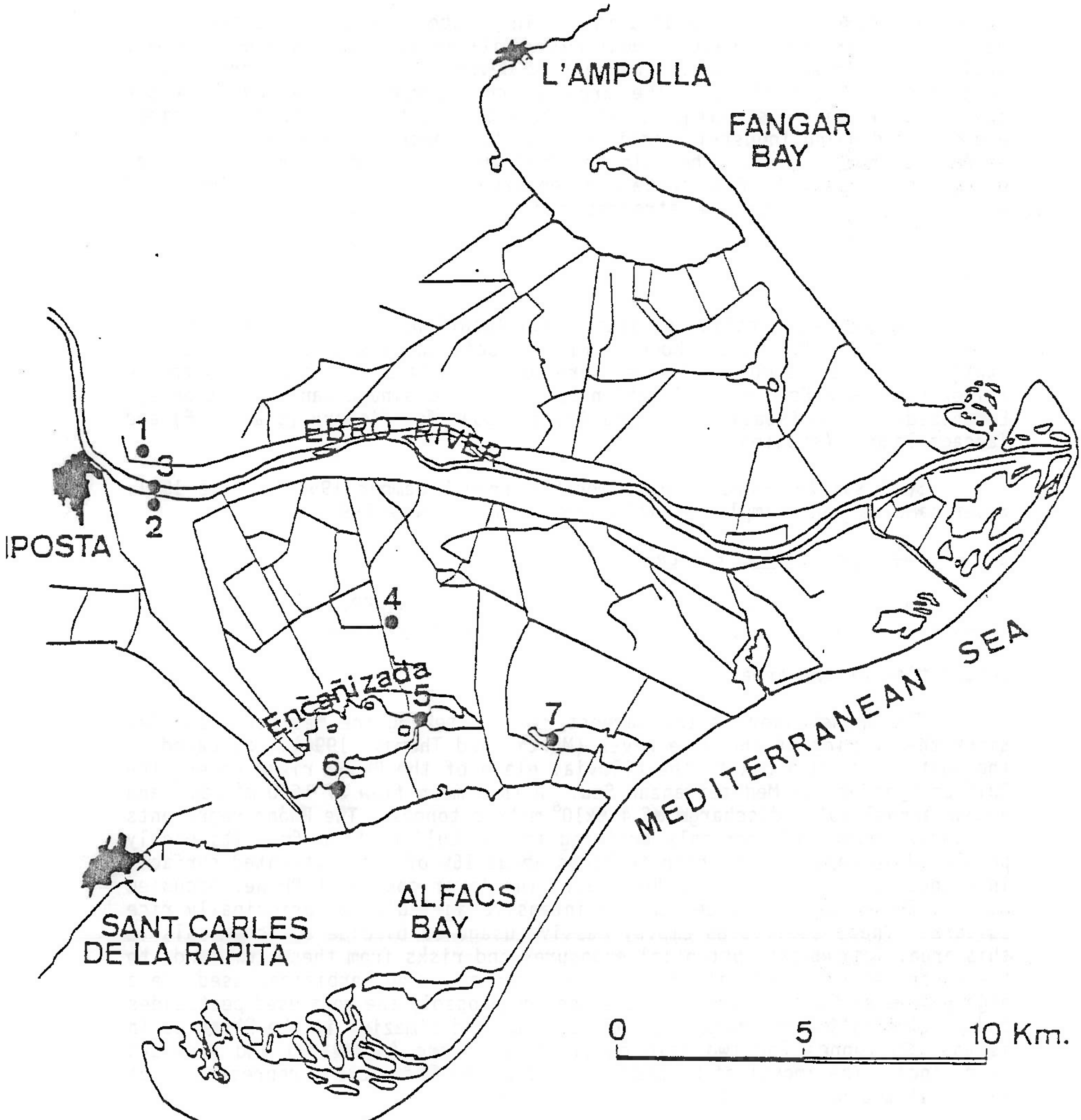



Fig. 2 Sampling sites in the Ebro delta

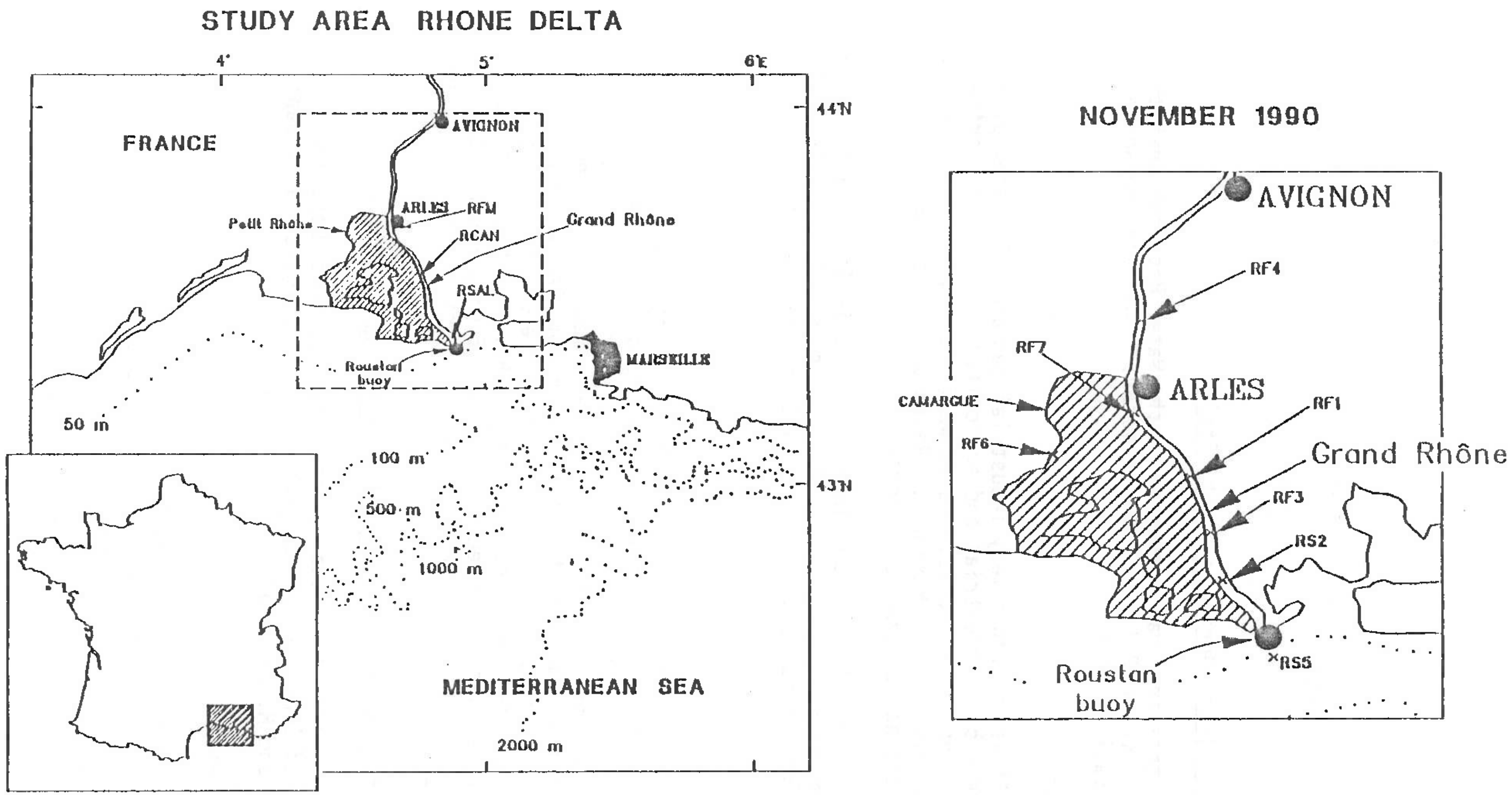



Fig. 3 Study area of the Rhône delta. The three sampling sites are: RFM - freshwaters of Rhône river; RCAN - drainage waters of rice crop canal; RS - low salinity waters of Rhône delta. Stations between RF4 and RS5 lie on a longitudinal transect. Shaded area indicates rice plantation in the Camargue region (around 19 thousands ha)

into the Rhône river, station -RCAN and (c) estuarine low salinity water, station -RSAL. Additionally two longitudinal transects of the Rhône delta were sampled in November 1990 and March 1991 (sampling sites between RF4 and RS5, Fig. 3). Water samples of 5 and/or 20 litres were collected from each station into glass bottles and transported within 2 to 3 hours to the laboratory (Laboratoire d'Ecologie des Systèmes Fluviaux, CNRS in Arles city), for further preparation. The large volume water samples were collected with all teflon equilibrated pumping system (IFREMER).

## 2.3 River Pô and Northern Adriatic coast, Italy

The survey in this area was conducted by the Water Research Institute (IRSA-CNR), Brugherio, Milan (Principal investigator: S. Galassi, co-workers: A. De Paolis and R. Ballestrini).

### Description of the area

The river Pô flows through a very industrialized and cultivated plain, receiving most of the urban, industrial and agricultural run off of Northern Italy. Lido delle Nazioni is a touristic area where sea water is influenced by fresh water from river Pô. Marina di Ravenna is located in a very industrialized area and has a commercial port.

About 50% of the herbicides used in agriculture in Italy (33000 t in 1987, including inorganic compounds) are used in the river Pô basin. In 1989, atrazine was banned for agricultural purposes in Italy and the prohibition is still in force.

### Sampling

The sampling area is shown in Fig. 4. River Pô water was collected at station A, Pontelagoscuro, near the town of Ferrara, at the closing section of the river basin which is about a hundred kilometers before the mouth. The two sampling stations of the Adriatic Sea, Lido delle Nazioni (B) and Marina di Ravenna (C) are located south of the river Pô mouth, ten and thirty kms respectively and and at a distance of five miles from the coast. Six sampling cruises were carried out between March and July 1991. In the sampling of April 20 only river water was collected and on July 16 only river water and sea water at station C were collected. The samples were stored at 4°C and extracted within 48 hours.

## 2.4 The river deltas in Thermaikos and Amvrakikos gulfs, Greece

The survey in this area was carried out by the Department of Chemistry, University of Ioannina, Greece (Principal investigator: T. Albanis, co-workers: T. Danis and M. Kourgia).

### Description of the area

The deltas of Axios, Loudias and Aliakmon rivers consist of a large wetland on the Thermaikos Gulf coast, which is protected by the Ramsar Convention (1971). The agricultural area of Thessaloniki (93,542 ha), located in Northern Greece, drains in this area through the above rivers (Fig. 5). During the last three years the cultivated crops were approximately 27.6%

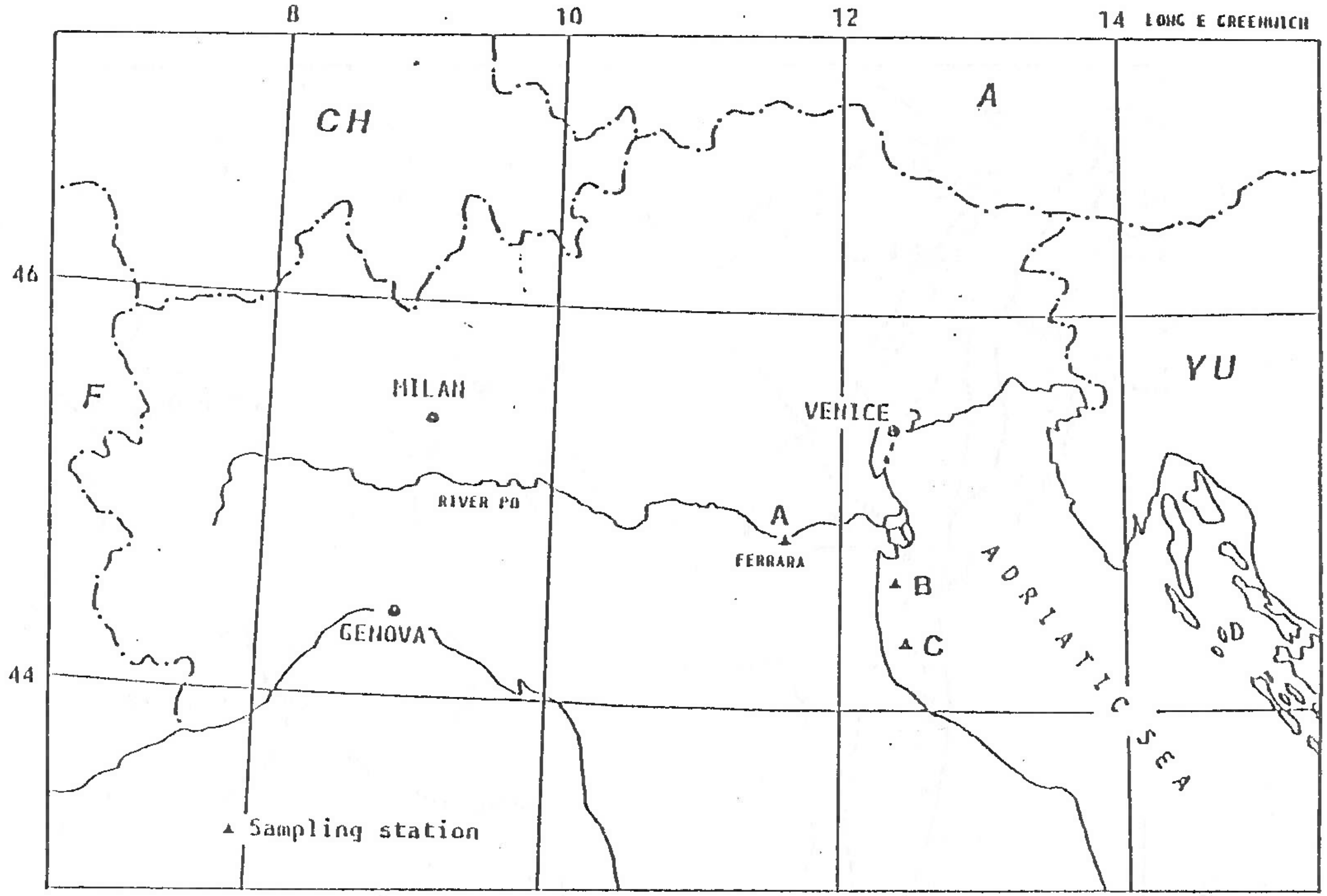



Fig. 4 Sampling sites in the river Pô and Northern Adriatic

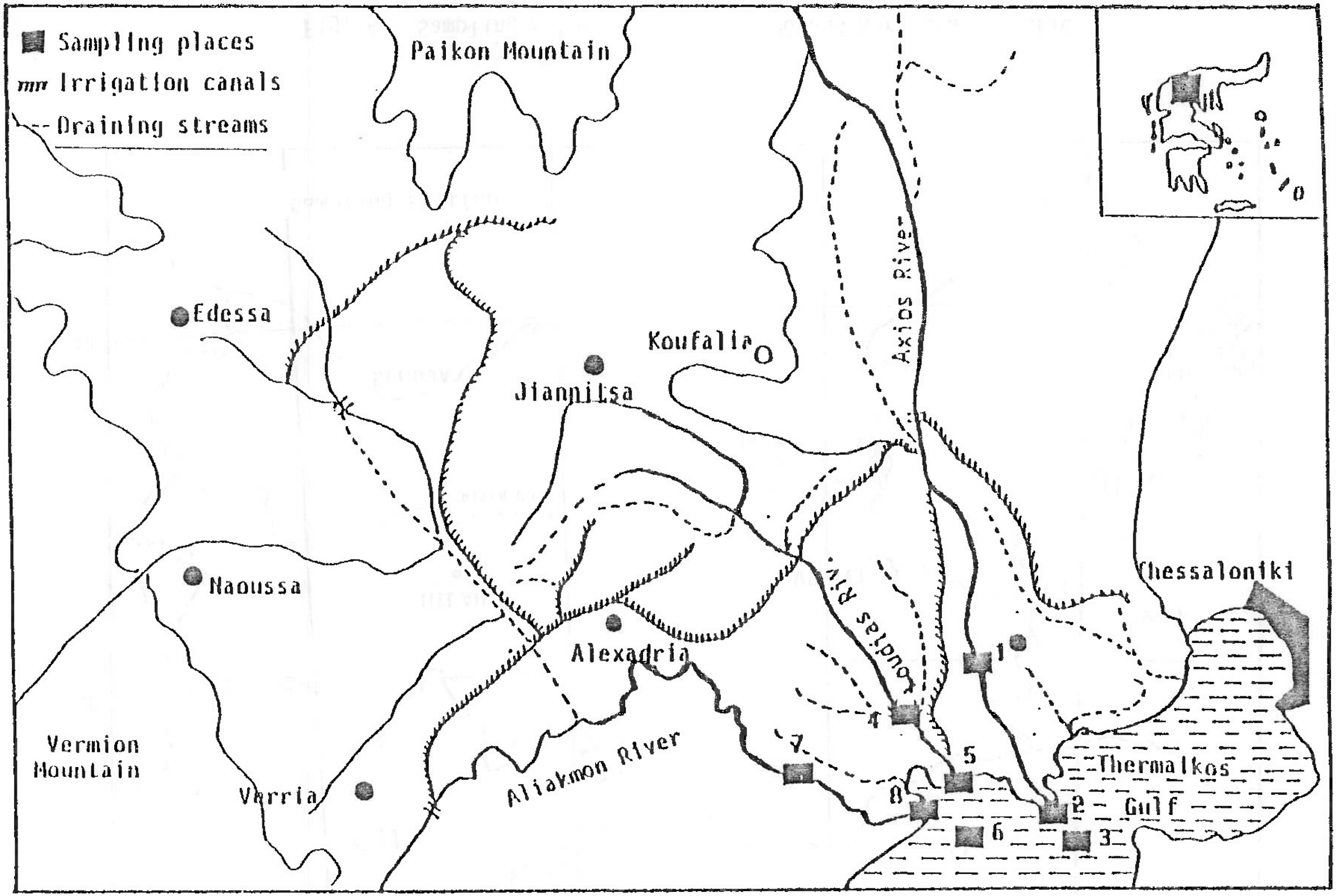



Fig. 5 The sampling stations in Thermaikos gulf and Thessaloniki plain

cotton, 20.1% corn, 21% trees, 13.5% rice, 4.9% tobacco, 3% alfa-alfa and 10% others (beets, vegetables etc). The water from Axios and Aliakmon rivers as well as from two smaller rivers, Moglinitsas and Arapitsa (Fig. 5) are the water sources for irrigation. During the 1991 cultivation season, from May to September, about 724 million $m^3$ water were used in the area of Thessaloniki plain and 80% of this was used during the period from July to August.

The mean annual water flow of Axios river is 118 $m^3$ $sec^{-1}$, of Loudias 21 $m^3$ $sec^{-1}$ and of Aliakmon 30 $m^3$ $sec^{-1}$ with large differences from year to year. The mean rainfall is about 362 mm (120.8 mm during winter, 121.4 mm during spring, 66.6 mm during summer and 133.5 mm during fall). The annual water deficit is 412.9 mm but the largest percentage of deficit appears in the summer, about 296.6 mm (71.8%).

The estimated annual use of herbicides in the Thermaikos area is about 220 tonnes active ingredient and the main chemicals are: alachlor, atrazine, 2,4-D, MCPA, metolachlor, simazine, molinate and trifluvalin.

The rivers Louros and Arachthos meet in the wetland of Amvrakikos gulf (Fig. 6) which is also protected by the Ramsar Convention. Amvrakikos gulf is an almost enclosed and protected marine area, which communicates with the adjacent lagoons via controlled accesses. Amvrakikos gulf is the recipient of run-off from a basin with a total area of 4,400 $km^2$ and the highest point 2,429 m. Total average annual run-off from rainfall into Amvrakikos gulf is estimated at $28x10^8$ $m^3$. The lowlands near the north gulf lagoons consist of saline soils and beyond them stretches an agricultural area with a surface of 74700 hectares. The main cultivations are citrus fruits 30%, olives 22%, corn 14%, alfa-alfa 9% and cotton 7.5%.

The estimated annual use of herbicides in the Amvrakikos area is about 35 tonnes of active ingredient. The herbicides alachlor, atrazine, 2,4-D, MCPA, metolachlor, simazine and trifluvalin are the most used compounds.

Sampling

Water and sediment samples from the estuaries and wetlands of Thermaikos gulf (8 stations, Fig. 5) and Amvrakikos gulf (7 stations, Fig. 6) were collected between January and December 1991. Three to four 2.5 L glass bottles of water were collected to allow analysis of all the groups of compounds specified in the study. Samples reached the laboratory 1-3 days after sampling.

2.5 <u>The river Nile delta (Rosetta branch)</u>

The survey in this area was conducted by the Environmental Chemistry Dept. CID-CSIC, Barcelona in collaboration with the Institute of Graduate Studies and Research, Alexandria (Principal investigator: D. Barceló, co-workers: M. El-Raey, H.Z. Ibrahim, S. Nasr, G. Durand).

Description of the area

The Rosetta branch flows north-westerly to the Mediterranean sea and it is part of the Nile river delta. This area includes industrial and agricultural activities. The main crop is cotton.

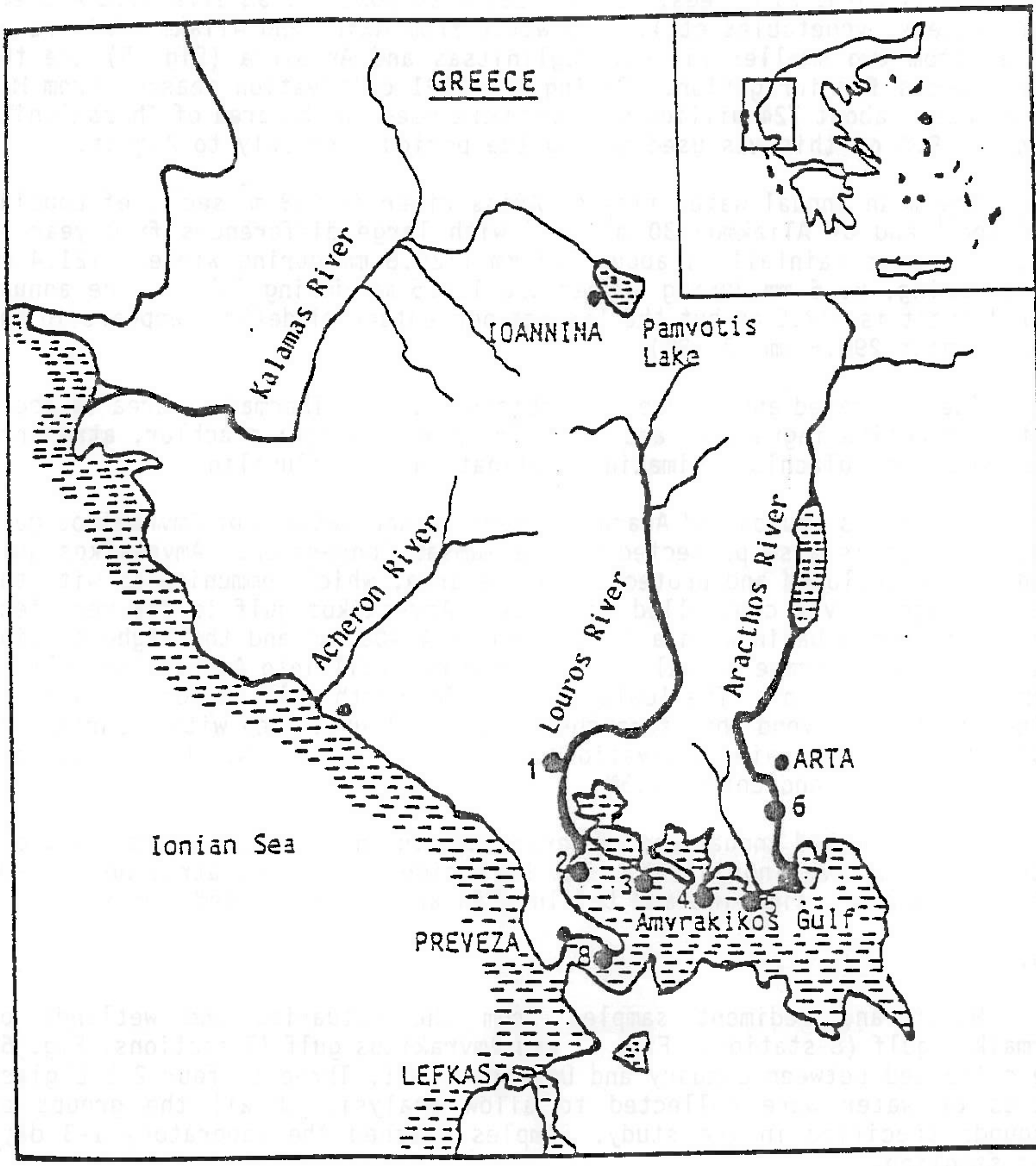



Fig. 6 The sampling stations in Amvrakikos gulf and the basin of Louros and Arachthos rivers

## Sampling

Water and sediment samples were taken from 6 locations on 10 November 1991 using a boat and appropriate equipment (Fig. 7). The samples were transferred to the laboratory; water samples were extracted the following day while sediment samples were stored at -20°C. The analyses were performed in Barcelona.

# 3. METHODOLOGY

## 3.1 Analytical protocols

Analyses of the herbicides followed the guidelines drafted during the IAEA/FAO/UNEP MED POL Workshop on the assessment of pollution by Herbicides and Fungicides held in Monaco from 30 October to 1 November 1991. Any differences in the chosen analytical techniques are summarised in Table 1 but the general scheme used by all participants is as follows:

### 3.1.1 Extraction, clean-up and quantification

#### 3.1.1.1 Water: Liquid-liquid extraction

Neutral compounds

One to five litres of water are extracted into dichloromethane (HMSO, 1985; Durand and Barceló, 1989).

Acidic compounds

Water is acidified with several ml of concentrated $H_2SO_4$ or phosphate buffer (pH ~ 2.5). Samples are then extracted with dichloromethane (HMSO, 1987).

#### 3.1.1.2 Sediments

Neutral compounds

Samples of sediment (10g) are soxhlet extracted for 12 h with methanol. The evaporated extract is redissolved in hexane in preparation for the "clean-up" (Durand *et al.*, 1989; Gruka *et al.*, 1986).

Acidic compounds

10g of sediment are mixed with 85 ml of 0.1M phosphate buffer (pH ~ 2.5). Dichloromethane is added to the mixture which is then ultra-sonicated. The extract is then isolated, evaporated, the residue displaced into hexane, and treated as for the "neutral" compounds (Durand *et al.*, 1989; Gruka *et al.*, 1986).

Florisil "clean-up"

Sediment extracts in hexane are added to a florisil column and eluted with n-hexane/ethyl ether (50:50; v/v) (Durand *et al.*, 1989). The extract is then reduced in volume and the residue redissolved in a solvent compatible with subsequent analyses.

#### 3.1.1.3 Quantification

Full details of the analytical techniques are provided in HMSO, 1985; Durand and Barceló, 1989; HMSO, 1987; Durand *et al.*, 1989; Gruka *et al.*, 1986.

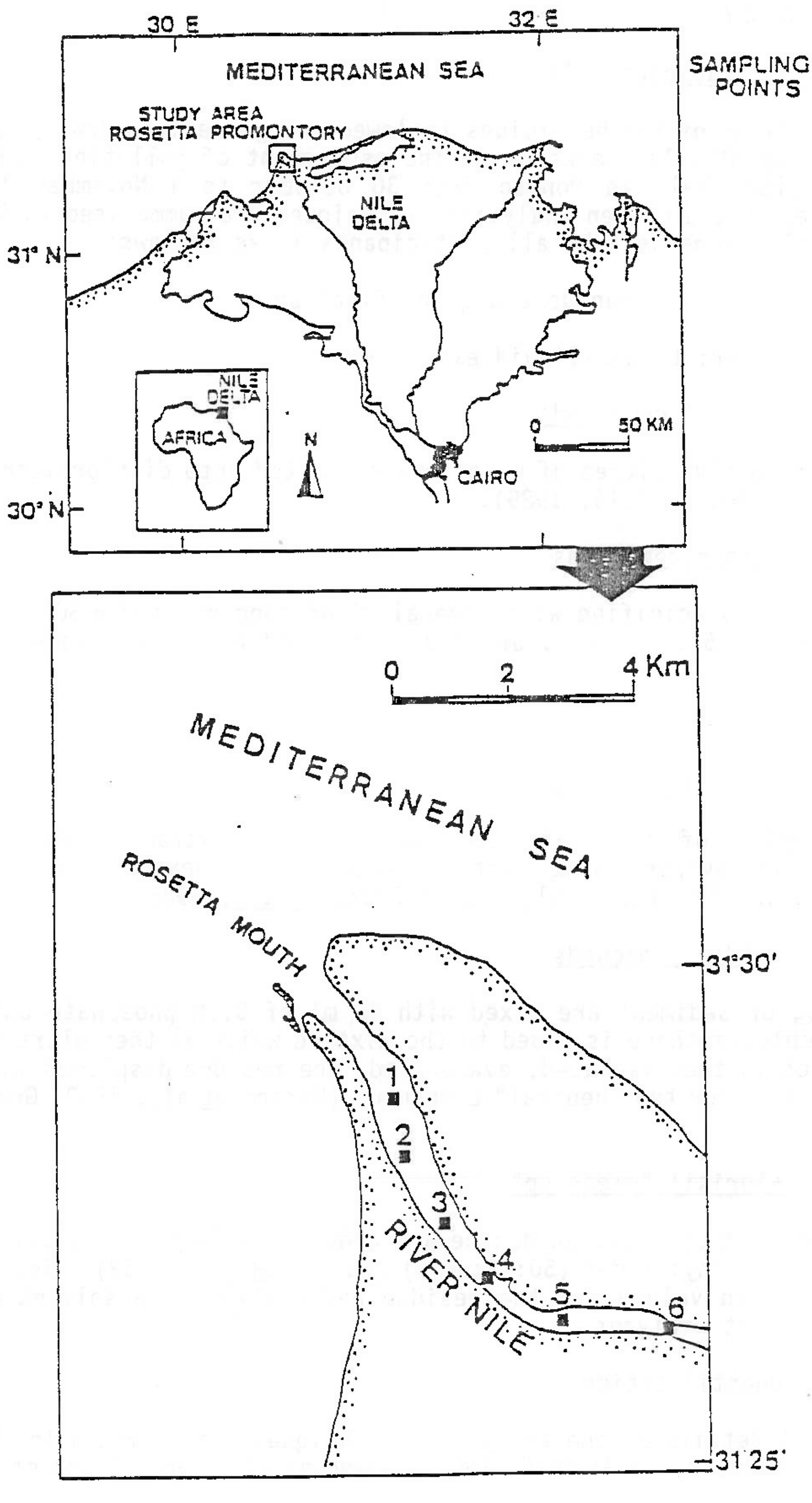



Fig. 7 Sampling sites in the Nile delta (Rosetta branch)

Table 1

Summary of variations betwen analytical protocols used by the participants.

| | France | Greece | Italy | Spain/Egypt |
|---|---|---|---|---|
| Filtration | GF/F | None | 0.45µm-river<br>None-saline | ✓ |
| Neutral extract | ✓ | ✓ | ✓ | ✓ |
| Acid Extract | ✓ | ✓ | ✓ | ✓ |
| Clean-up | None | Florisil | None | None |
| Neutral quantification | Ext.std.<br>cGC-NPD | Ext.std.<br>GC-NPD | Ext.std.<br>cGC-NPD | Ext.std.<br>cGC-NPD<br>LC-diode array UV<br>cGC-MS |
| Derivatisation | (to be analysed) | Methylation<br>diazomethane | Methylation<br>diazomethane | None |
| Acid quantification | (to be analysed) | GC-NPD<br>cGC-ECD | cGC-NPD | LC-diode array UV |
| Quality Assurance Parameters: | | | | |
| Reagent blanks | ✓ | ✓ | ✓ | ✓ |
| Recovery of spikes | Triazines | X | X | All compounds |
| Peak identification | Retention time<br>2 columns | Retention time<br>2 columns<br>2 temp.progs | Retention time<br>Confirmation<br>by GCMS | Retention time<br>GCMS<br>diode array<br>spectra |
| Reproducibility | instrumental<br>+ duplicate<br>sample<br>analyses | instrumental<br>+ duplicate<br>sample<br>analyses | instrumental<br>+ duplicate<br>sample<br>analyses | instrumental<br>+ triplicate<br>sample<br>analyses<br>+ (6 analyses<br>of one sample) |

The neutral compounds are usually separated and quantified by cGC-NPD or can alternatively be analysed by high performance liquid chromatography with U.V. detection (preferably by diode array/LC-DAD). Detection limits for the analysis of water (2 litres) are 1 to 10 ng $l^{-1}$ for cGC-NPD (according to response). For sediments (10g), detection limits are 1 to 10 ng $g^{-1}$ dry wt. for cGC-NPD.

For acidic compounds derivatisation is required and cGC-ECD analyses are most frequently used. Detection limits from these analyses are generally similar to those described for the neutral compounds.

The limit of detection under LC-DAD are worse than with GC-NPD or ECD analyses. They were estimated to be 10 ng $l^{-1}$ for herbicides exhibiting absorption maxima above 210 nm such as atrazine, simazine, chlortoluron, isoproturon and bentazone, whereas for molinate, alachlor, metolachlor and trifluralin, which exhibit UV maxima at the region below 210 nm, the limit of detection are ca. 10 times higher, 100 ng $l^{-1}$. For the two chlorinated phenoxy acids, 2,4-D and MCPA, that although exhibit maxima wavelength at 220 nm, the limit of detection is ca. 500 ng $l^{-1}$, due to its poor extraction efficiency and chromatographic behaviour.

### 3.2 Quality assurance

A harmonised general protocol was used by all the participating laboratories in order to minimise variability introduced through analytical methodologies. The testing parameters which were introduced by the individual participants to evaluate their techniques are summarised in Table 1.

The need to intercalibrate analyses using "reference" materials was endorsed by the meeting. At the time of the prior workshop in Monaco, no suitable materials were available. In the interim period however, sediment and lyophilysed water samples which have been characterised for several of the herbicides have become available. These will be distributed to all participating laboratories within the pilot survey in the near future. Results will be collated and evaluated by IAEA-MEL.

## 4. RESULTS AND DISCUSSION

This report presents the first quantitative and comparable results of concentrations of modern herbicides in estuaries of the major Mediterranean rivers.

### Water analyses

Comparisons of concentration ranges of some representative compounds, are shown in Table 2 and Figures 8, 9 and 10.

Despite some regional differences in uses of this group of agrochemicals, the obtained data set is in fairly good agreement for the different regions studied. It is apparent that five herbicides (atrazine, simazine, molinate, metolachlor and alachlor) are the most commonly encountered herbicides. It is, however, stressed that the selected analytical techniques are not applicable to all herbicides; absence of other compounds from the list might therefore reflect analytical incompatibility rather than absence.

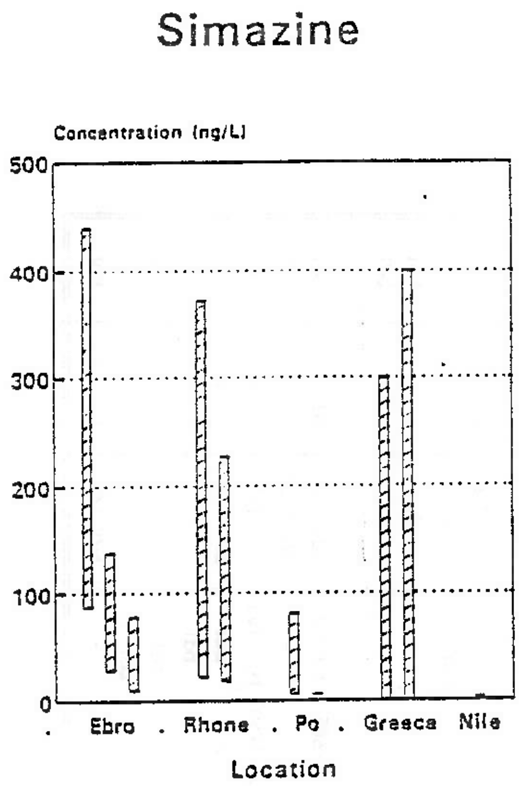
The concentrations found are similar to those reported by different authors in several studies. Hence, atrazine, one of the herbicides most widely used in the USA and European countries over the last 30 years, and employed for weed control among crops of corn, wheat, barley and sorghum and also on railroads (Barceló, 1991) has been detected in surface and groundwaters throughout the world. It has been detected in many US groundwaters at concentrations in the range of 0.17-4 $\mu g\ l^{-1}$ with median levels of 0.5 $\mu g\ l^{-1}$ and it is the most commonly detected compound in the so-called "corn-belt areas", at the Mississippi river (Pereira and Rostad, 1990), in Canadian rivers (Frank and Logan, 1988) and also in monitoring studies carried out in Europe, namely in Italian wells (Fielding et al., 1992), in the Pô river and effluents (Galassi et al., 1988) and in the Adige river (Benfenati et al., 1990). In other European countries such as Spain, in well water from Valencia (de Barreda et al., 1991), in surface and groundwaters from France (Legrand et al., 1990), in the river Rhine at the Dutch-German border (Hrubec, 1989), in river waters of the United Kingdom and in Swiss lakes (Barceló, 1991) as well as in the aquatic system of Ioannina, in Greece (Albanis et al., 1986). In most of the previous studies reported on atrazine, the second herbicide (also of a widespread use although with a lower

## Table 2

List of herbicides detected and their ranges in the different areas.

| | EBRO DRAINAGE CANAL | EBRO RIVER | EBRO DELTA LAGOONS | RHONE RIVER | RHONE DELTA | RIVER PO | NORTHERN ADRIATIC SEA | THERMAIKOS GULF | AMVRAKIKOS GULF | NILE DELTA |
|---|---|---|---|---|---|---|---|---|---|---|
| alachlor | bdl-862 | bdl-206 | bdl-267 | - | - | bdl-106 | bdl | bdl-1300 | bdl-1400 | bdl |
| atrazine | 58-308 | 17-190 | bdl-57 | 40-291 | 17-386 | 21-118 | bdl-18 | bdl-700 | bdl-260 | bdl |
| bentazone | bdl-5500 | bdl | bdl-1000 | - | - | 83-311 | bdl | bdl | bdl | - |
| chlortoluron | bdl | bdl | bdl | - | - | - | - | bdl | bdl | bdl |
| 2,4-D | bdl | bdl | bdl | - | - | - | - | bdl-1200 | bdl-500 | - |
| DEA | bdl | bdl | bdl | 2-8 | 4-6 | bdl-44 | bdl | - | - | bdl |
| DIA | bdl | bdl | bdl | 2-4 | 3 | bdl-6 | bdl | - | - | bdl |
| diuron | - | - | - | - | - | - | - | bdl-700 | bdl-600 | - |
| EPTC | - | - | - | - | - | bdl-1319 | bdl-187 | - | - | - |
| isoproturon | bdl | bdl | bdl | - | - | - | - | bdl | bdl | bdl |
| linuron | bdl | bdl | bdl | - | - | - | - | bdl | bdl | bdl |
| MCPA | bdl | bdl | bdl | - | - | - | - | bdl-800 | bdl-900 | - |
| metolachlor | bdl-68 | 32-132 | bdl-554 | - | - | bdl-605 | bdl-66 | bdl-500 | bdl-800 | bdl |
| metribuzin | - | - | - | - | - | - | - | bdl-1100 | bdl | bdl |
| molinate | 254-1400 | bdl-38 | bdl-568 | - | - | bdl-1750 | bdl-103 | bdl-900 | bdl | bdl |
| prometryne | - | - | - | - | - | bdl | bdl | bdl-500 | bdl | - |
| propanil | - | - | - | 1-3 | -1-2 | bdl | bdl | - | - | - |
| simazine | 87-440 | 28-138 | 10-78 | 22-372 | 18-227 | 6-81 | bdl-6 | bdl-300 | bdl-400 | bdl |
| terbutylazine | - | - | - | - | - | 4-149 | bdl-50 | - | - | - |
| trifluralin | * | bdl | bdl | - | - | - | - | bdl-460 | bdl-360 | bdl |

- : indicates not monitored
bdl : indicates below detection limits
* : detected but not quantified



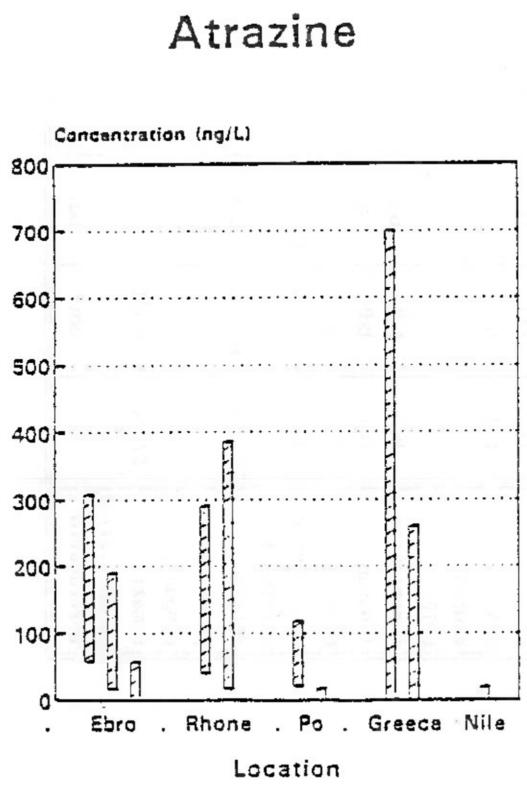




Fig. 8 Ranges in concentrations of simazine and atrazine in the selected Mediterranean locations (Bars indicate respectively the data listed in Table 2)

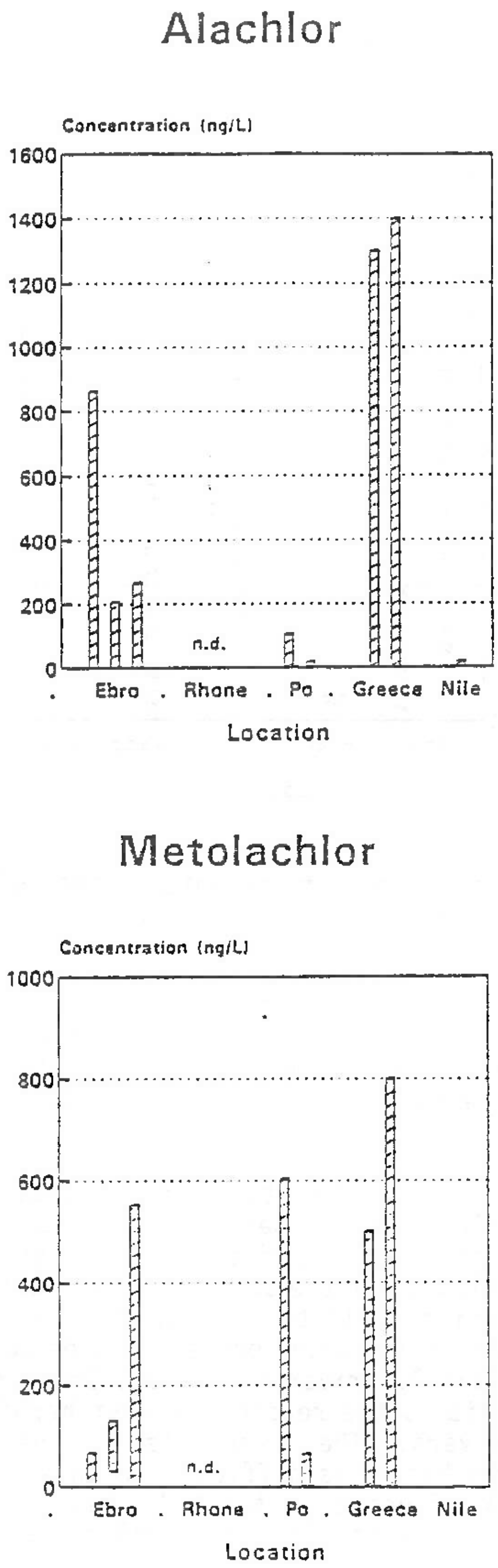



Fig. 9 Ranges in concentrations of alachlor and metolachlor in the selected Mediterranean locations (Bars indicate respectively the data listed in Table 2)

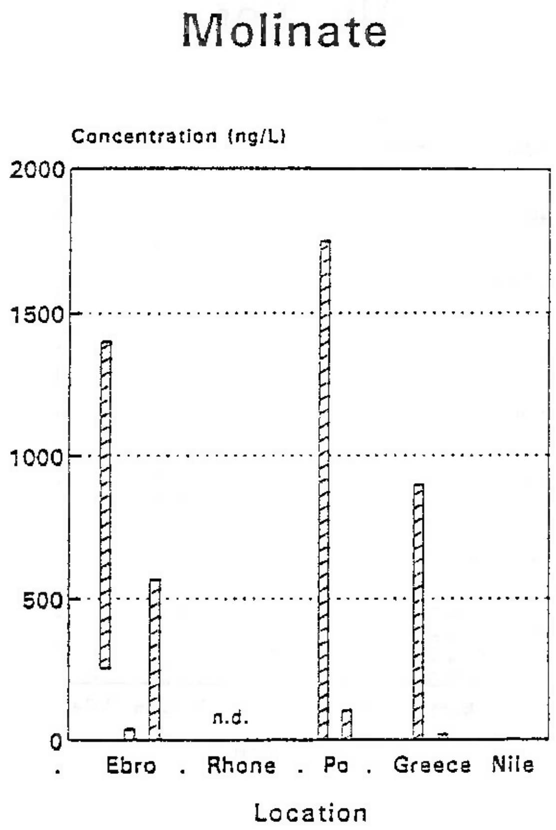



Fig. 10 Ranges in concentrations of molinate in the selected Mediterranean locations (Bars indicate respectively the data listed in Table 2)

concentration) was simazine and in some studies alachlor and metolachlor were also detected reaching levels up to 10 µg $l^{-1}$. Molinate reached high levels up to 90 and 150 µg $l^{-1}$ in a Spanish lake and in an Italian well respectively (Carrasco et al., 1987).

Apart from differences in the type of cultivations present in the areas selected for this pilot study, other circumstances should be taken into account when evaluating the reported data. First of all, the different analytical facilities available for the participating laboratories determines the number of compounds which could be monitored. Secondly, the different dilution capacity of the receiving water bodies must be considered. The Rhône and Pô, for instance have similar river flows, but Greek rivers have at least ten times lower flows. This is the reason why most herbicides reached their maximum levels in Greek rivers. The river Nile, on the contrary, seemed to be unpolluted by herbicides but it is difficult to understand if this lack of occurrence is due to lack of usage in the Nile basin, the construction of banks limiting soil drainage or the limited sampling regions.

The very low levels of atrazine in river Pô compared with other areas and previous periods in the same river are probably due to the banning of the compound in Italy for agricultural uses. The occurrence of high levels of terbutylazine or metolachlor can be related with the use of these herbicides as substitutes for atrazine.

Molinate and bentazone reached highest concentrations in the river Ebro and the river Pô in correspondence of the period of usage in rice crop fields. On the other hand, molinate and bentazone are used in about the same amount in Spain and Italy and the majority of rice fields are in the river Ebro and Pô basins, respectively.

Coastal waters contain detectable levels of some herbicides but the concentrations are lower by far than the river from which they receive waters. It is presumed therefore, that most of the herbicide pollution is derived from river inflow to coastal water.

Peak concentrations of some herbicides were observed corresponding to their application in the fields. However, the treatment period varies for each herbicide. Peak concentrations were observed in May for atrazine, simazine, molinate and metolachlor (Figs. 12, 14), in June for molinate and EPTC (Figs. 11, 13) and in September for simazine (Fig. 12).

Episodic peaks in concentrations occur in relation to meteorological and hydrological events like rainstorms, flood periods or daming practices. This was observed in April in the river Pô (Fig. 13) and in March in the Rhône river during a flood (Fig. 12) and during the period May to August in Thermaikos and Amvrakikos (Fig. 14). In one instance, a distinct relationship was observed between water discharge ($m^3$ $s^{-1}$) and simazine concentration in the Rhône delta.

Suspected point-sources of herbicide inputs were surveyed in irrigation waters of drainage canals of rice crops in Spain and France. The concentrations were shown to be high for herbicides being used locally.

The residual levels of herbicides present in different regions suggest that despite periodically occurring elevated concentrations, slow diffusive-like inputs are observed throughout the year. Furthermore, this is supported by observed residual levels of atrazine in Italy, where use of this herbicide was restricted/banned since 1989. The carry-over of chlorotriazines from one application to another is demonstrated by the study of its persistence in natural conditions in soil/sediment matrices in the Ebro delta in Spain (Fig. 15).

It appears from the data set that in order to estimate loads of herbicides into the Mediterranean sea, a study which integrates high variability of concentrations of herbicides in large estuaries and instantaneous water discharge records during period of sampling should be undertaken.

The herbicide levels determined in freshwater can be of concern for drinking purposes given that a limit of 0.1 µg $l^{-1}$ is fixed for drinking water for single pesticides and 0.5 µg $l^{-1}$ for total pesticides (EEC Directive 80/778).

On the basis of the available data, the concentrations found in freshwater and coastal water should not cause acute toxicity on aquatic organisms. However, nothing is known on the cumulative effect of mixtures of herbicides and other pollutants occurring in river and coastal water. Furthermore, some herbicides were found to cause effects on phytoplankton

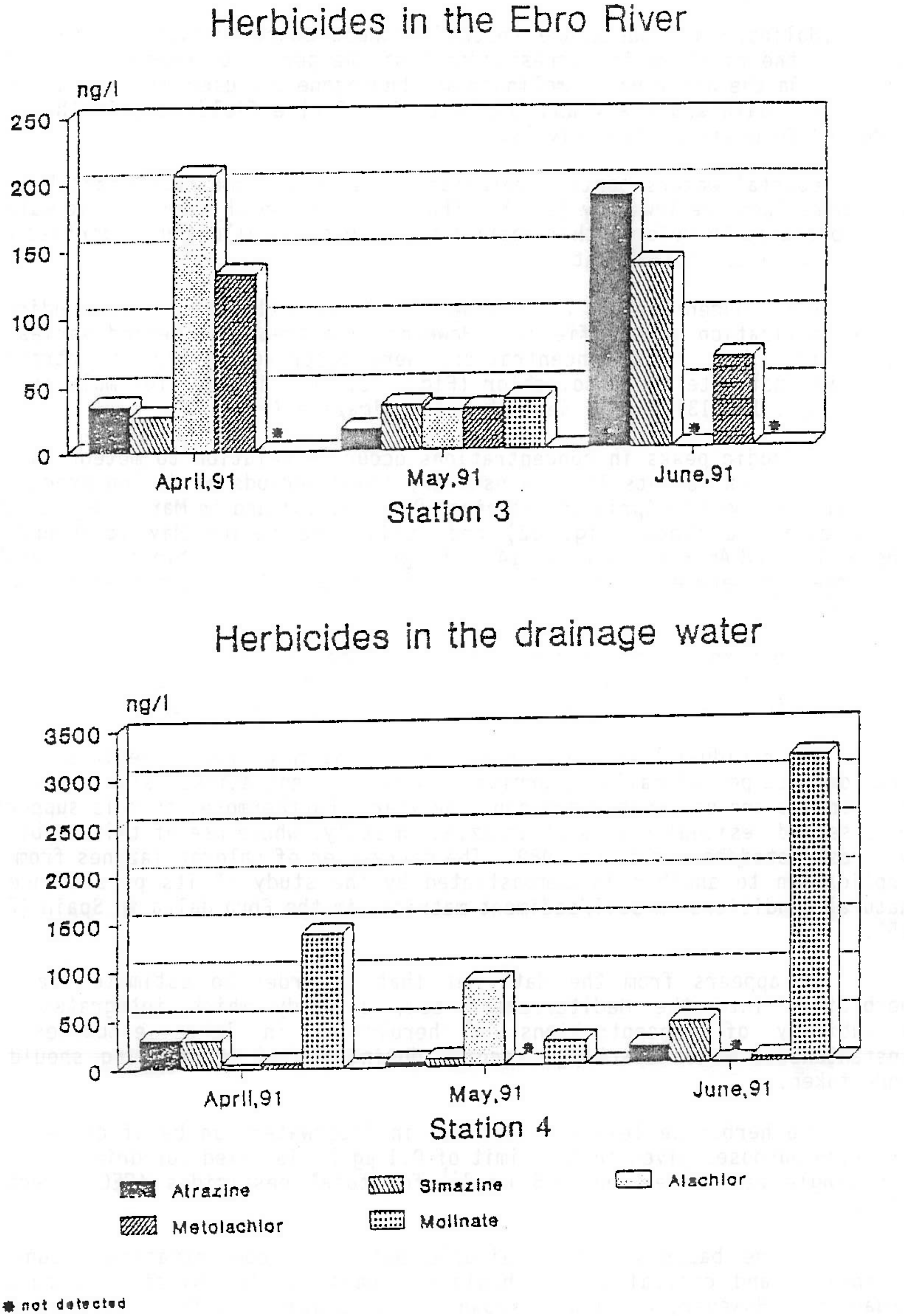



Fig. 11 Temporal trend in concentrations of selected herbicides in the river Ebro delta (1991)

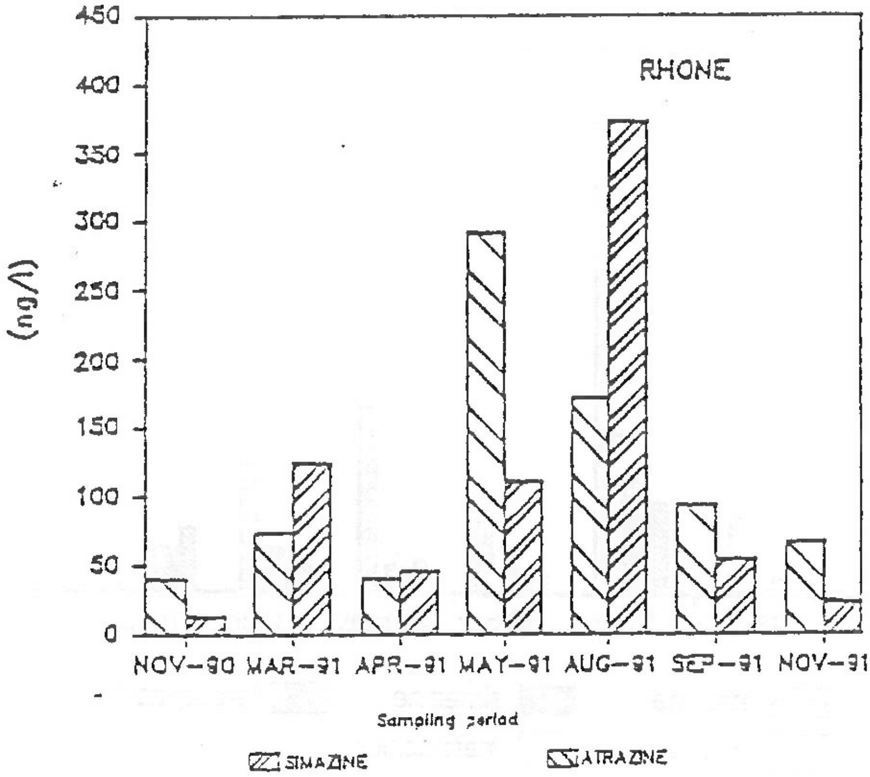



Fig. 12 Seasonal variations of the herbicides atrazine and simazine in the Rhône river (1991)

populations at concentrations much lower than those which cause acute toxicity (Bryfogle and McDiffett, 1979; De Noyelles et al., 1982). Data in this regard, is available only for a few compounds and more information is needed in order to assess the behaviour of herbicides in the real environment and their potential ecological impact.

Water samples from rivers and Gulfs in Greece were taken within days of local applications of herbicides. Whilst this information is useful in potentially identifying maximum concentrations, to afford comparability of the results with those from the other areas, they have been listed separately in Table 3.

Sediment analysis

Herbicide residues in sediments were determined only in the area of Ebro river (Spain) and in estuaries of rivers in Thermaikos and Amvrakikos gulfs (Greece). The concentrations of the herbicides atrazine and linuron in two soil samples of the Ebro delta are shown respectively in Figs 15 and 16. There are no previous data on the residue levels of herbicides in this area and it is difficult to conclude whether residue levels of these pesticides have accumulated significantly. Therefore these 1990-91 data will serve as a baseline for future studies on accumulation of herbicides in the region.

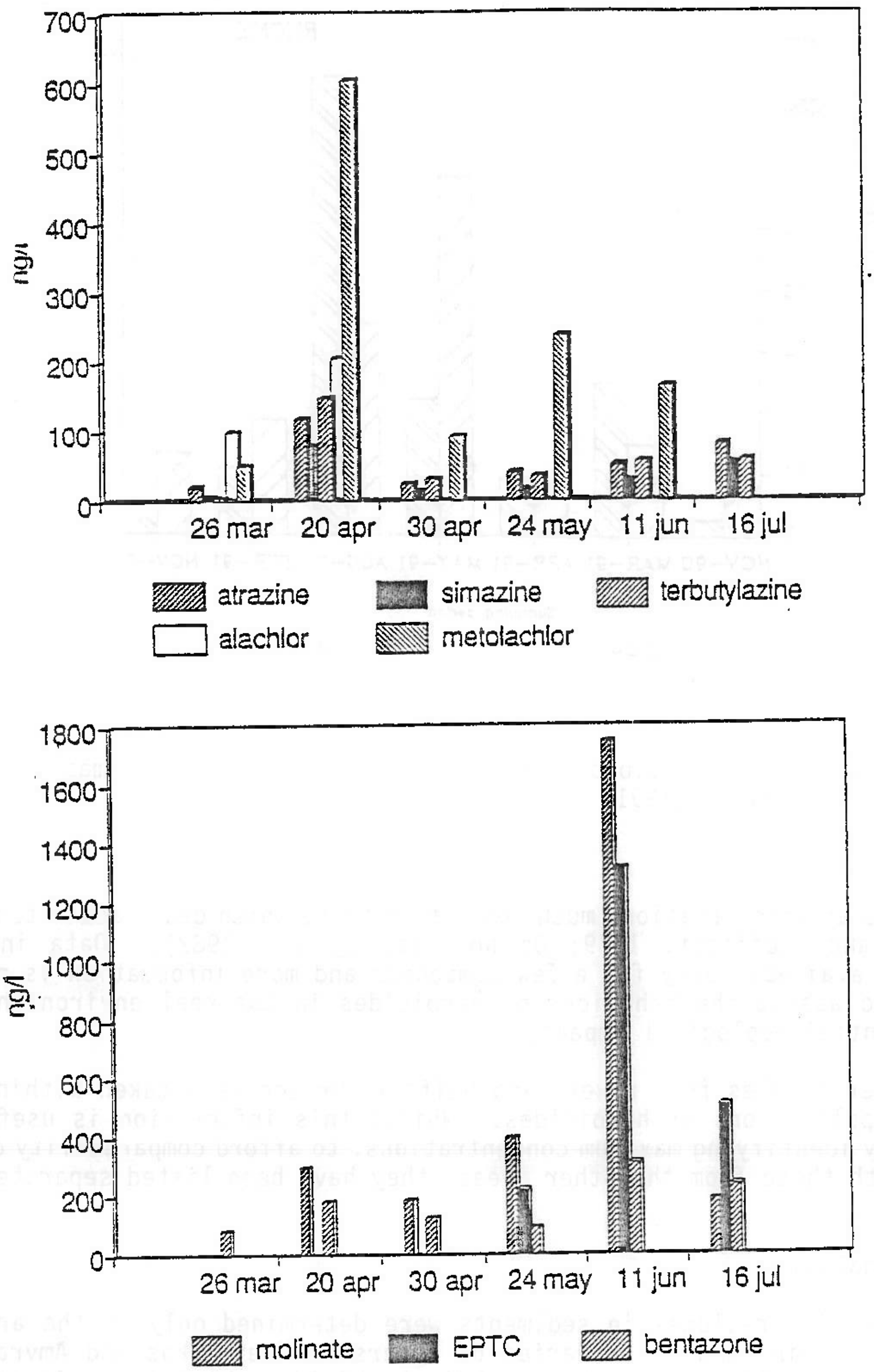



Fig. 13 Temporal trends in concentration of herbicides in the river Pô (1991)

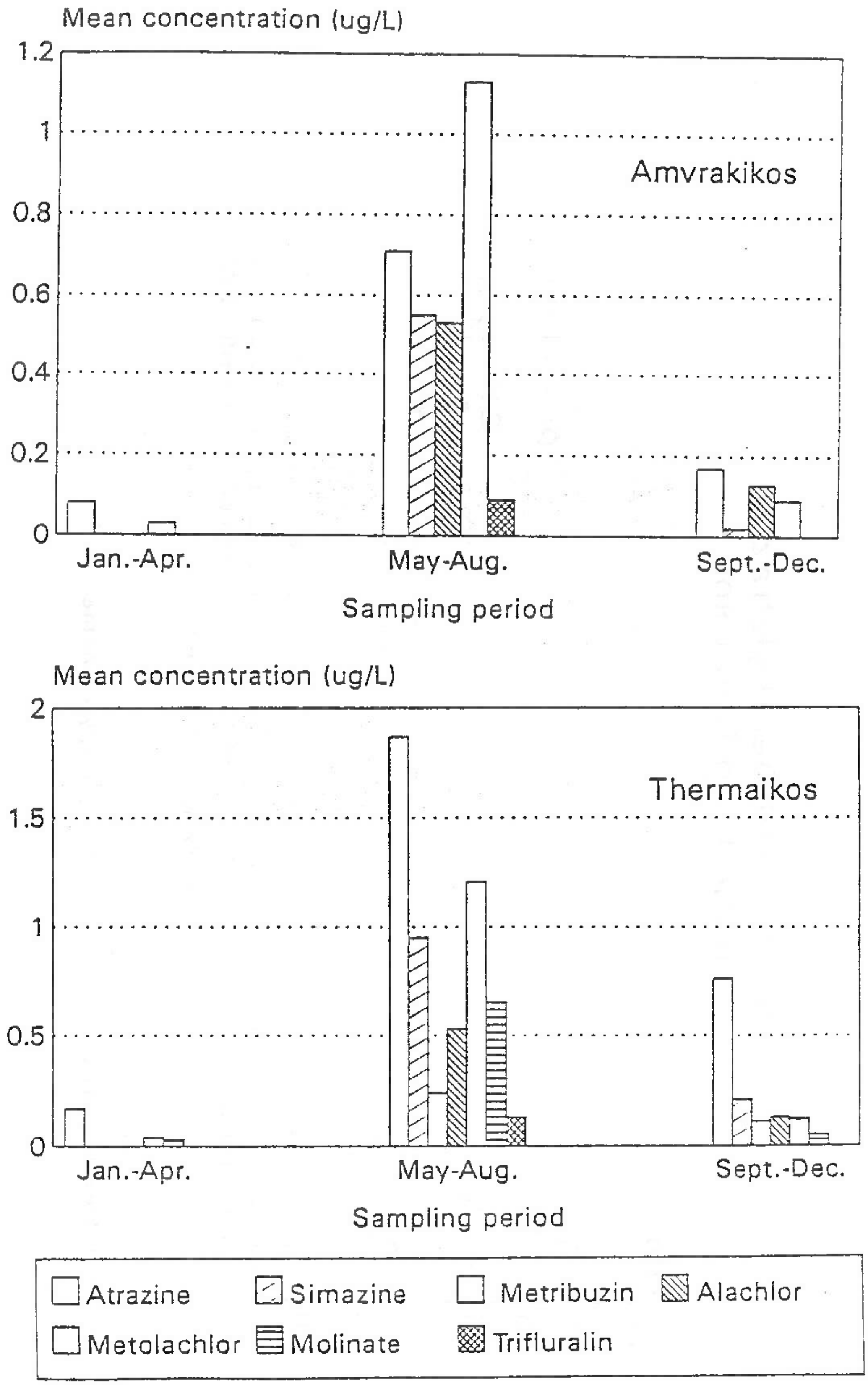



Fig. 14 Temporal variations in concentrations of herbicides in estuaries of rivers in Thermaikos and Amvrakikos gulfs (1991)

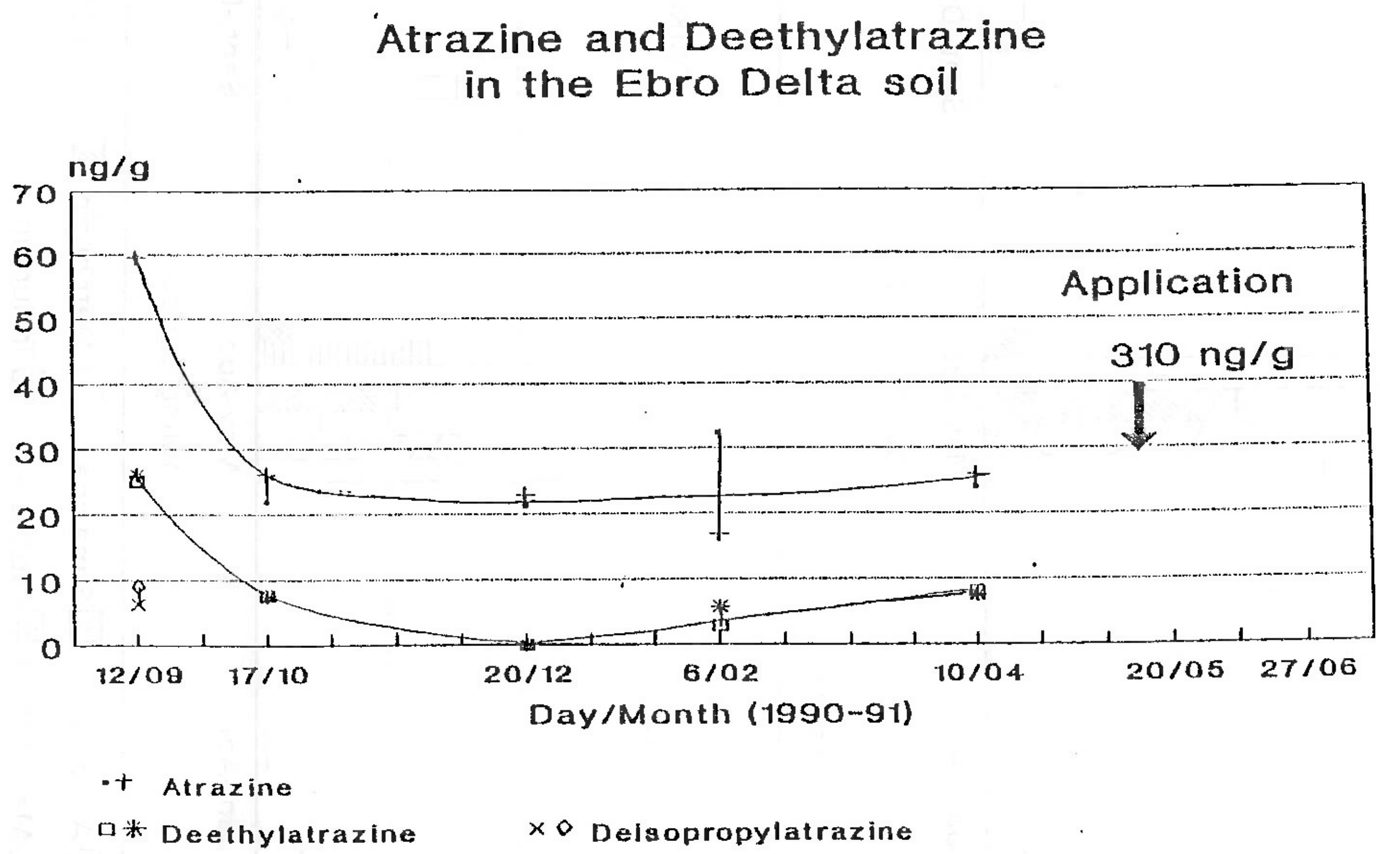



Fig. 15 Changes in concentrations of atrazine and deethylatrazine in the Ebro delta soil following application

Table 3

Concentrations of herbicides in water samples (mg $l^{-1}$) from Greek river estuaries in periods right after application (July 15, 1991 in Thermaikos and August 8, 1991 in Amvrakikos).

| Compound | Thermaikos, July 15 | | | Amvrakikos, August 8 | |
|---|---|---|---|---|---|
| | Estuary of | | | Estuary of | |
| | Axios | Loudias | Aliakmon | Louros | Arachthos |
| Alachlor | 1.3 | 2.1 | 0.2 | 1.7 | 0.9 |
| Atrazine | 2.2 | 3.4 | 0.9 | 2.9 | 4.1 |
| 2,4-D | 0.4 | 0.9 | 0.3 | 0.7 | 0.4 |
| Diuron | 0.2 | 0.7 | 0.2 | 0.2 | 0.3 |
| MCPA | 0.9 | 0.5 | 0.1 | 0.3 | 0.4 |
| Metolachlor | 3.5 | 2.4 | 0.5 | 1.9 | 0.5 |
| Metribuzin | 0.1 | 0.4 | 0.3 | n.d | n.d |
| Molinate | 2.1 | 3.8 | 0.6 | n.d | n.d |
| Prometryne | 1.2 | 1.5 | 0.6 | n.d | n.d |
| Simazine | 0.2 | 3.2 | 0.7 | 0.9 | 0.7 |
| Trifluralin | 0.09 | n.d | 0.19 | 0.37 | 0.14 |

n.d. = not detected

The concentrations of herbicide residues in sediments of river estuaries of the Thermaikos and Amvrakikos gulfs are shown in Fig. 17. The herbicides atrazine, simazine, alachlor, metolachlor and trifluralin show a significant accumulation in sediments which contain 3-4.5% organic matter. The accumulation is highest during summer. The other herbicides detected in sediments prometryne, metribuzin, molinate, 2,4-D, MCPA and diuron do not appear to have been significantly accumulated.

## 5. CONCLUSIONS

The following conclusions could be drawn from the results of the present pilot survey:

(a) The most commonly encountered herbicides in the regions studied were atrazine, simazine, alachlor, metolachlor and molinate.

(b) The ranges in concentrations for those compounds identified in (a) above were:

atrazine from b.d.l. to 700 ng $l^{-1}$
simazine from b.d.l. to 440 ng $l^{-1}$
molinate from b.d.l. to 3178 ng $l^{-1}$
alachlor from b.d.l. to 1400 ng $l^{-1}$
metolachlor from b.d.l. to 800 ng $l^{-1}$

In general, concentrations declined from freshwater locations through estuaries to marine waters.

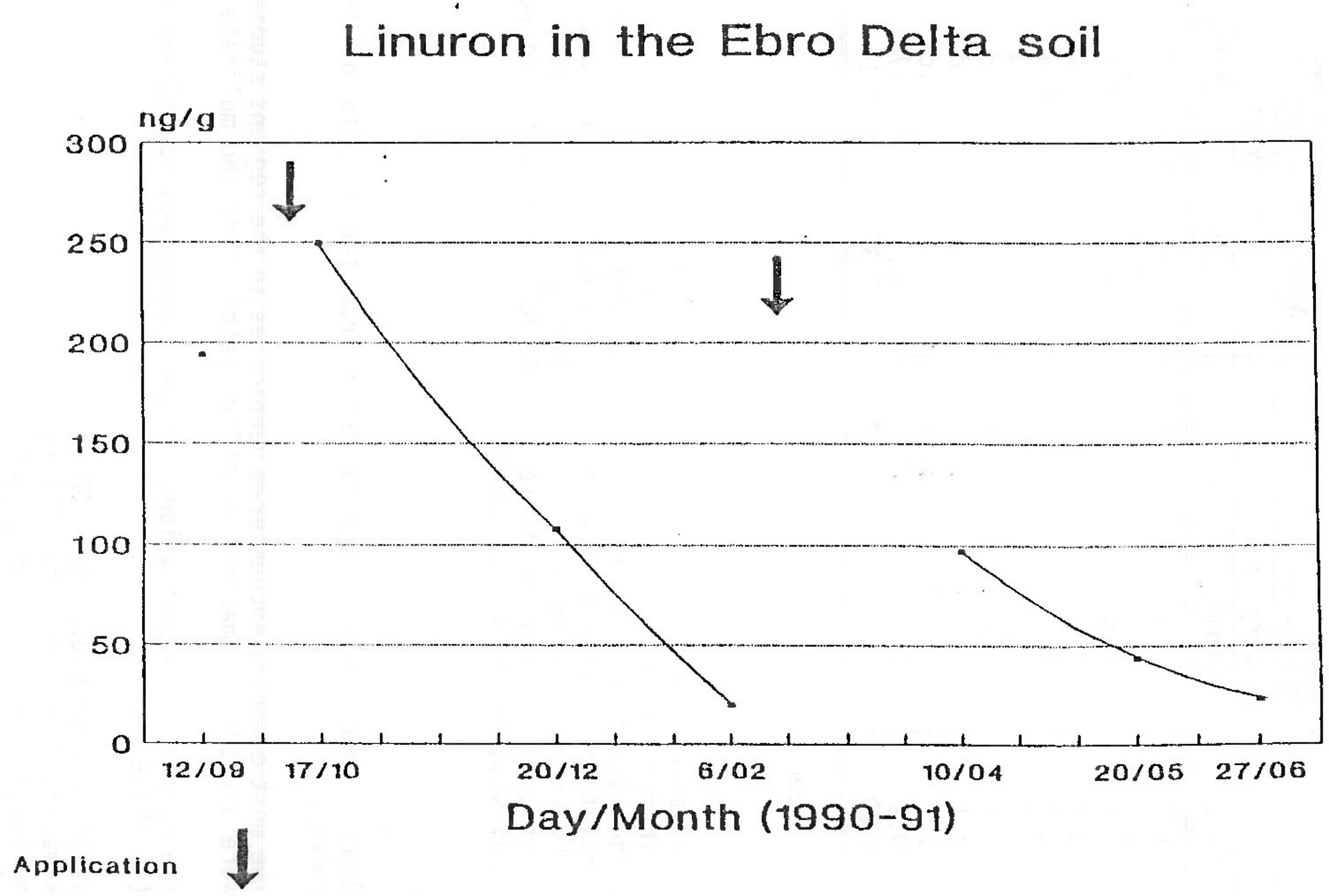
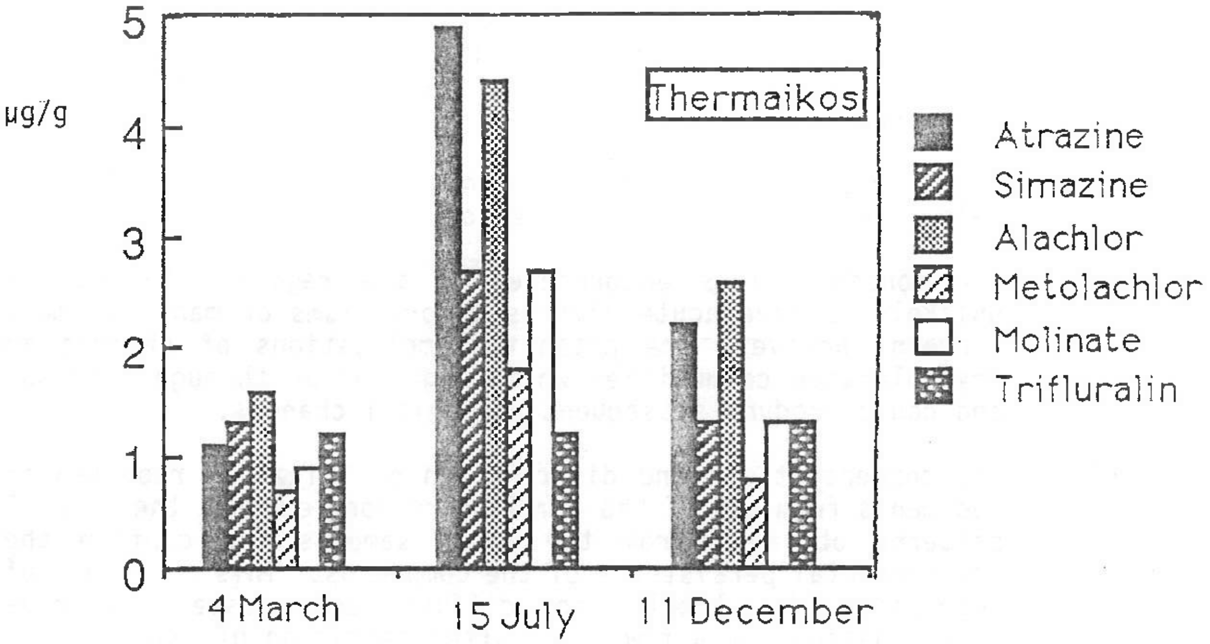



Fig. 16 Changes in concentrations of linuron in the Ebro delta soil following application



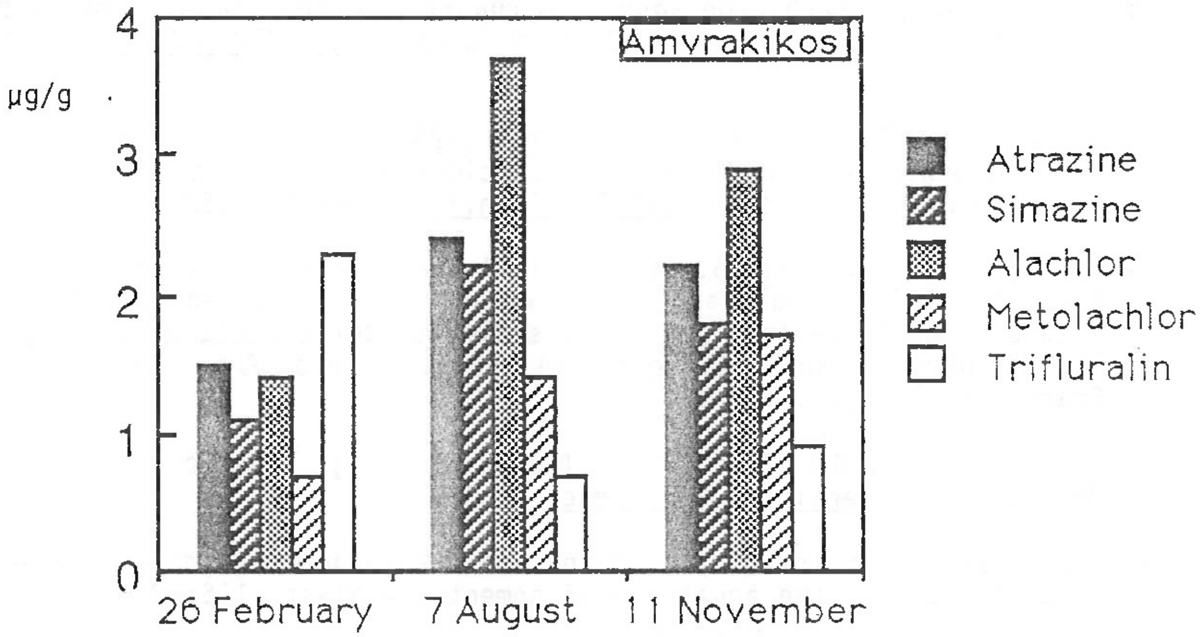




Fig. 17 Temporal trend in concentrations of selected herbicides in sediments from Thermaikos and Amvrakikos gulfs (1991)

(c) Large seasonal variations were observed with maximum herbicide run-off occurring immediately following application. Episodic hydrological and meteorological events were also shown to influence concentrations.

(d) Concentrations recorded during this survey are comparable (or below) those found in other regions of the World.

(e) The concentrations encountered in the regions studied are unlikely to have acute effects on organisms or man. Of more concern, however, are potential implications of changes in phytoplankton communities which might occur through "stress" and could produce subsequent ecological changes.

(f) The concentrations and distribution of triazines reported in sediments from two of the sampling regions endorse the spacial patterns observed from the water samples and confirm the environmental persistence of the compounds. This reservoir of herbicides is likely to diffuse and sustain aqueous contamination for a few years after cessation of use.

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