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REPORT OF THE FAO/UNEP/IAEA/WHO REVIEW MEETING

ON THE ORGANOPHOSPHORUS PILOT SURVEY

Barcelona, Spain, 24-26 January 1989

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

Convened jointly with:



UNEP



IAEA



WHO

Athens, 1989



## TABLE OF CONTENTS

	<u>Page No.</u>
Administrative Report	1
ANNEX I : List of participants	4
ANNEX II : Agenda	7
ANNEX III: FAO/UNEP/IAEA/WHO Pilot Survey of Organophosphorus Compounds in Selected Mediterranean Areas	9



ADMINISTRATIVE REPORT

1. Following a recommendation of the FAO/UNEP/IAEA/WHO Ad-hoc meeting on organophosphorus compounds (Athens, 18-20 November 1987), a pilot survey was undertaken during 1988 in selected Mediterranean areas to establish the levels of organophosphorus compounds (primarily fenitrothion, malathion, parathion-ethyl, parathion-methyl, tributyl phosphate and tris(2-chloroethyl)phosphate in the marine environment.
2. The present meeting was organised to review the results of the pilot survey and to discuss the need for recommending control measures to the Contracting Parties to the Barcelona Convention. It was jointly convened by FAO, UNEP, IAEA and WHO in the framework of the MED POL activities and was hosted by the Department of Environmental Chemistry, Centre for Research and Development, High Council for Scientific Research (CID-CSIC), Barcelona, Spain, at its premises from 24-26 January, 1989. It was attended by the principal investigators of the pilot survey and by representatives of IAEA and FAO. A list of participants appears in Annex I.
3. The meeting was opened by Mr. G.P. Gabrielides, FAO Senior Fishery Officer (Marine Pollution) on behalf of the Food and Agriculture Organization of the United Nations and of the Co-ordinating Unit for the Mediterranean Action Plan. He welcomed the participants and expressed his gratitude to the Centre for Research and Development for its invitation to host the meeting. He then explained the background and scope of the meeting.
4. The meeting unanimously elected Mr. D. Barceló, Senior Research Scientist at the Department of Environmental Chemistry, Centre for Research and Development, Barcelona, as Chairperson and Mr. D. Wynne, Senior Research Scientist, Kinneret Limnological Laboratory, Israel, as Rapporteur. Mr. G.P. Gabrielides acted as Technical Secretary.
5. The provisional agenda prepared by the Secretariat was unanimously adopted and appears in 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. The intercalibration results were presented by Mr. J.P. Villeneuve of ILMR. No organophosphorus compounds (OP's) could be detected in the sediment sample collected from the Venice lagoon and the doubt was expressed whether OP pesticides are used in the region. An exhaustive discussion took place concerning the difficulties encountered in organizing an intercalibration exercise owing to the high degradability of OP compounds. The view was also expressed that since laboratories are using the general methodology suggested by the Monaco meeting (April, 1988) and their recovery was higher than 90%, the results would be expected to be reliable.

It was finally agreed that to ensure comparability of results, the participants should meet in one laboratory (preferably ILMR) to undertake simultaneous analyses in freshly collected samples.

7. Mr. Barceló presented the summary report on the pilot survey which he prepared using the individual reports of the principal investigators. This report was extensively discussed and a modified version appears as Annex III.
8. The participants examined briefly the assessment document submitted by the consultant (G. Persoone) and the following comments were made:
  - (a) All pertinent information missing from the document (and found in the draft prepared by D. Barceló) should be added;
  - (b) Tables VIII and IX on toxicity data and NOEL should be removed being non-specific;
  - (c) It is not entirely valid to mention throughout the text that OP compounds are "non-toxic";
  - (d) It is not correct to assume that the only input of OPs is via river waters (p.25);
  - (e) Water quality criteria should be proposed for individual OP compounds whenever sufficient relevant information is available (as EPA). If such information is not available then a temporary global standard should be set until such time that there are details available. For this purpose both pesticide and non-pesticide OP compounds are to be considered together (eg. EEC);
  - (f) Different measures should be recommended for point and diffuse sources. For point sources emission control standards can be set. To control diffuse sources, education and training in the use and disposal of OP compounds should be undertaken;
  - (g) The purchase of OP compounds should be regulated by the appropriate national agency.
9. Under agenda item "Recommendations for future action" the meeting adopted the following recommendations which are based on the results of the pilot survey and on information from other sources:
  - (a) information on the production and use of OP compounds should be provided by the various Mediterranean countries;
  - (b) monitoring of selected Mediterranean areas for OP compounds should be expanded to identify:
    - (i) compounds other than those specified by the FAO/UNEP/IAEA/WHO ad-hoc meeting (Athens, 1987)

- (ii) seasonal variations in OP levels
  - (iii) regions other than those examined in the present pilot survey
  - (iv) other biota (eg. zooplankton, algae) which may be susceptible to OP compounds
- (c) where possible, all participants in the monitoring programme should analyse the same type of biota to enable comparison of data;
  - (d) selective and sensitive analytical procedures should be used (eg. HRGC-NPD/FPD);
  - (e) ILMR should study methods to prepare suitable samples for an intercalibration exercise.
10. This report was adopted by the participants of the meeting on Thursday, January 26, 1989.
11. 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 participants, warm thanks to the Centre for Research and Development, especially Mr. Barceló, for the kind hospitality accorded to them.

ANNEX I

LIST OF PARTICIPANTS

H. ABU EL-SEOUD ALY  
Professor of Organic and Pesticide  
Chemistry  
Faculty of Agriculture  
University of Alexandria  
Chatby  
Alexandria  
EGYPT

Tel. 5971860-1-2  
Telex 54467 UNIVY

D. BARCELO  
Centro de Investigación y Desarrollo  
C.S.I.C.  
Departamento de Química Ambiental  
Jorge Girona Salgado 18-26  
08034 Barcelona  
SPAIN

Tel. 2040600, 2050063  
Telex 97977  
Telefax 2045904

J. CID  
Centro de Investigación y Desarrollo  
C.S.I.C.  
Departamento de Química Ambiental  
Jorge Girona Salgado 18-26  
08034 Barcelona  
SPAIN

Tel. 2040600, 2050063  
Telex 97977  
Telefax 2045904

Silvana GALASSI  
Water Research Institute (IRSA) - CNR  
20047 Brugherio (Milano)  
ITALY

Tel. (39) 749577



Cinta PORTE  
Centro de Investigación y Desarrollo  
C.S.I.C.  
Departamento de Química Ambiental  
Jorge Girona Salgado 18-26  
08034 Barcelona  
SPAIN

Tel. 2040600, 2050063  
Telex 97977  
Telefax 2045904

D. WYNNE  
Israel Oceanographic and  
Limnological Research Ltd.  
The Yigal Allon Kinneret  
Limnological Laboratory  
P.O. Box 345  
Tiberias 14102  
ISRAEL

Tel. (67) 21444  
Telex 6693 IL  
Telefax (69) 35337

UN Organizations

FOOD AND AGRICULTURE  
ORGANIZATION OF THE  
UNITED NATIONS

G.P. GABRIELIDES  
Senior Fishery Officer  
(Marine Pollution)  
FAO Project Office  
Co-ordinating Unit for the Mediterranean  
Action Plan  
P.O. Box 18019  
Vas. Konstantinou 48,  
GR 116 10 Athens  
GREECE

Tel. 7244536  
Telex 222611 MEDU GR  
Telefax 7218246

INTERNATIONAL ATOMIC  
ENERGY AGENCY

J.P. VILLENEUVE  
ILMR/IAEA  
24, Avenue de Fontvieille  
98000 MONACO

Tel. 93504488  
Telex 479378 ILMR  
Telefax 257346

ANNEX II

AGENDA

1. Opening of the meeting
2. Background and scope
3. Election of officers
4. Adoption of the agenda
5. Organization of work
6. Intercalibration of methods
7. Pilot survey results
8. Assessment document and proposed measures
9. Recommendations for future action
10. Adoption of the report
11. Closure of the meeting



ANNEX III

FAO/UNEP/IAEA/WHO PILOT SURVEY OF ORGANOPHOSPHORUS  
COMPOUNDS IN SELECTED MEDITERRANEAN AREAS



TABLE OF CONTENTS

	<u>Page No.</u>
1. INTRODUCTION	12
2. SELECTED AREAS	13
2.1 Ebro and Llobregat estuaries (Spain)	13
2.2 River Po mouth and northern Adriatic coast (Italy)	16
2.3 Haifa Bay and the Lake Kinneret Watershed (Israel)	16
2.4 Rosetta Nile mouth and Edffina (Egypt)	19
3. METHODOLOGY	19
3.1 Sample preparation	19
3.1.1 Water	19
3.1.2 Sediment	21
3.1.3 Biota	21
3.2 Analytical techniques	21
3.3 Intercalibration	22
4. RESULTS AND DISCUSSION	23
4.1 Concentration of OP compounds in water	23
4.2 Concentrations of OP compounds in biota	26
5. CONCLUSIONS	28
6. REFERENCES	28

## 1. INTRODUCTION

Organophosphorus compounds (OP) is the general name for a group of roughly 250 chemicals manufactured all over the world. Approximately 140 of these compounds are pesticides and the remaining compounds are mainly industrial chemicals used as flame retardants, plasticizers and industrial hydraulic fluids and solvents.

Since the introduction of compound E605 (Ethyl parathion) by Schroder in 1944, substantial progress in agricultural practices and in the structure activity relationship of OP insecticides has been achieved. Other major OP insecticides such as malathion and fenitrothion were synthesized for the first time in 1950 and 1959, respectively (Eto, 1974).

Non-pesticide OP's in turn have been widely used since the 1940's in industrial and consumer products as both fire retardant plasticizers and high temperature functional fluids. The use of fire retardants during the 1960's and 1970's increased greatly due to the demand for improved fire safety in commercial products made from synthetic polymers (Muir, 1984; Boethling and Cooper, 1985).

Because of their rapid breakdown in water and their low environmental persistence the OP pesticides were introduced as an ecologically preferred alternative to the organochlorinated compounds then in use. However, the extensive use of these chemicals has resulted in a high contamination risk to various types of aquatic environments (eg. rivers, estuaries, lagoons and shallow waters). Organophosphorus pesticides have been determined in these environments at concentrations ranging from 10-20 ng l<sup>-1</sup> up to 127 µg l<sup>-1</sup> (Leistra *et al.*, 1984; Marin *et al.*, 1986; Wang *et al.*, 1987; Scott *et al.*, 1988). Although data on residue levels of organophosphorus pesticides in sediments and aquatic organisms are very limited, values ranging from 3-4 ng g<sup>-1</sup> up to 232 ng g<sup>-1</sup> for sediments and soil have been reported (Marin *et al.*, 1983; Lenarden *et al.*, 1984). In addition, different aquatic organisms such as clams, crayfish, rainbow trout and salmon were found to contain concentrations ranging from a few ng g<sup>-1</sup> up to 666 µg g<sup>-1</sup> (after eight days of application), with mean values between 20-100 ng g<sup>-1</sup> (Morrison and Wells, 1981; Holmes *et al.*, 1984).

The FAO/UNEP/IAEA/WHO Ad-hoc meeting on organophosphorus compounds (Athens, 18-20 November 1987) recommended that a pilot monitoring programme for organophosphorus compounds should be carried out in selected areas of the Mediterranean by laboratories with expertise in OP analyses of water, sediment and biota. The monitoring study should include at least four samplings per year, preferably related to the application time of OP pesticides (ie. prior, during and after), at sites close to the biggest river inputs into the Mediterranean sea. A site outside the area of potential contamination should also be included for reference purposes.



It was also agreed that the survey should include at least four pesticides (fenitrothion, malathion, parathion-ethyl and parathion-methyl) and two non-pesticides (tributyl phosphate (TBP) and tris(2-chloroethyl) phosphate (TCEP) chosen for their toxicity and increased use in the region. The principal investigators of the survey met at the International Laboratory of Marine Radioactivity of IAEA (Monaco, 13-15 April 1988) and discussed the analytical problems and intercalibration needs of this survey which was undertaken during 1988.

The results of the survey are presented below.

## 2. SELECTED AREAS

The selected areas are shown in Fig. 1 and they are two estuaries in the Mediterranean coast of Spain, the river Po mouth and Northern Adriatic coast (Italy), Haifa bay (including Kinneret watershed) and the Nile delta.

### 2.1 Ebro and Llobregat estuaries (Spain)

The survey in this area was conducted by the Department of Environmental Chemistry, CID-CSIC, Barcelona (principal investigator: D. Barceló, co-workers: C. Porte and J. Cid) in five locations (four in Ebro delta and one in Llobregat) as shown in Fig. 2.

#### Description of the areas

The Ebro Delta is an alluvial plain of about 350 km<sup>2</sup>, situated on the Western Mediterranean coast. About 20% of its surface consists of lagoons and marshes. The rest is devoted to intensive agriculture, principally rice culture. The area is considerably developed from the agricultural and industrial points of view, with an extensive use of pesticides and industrial activities at the lower course of Ebro, as well as in the coastal area. The Llobregat river is located south of the city of Barcelona and flows through heavily populated areas. Its water is used for various purposes (domestic and industrial), and drains a valley of 5100 km<sup>2</sup>. Its annual water output is 300 Hm<sup>3</sup> and the mean flow rate at the mouth is 8.8 m<sup>3</sup> s<sup>-1</sup>.

#### Sampling sites

Water samples were collected only from station A (Llobregat) and B (Ebro). Samples of mussels (Mytilus galloprovincialis) and red mullet (Mullus barbatus) were collected at stations C and D. Samples of mosquito fish (Gambusia affinis) were collected at station E, located at the canals of the Ebro Delta.

Water and biota were sampled monthly from March to June 1988 at station A, B, C and D. Station E was sampled only for Gambusia from April 1987 to February 1988.

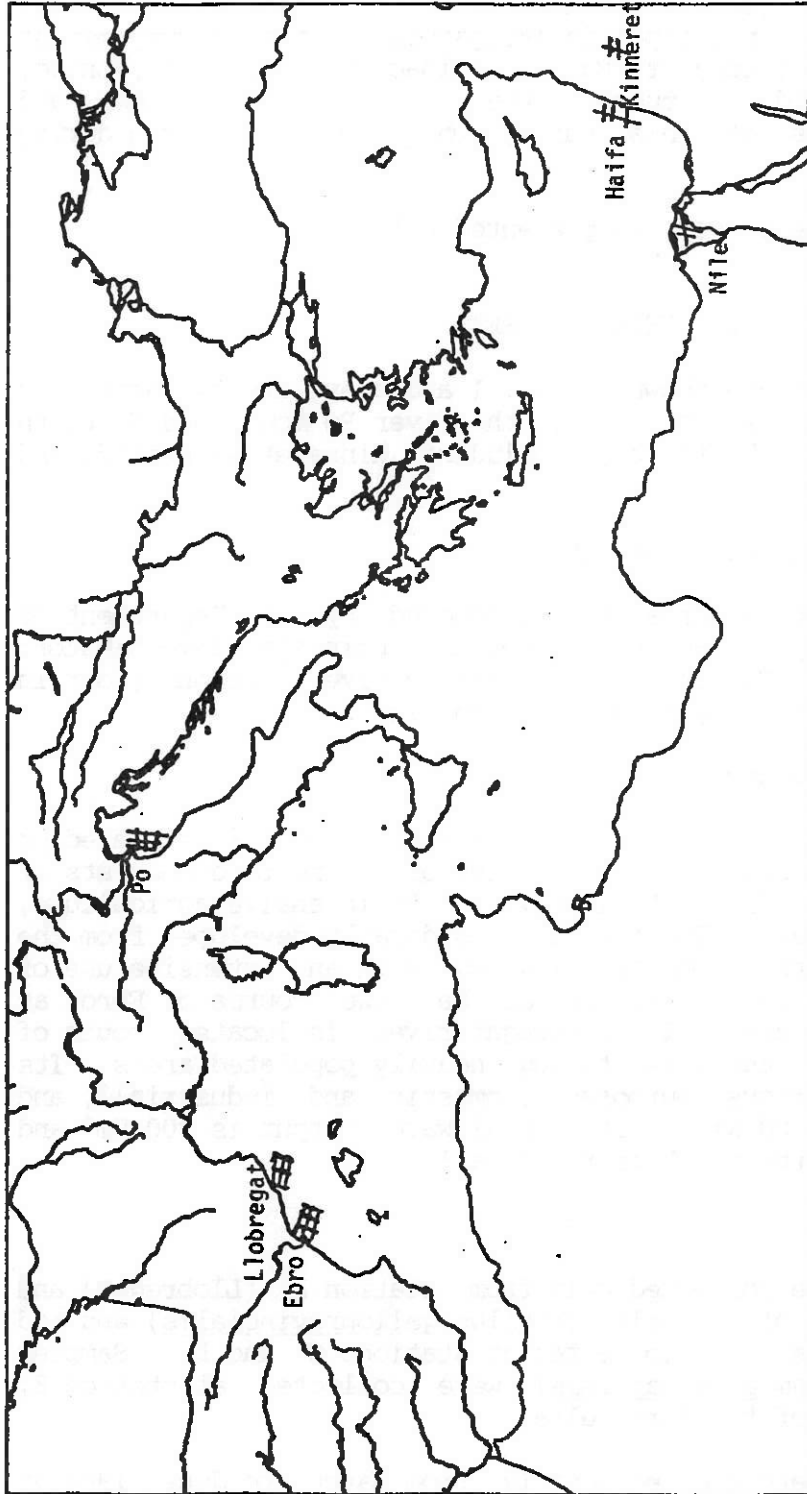


Fig. 1 The selected Mediterranean areas for the organophosphorus pilot survey

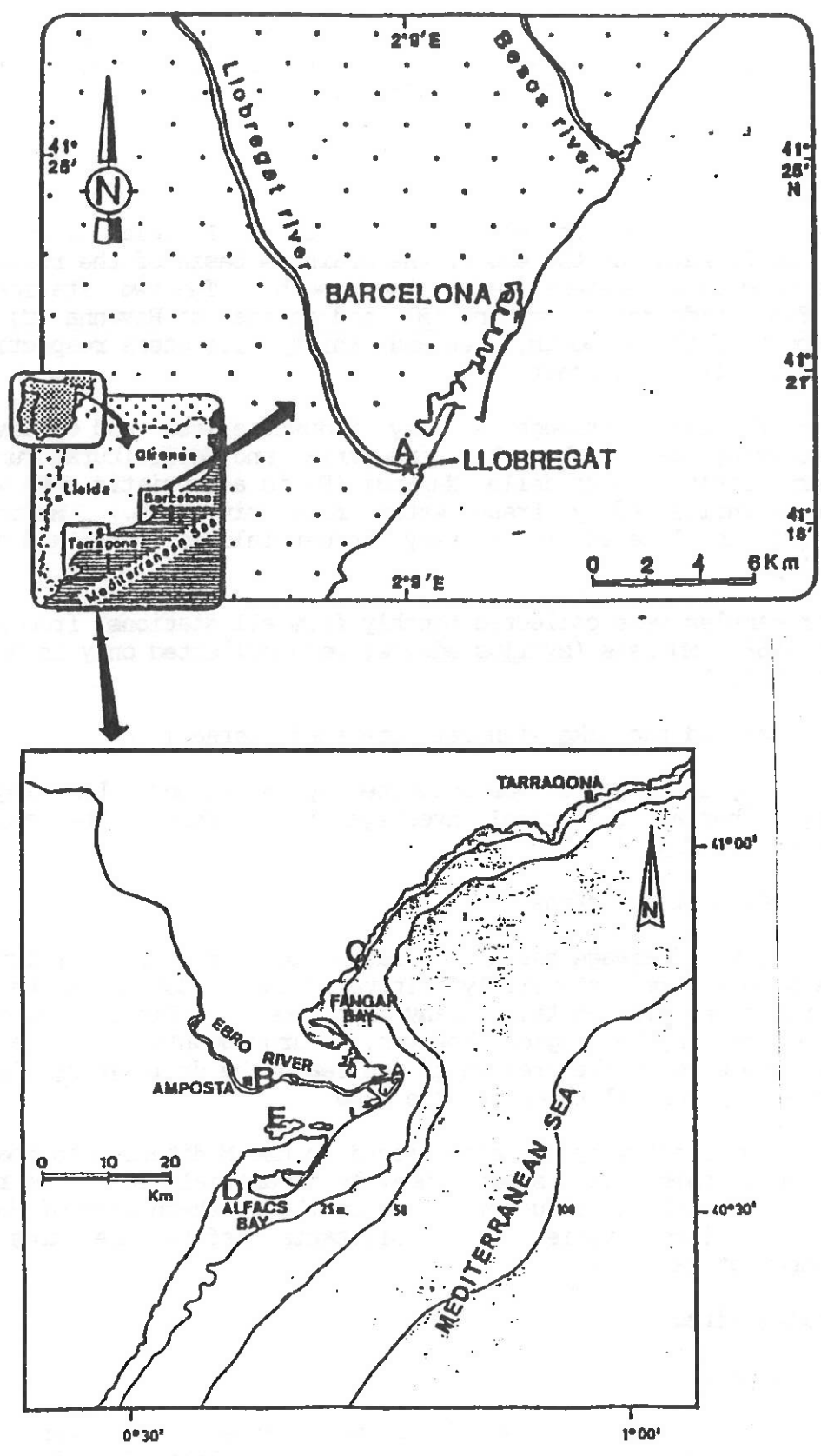


Fig. 2 Stations in the Llobregat and Ebro estuaries (Spain)

## 2.2 River Po mouth 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-worker: A. De Paolis). The sampling area is shown in Fig. 3.

### **Sampling sites**

River Po water was collected at station A, Pontelagoscuro, near the town of Ferrara, at the end of the drainage basin of the river and about one hundred kilometers before the mouth. The two stations of Adriatic Sea, Lido delle Nazioni (B) and Marina di Ravenna (C) were located south of the Po mouth, ten and thirty kilometers respectively and five miles from the coast.

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

Water samples were collected monthly from all stations from April to August 1988. Mussels (Mytilus edulis) were collected only in August from station C.

## 2.3 Haifa Bay and the Lake Kinneret Watershed (Israel)

The survey in this area was conducted by the Kinneret Limnological Laboratory, Tiberias, (principal investigator: D. Wynne). The sampling area is shown in Fig. 4.

### **Description of the areas**

The Kinneret drainage basin, situated in the north of Israel, comprises some 100 km<sup>2</sup> intensively cultivated land. Cotton is the main crop but the area also contains many fish ponds. Little industrial activity occurs in the region, however, large quantities of various pesticides are used in the area which can reach the drainage canals and thereby pose a potential threat to the Lake.

Agricultural activity is also found on the Mediterranean coastal plain, although this area is also heavily industrialized. The river Kishon flows through the industrial area of the northern city of Haifa, picking up a large variety of pollutants before reaching the Mediterranean at Haifa Bay.

### **Sampling sites**

#### Lake Kinneret

Samples were taken at two of the main arms of the river Jordan (1,2), at the point of entry of the river into the lake (3) and in the Kinneret itself (4).

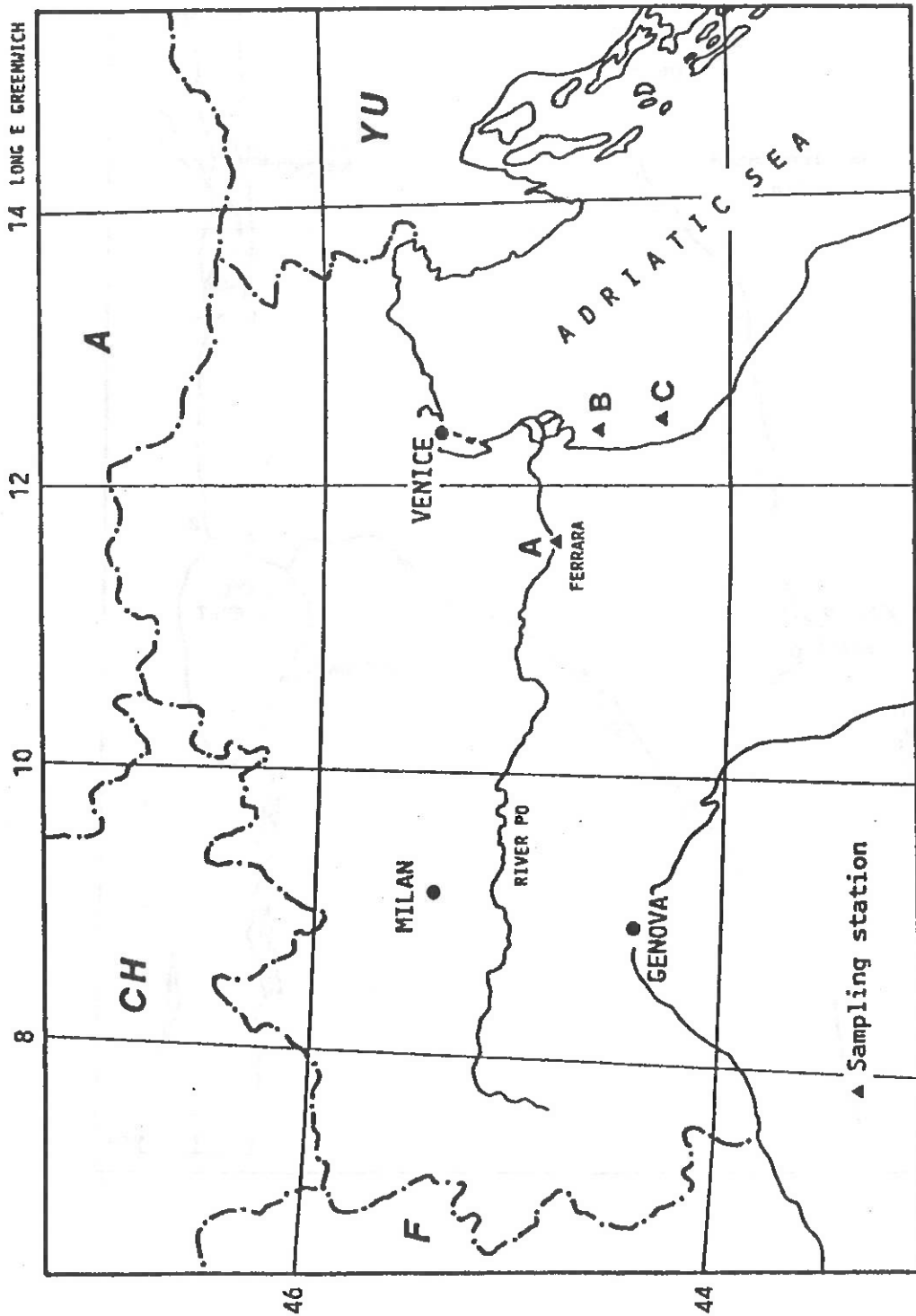


Fig. 3 Stations in the river Po (Italy)

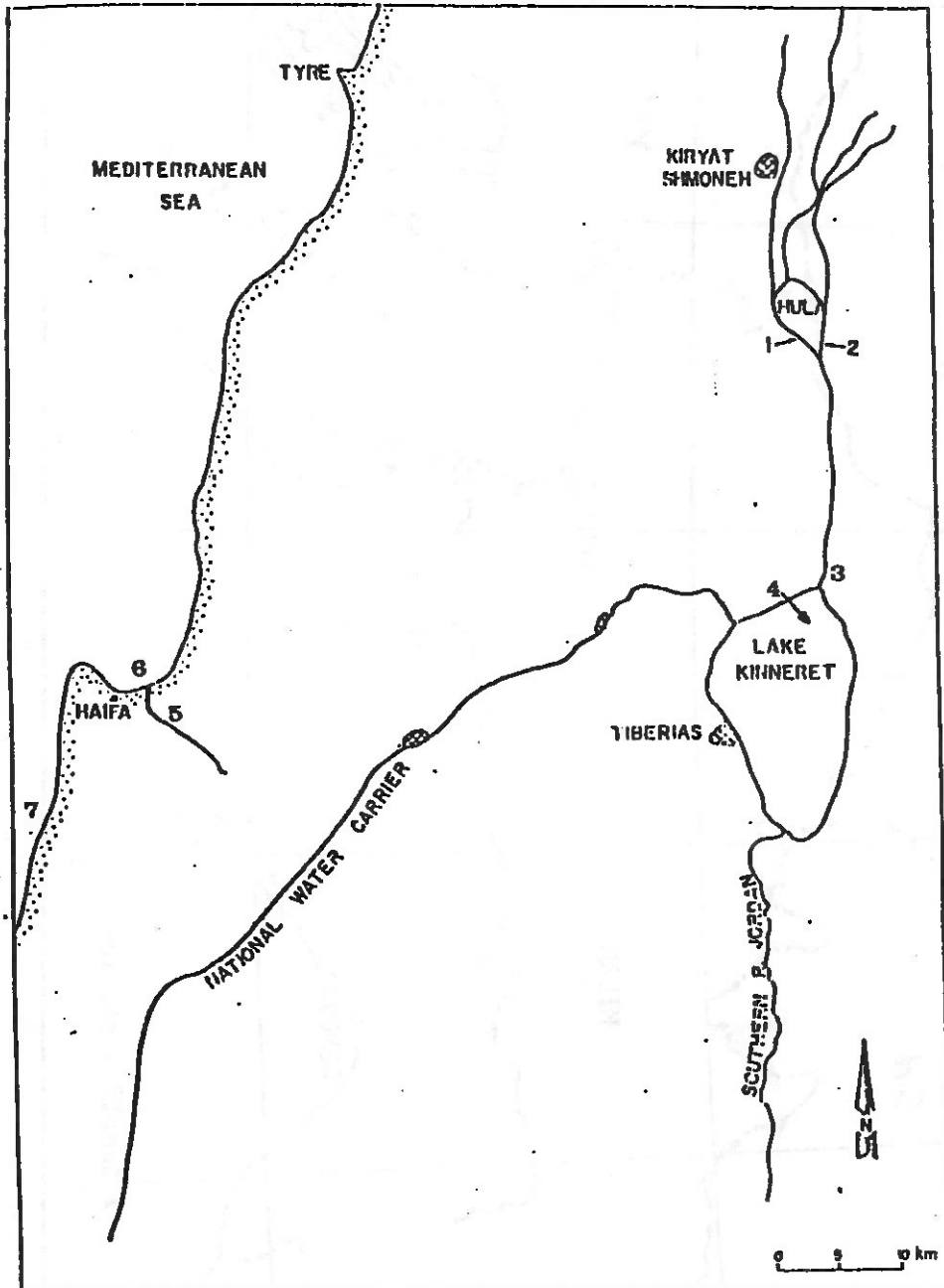


Fig. 4 Stations in the lake Kinneret and Haifa (Israel)

### Mediterranean coast

Two stations, one at the mouth of the river Kishon, in Haifa Bay (6) and the other one in the river itself (5), were taken as "polluted" sites. An additional station (7), situated further south from Haifa, at Atlit, was used as a control, "non-polluted" site.

Water, biota and sediment samples were collected from all stations monthly from April to July 1988.

#### 2.4 Rosetta Nile mouth and Edffina (Egypt)

The survey in this area was conducted by the Plant Protection Department, Pesticide Chemistry Division, Alexandria University, (principal investigator: H.A. Aly, co-worker: A. Abel-El- Hameed).

The sampling area is shown in Fig. 5. Site 3 could not be sampled due to high water current and lack of proper facilities. The sampling area is an intensive agricultural zone in the Nile delta and hence is expected to receive quite a high burden of various OP pesticides. Pest control programmes in Egypt rely heavily on OP-pesticides all over Egypt, according to the annual recommended programme issued by the Egyptian Ministry of Agriculture.

Sampling took place only in December 1988 for water and sediment at stations 1, 2 and 4.

### 3. METHODOLOGY

The sample methodology for the identification of organophosphorus compounds was carried out mainly as outlined in the IAEA Workshop report held in Monaco, (April 13-15 1988), with some modification concerning the clean-up procedures.

#### 3.1 Sample preparation

##### 3.1.1 Water

Samples of 1 to 4 l were extracted 3 times, 5 minutes each in a separatory funnel with 30-120 ml of methylene chloride (or by stirring with methylene chloride for half-an-hour in the case of the IRSA-CNR in Italy). The combined extracts were dried by a suitable amount of anhydrous sodium sulphate and concentrated in a rotary evaporator. After evaporation to a small volume (about 4 ml), 1-2 ml of ethyl acetate was added. Prior to GC, a clean-up procedure (Lores *et al.*, 1987) was applied when necessary.





The silica gel, which had been stored at 130°C was deactivated by the addition of 20% (w/w) distilled water and was equilibrated for 2 hours before use. Columns were prepared with 3.5 g silica gel, followed by 2.0 g of anhydrous sodium sulphate. The columns were washed with 10 ml of 1% acetic acid in hexane before and after sample introduction; the eluant was discarded. Fraction 1 consisted of 20 ml of 5% (v/v) ethyl ether in hexane and fraction 2 of 20 ml of 10% (v/v) ethyl ether in hexane. The eluants were collected and concentrated to 1 ml with a stream of nitrogen.

### 3.1.2 Sediment

Sediment samples (20-30g) were ground with anhydrous sodium sulphate (3g per g sediment) and extracted in a Soxhlet apparatus for 8 hrs with ethyl acetate. The extract was reduced in volume to 0.5 ml and injected into the GC.

### 3.1.3 Biota

A suitable amount of biota was homogenized and mixed with 2- 3g per g of anhydrous sodium sulphate and extracted between 8 and 18 hrs with an adequate volume of ethyl acetate in a Soxhlet apparatus. The solvent extract was evaporated to 5 ml by rotary evaporation and to 0.5 ml under a stream of nitrogen.

The clean-up procedures used were different for each laboratory.

C.S.I.C. used gel permeation chromatography, IRSA-CNR, ILMR and University of Alexandria used silica gel while Israel O.L. Research lab used florisil.

Recovery experiments done on the individual compounds gave between 90% and 100% recovery of spiked compounds.

## 3.2 Analytical techniques

### **Barcelona Laboratory**

GC-NPD. Gel permeation chromatography fractions were evaporated just to dryness, dissolved in iso-octane and injected into the GC 6000 Vega series (Carlo Erba, Milan, Italy) equipped with a nitrogen-phosphorus (NPD) detector. A 30 m, 0.25 mm i.d. column coated with 0.12  $\mu\text{m}$  of chemically immobilized SPB-5 (Supelco, Bellefonte, PA, USA) was used. Hydrogen was the carrier gas at 50  $\text{cm s}^{-1}$  and helium the make-up gas at 30  $\text{ml min}^{-1}$ . The injector and detector temperatures were held at 300 and 320°C, respectively. The column was programmed from 60 to 300°C at 6°C  $\text{min}^{-1}$ , keeping the final temperature for 15 min. The detection limit was 1  $\text{ng l}^{-1}$  for water and 1  $\text{ng g}^{-1}$  for biota.

GC-MS. A 5995 instrument interfaced to a 9825A data system (Hewlett-Packard, Palo Alto, CA, USA) was used. Helium was the carrier gas at 30  $\text{cm s}^{-1}$ . The same column as for GC-NPD analyses was used, programmed from 60 to 90°C at 15°C  $\text{min}^{-1}$  and from 90 to 300°C at

4°C min<sup>-1</sup>, keeping the final temperature for 10 min. Methane was used as the reagent gas at 1.5 Torr. The transfer line, ion source and analyzer were held at 280, 200 and 230°C, respectively. Scan acquisition was from m/z 40 up to 550 at 1.68 scan/s. Positive and Negative Chemical Ionization (PCI and NCI respectively) modes of operation were used for confirmatory purposes of the different organophosphorus compounds. The selectivity and sensitivity of NCI-MS over conventional electron impact (EI)-MS for organophosphorus pesticides has been reported in the literature (Busch *et al.*, 1978; Stan and Kellner, 1982). For the TBP and TCEP, PCI-MS has been recommended over EI-MS (Cairns *et al.*, 1983; D'Agostino and Provost, 1986).

#### **Milan Laboratory**

Capillary GC columns: SP 255 (25 m x 0.32 mm i.d.) with a film thickness of 2 µm and OV 17 (25 m x 0.32 mm i.d.) with a film thickness of 0.15 µm were used. Carrier gas: Helium at 1 ml min<sup>-1</sup>; Hydrogen: 30 ml min<sup>-1</sup>; Air: 300 ml min<sup>-1</sup> and Make-up Helium at 30 ml min<sup>-1</sup>. Oven temperature: 70 to 200°C, at 20°C min<sup>-1</sup>; 200-250°C at 4°C min<sup>-1</sup>; 250 to 270°C at 10°C min<sup>-1</sup>; 30 min at 270°C. The detector was an NPD, from Carlo Erba, kept at 270°C. An on-column system was used to inject samples (1-2 µl). The detection limit was 1-10 ng l<sup>-1</sup> (depending on the compound) for water and 0.1 µg g<sup>-1</sup> for mussels (freshweight).

#### **Tiberias Laboratory**

Three different packed GC columns have been used with EC and N.P. detectors. Oven temperature: isothermal at 200°C. The detection limit was <500 ng l<sup>-1</sup> (depending on the compound) for water.

#### **Monaco Laboratory**

Capillary GC column: SE 54 (25 m x 0.32 mm i.d.) with film thickness of 0.17 µm. Carrier gas: Helium at 1.5 ml min<sup>-1</sup>; Hydrogen: 3 ml min<sup>-1</sup>; Air: 300 ml min<sup>-1</sup> and Make-up at 30 ml min<sup>-1</sup> (He). Oven temperature programmed from 100°C to 220°C at 3°C min<sup>-1</sup>. A Hewlett Packard 5890 GC equipped with a NP detector was used. The injector was kept at 210°C and the detector at 250°C.

#### **Alexandria Laboratory**

A Shimadzu MC-4 GC was used equipped with FPD detector and SGE capillary column SE-30, (50 m x 0.25 mm i.d.). Column, injector and detector temperatures were 160, 250 and 250°C respectively, with a split ratio of 1:1000 and a detection limit of 700 ng l<sup>-1</sup> (water).

### **3.3 Intercalibration**

During the IAEA/FAO/UNEP Workshop on the methodology and intercalibration of organophosphorus compounds (Monaco, 13-15 April 1988) it was not possible to carry out any intercalibration exercise. It was decided that MESL/IILMR will prepare and distribute a set of intercalibration samples as soon as possible. Due to the lack of staff the preparation of these samples begun in July.

One sediment sample and one mussel sample (Mytilus galloprovincialis) were collected in the lagoon of Venice, freeze dried, ground, sieved and homogenised in Venice. These samples were dispatched to all participants of the Workshop in October 1988.

Results, reported by all participants were under the detection limit for all compounds of interest for both samples.

An intercalibration exercise for OP compounds requires a special approach due to their instability. The best way for conducting such an exercise would be to carry it out in one laboratory with all participants working on the same sample with their own method.

#### 4. RESULTS AND DISCUSSION

This monitoring survey was carried out from March to August 1988, although the Barcelona lab has also analysed biota samples from April 1987 to February 1988. The results of the monitoring survey on OP compounds at the different stations indicated in Figs. 2-5 are shown in Tables I and II.

##### 4.1 Concentration of OP compounds in water

Concentrations of OP compounds in water are shown in Table I. Stations A and B from Spain correspond to the Llobregat and Ebro river and Stations A, B and C from Italy correspond to river Po Ferrara, Lido Nazioni and Marina di Ravenna, respectively.

It should be noted that the levels of the non-pesticide OP compounds, such as TiBP, TBP and TCEP are of the same order of magnitude in both Spain and Italy and similar to values previously reported for river waters (Galassi and Guzzella, 1988; Galassi et al., 1988; Gomez-Belinchon et al., 1988). In Spain, the highest levels corresponded to Station A, at the Llobregat river, where more industrial activities are carried out. This is the first time that TCEP has been unequivocally determined in Spanish rivers, and levels up to  $0.3 \mu\text{g l}^{-1}$  indicate its use in the monitored area. In Italy, the highest levels were those of TBP and TCEP (in April) at Station C. This station is located near the commercial harbour of Ravenna, across which many cargo boats pass every day. It should be also mentioned that TCPB has been detected for the first time in Italian surface waters, reaching values similar to the other OP non-pesticide compounds. The levels of OP pesticides are rather low in Spain and Italy, with values below  $0.03 \mu\text{g l}^{-1}$ . In both Israel and Egypt no detectable levels of OP compounds were found in any water sample analysed.

At some sampling sites it was possible to show the monthly variation in the concentration of OP compounds in water. For example, at the river Po station in Italy OP pesticides reached a maximum in May, possibly corresponding to greatest agricultural runoff at this time (Fig. 6).

Table I

Concentration of OP compounds in water samples\*.

Compound	Spain		Italy			Israel (All Stats.)	Egypt (All Stats.)
	St.A	St.B	St.A	St.B	St.C		
Parathion-Me	nd-30	nd	nd	nd	nd	nd	nd
Parathion-Et	nd	nd	nd-9	nd-3	nd-2	nd	nd
Malathion	nd	nd	nd	nd	nd	nd	nd
Fenitrothion	nd	nd	nd	nd	nd	nd	nd
TBP	1-300	nd-20	4-300	8-34	3-1000	nd	nd
TCEP	nd-400	nd	nd-16	nd-110	nd-300	nd	nd
<u>Others</u>							
Diazinon	nd-30	nd	4	nd-2	nd-1		
Phorate	nd	nd	nd-4	nd	nd		
TiBP <sup>a</sup>	nd-900	nd	nd-200	40-200	13-64		
TCCP <sup>b</sup>	-	-	nd-139	nd-31	nd-9		

\*Concentrations in ng l<sup>-1</sup>; nd = below detection limit

a Tri-iso-butylphosphate

b Tris-chloro-isopropyl phosphate

Table II

Concentrations of OP pesticides in biota\*.

Compound	St.C	Spain		Italy (All Stats.)	Israel (All Stats.)
		St.D	St.E		
Parathion-Me	nd-2.2	nd-0.5	nd	nd	nd
Parathion-Et	nd	nd	nd	nd	nd
Malathion	nd	nd	nd-17	nd	nd
Fenitrothion	nd-16	nd	nd-306	nd	nd
<u>Others</u>					
Azinphos-Et	nd	nd	nd-31		
Coumaphos	nd	nd	nd-16		
Diazinon	nd-12	nd	nd		
Dioxathion	nd	nd	nd-28		
Fenthion	nd	nd	nd-35		
Paraoxon-Et	nd-16	nd	nd		
Ronnel	nd	nd	nd-9		
Tetrachlo- rinphos	nd	nd	nd-18		

\* Concentrations in ng g<sup>-1</sup> freshweight;

nd = below detection limit

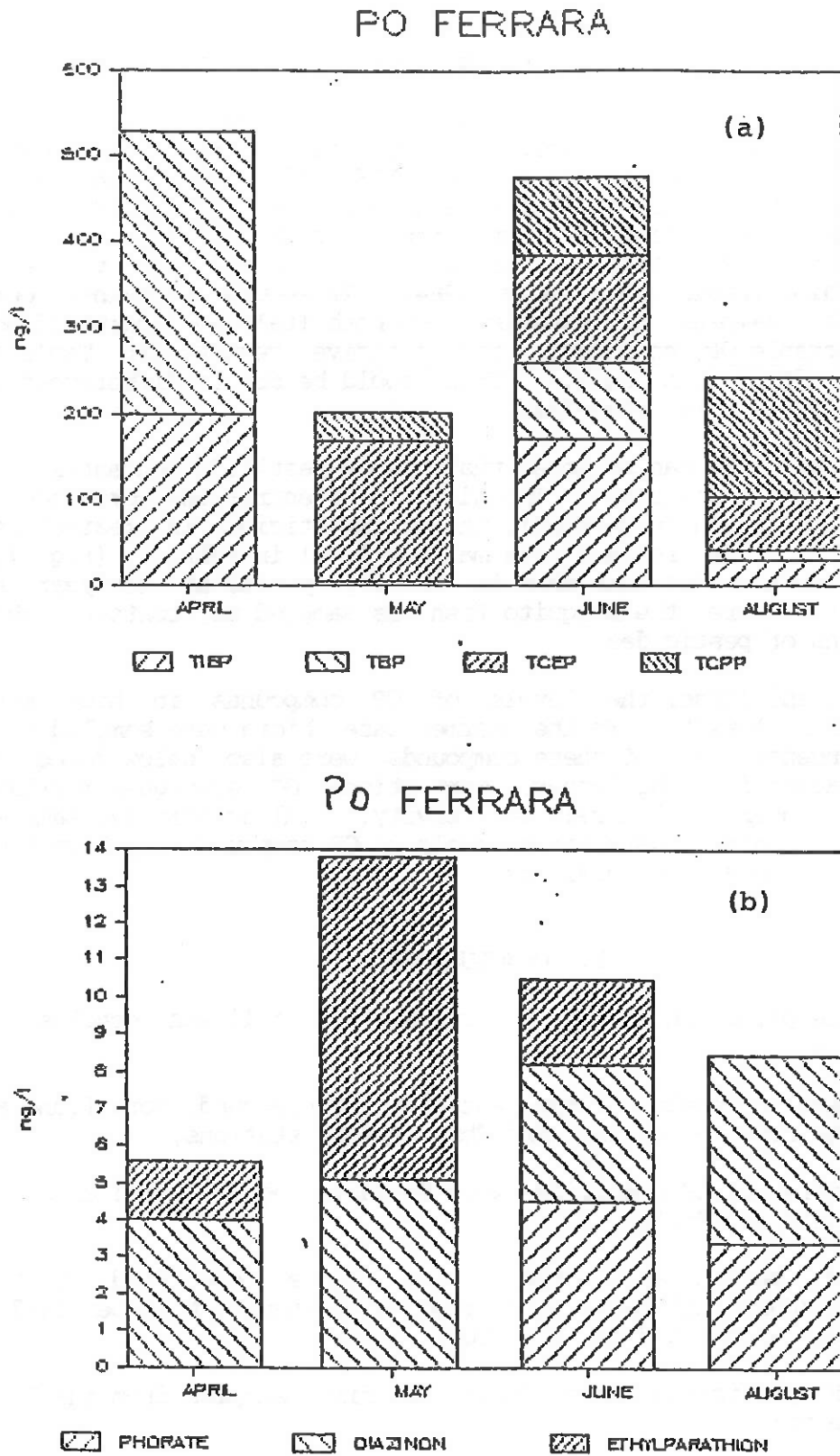


Fig. 6 Seasonal changes in industrial (a) and pesticide (b) OP compounds in the River Po

#### 4.2 Concentrations of OP compounds in biota

Concentrations of OP compounds in biota are shown in Table II.

It should be emphasized that only OP pesticides were found in biota samples and not OP compounds of industrial source. This may be related to the bioconcentration factors (BCF) of OP compounds, which are more than one order of magnitude higher for OP pesticides. So, whereas TBP and TCEP exhibit BCF for different fish species between 1-30, the BCF for OP pesticides vary from 70 up to 550, with values of 180 for Fenthion (Bruin, 1981; Muir, 1984). It should be pointed out, however, that samples of mussels from both Italy and Spain did not contain detectable OP compounds; the positive results in Table II (Spain) are from fish only. This could be due to differences in bioaccumulation in these organisms.

From Table II it can be noted that the OP pesticide concentrations were in the low  $\text{ng g}^{-1}$  range. The highest concentrations corresponded to Fenitrothion, which is currently the OP insecticide in greatest use at Station E. It reaches its maximum level in February (Fig. 7), probably due to the fact that this is the dry period of the year, so that the water where the mosquito fish was sampled may contain higher concentrations of pesticides.

In Italy and Israel the levels of OP compounds in biota were below detection levels. In the former case biota were sampled at a time when concentrations of these compounds were also below detection limits in water; for the latter, conventional GC techniques may have resulted in a lower analytical sensitivity. Alternatively, samples which did not contain detectable levels of OP compounds may have been collected from non-agricultural areas.

#### 5. CONCLUSIONS

From this pilot monitoring programme, the following conclusions could be drawn:

- (i) Similar levels of non-pesticide OP compounds were found at the river Po (Italy) and Ebro (Spain) stations;
- (ii) Different OP pesticides were found in agricultural areas of Spain and Italy;
- (iii) OP pesticides, other than those specified by the FAO/UNEP/IAEA/WHO ad-hoc meeting (Athens, November 1987), were also found in this study;
- (iv) OP pesticides were found in fish samples from the Ebro delta;
- (v) OP pesticides were not found in mussels from Spain and Italy;

# Organophosphorus pesticides in samples of GAMBUSA AFFINIS

EBRE DELTA (SPAIN) (Station E)

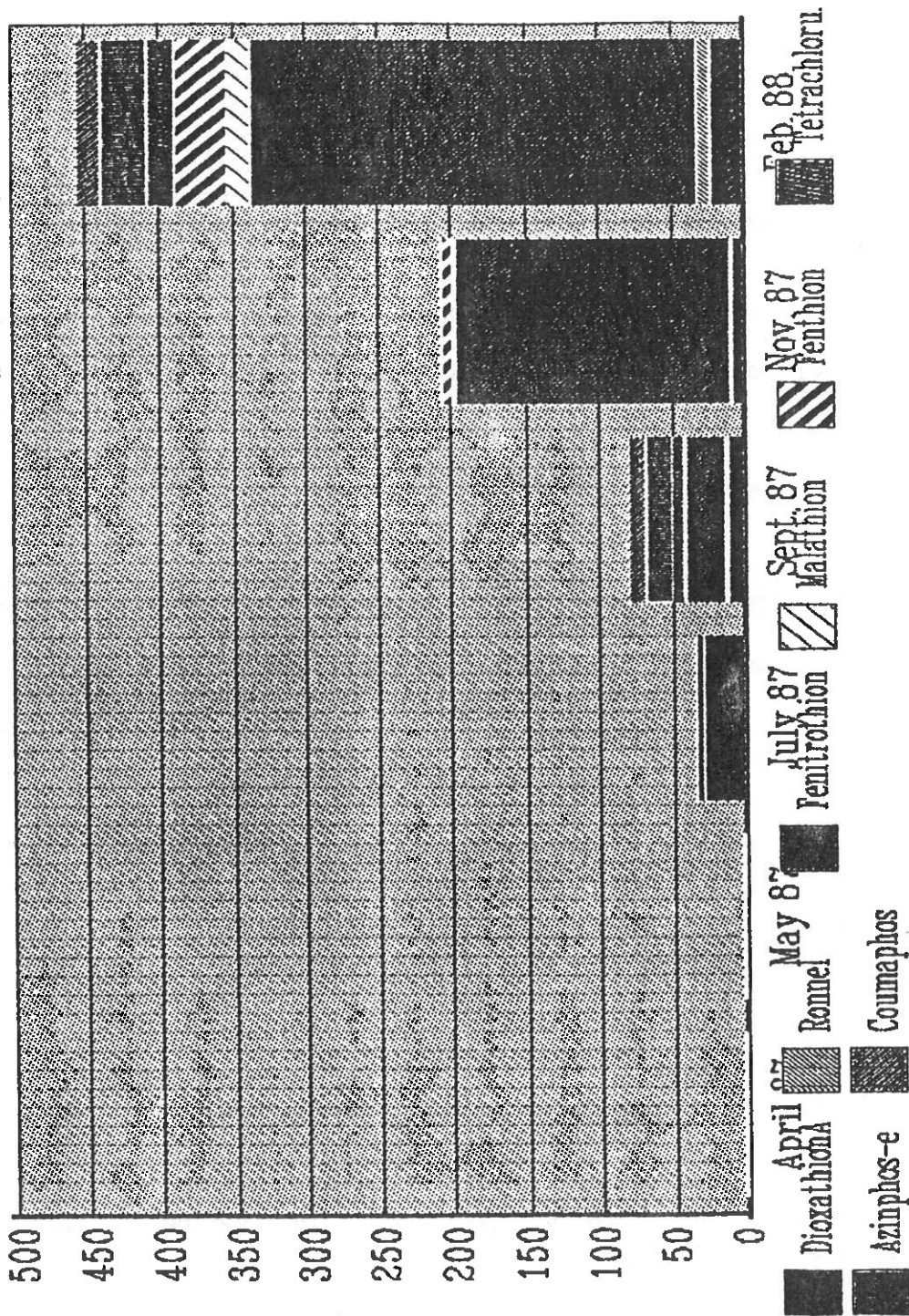


Fig. 7 Seasonal changes in OP pesticides in *Gambusia affinis* for the Ebro delta

- (vi) The methodology used in this pilot survey was adequate for the determination of OP compounds in the aquatic environment provided a low detection limit is attained;
- (vii) The results of this survey, together with those in the literature, warrant the recommendation of regulatory action.

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