



United Nations Environment Programme



UNEP(OCA)/MED WG.25/Inf.4
15 March 1991

Original: ENGLISH

MEDITERRANEAN ACTION PLAN

Joint Meeting of the Scientific and Technical
Committee and the Socio-Economic Committee

Athens, 6 - 10 May 1991

ASSESSMENT OF THE STATE OF POLLUTION OF THE MEDITERRANEAN SEA BY ORGANOPHOSPHORUS COMPOUNDS

In cooperation with



FAO



WHO



IAEA

U N E P
Athens, 1991

TABLE OF CONTENTS

	<u>Page No.</u>
EXECUTIVE SUMMARY	1
1. BACKGROUND	2
2. GENERAL FACTS ON ORGANOPHOSPHORUS COMPOUNDS	3
2.1 Chemistry	3
2.2 Physicochemical characteristics and environmental behaviour	7
2.3 Analytical methodologies	7
3. METABOLISM AND TOXICITY	12
3.1 Metabolism	12
3.2 Mode of action	12
3.3 Toxic manifestations	13
3.3.1 In humans and other mammals	13
3.3.2 In ecosystems	17
3.4 Effect levels	17
3.4.1 In animal experiments	17
3.4.2 In humans	18
3.4.3 In ecosystems	18
4. PRODUCTION AND USE	23
5. ORGANOPHOSPHORUS COMPOUNDS IN THE MEDITERRANEAN AREA: INPUTS, LEVELS AND HAZARDS	37
5.1 Sources, inputs and levels in the Mediterranean	37
5.2 Hazards to marine biota and humans	41
5.2.1 Marine biota	41
5.2.2 Human health hazard	42
6. EXISTING NATIONAL AND INTERNATIONAL REGULATIONS FOR THE PREVENTION OF MARINE POLLUTION BY ORGANOPHOSPHORUS COMPOUNDS	43
7. RATIONALE FOR ESTABLISHING MARINE POLLUTION CONTROL MEASURES IN THE MEDITERRANEAN REGION	46
8. REFERENCES	47

EXECUTIVE SUMMARY

Organophosphorus compounds is the general name for a large group of organic compounds containing phosphorus. The search for new compounds has led to the synthesis of more than 50 000 organophosphorus compounds and the registration of 250 of them as pesticides. In addition, a number of these compounds are used by industry and are known as non-pesticides but, in general, the commonly used compounds do not exceed one hundred.

The available information on the production and use of both organophosphorus pesticides and non-pesticides is limited, fragmentary and in some cases unreliable. On the basis of the limited information received from Mediterranean countries the organophosphorus pesticides, dimethoate, chlorpyrifos, malathion, methamidophos, phenthoate, dichlorvos, fenitrothion and parathion were the ones mostly used during the recent years. Other important compounds used were methidathion, fenthion and azinphos-methyl.

Eventhough in many cases they are looked at and treated as a group, organophosphorus compounds have varying physical and chemical properties eg. their solubility in water can vary as much as 10 000 times. In general, however, they are considered unstable in water but some of them can have a very high toxicity. The "no-observed effect level" for crustaceans, which appear to be the most sensitive group of marine biota, to organophosphorus compounds is well below 100 ng l⁻¹.

Organophosphorus compounds reach the marine environment through rivers, the atmosphere, agricultural run-off and industrial point sources. Information on their levels in the Mediterranean marine environment is very scarce. A MED POL study indicated that both pesticide and non-pesticide organophosphorus compounds can be detected in Mediterranean river estuaries and coastal areas subjected to pollution from these compounds. Some compounds were also detected in fish. However, in general, these concentrations are lower than those found in freshwater systems.

In most countries these compounds are controlled through the general legislation on pesticides and only very few countries have so far taken specific measures for the control of water pollution by organophosphorus compounds either in the form of emission standards or water quality criteria.

It is generally accepted that on the basis of the available information there is no human health hazard from the consumption of seafood and therefore specific measures are not warranted at the present stage.

As far as the aquatic ecosystems are concerned it is evident that fresh water ecosystems are exposed to a bigger danger than the marine ones. However, in view of the uncertainties conferred by excessive reliance on single species toxicity tests, lack of data on vulnerable biotopes and lack of data on behaviour of organophosphorus compounds in the marine environment, it is probable that potential impacts on marine ecosystems have been substantially underestimated and therefore the principle of precautionary approach could be followed.

1. BACKGROUND

According to the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-based Sources (LBS Protocol) the Contracting Parties shall take all appropriate measures to prevent, abate, combat and control pollution of the Mediterranean Sea Area caused by discharges from rivers, coastal establishments or outfalls, or emanating from any other land-based sources within their territories.

Article 5 of this Protocol stipulates that:

- The Parties undertake to eliminate pollution of the Protocol Area from land-based sources by substances listed in Annex I to this Protocol;
- To this end they shall elaborate and implement, jointly or individually, as appropriate, the necessary programmes and measures;
- These programmes and measures shall include, in particular, common emission standards and standards for use.

Organophosphorus compounds and substances which may form such compounds in the marine environment (with the exception of those which are biologically harmless or which are rapidly converted into biologically harmless substances) are included in Annex I to this Protocol.

The Meeting of Experts for the Technical Implementation of the LBS protocol (December, 1985) proposed that the measures to be recommended to the Contracting Parties for each group of substances should be based on an "assessment document" which should be prepared by the Secretariat. According to this proposal, which was adopted by the Fifth Ordinary Meeting of the Contracting Parties to the Barcelona Convention (September, 1987), such assessments should include inter alia chapters on:

- sources, point of entries and amounts of pollution for industrial, municipal and other discharges to the Mediterranean Sea;
- levels of pollution;
- effects of pollution;
- present legal, administrative and technical measures at national and international level.

Prior to the preparation of this assessment document a small ad-hoc meeting on organophosphorus compounds was convened in Athens in November 1987 (FAO/UNEP/IAEA/WHO, 1987). The meeting agreed on an annotated outline of the assessment document and recommended the initiation of a pilot monitoring study to collect relevant data from the Mediterranean region. The study centred on 4 pesticide and 2 non-pesticide compounds all of which have been used as case-examples

throughout the assessment document. The results of the study are found in document FIR/MEDPOL/OP/5 (FAO/UNEP/IAEA/WHO, 1989). In addition, the Co-ordinating Unit for the Mediterranean Action Plan compiled 870 bibliographic references on aquatic pollution by organophosphorus compounds and published them in MAP Technical Reports Series no. 44 (UNEP, 1990).

During 1989, document UNEP(OCA)/MED WG.12/4 was prepared by the Secretariat with the help of consultants and in close cooperation with FAO, WHO and IAEA, was reviewed by an ad-hoc meeting of experts (Athens, 7-8 March 1990), and was submitted to the Joint Meeting of the Scientific and Technical Committee and the Socio-Economic Committee (Athens, 28 May - 1 June 1990). The document evaluated information on the contamination of the marine environment by organophosphorus compounds, the ecological and human health significance of such contamination, and made recommendations to the Contracting Parties taking also into consideration the results of the pilot monitoring study.

The Joint Committee meeting took note of the draft recommendations included in the document, especially pointing out the difficulty of collecting, on a continuing basis, reliable and relevant data on the quantities of organophosphorus compounds produced and consumed as well as on their environmental concentration levels, fate and impact, and agreed that every effort should be made by all Contracting Parties to provide the secretariat by the end of September 1990 with i) quantities of organophosphorus compounds produced and consumed in each country, ii) present national legislative and administrative measures implemented for the control of pollution by organophosphorus compounds, and iii) available data on effects and levels of organophosphorus compounds in the Mediterranean coastal and estuarine areas.

On the basis of the above-mentioned information, the secretariat would then propose, if it was deemed necessary, a new set of recommendations for the next Joint Committee meeting in 1991 which, if approved, would be transmitted to the Contracting Parties for adoption.

The present document is an updated version of document UNEP(OCA)/MED WG.12/4 and includes the information received by the Contracting Parties before the end of February 1991.

2. GENERAL FACTS ON ORGANOPHOSPHORUS COMPOUNDS

2.1 Chemistry

The basic compound for the synthesis of organophosphorus compounds is phosphine (PH_3), which is alkylated or arylated to R_2PH or R_3P . The oxidation of phosphines gives phosphine oxides, $\text{R}_2\text{P}(\text{O})\text{H}$, R_3PO , and the conversion of the C-P bond to C-O-P bond phosphites, RO_3P . The combination of these two steps results in the formation of phosphinate esters, $\text{R}_2(\text{RO})\text{P}(\text{O})$, phosphonite esters, $\text{R}(\text{RO})_2\text{P}(\text{O})$, and phosphate esters, $(\text{RO})_3\text{P}(\text{O})$. Side chains can be halogenated, oxygen substituted with sulphur, and occasionally with nitrogen. Within the large group of organophosphorus compounds esters, especially phosphate esters, are of the greatest importance.

According to use, organophosphorus compounds and their derivatives can be divided into the following categories:

- (a) industrial use
 - flame retardants, plasticisers, solvents, antifoaming agents, industrial hydraulic fluids, lubricants, dispersants, detergents.
- (b) pesticides
 - insecticides, acaricides, nematocides, anthelmintic agents, fungicides, herbicides.

In most of the phosphate esters manufactured for industrial use the organic radicals fall into the following categories:

- (a) triaryl phosphates - either three identical aryl groups (cresyl, phenyl) or two phenyl and one other aryl group (e.g. monocresyl diphenyl phosphate);
- (b) aryl-alkyl phosphates - either two alkyl and one phenyl (e.g. dibutyl phenyl phosphate) or one alkyl and two aryl groups (e.g.) 2-ethylhexyl diphenyl phosphate);
- (c) trialkyl phosphates - three identical alkyl groups (e.g. tritributyl phosphate);
- (d) trihaloalkyl phosphates - three identical halogenated alkyl groups (e.g. tris 2-chloropropyl phosphate).

As biological and environmental behaviour can be altered by structural modifications around the phosphorus centre, the search for organophosphorus compounds which can satisfy a specific requirement in stability and selectivity resulted in the synthesis of more than 50 000 organophosphorus compounds and the registration of 250 as pesticides (Hutson and Roberts, 1985). The most frequently used 100 were reviewed by WHO (1986). Table I lists the major organophosphorus compounds presently manufactured and used. Though in most of the pesticides two of the organic radicals are either methyl or ethyl, the third radical is different in nearly every pesticide. Thus the third radical can be a longer alkyl group, alkyl derivative, aryl group, the combination of the two, a ring with sulphur or nitrogen. The R-O-P bond is often replaced by R-S-P and in few instances by R-N-P bond. In the first organophosphorus compound synthesized in 1944 the P=O bond was replaced by R=S bond. The majority of organophosphorus pesticides confirms to the formulae shown on Table II.

Other structures not shown in Table II are diphosphate esters and phosphoroamidates. Diphosphate esters consist of two identical organophosphorus compounds (phosphorothionate) moieties which are linked by oxygen (sulfotep) or by an organic radical sandwiched between two oxygen (temephos) or sulphur (dioxathione, ethione). In phosphoroamidates one (e.g. fenamiphos) or more (triamiphos) valencies are occupied by nitrogen.

Table I

Organophosphorus compounds currently manufactured and used.

A. Pesticides

- | | |
|--------------------------|---------------------|
| - acephate | - methamidophos |
| - amidithion | - methidathion |
| - azinphos-ethyl | - mevinphos |
| - azinphos-methyl | - monocrotophos |
| - bromophos | - naled |
| - bromophos-ethyl | - omethoate |
| - carbophenothion | - oxydemeton-methyl |
| - chlorpyrifos | - parathion-ethyl |
| - chlorfenvinphos | - parathion-methyl |
| - chlorthion | - phenthoate |
| - coumaphos | - phorate |
| - demeton | - phosalone |
| - demeton-S-methyl | - phosmet |
| - demeton-S-methylsulfon | - phosphamidon |
| - dialifor | - phoxim |
| - diazinon | - pirimiphos-ethyl |
| - dichlorvos | - pirimiphos-methyl |
| - dicrotopos | - prothoate |
| - dimethoate | - pyrazophos |
| - dioxathion | - ronnel |
| - disulfoton | - sulfotep |
| - ethion | - temephos |
| - fensulfothion | - tetrachlorvinphos |
| - fenthion | - thiometon |
| - fenitrothion | - triamiphos |
| - fonofos | - triazophos |
| - formothion | - trichlorfon |
| - leptophos | - vamidothion |
| - malathion | - zinophos |

B. Non-pesticides

- dibutyl phenyl phosphate
- cresyl diphenyl phosphate
- cumylphenyl diphenyl phosphate
- 2-ethylhexyl diphenyl phosphate
- isodecyl diphenyl phosphate
- isopropylphenyldiphenyl phosphate
- tributyl phosphate
- tricresyl phosphate
- triphenyl phosphate
- tris (2-chloroethyl) phosphate
- tris (2-chloropropyl) phosphate
- tris (1,3-dichloropropyl) phosphate
- tris (2-ethylhexyl) phosphate

Table II

Chemical structures of organophosphorus pesticides.
(Compiled from WHO, 1986). R denotes the twin alkyl radicals, R' indicates difference from R, X denotes the third (so called leaving) radical.

Phosphorus group	Outline of structure	Common or other name
Phosphate	$\begin{array}{c} O \\ \\ (R-O)_2-P-O-X \end{array}$	chlorfenvinphos, crotoxyphos, dichlorvos, dicrotophos, heptenphos, mevinphos, monocrotophos, naled, phosphamidon, TEPP, tetrachlorvinphos, triazophos
Phosphorothioate S-phosphoryl	$\begin{array}{c} S \\ \\ (R-O)_2-P-O-X \end{array}$	azothoate, bromophos, bromophos-ethyl, chloropyrophos, chloropyriphos-methyl, coumaphos, diazinon, dichlofenthion, fenchlorphos, fenitrothion, fenthion, parathion, parathion-methyl, pyrazophos, pyrimiphos-ethyl, pyrimiphos-methyl, thionazin
O-alkyl	$\begin{array}{c} O \\ \\ (R-O)_2-P-S-X \end{array}$	amiton, demeton-S-methyl, omethoate, oxydemeton-methyl, phoxim, vamidothion
S-alkyl	$\begin{array}{c} O \\ \\ R-S \backslash \\ P-O-X \\ / \\ R'-O \end{array}$	profenofos, trifenofos
Phosphorodithioate O-alkyl	$\begin{array}{c} S \\ \\ (R-O)_2-P-O-X \end{array}$	amidithion, azinphos-ethyl, azinphos-methyl, dimethoate, disulfoton, formothion, malathion, mecarbam, menazon, methidathion, morphothion, plenthoate, phorate, phosalone, phosmet, prothoate, thiometon
S-alkyl	$\begin{array}{c} S \\ \\ R-S \backslash \\ P-O-X \\ / \\ R'-O \end{array}$	prothiofos, sulprofos
Phosphonothioate	$\begin{array}{c} S \\ \\ R-O \backslash \\ P-O-X \\ / \\ R' \end{array}$	EPN, trichlornat, leptophos

2.2 Physicochemical characteristics and environmental behaviour

Table III gives the physical-chemical properties of six organophosphorus pesticides. The molecular weights of the six compounds in Table III are in a narrow range, but the range for all organophosphorus compounds is larger. It is from 213 to 466 for pesticides and from 140 (trimethyl phosphate) to 518 (3,5,5-trimethylhexyl) for other compounds. With the exception of tributylphosphate (TBP) organophosphorus compounds have relatively low vapour pressure and volatilization loss from water is minor. The high Henry constant (the ratio of molar concentrations in the liquid and vapour phase at equilibrium) of tributylphosphate indicates its relatively high volatilization from water.

The solubility of organophosphorus compounds in water shows great variation. Thus industrial alkylphosphate esters are soluble while tricresylphosphates are practically insoluble in water. The water solubility of pesticides shows similar variation and range from 0.4 mg l⁻¹ for chlorpyrifos to 4 000 mg l⁻¹ for vamidithion. An exception is acephate which is highly soluble in water with a saturation concentration of 67%.

The octanol-water partition coefficient ($\log K_{ow} = P_{ow}$) is usually below 3-4 (Bowman and Sans, 1983). As organophosphorus compounds have molecular weights below 600, the effect of lipophilicity on bioconcentration is not limited by molecular size. However, compared with organochlorine compounds with similar lipophilicity, organophosphorus compounds have a lower bioconcentration potential in aquatic organisms (Saeger *et al.*, 1979). This is attributed to their relative instability in water and organisms due to mechanisms of hydrolysis and ester cleavage. Fig. 1 illustrates the rather rapid disappearance of methyl-parathion from a pond, and Fig. 2 the disappearance of four arylphosphates from river water. Fig. 3 gives the biodegradation scheme of parathion in various biota. However, Jones and Zabel (1989) claim that for parathion a bioconcentration factor of 335 has been calculated for an unnamed fish in a model ecosystem.

The importance of biological factors has been demonstrated by the difference in the persistence of parathion in biotic and abiotic water. The half-life of parathion is usually few days, but in abiotic water no noticeable breakdown was observed in 40 days (Fisher and Lohner, 1987). Uptake by plants and particles is an important process which limits the availability of organophosphorus compounds for absorption by fish (Hutson and Roberts, 1985).

The environmental behaviour of organophosphorus pesticides has been evaluated by MacKay *et al.* (1985) with the help of a fugacity (partial pressure of the solute) model.

2.3 Analytical methodologies

Analytical methodologies for the fractionation and clean-up of organophosphorus pesticides in real environmental samples include the use of silica-gel (Lores *et al.*, 1987), Florisil (Neicheva *et al.*, 1988) or gel permeation (Lawrence, 1987). As regards the analytical

Table III

Physical-chemical properties of six major organophosphorus compounds.

	Ethyl-parathion	Methyl-parathion	Fenitrothion	Malathion	TBP	TCEP
Molecular weight	291.3	263.2	277.2	330.4	266.3	285.5
Boiling point (°C)	150 at 0.6mmHg	154 at 1mmHg	140 at 0.1mmHg	156 at 0.7mmHg	292 at 760mmHg	214 at 25mmHg
Melting point (°C)	6	35-38	0.3	2.85	-80	-55
Vapour pressure (mmHg/°C)	3.8-6.0X10 ⁻⁶ at 20°C	9.7-11.2X10 ⁻⁶ at 20°C	5.4X10 ⁻⁵ at 20°C	1.2X10 ⁻⁴ at 20°C	127 at 177°C	0.5 at 145°C
Henry's constant (mmHg/ppm at 25°C)	2.52X10 ⁻⁷	1.0X10 ⁻⁷	9.3X10 ⁻⁷	8.62X10 ⁻⁷	7.08X10 ⁻²	4.82X10 ⁻⁷
Water solubility (mg l ⁻¹)	24 at 25°C	55-60 at 25°C	30 at 20°C	145 at 25°C	280 at 25°C	7 000 at 25°C
Specific gravity	1.265 at 25°C	1.358 at 20°	1.3227 at 25°C	1.23 at 25°C	0.98	1.4 - 2.2
Log Kow	3.8	2-3.4	2.3-3.3	2.9	4	1.5
Log Koc (carbon water sorption coeff.)	2.8	3.3	2.8		3.5	2.2
Persistence (half-life in water at pH7 in days at room temperature)	2-8	2-4	1-2	2-8	6	24

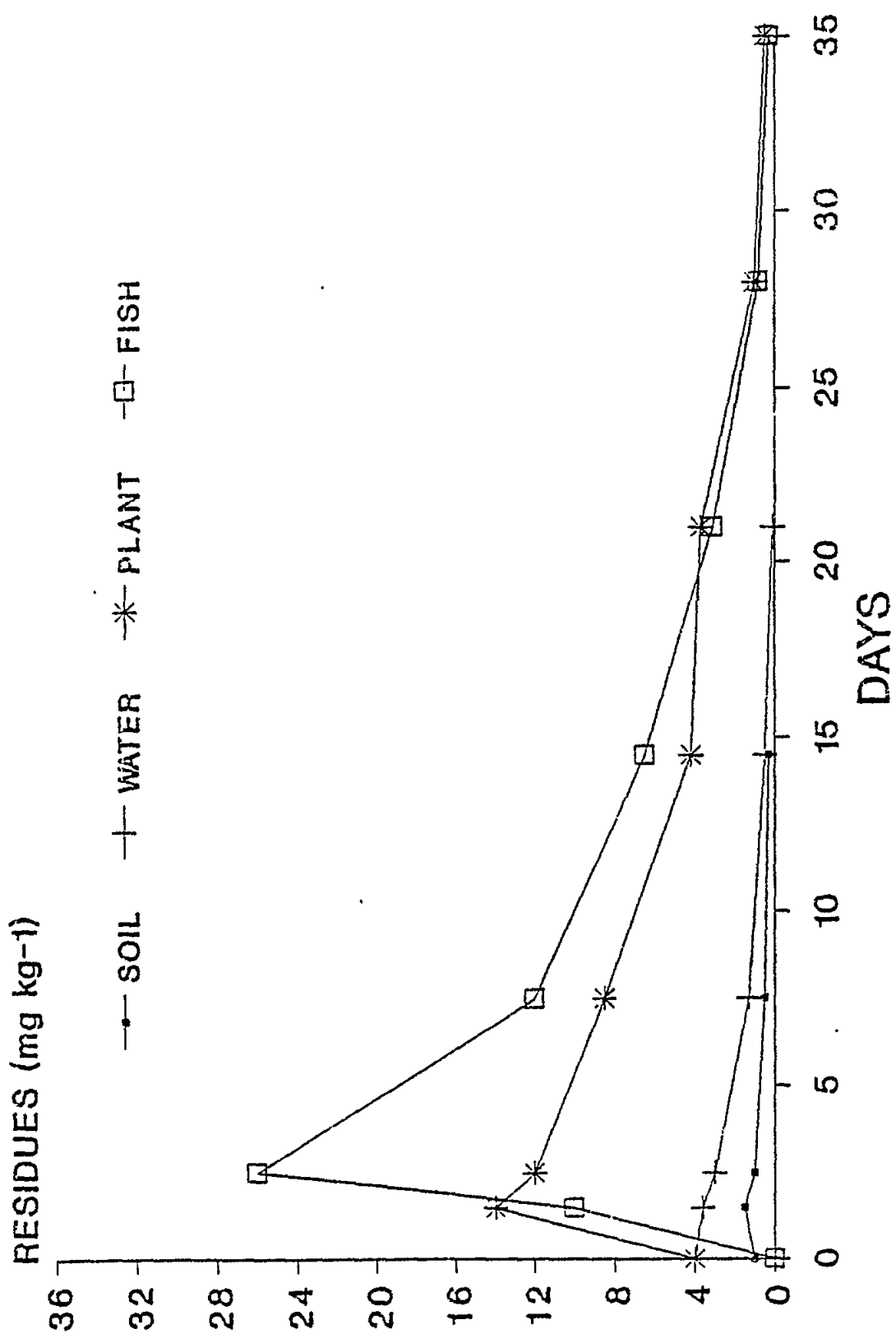


Fig. 1 Persistence of methyl parathion in a carp pond (from Sabbarhawi and Belsare, 1986)

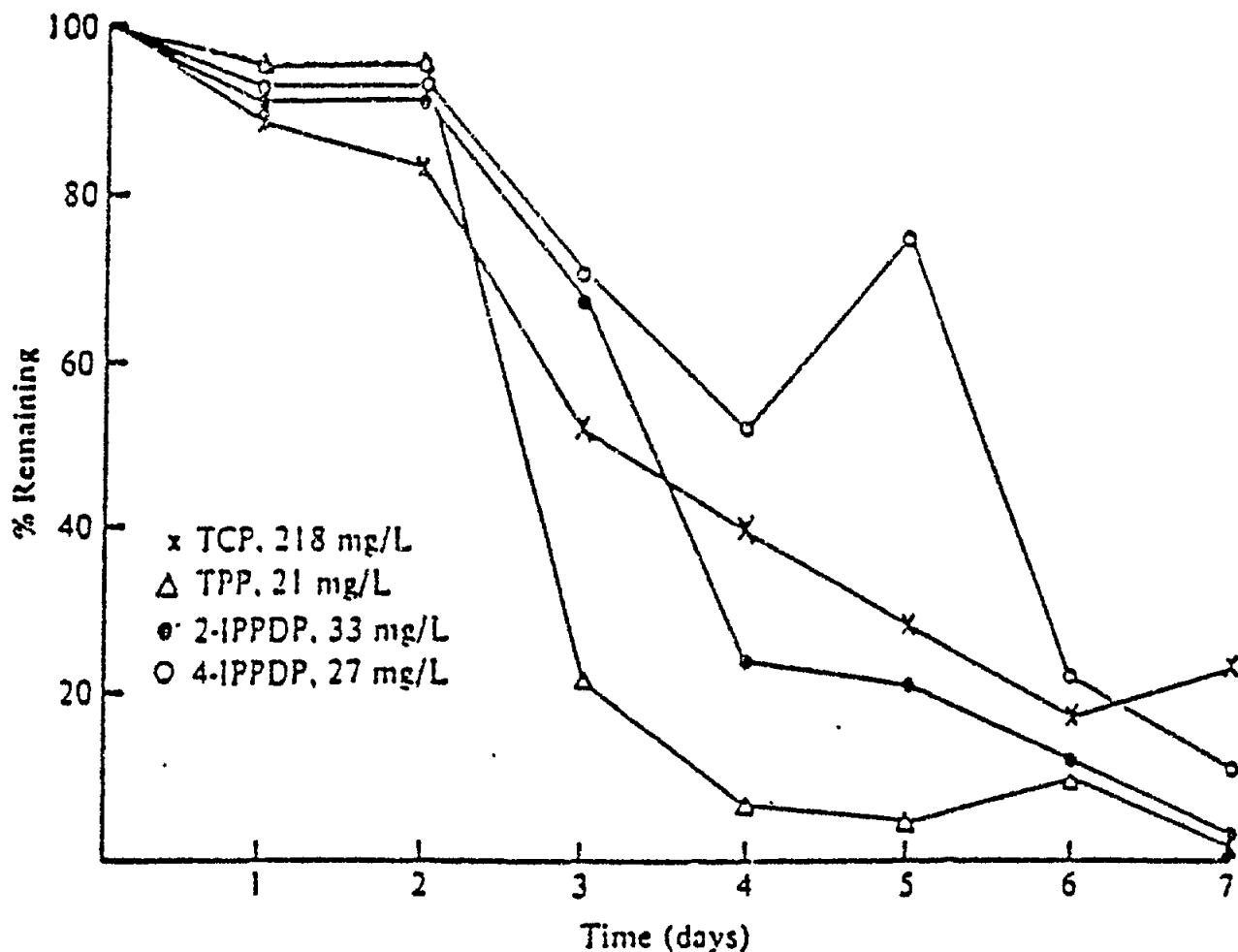


Fig. 2 Biodegradation of aryl phosphates in river water. Triphenyl phosphate (TPP), 2-isopropylphenyl diphenyl phosphate (2-IPPDP) and 4-isopropylphenyl diphenyl phosphate (4-IPPDP) were added as a mixture. TCP = tricresyl phosphate (from Latourette, 1979 in Boethling and Cooper, 1985).

part, capillary gas chromatography with thermionic nitrogen-phosphorus detector is usually the preferred method, with minimum detectable amounts between $0.01-0.1 \mu\text{g l}^{-1}$ in water (Wang *et al.*, 1987; Leistra *et al.*, 1984).

Other detectors employed in gas chromatography for the determination of organophosphorus compounds are the flame photometric detector (Prinsloo and De Beer, 1985; Onuska, 1984) or mass spectrometry in the electron impact (Wilkins *et al.*, 1985) or chemical ionization mode (Stan and Kellner, 1982; Cairns *et al.*, 1985). Due to the fact that some organophosphorus pesticides are thermally labile and/or polar, the use of liquid chromatographic techniques is advisable, either using ultraviolet (Osselton and Shelling, 1986) diode

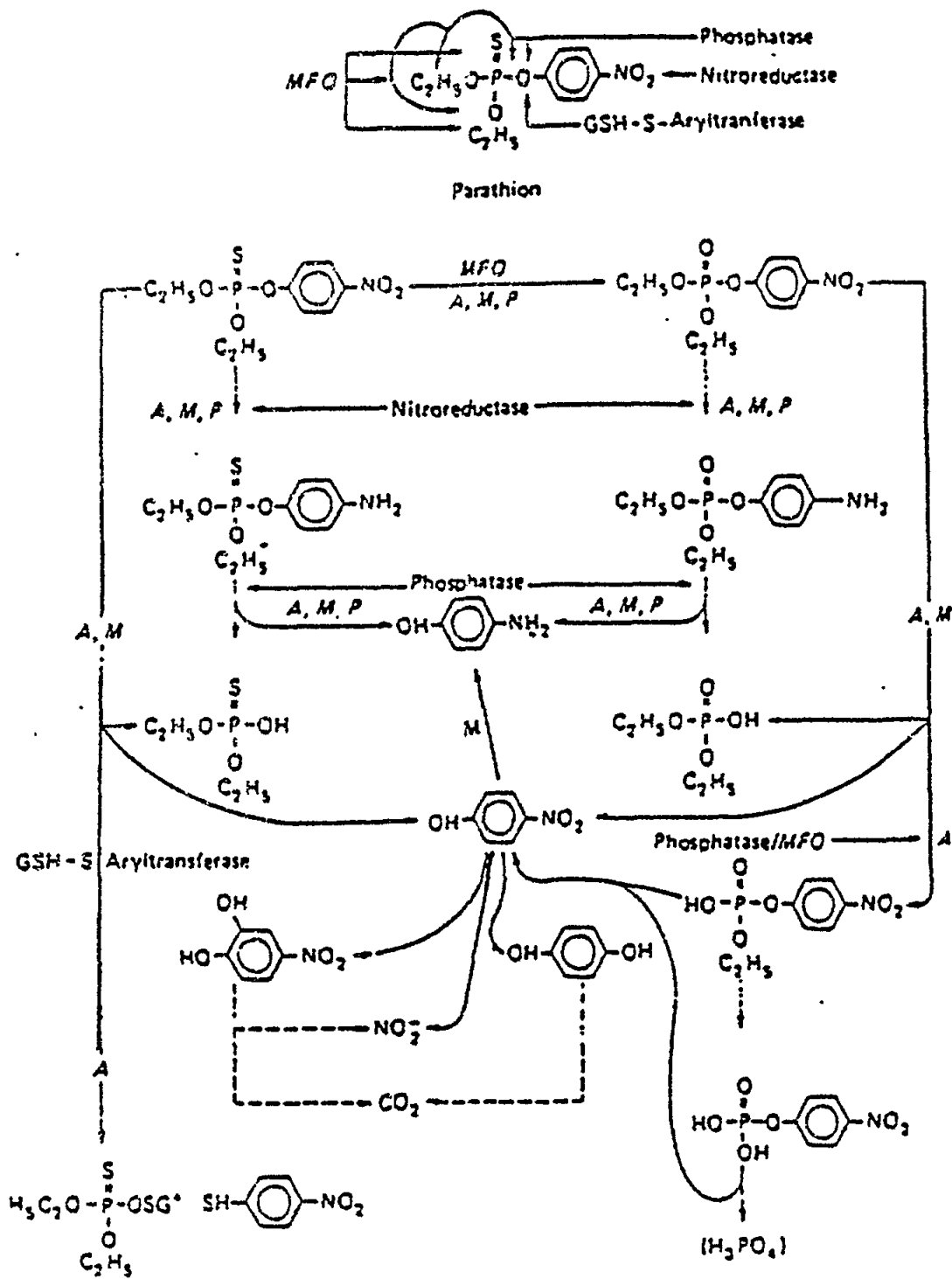


Fig. 3 A general scheme of the metabolic fate of parathion: A = animals, M = microorganisms, MFO = mixed function oxidase(s), and P = plants (from Mulla *et al.*, 1981)

array (Greve and Goewie, 1985), reductive amperometric (Clark et al., 1985) and mass spectrometry detectors (Barceló et al., 1987; Farran et al., 1988; Barceló et al., 1988). Recently a review of the use of liquid chromatography in pesticide analysis has been published (Barceló, 1988a).

Mass spectrometry detection in combination with gas and liquid chromatography has been recently applied for the determination of trialkyl and triaryl phosphates, including tris-2-chloroethyl phosphate (Cairns et al., 1983; D'Agostino and Provost, 1986; Barceló, 1988).

3. METABOLISM AND TOXICITY

3.1 Metabolism

Organophosphorus compounds undergo metabolic transformation in biological systems. Some of these transformations convert an inactive compound to an active one, others have the opposite consequence. In the case of parathion, its toxicity is enhanced by metabolic oxidation to diethyl 4-nitrophenyl phosphate. Any metabolic transformation which brings the structure of organophosphorus insecticides nearer to the structure of organophosphorus triesters, increases the ability to inhibit acetylcholinesterase (AChE) and converts a pro-insecticide to an active insecticide. Activation reactions are (Hutson and Roberts, 1985):

- (a) oxidative desulphuration of a thiophosphoryl group (conversion of P=S in parathion to P=O in paraoxon);
- (b) thioether oxidation to sulphoxide or sulphone (the conversion of C-S-C to C-S(=O) or C-S(=O)₂-C in fenthion or in disulfoton);
- (c) S-alkyl oxidation (the conversion of P-S-R to P-S(=O)-C in metamidophos or to P-S(=O)₂-R in profenofos);
- (d) oxidative N-demethylation (the conversion of N-R₃)₂ to NH-R₃ in dicrotophos or phosphamidon.

Deactivation reactions are (Hutson and Roberts, 1985):

- (a) hydrolytic removal of the X radical (the leaving group), mostly dearylation;
- (b) glutathione-dependent dearylation;
- (c) glutathione dependent dealkylation;
- (d) oxidative dealkylation.

3.2 Mode of action

The hydrolytic conversion of a triester to diester by acetylcholinesterase (AChE) is the most important step in the toxicology of organophosphorus compounds because this detoxification

reaction is associated with the toxification of acetylcholin. The physiological roles of acetylcholin and acetylcholinesterase are inter-linked. Acetylcholin is a transmitter of nerve impulses in cholinergic synapses and AChE prevents the build-up of toxic acetylcholin concentrations through the hydrolysis of released acetylcholin to cholin and acetate. Inhibition of AChE is associated with the most important clinical effects, however, a number of other enzymes are also known to be phosphorylated. These include acid phosphatase, aliesterases, lipases, trypsin, chymotrypsin, succinoxidase and dehydrogenase. While there is no known clinical significance attached to these interactions in humans, the possible impacts of similar reactions with enzyme systems of organisms in the wider environment remain unknown. Fig. 4 shows the enzyme reactions with (a) a substrate (b) an organophosphate and (c) a protective organophosphinate. In the first case, the liberation of the free enzyme is not inhibited and for good substrates (acetylcholine for AChE and phenyl valerate for NTE) the cycle can be completed as much as 10,000 times per minute. In the second case, inhibition occurs and the cycle proceeds at a negligible rate unless aided by nucleophilic reactivators. The hydrolysis of the diester leaves only an acidic negatively charged residue. This process, called aging, is a chemical change and can be monitored enzymically (time-dependent loss of responsiveness to reactivators). Aging rates of organophosphate-inhibited esterases depend on both the organophosphate and the enzyme but, for esterases, the R group is liberated into the medium. For NTE, however, aging involves intra-molecular transfer of R to a secondary site (commonly called site Z) on the NTE molecule. The presence in the inhibited NTE of a residual hydrolyzable bond (such as P-O-C from phosphates or phosphonates or P-NH-C from phosphoramidates) is obviously necessary for aging to occur and has been found to be an absolute requirement for neuropathic organophosphate esters. The intimate molecular mechanism of aging of inhibited NTE is not known and may be more complex than simple hydrolysis; the rate depends on steric factors but it is very high ($t_{1/2} = 1-4$ min) for simple dialkyl phosphates (Gallo and Lawryk, 1991).

The mode of action is the same in different animal phyla, though even within one order (e.g. fishes) there are substantial species differences in the hydrolysis of organophosphorus compounds (Hutson and Roberts, 1985).

Besides acetylcholinesterase, organophosphorus compounds can inhibit pseudocholinesterase, carboxylesterase, and various other esterases, among them the Neuropathy Target Esterase (NTE). The reaction of organophosphorus compounds with acetylcholinesterase and NTE is not different, the difference is in the outcome.

3.3 Toxic manifestations

3.3.1 In humans and other mammals

The acute toxic effects of organophosphorus compounds are the result of the excessive cholinergic stimulation in every mammalian species. In patients following the ingestion or inhalation of organophosphorus compounds the acute symptoms and signs of toxicity are either mimic the cholinergic effects of muscarine (e.g. pinpoint pupils, excessive bronchial secretion), or mimic the cholinergic

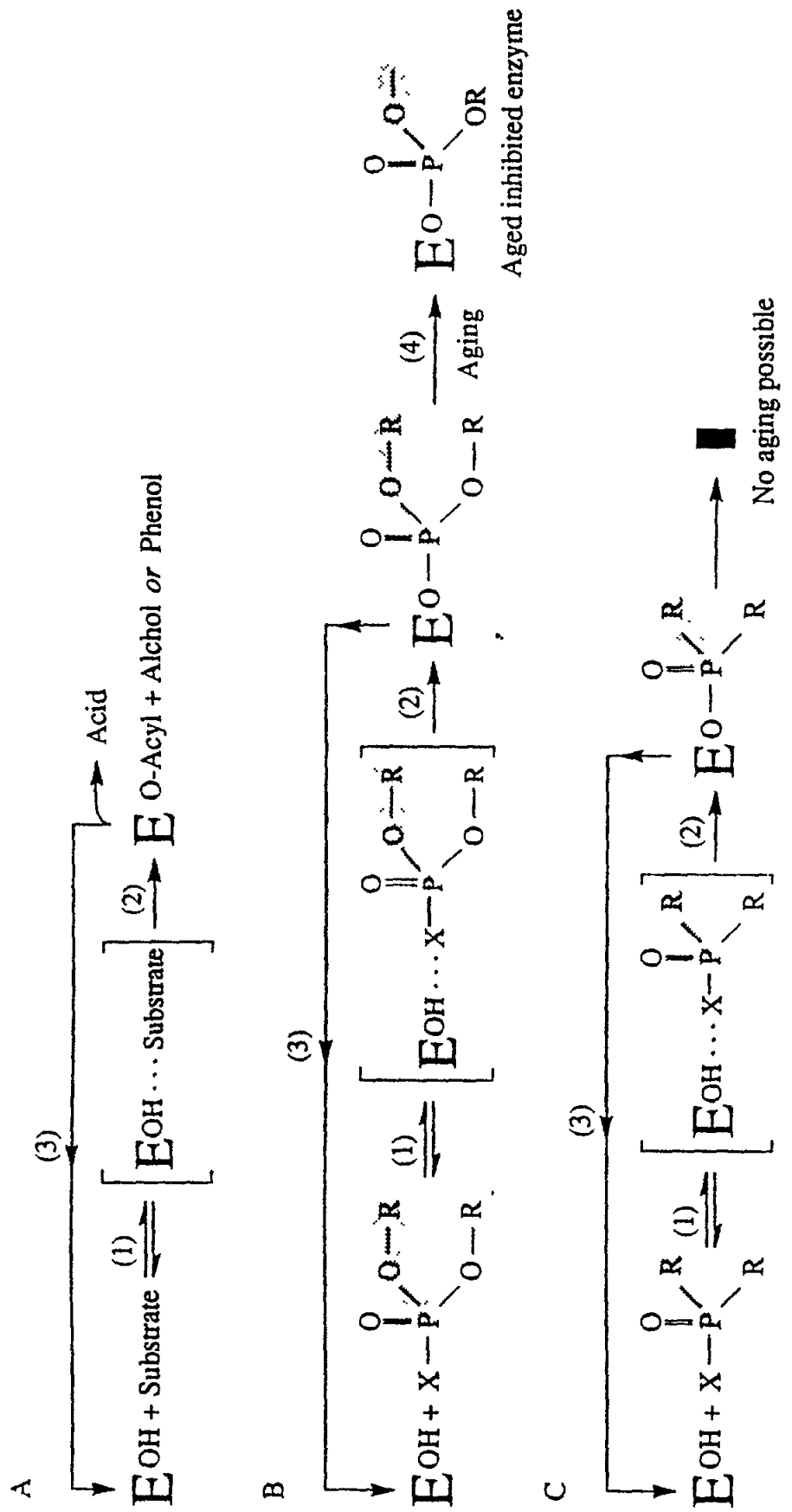


Fig. 4 Reaction steps for a typical β -esterase (organophosphate-sensitive serine hydrolase). A. Reaction with substrate. (1) is the reversible formation of a Michaelis complex. (2) is the formation of the acyl enzyme and one product. (3) is the liberation of the other product and free enzyme to repeat the cycle. B. Reaction with an organophosphate. Reactions (1)-(3) are analogous to those in A except that, for most organophosphates, (3) proceeds at a negligible rate unless aided by nucleophilic reactantors. Reaction (4) is a chemical change which can be monitored enzymically as "aging" (time-dependent loss of responsiveness to reactantors). C. Reaction with a protective organophosphinate. Reactions (1)-(3) take place but aging [reaction (4)] cannot occur because the residual R-P bonds in the inhibited esterase are not hydrolyzable (from Gallo and Lawryk, 1991)

effects of nicotine (e.g. fasciculation of muscles), or central nervous manifestations (e.g. anxiety, confusion). They begin within 30-60 min and are at a maximum at 2-8 hours after intake. In mild, moderate and severe intoxications the signs and symptoms in order of appearance are (Dreisbach and Robertson, 1987):

- a) Mild - Anorexia, headache, dizziness, weakness, substernal discomfort, tremor of tongue and eyelids, pin-point pupil, impairment of visual acuity.
- b) Moderate - Nausea, salivation, tearing, abdominal cramps, vomiting, sweating, slow pulse, spontaneous contraction of muscle fibres (fasciculation).
- c) Severe - Diarrhoea, pinpoint and non-reactive pupils, excessive bronchial secretion, respiratory difficulty, pulmonary oedema, cyanosis, involuntary defecation and urination, convulsions, coma. Death is caused by respiratory failure and heart block.

The induction of acetylcholin toxicity is a common characteristic of all organophosphorus compounds, at least after metabolic activation. Another toxic effect called organophosphorus compound induced delayed polyneuropathy (OPIDP) can be induced only by few organophosphorus compounds. The reason for this is that the inhibition of neuropathy target esterase (NTE) by phosphorylation is only the first condition of delayed neuropathy. The second condition is that the aging of NTE can be produced only by some organophosphorus compounds and nerve damage (paralysis) can be produced only in sensitive species. Cat, hen, some large animals, and man, are sensitive, while rodents, baboon, monkey and marmoset are insensitive.

Organophosphorus triesters used for industrial purposes which have the ability to produce delayed neuropathy are tri-ortho-cresyl phosphate (TOCP), mono-, di- and tri-o-tolyl, o-cresyldiphenyl, o-isopropyl-phenyldiphenyl, di- and monophenyl derivatives, tributyl phosphate, tris(2-chloroethyl) phosphate (Clayton and Clayton, 1981; Muir, 1984; Moretto and Johnson, 1987; Pellin *et al.*, 1987). The meta- and para-cresyl phosphates are not active. Pesticides which are able to cause delayed neuropathy in hens after a single dose include: amiphros, chlorpyrifos, coumaphos, cyanofenphos, desbromoleptophos, EPN, dichlorvos, isofenphos, leptofos, trichlorat (WHO, 1986; Moretto and Johnson, 1987; Vilanova *et al.*, 1987). The effect on NTE can be antagonised in a sensitive species by pretreatment with organophosphinate or sulfonyl fluorides. These become attached to NTE and inhibit its activity, but because they have no hydrolysable bond, they do not cause aging (WHO, 1986). Fig. 5 shows the reaction of NTE with organophosphorus compounds and organophosphinates.

The signs and symptoms of delayed neuropathy is tingling sensation, weakness, and ataxia. This progresses to paralysis of the lower limb. The upper limbs are affected only in severe cases.

There is no correlation between the potencies of organophosphorus compounds to inhibit acetylcholinesterase and induce delayed neuropathy.

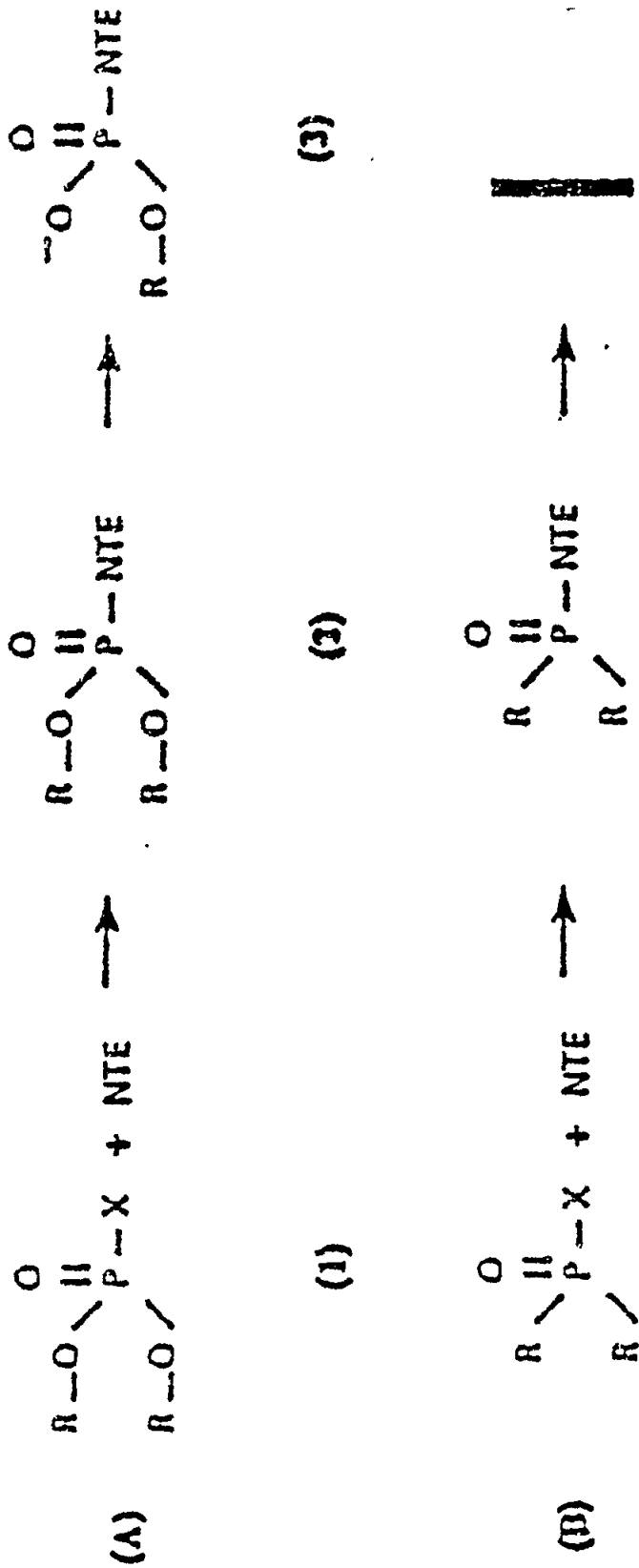


Fig. 5 Reaction of NTE with an organophosphorus compound (A) or an organophosphinate (B) (from Moretto and Johnson, 1987)

1. enzymatic activity, no known physiological role;
2. inhibited enzyme, no toxic effect;
3. in A. aged inhibited enzyme, initiation of the mechanism of OPIDP impossible, no aging possible; initiation of the mechanism of OPIDP impossible, blockage of the effect of neuropathic organophosphorus compounds

Experimental evidences indicate that organophosphorus esters are either not mutagenic in vitro or only weakly mutagenic. Acceptable tests do not indicate carcinogenicity. One report claimed that trichlorophon is teratogenic in pigs, but few teratogenic effects have been reported for other compounds (WHO, 1986).

3.3.2 In ecosystems

Organophosphorus insecticides frequently caused death from acute poisoning of the wild fauna. Thus the use of phosphamidon to control leafroller caterpillars on conifers in Montana, USA, caused a 87% decrease in the bird population (Ramade, 1987). In an other incidence 5 000 to 25 000 birds died following a fenthion application at 95.0 mL/hectare (Seabloom *et al.*, 1973). Contrary to the terrestrial environment there is hardly any information on the effects of organophosphorus compounds on the aquatic ecosystem where toxic mechanisms may not be restricted to an anticholinesterase effect.

No information is available on disturbances of marine ecosystems by organophosphorus compounds. In freshwater ecosystems temporary effects have been reported occasionally. At ambient environmental levels, short-term intoxication is not likely to occur and no hazard is to be expected from ethyl-parathion or methyl-parathion applications though in agricultural areas, crustaceans may be affected temporarily. For fenitrothion, results of extensive monitoring programs carried out in Canada in zones sprayed with this pesticide, revealed a temporary disturbance of populations of aquatic invertebrates, but no effects were noted on aquatic vertebrates. Although the doses used in Japan may be up to ten times higher than those in Canada, no evidence of impingement on aquatic ecosystems has been reported in scientific literature. No information has been found on ambient levels of fenitrothion and the eventual consequences in aquatic biotopes in the EEC countries. With regard to malathion it has been shown that chronic exposure to concentrations of $15 \mu\text{g l}^{-1}$ can result in 80% mortality of some species of marine crustaceans; it should be emphasized that such concentrations are quite close to ambient levels resulting from practical application rates in mosquito control programmes.

Monitoring studies of river water, drinking water, sediments and biota, in the United States, Canada, Western Europe and Japan have revealed the presence of TBP at concentrations less than one $\mu\text{g l}^{-1}$; taking into account the very low persistence of this compound, the hazard at such low ambient levels can be considered to be negligible.

Also, no data are available on the interaction of organophosphorus compounds with the microlayer and given their lipophilicity and the possibility that degradation through hydrolysis may be different (as far as kinetics are concerned) in this chemically unique biotope, there is clearly a need for an in-depth study of the effects of these compounds on the neustonic community which includes the eggs and developmental stages of many important species.

3.4 Effect levels

3.4.1 In animal experiments

The acute toxicities of organophosphorus pesticides show wide variation. The most toxic disulfoton, mevinphos, and parathion, have

an oral LD50 in rats of below 5 mg kg⁻¹ and the LD50s of the least toxic bromophos, malathion and primiphos-methyl are over 2 000 mg kg⁻¹ (WHO, 1986). Most of industrial organophosphorus compounds have oral LD50 values over 500 mg kg⁻¹ in the rat.

Compared with a pure compound the technical grade may be more or less toxic. Impurities in technical malathion increases toxicity (WHO, 1986).

WHO (1986) tabulates data on 17 organophosphorus pesticides with potential to cause delayed neuropathy in hens. The single dose which elicited delayed neuropathy was in the range of 25 to 150 mg kg⁻¹ for mipafox (N,N-diisopropylphosphorodiamidic fluoride), EPN, desbromoleptophos, chlorpyrifos, cyanofenphos, isofenphos, dichlorvos, and cuamophos.

3.4.2 In humans

As the common consequence of different organophosphorus pesticides is the inhibition of acetylcholinesterase, exposure and the severity of adverse effects are usually related to the decrease in red blood cell or plasma acetylcholinesterase activity. A decrease by 30-50% or more indicates exposure and necessitates removal. Signs of poisoning does not occur until blood levels are below 50%, while severe poisoning is usually associated with depression below 20%. Because normal variation in enzyme activity is large, determination must start before exposure and thereafter monitoring should be repeated at weekly intervals.

The possibility to monitor exposure to organophosphorus compounds with the potential to cause delayed neuropathy has been explored, but its feasibility needs further research.

Differences in the toxicity of various organophosphorus compounds are reflected by differences in the levels of both threshold limit values for inhalation exposure and acceptable daily intakes. The American Conference of Governmental Industrial Chemists set the following threshold atmospheric concentrations for occupational inhalation exposure: 0.05 mg m⁻³ for TEPP; 0.1 mg m⁻³ for fonofos, mevinphos, parathion, phosdrin and tri-o-cresyl phosphate; 0.2 mg m⁻³ for dioxathion, parathion-methyl; 0.5 mg m⁻³ for EPN; 3 mg m⁻³ for naled and triphenyl phosphate; 5 mg m⁻³ for crumofate and tributyl phosphate; 10 mg m⁻³ for malathion and temephos (Clayton and Clayton, 1981).

The acceptable daily intakes of 47 organophosphorus pesticides are listed by WHO (1986). They range from 0.00002 mg kg⁻¹ for phorate through 0.005 mg kg⁻¹ for parathion to 0.1 mg kg⁻¹ for crumofate.

3.4.3 In ecosystems

In view of the widespread use of organophosphorus compounds it is not surprising that extensive studies have been performed over the years on the dose(or concentration)-effects of these compounds to various groups of terrestrial and aquatic organisms, as well as to mammal species (as surrogates for man), to determine the hazard of these chemicals to the environment.

With regard to the impact of organophosphorus pesticides on the aquatic environment, extensive and very detailed literature studies have been made during recent years on request of the EEC, and extensive reviews have been published on parathion, methyl-parathion and fenitrothion by Persoone et al. (1985) and on malathion by Premazzi (1983).

Table IV summarizes the information collected by Persoone et al. (1985) relevant to this particular report, on the acute toxicity of parathion, methyl-parathion and fenitrothion to estuarine and marine biota. This table shows that crustaceans are the most sensitive marine organisms. The two species which gave exceptionally low LC₅₀ values were Homarus americanus (0.1 $\mu\text{g l}^{-1}$) and Penaeus sp. (0.02 $\mu\text{g l}^{-1}$).

The major ecotoxicological as well as toxicological data for four pesticides and two non-pesticide organophosphorus compounds have been summarized in Table V. Information for some other important pesticides follows (Jones and Zabel, 1989; Jones et al. 1988). The 24 hr LC₅₀ of dichlorvos to trout is 170 $\mu\text{g l}^{-1}$ and its 48 hr EC₅₀ to Daphnia is 0.066 $\mu\text{g l}^{-1}$. The lower reported 96 hr LC₅₀ for azinphos-methyl to fish (pike) is 0.36 $\mu\text{g l}^{-1}$ and to invertebrates (Gammarus) 0.1 $\mu\text{g l}^{-1}$. For azinphos-ethyl, a 96 hr LC₅₀ of 19 $\mu\text{g l}^{-1}$ has been reported for rainbow trout and a 48 hr LC₅₀ of 1.8 $\mu\text{g l}^{-1}$ for Daphnia. 96 hr LC₅₀s for dimethoate usually vary from <1 to 10 mg l^{-1} while a bioconcentration factor of 117 has been reported for Tetrahymena pyriformis exposed to 1 mg l^{-1} for 12 hours. A concentration of 1 mg l^{-1} of fenthion more than halved the photosynthesis of a marine flagellate. The 96-hour LC₅₀ of chlorpyrifos to atherinid fishes is reported to range from 0.4 to 6.7 $\mu\text{g l}^{-1}$ (Borthwick et al., 1985).

From the above data, it can be seen that organophosphorus pesticides are very toxic to aquatic biota. Insect larvae and crustaceans are extremely sensitive to intoxication by these products, although there are wide differences in sensitivity between different species of the same group. Acute effects on freshwater insects and crustaceans, as well as on marine crustaceans, are reported in the scientific literature at concentration levels below 1 $\mu\text{g l}^{-1}$. Other categories of biota are, in general, less sensitive, though acute effects often occur at concentrations below 1 mg l^{-1} .

Chronic effects have been found at and even below the 0.1 $\mu\text{g l}^{-1}$ level for the most sensitive biota (insects and crustaceans); fish species, in general, can be affected by <50 $\mu\text{g l}^{-1}$ of some organophosphorus pesticides when exposed for weeks to the compounds.

Experimental field studies have revealed that aerial application of organophosphorus pesticides (at practical rates) can lead to substantial mortalities of non-target insects and crustaceans.

In contrast to the wealth of ecotoxicological information available for organophosphorus pesticides, there are but few data on the effects of non-pesticide organophosphorus compounds to biota. Muir (1984) and Boethling and Cooper (1985) have attempted to collect and interpret some of the data reported in literature on alkyl and arylphosphate toxicity. Although some of the non-pesticide organophosphorus compounds are also very toxic to aquatic biota, the range is highly variable and species - as well as chemical - dependent.

Table IV

Effect concentrations of three important organophosphorus pesticides to estuarine and marine biota (from Persoone *et al.*, 1985).

Pesticide	Group of organisms	Effect	Concentration (in $\mu\text{g l}^{-1}$)
PARATHION	ALGAE	reduction of photosynthesis	1 000
	INVERTEBRATES		
	Molluscs	mortality (LC50)	330-10 000
	Crustaceans	mortality (LC50)	0.2- 4 300
VERTEBRATES			
	Fish	mortality (LC50)	15-65
METHYL-PARATHION	INVERTEBRATES		
	Molluscs	mortality (LC50)	1 200-25 000
	Crustaceans	mortality (LC50)	0.33-28
	VERTEBRATES		
	Fish	mortality (LC50)	60-76 000
FENITROTHION	ALGAE	growth (EC50)	3 000-3 900
	INVERTEBRATES		
	Coelenterates	mortality (LC50)	30 000
	Molluscs	mortality (LC50)	2 500-6 700
	Crustaceans	mortality (LC50)	<0.1-410
VERTEBRATES			
	Fish	mortality (LC50)	670-5 000

Acute toxicity levels indeed range from 150-200 $\mu\text{g l}^{-1}$ for some compounds on different aquatic biota (insects, crustaceans, fish, and quite surprisingly also lake phytoplankton), to over 6 700 mg l^{-1} for other compounds on particular species of fish.

Chronic effects (mortality and growth impairment) resulting from long-term exposure (several weeks) to aryl phosphates has been observed at concentrations as low as a few $\mu\text{g l}^{-1}$ in freshwater crustaceans as well as in fish.

Table V

Major toxicological data on 4 pesticide and 1 non-pesticide organophosphorus compound of concern to the Mediterranean.

	PARATHION (1)	PARATHION-METHYL (1)	FENITROTHION (1)	MALATHION (2)	TBP (3)
Acute aquatic toxicity ($\mu\text{g l}^{-1}$)	0.2-10 000	0.3-76 000	0.1-30 000	0.3-30 000	(8.8)
Chronic aquatic toxicity ($\mu\text{g l}^{-1}$)	0.1	0.1	0.1	0.1	
Acute oral LD50 in rats (mg kg^{-1}) (4)	3.6-13	14-24	250-500	2 800	3 000
Chronic toxicity for mammals (mg kg^{-1})	1-3	2-28	0.2-9	120	
Bioaccumulation	moderate	low to moderate	low to moderate	low	moderate
Bioconcentration factor (BCF)	up to 750	7 (insuff.data)	up to 940 (mosses) 180-250 (fish)	no data	
Mutagenicity	- (to be confirmed)	± (organism dependent)	-	+	-
Carcinogenicity	"equivocal" evidence	-	-	-	-

(1) Persoone *et al.*, 1985

(2) Premazzi (1983)

(3) Muir (1984)

(4) Clayton and Clayton (1981)

The acute aquatic toxicity figure for TBP (8.8 mg l^{-1}) in Table V (which is the only effect data that could be found for the aquatic environment) originates from an experiment with fish and should be interpreted with caution. It is indeed possible (and very likely) that as for other pesticide and non-pesticide organophosphorus compounds, several groups of aquatic biota are much more sensitive to TBP than fish.

In the reports on organophosphorus pesticides by Persoone *et al.* (1985), NOEL's (no observed effect level) are given for parathion, methyl-parathion and fenitrothion, which are either experimental or have been extrapolated from acute or chronic toxicity data (Table VI).

From Table VI it appears that for the most sensitive biota in the marine environment (crustaceans) no-effect levels for organophosphorus pesticides are below $0.1 \mu\text{g l}^{-1}$.

Table VI

No effect levels ($\mu\text{g l}^{-1}$) of three major organophosphorus pesticides for estuarine and marine biota (from Persoone *et al.*, 1985).

Pesticide	Group of organisms	Reported in literature	Extrapolated from acute and chronic toxicity data
PARATHION	ALGAE	-	100
	INVERTEBRATES		
	Molluscs	25-30	600
	Crustaceans	<0.1*	<0.1*
VERTEBRATES	Fish	<10*	4
	METHYL-PARATHION		
INVERTEBRATES	Molluscs	-	>1 000
	Crustaceans	0.10-0.32	<0.2
	VERTEBRATES		
Fish	56-10 000 *	-	
FENITROTHION	ALGAE	<100	300
	INVERTEBRATES		
	Coelenterates		3 000
	Molluscs		25
	Crustaceans		<0.1
VERTEBRATES	Fish	10	100-500

* lowest concentration at which a sublethal or chronic effect was noted

A few experimental no-effect levels have also been reported in scientific literature for non-pesticide organophosphorus compounds. For the waterflea *Daphnia*, NOEL's range from $17 \mu\text{g l}^{-1}$ to $460 \mu\text{g l}^{-1}$ for one particular arylphosphate ester (Boethling and Cooper, 1985); the 30-fold difference found between the lowest and the highest NOEL is due to differences in the commercial formulation of the same organophosphorus ester. Exposure of rainbow trout for more than one month to levels of arylphosphates of as low as $0.2 \mu\text{g l}^{-1}$ has been shown to cause many adverse effects: behavioural, morphological as well as physiological. No information is available on no-effect levels for TBP to aquatic biota, and only one figure has been found for the chronic effect on one fish species; it would be meaningless to try to derive a "safe concentration" for the aquatic environment from this sole figure.

On the basis of all toxicological information available on non-pesticide organophosphorus compounds, it appears that the NOEL's for the most toxic non-pesticide organophosphorus compounds to the most sensitive biota in the marine environment, are of the same order of magnitude as those for organophosphorus pesticides, i.e. below $0.1 \mu\text{g l}^{-1}$.

All the discussion in section 3 is based, due to lack of other data, on the evaluation of relative LC50 values and a word of caution is necessary at this stage. As it is known, toxicity tests are conducted in the laboratory under arbitrarily defined conditions which are incapable of perfectly simulating environmental conditions. They enable interlaboratory comparisons to be made of the possible toxic effects of a substance or an effluent but they have only limited value in assessing the effect of this substance in actual environmental conditions in which many other factors may have an influence (SIS, 1985). While LC50s allow a broad classification of likely environmental hazard to the particular target species tested (Cairns, 1984; 1989) it is not possible to reliably extrapolate the results to organismal communities. Lampert *et al.* (1989) have shown that the community response of the herbicide atrazine may occur at levels well below those at which effects are observed in test species.

4. PRODUCTION AND USE

The available figures on production and use of both organophosphorus pesticides and non-pesticides is scarce and fragmentary at the national as well as at the international level. In addition, different figures are reported by different sources and this indicates the difficulties in obtaining accurate and reliable data. In most of the Mediterranean countries no proper records of pesticide consumption quantities are kept and in many instances the only available figures are those of the Ministry of Finance or the Customs Department. Such figures are created for a different purpose and do not necessarily satisfy the needs of the scientists. However, a number of countries have provided some figures, to a large extent estimations, which are presented below.

4.1 Albania

No information was received from this country.

4.2 Algeria

No information was received from this country.

4.3 Cyprus

There is no industrial production of organophosphorus compounds in Cyprus and all quantities used are imported. During the years 1987-1989 the following quantities of organophosphorus-based pesticides were imported. These figures, however, are for formulated products and should be reduced by 60% for active ingredients.

1987: 313.4 tons
 1988: 389.0 tons
 1989: 263.0 tons

The following organophosphorus pesticides are normally used on the island:

acephate, azinphos-ethyl, azinphos-methyl, chlorpyrifos, diazinon, DDVP(dichlorvos), dimethoate, ethion, fenitrothion, fenthion, formothion, heptenophos, isazophos, malathion, mecanban, methamodophos, methidathion, omethoate, proparzite, phenamiphol, phorate, phosalone, parathion-ethyl, parathion-methyl, temephos, thiometon, thiazophol, trichlorfon.

4.4 Egypt

The following table (Table VII) provided by the Egyptian Environment Affairs Agency indicates the amounts of organophosphorus pesticides imported and produced locally in Egypt.

Table VII

Quantities of organophosphorus pesticides (in tons)
 imported in Egypt during the period 1984-1989.

Pesticide	1984	1985	1986	1987	1988	1989
Actellic (tech.)	64	71	---	---	---	---
Cyonox	---	30	300	150	300	---
Cytrolane	336	---	---	---	---	---
DC-702	613	755	---	---	---	---
Diazinon	14	---	---	---	---	---
Dimethoate	100	112	698	---	---	---
Dimethoate (tech.)	30	315	600	32	470	300
Dursban (48%)	376	285	600	605	400	350
Hostathion (40%)	716	617	---	187	134	90
Malathion (57%)	---	70	---	486	---	---
Malathion (tech.)	294	29	---	275	---	---
Sumithion (tech.)	60	57	134	40	---	60
Volaton	13	80	150	---	---	---
Total	2604	2421	2482	1775	1304	800

Locally produced organophosphorus pesticides (annually since 1988)
 Malathion (tech.) 100-110 tons, Dimethoate (tech.) 150-190 tons

According to Abdel-Gawaad (1990) all active ingredients needed for the formulated pesticides are imported. It also states that the import of organophosphorus pesticides has been high since 1973 but in the last five years pyrethroids appear to replace halogenated hydrocarbons and organophosphorus pesticides. According to this report the quantities of organophosphorus pesticides (in tons) actually used in Egypt in the period 1984-1989 appear in Table VIII.

4.5 France

The statistics in France refer to total organophosphorus compounds and not to individual compounds.

During 1989, 1 478 tons (active ingredient) were produced in France and about 1 600-2 000 tons were used in formulated pesticides for agricultural use. These figures refer to the total French territory and not only to the Mediterranean basin.

Monitoring of organophosphorus compounds in the marine environment does not take place since priority is given to more dangerous substances.

4.6 Greece

Most of the pesticides used in Greece are imported in a ready-to-use form. However, a few of them are produced locally using imported active ingredients. 10-20% of the imported quantities are exported as ready-made formulations. The figures for the quantities of pesticides used in the country are only estimates.

The quantities (in tons) of certain pesticides used for agricultural purposes during 1988 in Greece were provided by the Ministry of the Environment and appear in Table IX.

Psonas (1990) concludes in his report that the above figures are quite reliable. The data in Table X which indicates the estimated quantities (in tons of active ingredient) of the organo-phosphorus pesticides imported in Greece during the years 1987-89 are extracted from this report. Fig. 6 (extracted from the same report) indicates the import and use figures for selected organophosphorus pesticides during the same period.

4.7 Israel

No information was received from this country.

4.8 Italy

No information was received from this country.

According to ISTAT (1984) 19 000 tons of organophosphorus pesticides were used in Italy during 1983 but different figures were reported to FAO.

4.9 Lebanon

No information was received from this country.

Table VIII

Quantities of organophosphorus pesticides (in tons) which were used in Egypt in the period 1984-1989*

Name	Common name	84/85	85/86	86/87	87/88	88/89	Total
Actellic	Pirimiphos methyl	46 251	31 000	46 251	6 500	61 900	191 902
Basuden	Diazinon	148 400	113 000	39 600	42 800	30 600	374 400
Bolstar combi	Sulprofos	6 188	502 300	470 370	142 600	136 200	6 188
Cidial	Phenthoate	1098 174		134 880			2349 644
CRD Hostathion	Triazophos	406 925		10 770	7 000	12 000	541 805
Curacron	Prophenophos	262 116	26 740	14 680	9 800	5 000	318 626
Cyolane	Phosfolan	46 489	37 300	182 180	85 000	31 500	113 269
Cyonox	Cyanophos	3 900	48 800	6 800	6 100	3 000	351 380
Cytrolane	Mephosfolan	211 773	14 700	884 260	153 510	87 390	242 373
DC 702	(Dursban + Demilin)	910 546	80 300	1180 000	975 000	790 000	2056 006
Dimethoate	Dimethoate	557 428	445 000	810			3947 428
Disyston	Disulfoton	723		89 600	155 000	525 000	1 533
Dursban	Chlorpyrifos	331 462	90 000	4 500	6 600	9 000	1191 068
Gardona	Tetrachlorvinphos	11 748	9 200	6 800	4 200	2 900	32 948
Gusathion	Azinphos-methyl	12 302	8 000	586 680	40 000	29 700	34 202
Kelthane	Dicofol	100 813	187 700	133 500	100 000	302 000	944 893
Kelthane-dimethoate		308 054	173 880	72 900			755 643
Kitazin	IBP	11 662		210 600	379 800	239 700	84 562
Malathion	Malathion	264 770	37 610	78 700	100 000	80 500	1130 480
Nuvacron	Monocrotophos	1 064	200	48 920	134 500	74 700	1 264
Ridomil + Mancozeb		77 400	88 900	87 100	73 000	381 000	425 500
Selecron	Profenfos		50 300				308 420
Sumithion	Fenitrothion						198 200
Supracide	Methidathion	1 238					1 238
Tamaron compi	Methamidophos	448 589	59 000	337 800	257 400	448 900	1591 689
Valexon		75 878	165 800	108 910	23 000	13 100	368 688
Zolone	Phosalone				11 540		
Total		5383 899	2109 730	4636 611	2723 350	2639 290	17581 340

* Data from Abdel-Gawaad (1990)

Table IX

Quantities (in tons) of certain pesticides used for agricultural purposes during 1988 in Greece.

Compound	Quantity(tons)
2,4 D	110
Dimethoate	160
Limuron	10
MCPA	150
Mecoprop	8
Simazine	90
Triphenylthin acetate	40
Xylen	500
Atrazine	150
Bromoxynil	4
Ioxynil	2
Methyl Bromide	790
Alachlor	110
Aldicarb	10
Aminotriazole	160
Azinphos ethyl	80
Azinphos methyl	15
Fenitrothion	5
Fenthion	130
Malathion	50
Parathion	30
Parathion methyl	100
Dichlorvos	10
Total	2714

4.10 Libya

Table XI, provided by Technical Centre for Environmental Protection, Ministry of Health, shows the quantities (in kg or L of active ingredient) of organophosphorus pesticides used in Libya during the years 1987-1990.

4.11 Malta

Organophosphorus compounds are not manufactured in Malta which relies wholly on imports. During 1986, 45 000 kg were imported consisting mainly of malathion, dimethoate and dichlorvos.

4.12 Monaco

Organophosphorus compounds are not produced in the Principality and the quantities used are negligible.

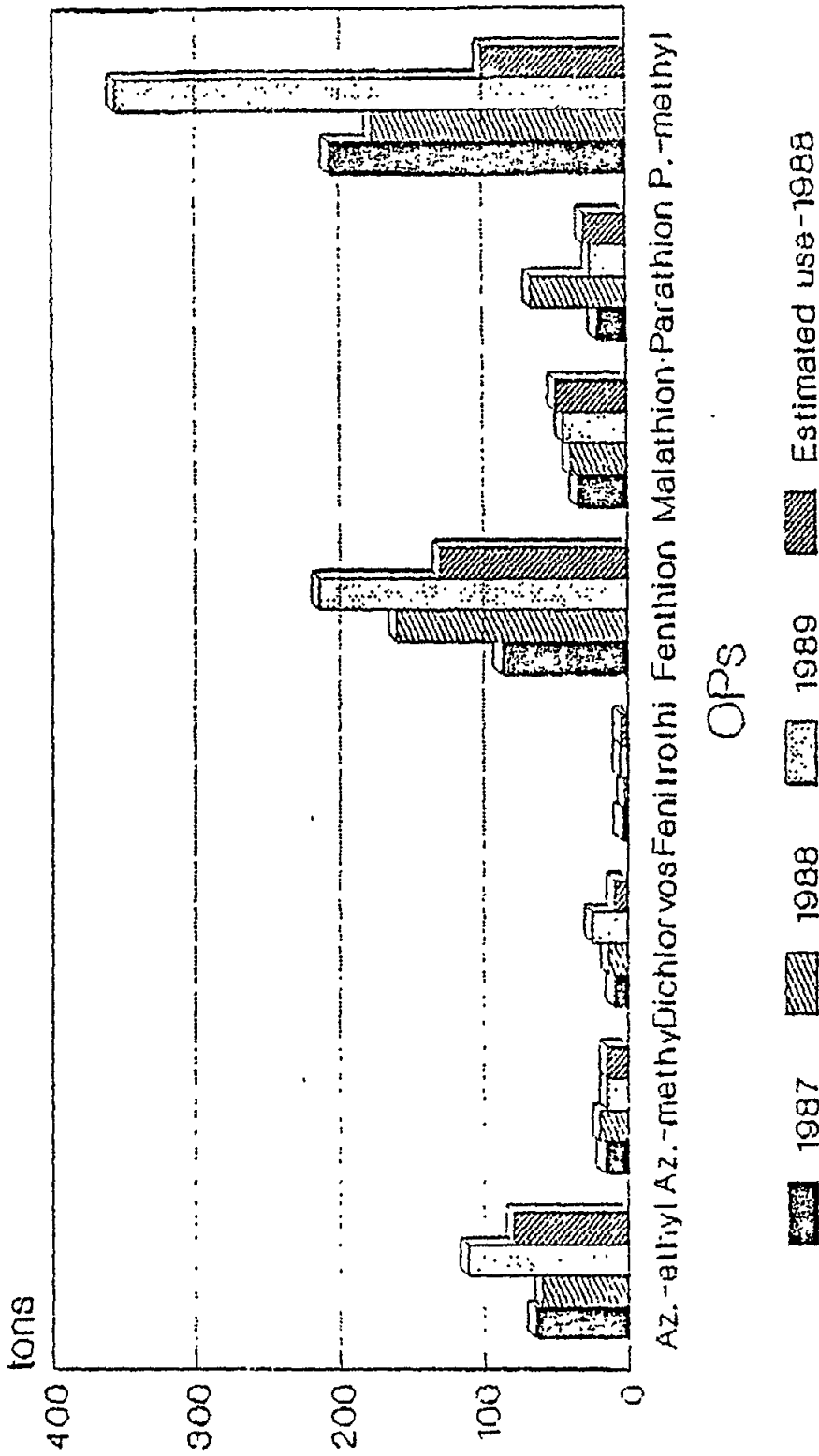


Fig. 6 Import and use figures for selected organophosphorus pesticides (after Psomas, 1990)

Table X

Estimated quantities (in tons of active ingredient) of organophosphorus pesticides imported in Greece during the years 1987-89*.

Pesticide	1987	1988	1989	% of active ingredient
acephate	9.8	9.0	21.0	75
azinphos-ethyl	65.3	60.2	111.5	40
azinphos-methyl	17.0	19.7	15.1	20-25
carbophenothion	11.7	7.0	7.0	25-45
chlorfenviphos	1.1	1.1	?	10-25
chlormephos	10.5	2.5	8.5	5
chlorpyrifos	34.5	74.6	117.9	5-48
chlorpyrifos-methyl	4.8	4.8	12.0	24
demeton-s-methyl	33.0	19.6	36.0	46-50
diazinon	7.6	8.9	51.3	10-60
dichlorvos (DDVP)	20.3	13.8	25.6	7.6-50
dimethoate	303.1	108.4	106.6	40
disulfoton	30.1	52.2	64.0	10
ethion	3.0	3.4	4.5	48.3-50
fenitrothion	4.8	2.4	5.3	50
fenthion	87.8	160.4	213.5	50
formothion	660.0	660.0	660.0	33
heptenophos	1.0	4.1	6.0	55
malathion	35.4	40.0	45.0	1-65
mecarbam	80.0	47.5	42.8	68
mephosfolan	625.0	?	?	25
methamidophos	213.8	296.8	317.3	56.5-60
methidathion	71.0	53.8	230.4	40
mevinphos	320.0	?	?	10
monocrotophos	93.7	54.9	117.8	40-60
omethoate	24.3	24.3	29.2	50
oxydemeton-methyl	3.5	?	?	50
parathion	21.5	56.4	25.3	10-20
parathion-methyl	207.2	177.4	355.8	10-40
phenamiphos	35.0	24.5	42.6	10-40
phenthoate	?	5.0	5.0	50
phorate	65.2	125.1	180.8	5-10
phosalone	31.5	19.5	31.0	30-35
phosmet	16.3	40.1	57.7	3-50
phosphamidon	18.0	28.1	47.6	50
pirimiphos-methyl	3.4	10.1	20.0	2-50
prophenophos	1.3	1.7	4.3	50
quinalphos	2.0	3.0	4.3	25
terbufos	27.9	34.0	51.5	5
thiometon	1.8	1.3	?	25
triazophos	18.0	21.0	27.7	42
trichlorphon	5.0	3.0	14.0	50-80
vamidothion	8.8	?	?	40
pyrazophos	8.1	10.9	7.1	29.4-30
glyphosate	66.6	127.4	122.4	9-18

* Data from Psomas (1990)

Table XI

Quantities (in kg or L of active ingredient) of organophosphorus pesticides used in Libya during the years 1987-1990.

Organophosphorus pesticide	1987	1988	1989	1990
dimethoate	8 000	39 992		40 000
pirimiphos-methyl	5 004	28	5 000	5 000
fenthion	750	15 000		5 000
fenitrothion	375	51 000	10 000	
dichlorvos	50		15 000	
malathion		105 735		17 100
diazinon		1 500	10 000	1 500
methidathion		12 000	10 000	
formothion			8 000	1 650

4.13 Morocco

No information was received from this country. However, from a report by Besri *et al.* (1990) the information appearing in Table XII regarding the use of pesticides in Morocco was obtained.

4.14 Spain

No information was received from this country.

4.15 Syria

No information was received from this country.

4.16 Tunisia

No information was received from this country. However, from a report by Bouguerra (1990) the information appearing in Table XIII regarding quantities of organophosphorus pesticides imported during the years 1988-1990 was obtained. No pesticides are produced in the country and exports are negligible.

4.17 Turkey

Turkey imported in 1985, 130 tons of pesticide and non-pesticide organophosphorus compounds while this figure was reduced in 1986 to 67 tons.

4.18 Yugoslavia

The information given here is included in a report by Fröbe and Drevenkar (1991) which was submitted to us by the MED POL National Coordinator.

Table XII

Extent of use of organophosphorus pesticides in the principal crop cultivations*.

Cultivation	Quantity of pesticides consumed (in tons)				Quantity of organophosphorus pesticides (in tons)				Percentage of organophosphorus pesticides to total pesticides					
	IA	N	F	H	Total	IA	N	F	H	Total	IA	N	F	H
Vegetables	331	889	3192	43	4455	6	56	4	-	66	1.81	06.30	0.13	-
Sugar beets	109	-	70.33	105.5	284.83	78	-	-	-	78	71.56	-	-	-
Citrus produce	831	-	39	10	880	690	-	39	10	739	83.03	-	100	100
Vineyards	186.31	-	643.67	-	829.98	14.69	-	-	-	14.69	7.88	-	-	-
Banana plantations	7.2	206	3.6	-	216.8	-	108	-	-	108	-	52.43	-	-
Olive trees	69.24	-	78.82	-	148.06	68.07	-	-	-	68.07	98.31	-	-	-
Rose plants	49.66	-	60.61	-	110.27	30.55	-	-	-	30.55	61.52	-	-	-
Total	1583.41	1095	4088.03	158.5	6924.94	887.31	164	43	10	1104.31	56.04	14.98	0.01	6.3

-- : Negligible amounts

IA: Insecticide, acaricide

N: Nematicides with an insecticide side effect

F: Fungicide

H: Herbicide

* Data from Besri et al. (1990)

Table XIII

Imports of organophosphorus pesticides in Tunisia
(in Kg) for the years 1988-1990*.

Compound	1988	1989	1990
azinphos-methyl	3 000	-	-
fenitrothion	4 200	3 000	-
malathion	327 000	15 000	-
parathion-ethyl	30 750	30 000	11 000
fenthion	10 000	6 600	1 000
dichlorvos	80 000	80 000	160 000
dimethoate	12 000	85 080	20 000
methidathion	-	15 000	12 000
pirimiphos-methyl	-	15 000	35 000
phorate	-	-	3 000
phosalone	19 000	5 000	6 000
chlorpyrifos	105 000	36 000	30 000
omethoate	2 000	-	-
isofenphos	2 000	-	-
temephos	2 000	4 000	10 000
heptenophos	1 000	9 000	2 160
naled	5 000	-	-
methamidophos	3 000	5 000	1 000

* Data from Bouguerra (1990)

The total production of organophosphorus pesticides in Yugoslavia is based exclusively on imported active substances. There is no domestic industrial synthesis of these compounds from phosphorus containing precursors. "Production" refers solely to manipulation with imported pure active substances to prepare different formulations by dilution in appropriate solvents or mixing with neutral additives. These formulations, containing from 1 to 50 % of active ingredient, are commercially available as final preparations for agricultural plant protection. There are no data referring to export of either pure active substances or of their formulations to the foreign market. Therefore, as in most Mediterranean countries, consumption of organophosphorus pesticides in Yugoslavia is assumed to be equivalent to imported quantities.

Data are not available for the exact quantities of each active ingredient used. Data, however, exist on total insecticides used and their formulations which are three: granular, containing 10% of active ingredient, powder, containing 1-3% of active ingredient and emulsion/suspension, containing up to 50% of active ingredient. Assuming that 60% of all insecticides are organophosphorus insecticides and that the active ingredients in the various formulations are 10% for granular, 3% for powder and 50% for emulsion/suspension the following figures are yielded (Table XIV).

The data above are plotted in Fig. 7 to illustrate the decreasing pattern in both production and consumption of organophosphorus insecticides during the 1987-1990 period.

Table XIV

Quantities of organophosphorus insecticides (in metric tons) produced and consumed in Yugoslavia during the period 1987-1990 (for 1990 only first six months are included).

Assumptions: a) 60% of all insecticides are organophosphorus insecticides;
 b) active organophosphorus ingredients in:
 granular = 10%
 powdered = 3%
 emul/sus = 50%

	1987	1988	1989	1990 (I-VI)
	Produc. Consum.	Produc. Consum.	Produc. Consum.	Produc. Consum.
Total organophosphorus insecticides	8488 8677	8196 7841	6788 6771	5101 4942
Active organophosphorus ingredients	1352 1412	1385 1404	1347 1232	970 956

Note: When consumption exceeds production, the difference comes from the previous year's supply.

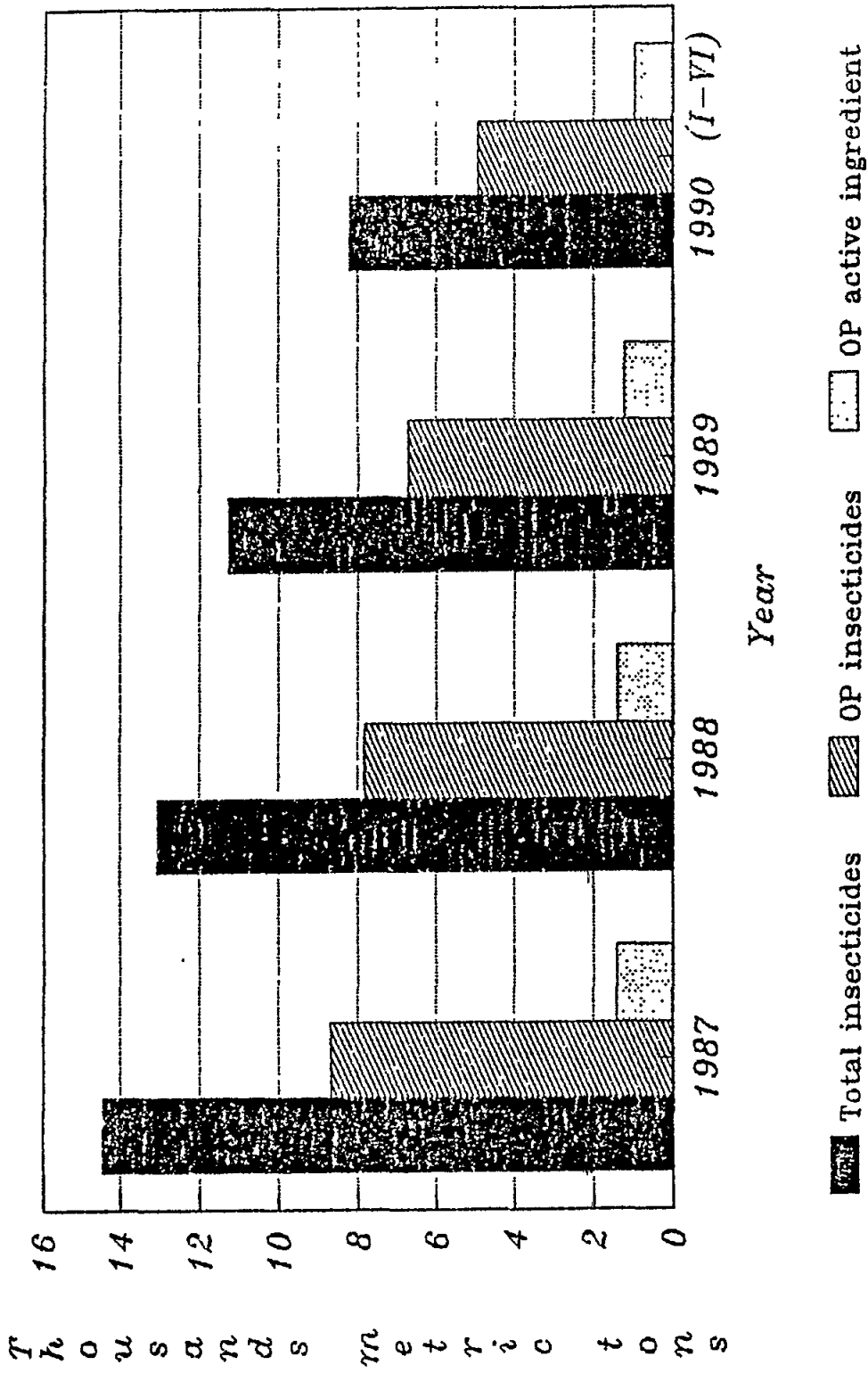


Fig. 7 Insecticide consumption in Yugoslavia (from Fröbe and Drevenkar, 1991)

4.19 Important organophosphorus pesticides

As can be seen from the above, only for 4 out of the 18 countries was it possible to obtain consumption figures per compound. However, it was possible to obtain figures for total quantities used for another 6 countries one of which also provided a list of the compounds used. According to these limited data, dimethoate, chlorpyrifos, malathion, methamidophos, phenthoate, dichlorvos, fenitrothion and parathion were the pesticides used in large quantities during the recent years. Other important compounds used were methidathion, fenthion and azinphos-methyl. Some more information is provided herebelow on some of these important compounds.

The total production of parathion in the EEC countries was estimated at 15 000 tons in 1974, 3 500 tons in 1979 and 6 000 tons in 1984; consumption values decreased from 3 500 to 1 000 tons. In the United States the production of this pesticide had decreased from 7 530 tons in 1965, to 6 940 tons in 1970, and to 4 535 tons in 1972 while the consumption in 1982 was estimated to be 3 125 tons. In 1989, the total world production of parathion and parathion-methyl was 40 000 tons and in the EEC countries 12 000 tons out of which only 1 000 tons were utilised.

The EEC production and use of parathion-methyl in 1974 was approximately 15 000 and 3 500 tons respectively. In 1984, production and consumption decreased to 8 000 and 1 000 tons respectively. In the United States the 1982 production was 23 000 tons and the consumption 7 700 tons. Since total world production of parathion-methyl in 1973 was as high as 60 000 tons, one may thus expect a decrease in production and use of this pesticide in the EEC countries in the years to come (ECDIN).

Fenitrothion is quite well-known in Canada since it has been applied by aerial spraying on forests in amounts approaching 1 000 tons/year since 1967 to combat spruce budworm pests. Data available for the EEC countries indicate a total use of 800 tons for 1979 and 300 tons for 1989.

Total world production of malathion in 1980-81 was estimated to be around 30 000 tons. The total world consumption of malathion during the same period is shown in Table XV (Premazzi, 1983). 2 100 tons (active ingredient) of this amount was used in the Mediterranean countries (40% of which was in Spain) versus 9 700 tons in Asia. In the EEC countries the production of malathion has increased from 5 750 tons in 1974 to 10 000 tons in 1984 while the annual consumption was close to 2 000 tons. In the United States the annual use of this pesticide over the period 1972-1982 has varied only slightly: from 7 350 tons (1972) to 6 350 tons (1982). In 1988 the total world production was 25 000 tons. During the same year, production in the EEC countries was 14 000 tons out of which only 1 000 tons were utilised.

The annual production in the EEC countries is estimated to be 6000-8000 tons for dimethoate, 500-1000 tons for fenthion, 2000-4000 tons for dichlorvos and 5000-10 000 tons for azinphos-methyl.

Table XV

Total consumption of malathion in various continents and countries (period 1980-1981) (Premazzi, 1983).

Area	tons/yr active constituent	Area	tons/yr active constituent
<u>Western Europe</u>	1 515	<u>New Guinea</u>	100
<u>EEC Countries</u>	640	<u>Asia</u>	9 680
Spain	850	Pakistan	4 000
Italy	250	Sri Lanka	2 150
France	220	India	1 500
Greece	150	South Korea	400
Portugal	15	Iran	350
Finland	10	Turkey	200
Germany	10	Iraq	200
Belgium	5	Japan	170
Netherlands	5	Taiwan	150
<u>North America</u>	7 350	Malaysia	150
USA	7 000	Thailand	100
Canada	350	Nepal	100
<u>Central and South America</u>	4 037	Philippines	80
Brazil	1 650	Lebanon	50
Argentina	800	Syria	50
Cuba	450	Saudi Arabia	20
Columbia	400	Indonesia	10
Mexico	300	<u>Africa</u>	905
Guatemala	170	Morocco	300
El-Salvador	150	Kenya	150
Venezuela	50	Egypt	140
Uruguay	20	South Africa	130
Peru	18	Algeria	50
Nicaragua	15	Libya	50
Ecuador	9	Tunisia	40
Chile	5	Zambia	20
<u>Australia</u>	250	Ethiopia	10
<u>New Zealand</u>	10	Tanzania	10
		Nigeria	5
	<u>TOTAL</u>		<u>23 850</u>

4.20 Non-pesticide organophosphorus compounds

The total production of non-pesticide organophosphorus compounds in the United States in 1986 has been estimated to be 77 000 tons while in 1977 it was 47 000 tons. Despite the fact that tributylphosphate (TBP) and tris(2-chloroethyl)phosphate (TCEP) are two of the most commonly produced and used compounds only very limited information is available about them. In the EEC countries 10 000 tons of TBP were produced and used in 1979 as well as in 1983, versus only 2 500 tons in 1972. The consumption in the United States during 1983 was 1 360 tons (Muir, 1984; ECDIN/EEC). Compounds such as TBP are now consumed to a higher extent in Europe rather than in the United States.

5. ORGANOPHOSPHORUS COMPOUNDS IN THE MEDITERRANEAN AREA: INPUTS, LEVELS, AND HAZARDS

The FAO/UNEP/IAEA/WHO ad-hoc meeting on organophosphorus compounds (18-20 November, 1987) decided on the basis of the then available information on the quantities currently produced and/or used in the Mediterranean countries and taking into account their toxicity, persistence and bioaccumulation, that six organophosphorus compounds should be treated as "case-examples" for the purpose of the assessment and the pilot survey. Four of the six compounds are pesticides (ethyl-parathion, methyl-parathion, fenitrothion and malathion) while the other two are non-pesticide organophosphorus compounds [tributyl phosphate (TBP) and tris(2-chloroethyl) phosphate (TCEP)].

5.1 Sources, inputs and levels in the Mediterranean

The types of marine areas at risk from contamination by organophosphorus compounds are:

- river mouths and estuaries
- lagoons
- shallow waters
- marshes

Agricultural run-off, directly or indirectly through rivers and streams, is by far the largest input of organophosphorus compounds in the marine environment. Industrial effluents containing organophosphorus residues may, however, also be discharged directly into shallow waters through pipelines from on-shore plants.

A third source of pollution is aerial transportation of both non-pesticide and pesticide organophosphorus compounds. Common organophosphorus pesticides are appreciably volatile and considerable losses from treated crops may take place into the atmosphere. Volatilization following application and subsequent wet and dry deposition probably does constitute a major route of entry of these pesticides in the marine environment. Such environmental behaviour is well established for other major groups of anthropogenic contaminants and requires quantification and evaluation for the organophosphates in view of potential surface-microlayer impacts.

Information on point sources of the organophosphorus compounds into the Mediterranean is scarce. Most of the information available is related to surface waters. In the Tiber river maximum concentrations of malathion of 0.5 - 0.6 $\mu\text{g l}^{-1}$ have been detected during the years 1970-73 (Leone and Puccetti, 1971, 1978). Values have also been published for different pesticides in surface waters of the Ferrara Province during the period 1975-84 (Baldi *et al.*, 1986). For malathion, the concentrations were usually below 0.4 $\mu\text{g l}^{-1}$, although, in 1977 and 1982, 2.6 and 4.2 $\mu\text{g l}^{-1}$ respectively were noted. Parathion-methyl concentrations were usually lower than 1 $\mu\text{g l}^{-1}$; a maximum level of 11.1 $\mu\text{g l}^{-1}$ was found in 1981. Parathion-methyl values were essentially below 0.1 $\mu\text{g l}^{-1}$, except in 1976 where a 4.4 $\mu\text{g l}^{-1}$ concentration was recorded. No fenitrothion has been detected in any water sample in this Italian Province. In France, 2 to 4 $\mu\text{g l}^{-1}$ parathion-ethyl and malathion have been reported in the river Saône in 1968 (Mestres *et al.*, 1969), as compared to values below 8 $\mu\text{g l}^{-1}$ in

the drainage waters of the Camargue in 1978 (Podjelski and Dervieux 1978). In the latter drainage waters, the concentration of the pesticide decreased from $5 \mu\text{g l}^{-1}$ to $0.2 \mu\text{g l}^{-1}$ three days after application.

In Spain, values have been reported for fenitrothion in lake Albufera at Valencia (Carrasco *et al.*, 1987). For the period 1983-85, concentrations varied from 0.1 to $2.0 \mu\text{g l}^{-1}$; these values decreased each time to non detectable levels (below $0.05 \mu\text{g l}^{-1}$) within two weeks. Fenitrothion levels in *Gambusia affinis* up to 306 ng g^{-1} have been reported (Barceló *et al.*, 1990) and in soils from the Ebro delta up to 1 ng g^{-1} (Durand, 1989). For the non-pesticide TBP, data were published in 1987 for the Besos river mouth in Spain, (Gomez-Belinchon *et al.*, 1988); the organophosphorus levels ranged from 0.02 to $1 \mu\text{g l}^{-1}$, with some peaks of $14 \mu\text{g l}^{-1}$. In the Llobregat estuary TBP and TCEP were found at concentrations of up to 0.3 and $0.4 \mu\text{g l}^{-1}$ respectively (Barceló, 1990). In Italy, TBP has been monitored in surface and drinking waters in Northern Italy in 1987. TBP levels in the river Po varied from 0.02 - $0.03 \mu\text{g l}^{-1}$ in Ferrara, to 0.04 - $0.13 \mu\text{g l}^{-1}$ in Turin (Galassi *et al.*, 1986).

In Greece, organophosphorus pesticides (diazinon, azinphos, methyl and parathion-methyl) have been detected in the Ioannina lake and in the Kalamas river during the period 1984-1985 (Albanis *et al.*, 1986). Fig. 8 shows that the concentration of these compounds fluctuate seasonally, with the highest concentrations in the summer when rainfall is lower and pesticides are intensively used.

In Yugoslavia, Drevenkar *et al.* (1986) detected phosalone, methidathion and demeton-S-methyl in the water of two ponds adjacent to orchards treated with organophosphorus insecticides and studied their degradation. They observed a considerable increase in the concentrations of the degradation products, dialkyl phosphorothioates and phosphorodithioates during and immediately after the spraying season.

Most of the information available worldwide at present, concerns contamination levels in surface waters (mainly lakes and river waters) in western Europe, Canada and the United States. Concentrations in seawater or sediments are scarce or lacking. A pilot survey organised in the framework of the Long-term Programme for Pollution Monitoring and Research in the Mediterranean (FAO/UNEP/IAEA/WHO, 1989) found lower values in two Mediterranean estuaries (Ebro and Llobregat in Spain) and in the Northern Adriatic coast (Lido delle Nazioni and Marina di Ravenna in Italy) than those reported for surface waters. The study was not supported by data quality assurance. The summary of the findings is as follows:

- (a) Fenitrothion and malathion were not detected in any of the sampling sites. Parathion-methyl was present only in the Llobregat estuary, where concentrations ranged from <1.0 to 30 ng l^{-1} . Parathion was detected at the two Adriatic sites where concentrations ranged from <1.0 to 3 ng l^{-1} . Phorate was not detected while diazinon was detected at every site with the exception of Ebro estuary. Concentrations were low in the Adriatic (<1.0 to 2 ng l^{-1}) but in the Llobregat estuary they ranged from <1.0 to 30 ng l^{-1} .

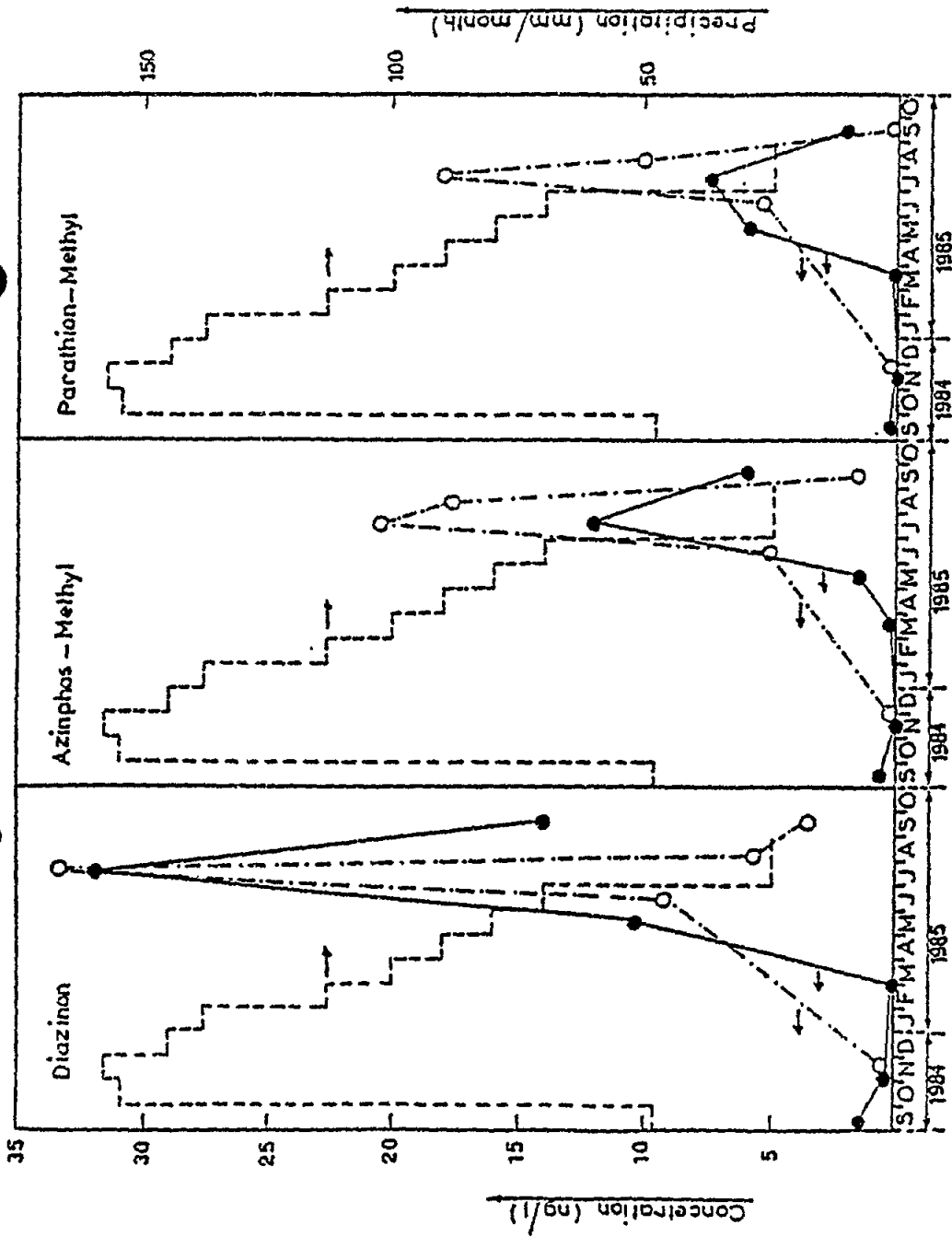


Fig. 8 Mean values of the pesticides Diazinon, Azinphos-methyl and Parathion-methyl in the Ioannina lake (.-.) and in the Kalamas river (o-.-.-o) in Greece over one year period. The dotted line (---) represents the average height of rainfall (mm/month) in the area for a fifteen year period (from Albanis et al., 1986)

- (b) Industrial organophosphorus compounds usually gave higher concentrations than pesticides. The concentration of tributyl phosphate was 1-300, <1.0 to 20, 8 to 34 and 3 to 1 000 ng l⁻¹ at the Llobregat estuary, Ebro estuary, Lido Nazioni and Marina di Ravenna respectively. The corresponding concentrations were for tris-2-chloroethyl phosphate: <1.0 to 400, <1.0, <1.0 to 100 and <1.0 to 300; for tris-isobutyl phosphate: <1.0 to 900, <1.0, 40 to 200, 13-64. Trischloro-isopropyl phosphate was estimated only at the two Adriatic sites, where concentrations ranged from non detectable to 31 in Lido Nazioni and from non detectable to 9 ng l⁻¹ in Marina di Ravenna.
- (c) The pilot study included two other areas which were the Haifa Bay and the Nile delta. At these sites no organophosphorus pollution could be detected but the detection limits (500 and 700 ng l⁻¹) were high and therefore the negative results only exclude the possibility of toxic contamination.
- (d) The survey included estimations in biota. In the Adriatic sites all the organophosphorus compounds were below the detection limit in the biota (mussels). In the Ebro estuary organophosphorus pesticides were detected in Mullus barbatus the maximum values of which were: diazinon, 12 ng g⁻¹; fenitrothion, 16 ng g⁻¹; paraoxon, 16 ng g⁻¹; parathion-methyl 2.2 ng g⁻¹. Industrial organophosphorus compounds could not be detected in biota. In the canals of the Ebro delta the presence of azinphos-ethyl, coumaphos, dioxathion, fenchlorphos (Ronnel), fenitrothion, fenthion, malathion, and tetrachlorvinphos was identified in Gambusia affinis. Maximum concentrations were 306 ng g⁻¹ fresh weight for fenitrothion, and 9 to 35 ng g⁻¹ for the others.

Ambient parathion levels in river and lake water in Europe and the United States range from non-detectable to 0.07 µg l⁻¹, most samples showing no contamination. In the Netherlands, Leistra et al. (1984) report that leaching of organophosphorus compounds (such as e.g. parathion) from glasshouse soils can contribute substantially to the pollution of water courses (0.1 to 2.0 µg l⁻¹).

For parathion-methyl concentrations are between 0.02 to 0.04 µg l⁻¹ in most cases, in different lakes and surface waters in the United States. Following a four year survey of 144 estuaries in 21 states of the United States, residues in aquatic biota only showed 2 cases of contaminated fish (out of 1524 samples).

For fenitrothion, concentrations in Canadian waters range from 2.3 to 16.3 mg l⁻¹ and mainly result from run-off from contaminated soils following spraying. Within a few days the levels had usually decreased to values below 1 mg l⁻¹. The median fenitrothion concentrations detected in aquatic biotopes in Quebec after spraying ranged from 1 to 8 µg l⁻¹ (Morin et al., 1986). One study has reported levels of up to 0.7 mg l⁻¹ (Moody et al., 1978).

Organophosphorus compounds may reach the sea when mangrove swamplands are sprayed for mosquito control. In Florida fenthion was sprayed aerially as a thermal fog at a rate of 28.0 mg m^{-2} from approximately 30 meters height and deposition on the recipient surface water (a ditch which communicated with the estuarine through a river) and concentration were estimated after three different test runs. Depositions were 1.86, 0.125, and 0.03 mg m^{-2} and peak concentrations 1.6, 0.16 and 0.16 ng l^{-1} respectively. Concentrations declined with zigzags (due to tidal changes) to non-detectable levels in 24 hours (Wang *et al.*, 1987).

Malathion concentrations in surface water of $0.3 \text{ } \mu\text{g l}^{-1}$ at Essex in the United Kingdom and $0.01 - 0.07 \text{ } \mu\text{g l}^{-1}$ in the river Rhine in the Federal Republic of Germany have been reported.

Contamination of sediments has been found to occur in the vicinity of pesticide manufacturing plants. In Denmark, marine sediments close to a company producing organophosphorus pesticides contain levels of malathion, parathion and methyl parathion ranging from 1 ng g^{-1} up to 3.8 ng g^{-1} (Kjølholt, 1985).

For the non-pesticide organophosphorus compounds, and particularly for TBP, concentrations in the river Rhine vary from 0.03 to $0.3 \text{ } \mu\text{g l}^{-1}$, with occasional values of $1 \text{ } \mu\text{g l}^{-1}$. TBP has frequently been detected in different lakes and rivers in the U.K., Norway, Switzerland, the Federal Republic of Germany, the Netherlands, the U.S.A. and Canada. The maximum levels were $10 \text{ } \mu\text{g l}^{-1}$ in the river Wall in the Netherlands and $2 \text{ } \mu\text{g l}^{-1}$ in the Delaware river in the U.S.A.

Concentrations of phosphate esters in sediments and fish tissue can, however, be 100 to 1000 fold higher than those in water, (ECCDIN/EEC; Muir, 1984; N.R.C., 1975).

Nevertheless surveys carried out in the United States and Japan suggest that, with the exception of a few compounds (such as TPB), phosphate esters are not widespread contaminants of aquatic environments.

5.2 Hazards to marine biota and humans

5.2.1 Marine biota

Information on levels in the Mediterranean is very limited to allow a proper evaluation of the hazards to marine biota. A proper monitoring programme has not been carried out in the Mediterranean and reported concentration values are not supported by quality assurance data. In addition, there is no information at all on the microlayer which is distinctly different from other portions of the aquatic environment (Albright, 1980). Anthropogenic enrichment of the microlayer has been recorded for many pollutants and this could also be true for organophosphorus compounds in view of their lipophilicity. The neustonic community includes the eggs and developmental stages of many species and is of critical importance to decapods and fishes during the reproductive season which coincides with the period of maximal pesticide application.

The FAO/UNEP/IAEA/WHO (1989) pilot study indicated that in two estuaries and two Adriatic sites 5 miles from the coast, the concentrations of organophosphorus pesticides in water even though they largely lie below 10 ng l^{-1} , they may reach values of up to 30 ng l^{-1} . Similarly, concentrations of non-pesticide organophosphorus compounds occasionally reached levels of 1000 ng l^{-1} . As shown in section 3 and Tables IV, V and VI, concentrations as low as $<100 \text{ ng l}^{-1}$ can be toxic to aquatic biota. The concentration of organophosphorus pesticides in rivers which flow into the Mediterranean sea ranges from non-detectable to $5.0 \text{ } \mu\text{g l}^{-1}$, with occasional peaks of $>10 \text{ } \mu\text{g l}^{-1}$. For industrial pesticides, concentrations in rivers range from 0.02 to $1.3 \text{ } \mu\text{g l}^{-1}$, with an outlier maximum of $14 \text{ } \mu\text{g l}^{-1}$ for TBP. Average concentrations for both agricultural and industrial organophosphorus compounds are below $0.1 \text{ } \mu\text{g l}^{-1}$. However, one cannot calculate mass balances simply on the basis of riverine inputs since there is considerable uncertainty attached to such estimates and even very low concentrations of compounds in the water can still represent a considerable contribution to the mass transport. In addition, no values are available for aerial inputs. It is probable that this route of entry is of major importance since many of these pesticides being quite volatile can find their way into the atmosphere during application and then into the sea through wet and dry deposition.

5.2.2 Human health hazard

The route of exposure to organophosphorus compounds through the sea or seaproducts is either dermal (contact with contaminated water) or oral (ingestion of contaminated seafood or water). Intoxication can occur when intake exceeds the no-effect level. Considering the environmental instability of organophosphorus compounds, low bioconcentration potential, and low reported concentrations in surface waters, it is reasonable to conclude that organophosphorus compounds in the marine environment are not human health hazards. This view is supported by the comparison of non-toxic levels of exposure with concentrations found by the FAO/UNEP/IAEA/WHO (1989) pilot survey.

Parathion has a recommended occupational exposure limit of 0.1 mg m^{-3} . As the respiration volume of a 70 kg man is 12 m^3 during 8 h work, the average permissible daily intake during a 5 day working week is 0.86 mg per day. The acceptable daily intake (ADI) of parathion given by FAO/WHO (WHO, 1986) is 0.005 mg kg^{-1} ($0.35 \text{ mg}/70 \text{ kg day}^{-1}$). In either case the pollution of seafood must exceed $1.6 \text{ } \mu\text{g g}^{-1}$ fresh weight to deliver intake above the acceptable level when one fishmeal (200 g) is consumed daily. As the ADI of malathion is 0.02 mg kg^{-1} and the NOEL reported by the National Research Council of Canada for fenitrothion is 0.33 mg kg^{-1} , the toxicologically hazardous concentration in seafood for these two pesticides is over 7.0 and $115 \text{ } \mu\text{g g}^{-1}$ fresh weight respectively. The ADI for fenthion is 0.001 mg kg^{-1} and for azinphos-methyl $0.0025 \text{ mg kg}^{-1}$. In the study sites of the FAO/UNEP/IAEA/WHO (1989) survey the concentration of industrial organophosphorus compounds did not reach the detection limit while the maximum concentration of pesticides remained about one thousand times below the concentration which could supply the allowable daily intake for consumers of one fishmeal per day.

6. EXISTING NATIONAL AND INTERNATIONAL REGULATIONS FOR THE PREVENTION OF MARINE POLLUTION BY ORGANOPHOSPHORUS COMPOUNDS

In most of the Mediterranean countries, pollution by organophosphorus compounds is regulated through the general legislation. Only in very few countries specific legislation exists.

In Cyprus, the Pest Control Products Law and subsequent amendments and regulations control the use of pesticides in which organophosphorus based pesticides are also included. In addition, regulations based on the Sales of Foods and Drugs Law control the maximum permissible levels of organophosphorus pesticides in food. However, marine food is not covered.

In France, no restrictions are imposed on their use or sale but production industries may have to follow the provisions of Law no. 76-663 for the protection of the environment.

In Libya, Law 7 of 1982 on the Protection of the Environment and subsequent legislation and regulations control the import, manufacture, transport and use of organophosphorus pesticides for the protection of water resources, agricultural products, livestock and human life.

In Malta, organophosphorus pesticides are regulated by the Pesticide Control Act of 1966 which is in the process of being updated. In Monaco, they are controlled by the general legislation on phosphorus containing compounds and in Turkey by the general legislation on environmental protection and control.

The only Mediterranean countries where legislation exists on effluent standards or water quality criteria are Italy and Yugoslavia. In Italy, Law 319/1976 sets the acceptable concentration for total organophosphorus pesticides in effluents to 0.1 mg l^{-1} . In Yugoslavia, all surface waters, ground waters and coastal sea areas are classified into four categories according to their intended use and degree of pollution. Category I includes waters intended for fish and shellfish cultures, category II waters are intended for bathing and recreation, category III for agriculture or fishing and category IV includes all other waters such as closed harbours. The Federal Act of 1978 on Maximum Allowable Concentrations of Radionuclides and Hazardous Chemicals in Surface and Coastal Sea Waters of Yugoslavia regulates 223 hazardous substances out of which 19 are organophosphorus compounds. The maximum permissible levels of these 19 compounds in the different waters are shown in Table XVI.

The concentrations in Table XVI are under revision and it is recommended that the total concentration of organophosphorus and carbamate insecticides should not exceed 0.0001 mg l^{-1} . For parathion the recommended value is $0.00004 \text{ mg l}^{-1}$. In some Republics of Yugoslavia the regulations are stringer. For example, the concentrations allowed in the Republic of Croatia are shown in Table XVII.

Table XVI

Maximum allowable concentrations of organophosphorus compounds in surface and coastal sea waters in Yugoslavia according to the Federal Act.

Compound name	Maximum allowable concentration, (mg l ⁻¹)	
	in surface water or coastal sea of category	
	I and II	III and IV
1. Acetophos	0.03	-
2. Diethylphosphorodithioic acid	0.1	1.0
3. Diethylchlorophosphorothioate	0.02	-
4. Dimethyl-S-ethylmercaptoethyl-phosphorodithioate	0.001	1.0
5. Potassium diethylphosphorodithioate	0.2	2.0
6. Carbofos	0.05	1.0
7. Cresyl phosphorodithioate	0.001	0.05
8. Mercaptophos	0.01	1.0
9. Metaphos	0.02	0.5
10. Methylacetophos	0.03	-
11. Methylsystox	0.03	-
12. Ethyldichlorophosphorothioate	0.02	0.02
13. Thiophos	0.003	1.0
14. Tributyl phosphate	0.01	5.0
15. Phosalone	0.0005	-
16. Phosbutyl	0.03	-
17. Phosphamid	0.03	1.0
18. Chlorophos	0.05	10.0
19. Potassium diisopropylphosphorodithioate	0.02	1.0

Regulations also exist in some countries outside the region. In the USSR and Sweden the maximum allowable concentration of parathion in surface waters is 3 $\mu\text{g l}^{-1}$. In Mexico it is 100 $\mu\text{g l}^{-1}$ in estuaries and 1 $\mu\text{g l}^{-1}$ in coastal waters. In the U.S.A., the Environmental Protection Agency has set water quality criteria for the protection of freshwater and marine aquatic biota at 0.05 $\mu\text{g l}^{-1}$ for parathion, 0.1 $\mu\text{g l}^{-1}$ for malathion, 0.01 $\mu\text{g l}^{-1}$ for azinphos-methyl and 0.1 $\mu\text{g l}^{-1}$ for demeton. In the USSR the maximum allowable surface water concentration is 50 $\mu\text{g l}^{-1}$ for malathion and 250 $\mu\text{g l}^{-1}$ for fenitrothion.

In the U.S.A. the emission limits are regulated for hazardous substances by the Water Pollution Control Act. Thus, the discharge of parathion-methyl from any point source into USA waters requires a permit. Inspection, monitoring, and reporting requirements are specified after issue of permit. Even if it is not stated in the permit, discharge of the substance must be reported when it exceeds the highest of the following levels: (a) 100 $\mu\text{g l}^{-1}$, (b) 5 times the maximum concentration established by EPA.

Table XVII

Maximum allowable concentrations of organophosphorus compounds in surface and coastal sea waters in the Republic of Croatia according to the Republican Act.

Compound name	Maximum allowable concentration, ($\mu\text{g l}^{-1}$)				
	category	surface water		coastal sea	
		I/II	III/IV	I/II	III/IV
Carbofos (Malathion)		0.1	1.0	0.1	1.0
Mercaptophos (Demeton)		0.1	1.0	0.1	1.0
Thiophos (Parathion)		0.04	0.4	0.04	0.4
Total organophosphorus and carbamate insecticides		0.1	1.0	0.1	1.0

Phosphate, inorganic (as P)		100	100	25	25

Tributylphosphate		10	100	10	100

It is obligatory that owners/operators of vessels or offshore facilities should notify the USA government of any discharge of parathion, parathion-methyl and malathion in or on navigable waters adjoining shorelines or the contiguous zone. Discharges of more than 45.4 kg (100 pounds) parathion-methyl, 4.5 kg (10 pounds) malathion and 0.45 kg (1 pound) parathion in any 24 hour period are considered as violation of the Federal Water Pollution Control Act.

Other international regulations deal with allowable concentrations in the working atmosphere and in foodstuffs. In the Netherlands and the Federal Republic of Germany maximum residue levels in vegetable and fruit are 0.05 mg kg^{-1} for fenitrothion and parathion, 0.1 mg kg^{-1} for parathion-methyl and 0.5 mg kg^{-1} for malathion.

In 1982, EEC prepared a list of 129 potentially dangerous substances based on their toxicity, persistence and bioaccumulation. This is in fact List I of the Annex to Directive 76/464/EEC. In February 1990 the Commission proposed to the Council that priority should be given to some of these substances for the purpose of fixing limit values and quality objectives. Among them are the following organophosphorus compounds: azinphos-methyl, azinphos-ethyl, fenitrothion, fenthion, malathion, parathion, parathion-methyl and dichlorvos.

The Final Declaration of the Third International Conference on the Protection of the North Sea (The Hague, 7-8 March 1990) includes a comprehensive set of common actions for the protection of the North Sea which have been adopted by the participants. In the section of "Inputs of Hazardous Substances" they agreed to achieve a significant reduction (of 50% or more) of:

- inputs via rivers and estuaries between 1985 and 1995 for each of the substances in Annex 1A part (a); and
- atmospheric emissions by 1995 or 1999 at the latest of the substances specified in the same Annex above

The Annex in question includes 36 substances termed as "priority hazardous substances" of which 8 are organophosphorus pesticides. These are: azinphos-ethyl, azinphos-methyl, fenitrothion, fenthion, malathion, parathion, parathion-methyl and dichlorvos.

In addition, the Final Declaration includes 14 examples of measures to reduce inputs of pesticides. These vary from the promotion of non-chemical means of pest control to education of farmers and regulations for their use.

7. RATIONALE FOR ESTABLISHING MARINE POLLUTION CONTROL MEASURES IN THE MEDITERRANEAN REGION

The scientific rationale for control depends on whether (a) the levels actually encountered in the marine environment are close to those which are likely to prove harmful to the ecosystem or cause adverse effects in man through any exposure route; (b) harmful levels may eventually be reached if inputs are not controlled.

A definite answer to the above questions cannot be given since there are many uncertainties involved. Firstly, the information about the levels in the marine environment is very limited; information mostly concerns the water column and comes from hot-spot areas. Secondly, the NOEL's are usually extrapolated from acute toxicity values on single species and this exercise has been seriously criticised by many scientists (see Johnston and MacGarvin, 1989). Thirdly, there is complete lack of information on certain important issues such as the aerial inputs and the surface microlayer.

It is evident, however, that freshwater systems are exposed to a greater danger than marine ones as far as organophosphorus pesticides are concerned, and this is reflected in the fact that scientific work has concentrated largely on freshwater systems. Concentrations reported, usually refer to lakes and rivers and even toxicological data refer mostly to fresh water species.

Organophosphorus pesticides are considered to be generally biodegradable and are therefore expected to degrade to a large extent before reaching the marine environment. This is not necessarily the case when these and non-pesticide compounds are discharged directly into the marine environment from point sources.

The MED POL pilot study indicated that organophosphorus compounds can be detected in the marine environment and especially the non-pesticide ones. In Spain, organophosphorus pesticides were also detected in fish. However, the concentrations were small and it is considered that they would not present a hazard to human health through the marine food chain. It is not therefore necessary to recommend at this stage, any measures specifically aimed at protecting human health.

Concentrations in rivers range from non-detectable to $5 \mu\text{g l}^{-1}$ while in coastal sea areas they are usually much lower and in hot-spot areas (as shown by the MED POL study) they may reach high values approaching $1\ 000 \text{ ng l}^{-1}$.

The lowest concentration of certain organophosphorus compounds found to cause damage to crustaceans, which is the most sensitive group of marine organisms to these compounds, is less than 100 ng l^{-1} . If Environmental Quality Objectives (EQOs) were to be set a safety factor of 10 would have been used. In fact, given our current knowledge on this group of chemicals it is simply not possible to set EQOs or to reliably enforce them.

This document does not show convincingly that organophosphorus compounds are a hazard to marine life or human health but equally so it does not show that they are environmentally benign. On the contrary, some of them are very toxic and there are indications that they could be harmful to marine life. In fact, this is an area where the precautionary action approach should be applied. This approach was adopted by the Sixth Meeting of the Contracting Parties to the Barcelona Convention (Athens, 3-6 October 1989).

8. REFERENCES

- Abdel-Gawaad, A.A. (1990), Ecotoxicological impact of organophosphorus pesticides in Egypt, Report prepared for Greenpeace International, 6 p.
- Albanis, T.R., P.J. Pomonis and A.Th. Sdoukos (1986), Organophosphorus and carbamate pesticide residues in the aquatic system of Ioannina basin and Kalamas river (Greece), Chemosphere, 15:1023-1034.
- Albright, L.J. (1980), Photosynthetic activities of phyto neuston and photoplankton. Can.J.Microbiol., 26:389-392.
- Baldi, M., A. Bovolenta, L. Penazzi, A. Fantini e D. Finessi (1986), Residui di organoclorurati e di organofosforati in acque superficiali della provincia di Ferrara. Dieci anni di indagini: 1975-1984, Boll.Chim.Igien., 37:449-480.
- Barceló, D. (1988), Application of thermospray liquid chromatography-mass spectrometry for determination of organophosphorus pesticides and trialkyl and triaryl phosphates, Biomed. Environ. Mass.Spectrom., 17:363-369.
- Barceló, D. (1988a), A review of liquid chromatography in environmental pesticide analysis, Chromatographia, 25:928-936.

- Barceló, D., F.A. Maris, R.B. Geerdink, R.W. Frei, G.J. De Jong and U.A.Th. Brinkman (1987), Comparison between positive, negative and chloride-enhanced negative chemical ionization of organophosphorus pesticides in on-line liquid chromatography-mass spectrometry, J.Chromatogr., 394:65-76.
- Barceló, D., C.Porte, J. Cid and J. Albaigés (1990), Determination of organophosphorus compounds in coastal environments by gas chromatography nitrogen phosphorus and main spectrometric detection. Intern.J. Environ. Anal. Chem. 38:199-209.
- Besri, M., N. Chtaina and A. Dahchour (1990), Les pesticides organophosphorés au Maroc, Report prepared for Greenpeace International, 21 p.
- Boethling, R.S. and J.C. Cooper (1985), Environmental fate and effects of triaryl and tri-alkyl/aryl phosphate esters, Residue Reviews, 94:49-99.
- Borthwick, P.W., J.M.Jr Patrick and D.P. Middaugh (1985), Comparative acute sensitivities of early life stages of Atherinid fishes to chlorpyrifos and thiobencarb. Arch. Environ. Contam. Toxicol., 14:465-473.
- Bouguerra, M.L. (1990), Figures on insecticide trade in Tunisia, Report prepared for Greenpeace International, 14 p.
- Bowman, B.T. and W.W. Sans, (1983), Determination of octanol-water partition coefficients (Kow) of 61 organophosphorus and carbamate insecticides and their relationship to respective water solubility (S) values, J. Environ. Sci. Health, B18(6):667-683.
- Cairns, J. (1984), Are single species toxicity tests alone adequate for estimating environmental hazard? Environ. Monit. Assess., 4:259-273.
- Cairns, J. (1989), Applied ecotoxicology and methodology, In Aquatic ecotoxicology: Fundamental concepts and methodologies, edited by A. Boudou and F. Ribeyre, Boca Raton, Florida, U.S.A., CRC Press, Inc. pp.275-290.
- Cairns, Th., E.G. Siegmund, R.A. Jacobson, T. Bang, G. Petzinger, W. Morris and D. Heikes (1983), Application of mass spectrometry in the regulatory analysis of pesticides and industrial chemicals in food and feed commodities, Biomed. Mass. Spectrom., 10:301-315.
- Cairns, Th., E.G. Siegmund and J.E. Froberg (1985), Identification of Diazinon and its metabolites in spinach by chemical ionization mass spectrometry, Bull. Environ. Contam. Toxicol., 35:291-295.
- Carrasco, J.M. M. Planta, V. Gomez-Casals and V. Moragues (1987), Pesticide residues in lake Albufera, Valencia, Spain, J. Assoc. Off. Anal. Chem., 70:752-753.

- Clark, G.J. A.R. Goodin and J.W. Smiley (1985), Comparison of ultraviolet and reductive amperometric detection for determination of ethyl and methyl parathion in green vegetables and surface water using high-performance liquid chromatography, Anal.Chem., 52:2223.
- Clayton, G.D. and F.E. Clayton eds, (1981), *Patty's Industrial Hygiene and Toxicology*. J. Wiley & Sons, New York. vol. 2. pp.2359-2383, 4801-4843.
- D'Agostino, P.A. and L.R. Provost (1986), Capillary column ammonia chemical ionization mass spectrometry of organophosphorus chemical warfare agents and simulants, Biomed.Mass.Spectrom., 13:231-236.
- Dreisbach, R.H. and W.O. Robertson (1987), *Handbook of Poisoning*. 12th edition. Appleton & Lange, Norwalk, Connecticut. pp.110-118.
- Drevenkar, V., Z. Fröbe, B. Stengl, and B. Tkalcevic (1986), Orchard spraying with organophosphorus pesticides: Occurrence and fate of parent compounds and phosphorus containing hydrolytic products in adjacent ponds. In *Organic micropollutants in the aquatic environment*, Proceedings of the Fourth European Symposium, Vienna 1985, Commission of the European Communities, edited by G. Angeletti and A. Bjorrseth, Dordrecht 1986, D. Reidel Pub.Comp., pp.342-348.
- Durand, G., R. Furteza and D. Barceló (1989), Determination of chlorotriazines and organophosphorus pesticides in soil samples by two different clean-up methods. Chromatographia, 28:597-604.
- E.C.D.I.N. Service (CEC, Joint Research Centre, Ispra), Italy.
- Farran, A., J. De Pablo and D. Barceló (1988), Identification of organophosphorus insecticides and their hydrolysis products by liquid chromatography in combination with UV and thermospray-mass spectrometry detection, J.Chromatogr., 455:163-172.
- FAO/UNEP/IAEA/WHO (1987), Report of the FAO/UNEP/IAEA/WHO Ad-hoc Meeting on Organophosphorus compounds (Athens, 18-20 November 1987). Document FAO/OP/4 14p. (mimeo).
- FAO/UNEP/IAEA/WHO (1989), Report of the FAO/UNEP/IAEA/WHO Review Meeting on the Organophosphorus Pilot Survey (Barcelona, 24-26 January 1989), Document FIR/MEDPOL/OP/5, 29 p.(mimeo).
- Fisher, S.W. and T.W. Lohner (1987), Changes in the aqueous behavior of parathion under varying conditions of pH. Arch. Environ. Contam. Toxicol., 16:79-84.
- Fröbe, Z. and V. Drevenkar (1991), Production, consumption, available data on presence in waters, and legislative measures for the control of organophosphorus compounds in Yugoslavia. Report of the Institute for Medical Research and Occupational Health, University of Zagreb, Laboratory of Organic Analytical Chemistry, 33 p.

- Galazzi, S., I. Camoni, V. Leoni, A. Liberatori and L. Viganò (1986), Gruppo 5: pesticidi clorurati e fosforati, Convegno per la revisione dei limiti della legge 319 per gli scarichi in acque superficiali, Roma.
- Gallo, M.A. and N.J. Lawryk (1991), Organic Phosphorus pesticides. In Handbook of pesticide toxicology, edited by W.J. Hayes and E.R. Laws, Vol. 2: Classes of pesticides. New York, Academic Press Inc. pp.917-1123.
- Gomez-Belinchon, J.I., J.O. Grimalt and J. Albaigés (1988), Analysis and persistence of tributyl phosphates in riverine and marine coastal waters. Chemosphere, 17:2189-2197.
- Greve, P.A. and C.E. Goewie (1985), Developments in the determination of organophosphorus pesticides, Intern.J. Environ. Anal. Chem., 20:29-39.
- Jones, A. and T.F. Zabel (1989), Information related to the first priority candidate 'red list' substances, Report PRU 2092-M of the Water Research Council, Medmenham, U.K., 49 p.
- Jones, A., S. Hedgecote and T.F. Zabel (1988), Information related to proposed 'red list' substances, Report PRU 1901-M/2 of the Water Research Council, Medmenham, U.K., 54 p.
- Johnston, P. and M. MacGarvin (1989), 0-2000: Assimilating lessons from the past, Greenpeace Paper 28, submitted at the Third North Sea Conference (The Hague, 7-8 March 1990), 32 p.
- Hutson, D.H. and T.R. Roberts (1985), Insecticides. J. Wiley & Sons, Chichester. vol. 5 pp.11-21, 64-74, 256-261.
- Kjølholt, J. (1985), Occurrence of organophosphorus compounds in polluted marine sediments near a pesticide manufacturing plant, Chemosphere, 14:1763-1770.
- Lampert, W., W. Fleckner, E. Pott, U. Schober and K.U. Störkel (1989), Herbicide effects on planktonic systems of different complexity, Hydrobiologia, 188/189:415-424.
- Latourette, H.K. (1979) in Boethling and Cooper (1985).
- Lawrence, J.F. (1987), Analytical methodology for organophosphorus pesticides used in Canada, Intern.J. Environ. Anal. Chem. 29:289-303.
- Leistra, M., L.G.M.Th. Tuinstra, A.M.M. Van Der Burg and S.J.M. Crum (1984), Contribution of leaching of diazinon, parathion, tetrachlorvinphos and trizophos from glasshouse soils to their concentration in water sources, Chemosphere, 13:403-413.
- Leoni, V. and G. Puccetti (1971), Cromatografia su strato sottile di pesticidi organo-fosforici in rapporto a studi di contaminazione ambientale (acque superficiali italiane). Il Farmaco, 7:382.

- Leoni, V. and G. Puccetti (1978), Stato di inquinamento da pesticidi del fiume Tevere e del suo bacino imbrifero. Quaderno, no.27, I.R.S.A.
- Lores, E.M., J.C. Moore and P. Moody (1987), Improved silica gel clean up method for organophosphorus pesticides, Chemosphere, 16:1065-1069.
- Mackay, D., S. Paterson, B. Cheung and W. Brock Neely (1985), Evaluating the environmental behaviour of chemicals with a level III fugacity model, Chemosphere, 14:335-374.
- Mestres, R., G. Leonardi, Ch. Chevalier and J. Tourte (1969), Pesticides residues XIX. Determining pesticide residues in natural waters. 1. General analytical methods. Ann.Fals. Exp.Chim., 62(685):75-85.
- Moody, R.P., R. Greengal, L. Lockhart and P. Weinberger (1978), The fate of fenitrothion in an aquatic ecosystem, Bull. Environ. Contam. Toxicol., 19:8-14.
- Moretto, A. and M.K. Johnson (1987), Toxicology of organophosphorus compounds and carbamates In Toxicology of pesticides: experimental, clinical and regulatory aspects, edited by L.G. Costa et al., Springer Berlin, Verlag, pp.33-48.
- Morin, R., G. Gaboury and G. Mamarbachi (1986), Fenitrothion and Aminocrab residues in water and balsam for foliage following spruce budworm spraying programs in Quebec, 1979 to 1982, Bull. Environ. Contam. Toxicol., 36:622-628.
- Muir, D.C. (1984), Phosphate esters in the handbook of environmental chemistry, ed. by O. Hutzinger, Springer-Verlag Berlin, vol. 3, part C, pp.41-66.
- Mulla, M.S., L.S. Mian and J.A. Kawechi (1981), Distribution, transport and fate of the insecticides malathion and parathion in the environment. Residue Rev., 81:1-159.
- Neicheva, R., E. Kovacheva and G. Marudov (1988), Determination of organophosphorus pesticides in apples and water by gas-liquid chromatography with electron capture detection, J.Chromatogr., 437:249-253.
- N.R.C. (1975), Associate Committee on Scientific Criteria for Environmental Quality, Fenitrothion: The effects of its use on environmental quality and its chemistry, N.R.C.C., Publication No. 14104.
- Onuska, F.I. (1984), Pesticide residue analysis by open tubular column gas chromatography: Trials, tribulations and trends, J.High Resolut. Chromatogr. Chromatogr. Comm., 7:660-670.
- Osselton, M.N.D. and R.D. Shelling (1986), Chromatographic identification of pesticides, J.Chromatogr., 368:265.

- Pellin, M., J.L. Vicedo and E. Vilanova (1987), Sensitivity to tri-o-cresylphosphate neurotoxicity on n-hexane exposed hens as a model of simultaneous hexacarbon solvent and organophosphorus occupational intoxication, Arch.Toxicol., 59:311.
- Persoone, G., P. Vanhaecke and E. Gobbers (1985), Evaluation of the impact of parathion, methyl-parathion, fenitrothion and fenthion on the aquatic environment. Report to the EEC, XI/785/83, 579 p.
- Podjelski, J. and A.M. Dervieux (1978), Persistence of four pesticides in rice field water in the Camargue; characterization of their effects on the ecosystem, Trav.Soc.Pharm.Montpellier, 38(2):153-163.
- Premazzi, G. (1983), Evaluation of the impact of malathion on the aquatic environment, EEC, Joint Research Centre, Ispra Establishment, Italy, 67 p.
- Prinsloo, S.M. and P.R. De Beer (1985), Gas chromatographic retention data for pesticides on nine packed columns: I. Organophosphorus pesticides using flame photometric detection, J.Assoc.Off. Anal.Chem., 68:1100.
- Psomas, S. (1990), Organophosphorus pesticides in Greece. Part I. Trade and use of organophosphorus pesticides, Interim Report prepared for Greenpeace International, 24 p.
- Ramade, F. (1987), Ecotoxicology. J.Wiley & Sons, Chichester. 136 p.
- Saeger, V.W., O. Hicks, R.G. Kaley, P.R. Michale, J.P. Mieure and E.S. Tucker (1979), Environmental fate of selected phosphate esters, Environ.Sci.Technol., 13:840-844.
- Sabbarhawl, A.K. and D.K. Belsare (1986), Persistence of methyl parathion in a carp rearing pond, Bull.Environ.Contam.Toxicol., 37:705-709.
- Seabloom, R.W., G.L. Pearson, L.W. Oring and J.R. Reilly (1973), An incident of fenthion mosquito control and subsequent avian mortality. J.Wildl.Dis., 9:18-20.
- SIS (1985), Water quality-determination of the inhibition of the mobility of Daphnia magna Straus (Cladocera, Crustacea), Report of the Swedish Institute for Standards, 15 p.
- Stan, H.J. and G. Kellner (1982), Negative ionization mass spectrometry of organophosphorus pesticides, Biomed.Mass. Spectrom. 9:483-492.
- UNEP (1990), Bibliography on aquatic pollution by organophosphorus compounds. MAP Technical Reports Series no.44, UNEP, Athens, 98 p.

- Vilanova, E., M.K. Johnson and J.L. Vicedo (1987), Interaction of some unsubstituted phosphoramidate analogs of methamidophos (O,S-Dimethyl Phosphrodithioamidate) with acetylcholinesterase and neuropathy target esterase of hen brain, Pestic.Biochem.Physiol., 28:224-238.
- Wang, T.C., R.A. Lenahan and J.W.Jr Tucker (1987), Deposition and persistence of aeriially-applied fenthion in a Florida estuary, Bull.Environ.Contam.Toxicol., 38:226-231.
- W.H.O. (1986), Organophosphorus insecticides: a general introduction, Environmental Health Criteria, WHO, Geneva.
- Wilkins, J.P.G., A.R.C. Hill and D.F. Lee (1985), Organophosphorus sulphides, sulphoxides and sulphones. Parts 2. Characterization by gas chromatography-mass spectrometry, Analyst, 110:1045-1051.