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REPORT OF THE FAO/UNEP/IAEA/WHO AD HOC MEETING
ON ORGANOPHOSPHORUS COMPOUNDS
(Athens, 18-20 November 1987)

In co-operation with :



FAO




IAEA



WHO

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Athens, 1988

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	ORGANISATION DES NATIONS UNIES POUR L'ALIMENTATION ET L'AGRICULTURE	
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Introduction

Organophosphorus compounds are used in large quantities in the Mediterranean region, usually for pest control but also for other purposes, and eventually they may reach the marine environment. Most of these compounds are highly toxic and some of them are relatively persistent and bioaccumulative.

Organophosphorus compounds and substances which may form such compounds in the marine environment are listed in Annex I to the Protocol for the Protection of the Mediterranean sea against Pollution from Land-based Sources which is one of the Protocols to the Convention for the Protection of the Mediterranean sea against Pollution (Barcelona Convention). According to article 5 of this Protocol

" 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 should 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".

The Contracting Parties to the Barcelona Convention agreed that the above Protocol should be implemented progressively, through a step-by-step process, according to a long-term workplan and timetable. They also decided that an assessment of the state of pollution in the Mediterranean sea should be prepared for each of the group of substances listed in Annex I to the Protocol. On the basis of such assessments control measures would be recommended. One of the objectives of the present meeting was to prepare an annotated outline for this assessment document and propose further research and monitoring work.

The meeting took place at the premises of the Coordinating Unit for the Mediterranean Action Plan in Athens, from 18-20 November 1987. It was attended by five participants from five countries and by representatives of FAO, UNEP, WHO and IAEA. A list of participants is given in Annex I.

Agenda item 1 : Opening, background and scope of the meeting

The meeting was opened by Mr G.P. Gabrielides, Senior Fishery Officer (Marine Pollution) on behalf of the Food and Agriculture Organization of the United Nations and by Mr. A. Manos, Coordinator of the Mediterranean Action Plan, on behalf of the United Nations Environment Programme. After welcoming the participants, Mr. Gabrielides explained that the meeting was convened jointly by FAO, UNEP, WHO and IAEA in the framework of the preparatory activities for the implementation of the Land-based Sources Protocol.

Organophosphorus compounds are included in Annex I to the above Protocol and, according to Article 5, the Contracting Parties shall elaborate and implement the necessary programmes and measures to eliminate pollution of the Mediterranean Sea from land-based sources by substances covered in this Annex. A document entitled "Assessment of the state of pollution of the Mediterranean Sea by organophosphorus compounds and proposed measures" should be prepared and presented to the Scientific and Technical Committee before submitting it to the Contracting Parties meeting. The main objectives of this meeting were:

- (a) to prepare an annotated outline for this assessment document;
- (b) to decide to which organophosphorus compounds the present document should refer;
- (c) to propose any further research and monitoring work;
- (d) to make any other relevant recommendations.

Mr. A. Manos after welcoming the participants, described the institutional aspect of the Mediterranean Action Plan and especially the close cooperation between the various UN agencies. Mr L. Jetic, Senior Marine Scientist, with UNEP, outlined the components of the Mediterranean Action Plan concentrating on the Long-term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL Phase II). He explained the various activities for the technical implementation of the Land-based Sources Protocol which is one of the four Protocols to the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention) and entered into force in 1983. Organophosphorus compounds are only one of the groups of substances for which an "assessment" document should be prepared, and a calendar was presented for all substances. He stressed the point that special emphasis should be given to the last section of the document, i.e. proposed measures.

Mr L.J. Saliba, Senior Scientist of the World Health Organization, outlined his Organization's involvement in the MED POL Programme and the activities relating to the technical implementation of the Land-based Sources Protocol.

Agenda item 2 : Administrative arrangements

The Group unanimously elected Mr G. Persoone as Chairperson and Mr D. Wynne as Rapporteur. Mr G.P. Gabrielides acted as Technical Secretary.

The meeting was conducted in English, and met in plenary sessions only.

The provisional agenda (Annex II) and work programme were adopted.

Agenda item 3 : List of organophosphorus compounds and substances on which the assessment should be based

After some discussion, the Working Group decided to split organophosphorus compounds into two broad groups: pesticides (including insecticides, herbicides, fungicides, etc.) and non-pesticides (alkyl, aryl and haloalkyl phosphates). This latter group is used in general as fire-retardants, metal extractants etc.

The organophosphorus compounds currently manufactured (approx. 140 pesticides and numerous non-pesticides) cover a wide range of physico-chemical properties, as well as toxicities. Because of lack of immediately available information the Working Group did not feel able to prepare a priority list. However a list of 24 organophosphorus compounds (Annex III) known to be currently used in four Mediterranean countries (France, Israel, Italy, Spain) was prepared. For practical reasons, the Working Group suggested that the assessment document should consider compounds that are used in large quantities, both in the Mediterranean region and on a global scale, are known to be very toxic to aquatic life and on which sufficient information is available. These compounds are the following:

- Pesticides: Parathion
 Methyl-parathion
 Fenithrothion
 Malathion
- Non-pesticides: Tributyl phosphate
 Tris-2-chloroethyl phosphate

Agenda item 4 : Annotated outline of the assessment document

The Working Group discussed in detail various aspects of the pollution of the Mediterranean by organophosphorus compounds. As a result the Group developed an annotated outline for the assessment document which is presented in Annex IV.

Agenda item 5 : Discussion of future work

The Working Group discussed future work and the following points were suggested:

- A. A pilot monitoring programme for organophosphorus compounds should be carried out in selected areas of the Mediterranean by laboratories with expertise in organophosphorus analyses of water, sediment and biota. The monitoring programme should include at least 4 samplings per year, preferably related to application time of organophosphorus pesticides (i.e. prior, during and after), at sites close to the biggest river inputs into the sea. A site, outside the area of potential contamination, should also be included for reference purposes.
- B. Data should be collected from the 17 Mediterranean countries on:
 - (i) the production and use of both organophosphorus pesticide and non-pesticide compounds;
 - (ii) the location of production plants and application areas;
- C. A series of methods for sampling and storage of water, sediments and biota as well as extraction and analysis of the organophosphorus compounds should be developed. Intercalibration exercises between the laboratories involved in analyses of organophosphorus compounds should be set up, by the IAEA Monaco Laboratory.

- D. A literature search should be set up, as soon as possible, to provide up to date information on the distribution pathways and fate, toxicity, persistence and bioaccumulation potential for all the organophosphorus compounds of quantitative importance in the Mediterranean, both to aquatic biota and to humans.
- E. In the absence of appropriate information, pertaining to paragraph "D" above, suitable experimental data must be generated.
- F. Predictive hazard models for those organophosphorus compounds of highest quantitative importance and highest toxicity, persistence and/or bioaccumulation potential should be set up, to determine potential risk at sites with high exposure probability.

Agenda item 6 : Rationale for the recommendation of control measures

In the opinion of the Working Group, control measures for organophosphorus compounds in the Mediterranean should be recommended for the following reasons:

- (i) The toxicity of most of these compounds, for humans and for several categories of marine biota, is high to extremely high.
- (ii) Some organophosphorus compounds are known to be relatively persistent and bioaccumulative.
- (iii) Organophosphorus compounds are currently used for pest control as well as for various other purposes in many Mediterranean countries and substantial amounts can eventually reach the marine environment.

Agenda item 7 : Recommendations

- (i) The assessment should be confined to those organophosphorus compounds which are known to be very toxic and used to a large extent in Mediterranean countries and on which information is immediately available. The assessment should at least deal with the following 6 compounds.

Pesticides: Parathion
 Methyl-parathion
 Fenithrothion
 Malathion

Non-pesticides: Tributyl phosphate
 Tris-2-chloroethyl phosphate

- (ii) The form of the assessment should follow the outline set out in Annex IV.
- (iii) A pilot monitoring programme should be carried out for at least the 6 compounds given above in selected areas of the Mediterranean.

- (iv) Standard methodologies should be worked out for sampling and storage of water, sediment and biota, and for the subsequent extraction and analysis of the compounds from such samples.
- (v) An intercalibration exercise should be conducted on reference samples of marine waters, sediment and biota for these compounds.
- (vi) Information should be collected from each Mediterranean country on the production and use of organophosphorus compounds currently used.
- (vii) World literature should be searched for data on the physico-chemical characteristics, distribution pathways, toxicity, persistence and bioaccumulation potential of organophosphorus compounds which are, or are expected to be, used extensively in Mediterranean countries in the future. In the absence of such information, the relevant data should be generated.
- (viii) A case to case predictive hazard evaluation for some organophosphorus compounds which will not be considered in the assessment document should be made for specific sites which may be at risk.
- (ix) The Group recommends that control measures be taken on organophosphorus compounds based on the rationale explained above.
- (x) Although specific control measures for organophosphorus compounds in the Mediterranean could not be recommended by the Group, the following measures are proposed for consideration:
 - (a) The adoption of common Mediterranean water quality objectives and emission standards;
 - (b) The performance of regular monitoring of water, sediment and biota in high risk areas;
 - (c) Governmental control on the emission standards for both production and treatment plants in coastal areas of the Mediterranean;
 - (d) Governmental control of the purchase and spraying quotas for specific organophosphorus pesticides in areas from which Mediterranean waters can be contaminated directly or indirectly.
 - (e) Education and training as well as extension service programmes should be set up in the Mediterranean countries for the appropriate use of organophosphorus compounds.

Agenda item 8: Adoption of the report and closure of the meeting

The report was adopted unanimously and the Chairperson closed the meeting at 14:00 on Friday 20 November 1987.

ANNEX I

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ANNEX II

AGENDA

1. Opening, background and scope of the meeting
2. Administrative arrangements
3. List of organophosphorus compounds and substances on which the assessment should be based
4. Annotated outline of the assessment document
5. Discussion on future work
6. Rationale for the recommendation of control measures
7. Recommendations
8. Adoption of the report and closure of the meeting

ANNEX III

LIST OF ORGANOPHOSPHORUS COMPOUNDS CURRENTLY
USED IN FRANCE, ISRAEL, ITALY AND SPAIN

a) pesticides

- | | |
|-------------------|---------------------|
| - azinphos-ethyl | - mevinphos |
| - azinphos-methyl | - monocrotophos |
| - chlorpyrifos | - parathion |
| - diazinon | - parathion-methyl |
| - dichlorvos | - phorate |
| - diethion | - phosphamidon |
| - dimethoate | - pirimiphos-methyl |
| - ethion | - prothoate |
| - fenitrothion | - tetrachlorvinphos |
| - malathion | - trichlorphon |
| - methidathion | - vamidothion |

b) non-pesticides

- tributyl phosphate
- tris-2-chloroethyl phosphate

ANNEX IV

ANNOTATED OUTLINE OF THE ASSESSMENT DOCUMENT ON ORGANOPHOSPHORUS COMPOUNDS

1. Introduction

- Historical background.
- General facts on organophosphorus compounds, including mode of action, commercial formulations and names.
- Classification according to use, i.e. pesticides and non-pesticides.
- Total amounts of organophosphorus pesticides produced and used in the Mediterranean and at world level, compared with other categories of pesticides.
- General trends in production and use.
- Variability in physico-chemical characteristics and, as a result, in the hazard to the environment and man.
- List of organophosphorus compounds currently manufactured (both pesticides and non-pesticides).

2. Selection of organophosphorus compounds of concern to the Mediterranean

- A priority list of these chemicals based on:
 - (i) quantities currently produced and/or used in large amounts in Mediterranean countries; and
 - (ii) the toxicity of each compound, as well as persistence and bioaccumulation potential.
- Justification of restricting of the assessment document to certain compounds of the priority list.

3. Sources and inputs into the Mediterranean

- Available information on point source and non-point source inputs of priority compounds including industrial and municipal discharges as well as industrial and agricultural uses.
- Comparison of sources and inputs into the Mediterranean with other regions.

4. Environmental distribution, pathways and fate

- Variability in physico-chemical characteristics (solubility, vapour pressure and molecular weight), which result in differences in pathways of environmental distribution, accumulation and degradation.
- Characteristics of distribution, bioaccumulation potential and persistence (abiotic-biotic degradation; half-lives) for the compounds chosen.
- Levels of these compounds in Mediterranean waters, sediment and biota. Comparison with data from sites outside the Mediterranean. Data reliability.

5. Effects on marine biota and ecosystems

- Mechanisms of toxicity of organophosphorus compounds (mode of action).
- Lethal, sublethal and no-effect levels of the compounds for various categories of marine biota emphasizing the influence on toxicity of various commercial formulations.
- Mutagenic, teratogenic and carcinogenic potential.
- Field studies and effects at the ecosystem level.

6. Human exposure

- Mode of action, toxicity and metabolic pathways in humans for organophosphorus compounds in general, and the compounds selected in particular.
- Major human uptake as related to occupational exposure (inhalation, dermal contact, ingestion).

7. Hazard assessment to marine biota and humans

- Types of marine areas at risk by contamination from organophosphorus discharges, such as river mouths and estuaries, lagoons and shallow waters, and marshes.
- Actual levels of compounds chosen in the Mediterranean. Comparison with experimental figures and calculated no-effect levels to extrapolate the present degree of hazard to aquatic biota.
- Hazard to humans through contact with polluted water or ingestion of contaminated seafood.

8. Existing national and international provisions for the prevention of marine pollution

- Review existing regulations on organophosphorus compounds in Mediterranean and other countries.

9. Rationale for establishing control measures in the Mediterranean region

- The rationale will be based on:
 - (i) toxicity levels (acute and chronic) and available no-effect levels (experimental or calculated) for the compounds chosen;
 - (ii) quality objectives derived from the above;
 - (iii) feasibility of monitoring quality objective levels in the areas of concern.
- Guidance to Mediterranean countries on emission standards for point source inputs located near the coastal region (treatment plants and production units).
- Calculation of such emission standards for the compounds chosen on the basis of water quality objectives and assuming an appropriate dilution factor.
- Regulatory actions for non-point source pollution.

10. Proposed measures

- Adoption of water quality objectives and emission standards.
- Governmental control of emission standards in coastal production and treatment plants.
- Regular monitoring of water, sediment and biota in risk areas.
- Governmental setting and control of application quotas for organophosphorus pesticides.
- Adequate education, training and extension services for the appropriate use of organophosphorus pesticides.

11. References