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	<b>ORGANISATION DES NATIONS UNIES POUR L'ALIMENTATION ET L'AGRICULTURE</b>	
	<b>ORGANIZACION DE LAS NACIONES UNIDAS PARA LA AGRICULTURA Y LA ALIMENTACION</b>	

**REPORT OF THE FAO/UNEP/IAEA/WEO AD-HOC MEETING**

**ON ORGANOTIN COMPOUNDS**

**Athens, 5-7 October 1987**

In cooperation with:



UNEP



IAEA



WEO

F A O

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## BACKGROUND

Attention has focussed recently on the increasing use of organotin compounds - in particular tributyl tin - as the active biocidal agents in antifouling paints. Concern over the effects of TBT first arose in France, where severe problems were encountered in commercial oyster fisheries in areas where there was intense boating activity and relatively poor water exchange. The French Government in 1982, was the first to take action against the use of organotin compounds. Studies in the U.K. has led the Government to take similar action. It is likely that the European Commission will propose similar measures for the EEC countries.

Organotin 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 of the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention). According to article 5 of the Protocol which entered into force in 1983,

" 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".

According to a decision of the Contracting Parties to the Barcelona Convention, the Secretariat is responsible for preparing an assessment of the state of pollution by these substances highlighting the problems and recommending, if necessary, specific measures to be undertaken by the Parties.

The assessment will include inter alia chapters on sources and inputs, levels in the various compartments of the marine environment, effects on marine biota and humans and present legal and administrative measures at national and international level.

The present meeting was expected to review the presently available information on the above topics, pin-point gaps, decide on the specific organotin compounds to which immediate attention should be given and recommend a programme of action which would include among other things

- a) proposals for immediate undertaking of control measures,
- b) proposals for further research and monitoring work.

The meeting took place in Athens on 5-7 October, 1987 at the Coordinating Unit for the Mediterranean Action Plan. It was attended by six participants from five countries together with representatives from FAO, UNEP and IAEA. A list of participants is given in Annex I.

### 1. OPENING OF THE MEETING

The meeting was opened by Mr. G.P. Gabrielides, Senior Fishery Officer (Marine Pollution) on behalf of the Food and Agriculture Organisation of the United Nations. He welcomed the participants and expressed his wishes for the success of the meeting. Mr. A. Manos, Coordinator of the Mediterranean Action Plan, welcomed the participants on behalf of the United Nations Environment Programme and described the close relationship between various UN agencies, particularly FAO and UNEP, within the Action Plan. He described the work of the Unit in the context of the Barcelona Convention and its related protocols especially the Land-based Sources Protocol; a new action plan had been recently agreed and so the Unit had both a mandate and a time table to propose measures to control the inputs of substances listed in Annexes I and II of the above protocol.

### 2. SCOPE AND PURPOSE OF THE MEETING

Mr. G.P. Gabrielides outlined the reasons for calling this ad-hoc meeting. Organotin compounds are listed in Annex I to the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-based Sources. Therefore, a review has to be prepared of the existing information on their use, environmental concentrations and harmful properties as for other Annex I substances. Based on this review a set of recommendations will be made for monitoring, research and regulatory action. These recommendations have to be firmly based on the scientific evidence available. Mr. L. Jetic, Senior Marine Scientist, UNEP, outlined the timetable for the review of Annex I substances. A review of significant organotin compounds could be put before a meeting of the Scientific and Technical Committee in 1988 for consideration at the meeting of the Contracting Parties of the Convention for the Protection of the Mediterranean Sea against Pollution in 1989. In the meantime funds were available for a limited monitoring and research programme during 1988.

### 3. ELECTION OF OFFICERS

The meeting unanimously elected Mr. T. Balkas, Chairman, Mr. C. Alzieu, Vice-Chairman and Mr. R. Lloyd, Rapporteur. Mr. G.P. Gabrielides acted as Technical Secretary.

### 4. ADOPTION OF THE AGENDA

The provisional agenda was unanimously adopted and appears as Annex II.

### 5. ORGANISATION OF WORK

As this was an ad-hoc Group with limited membership, it would meet in Plenary Session only. The Chairman and Technical Secretary explained the order in which the agreed programme of work would be carried out.

## 6. STATUS OF PRESENT KNOWLEDGE

The primary function of the Working Group was to discuss the extent of the information available on the impact of organotin compounds on the marine environment and to focus on those immediate problems which required priority review. A paper "Organotin compounds in the Mediterranean: Research needs for the evaluation of inputs, fate and effects of ecological relevance" by Mr. E. Bacci had been circulated to participants and formed the basis of a general discussion on the potential importance of tributyltin compounds in the marine environment. In presenting this paper, Mr. Bacci stressed the importance of the need for such a risk assessment for these organotin compounds.

The Working Group reviewed the information available on the ecotoxicological properties of organotin compounds, reinforced by theoretical models based on their quantitative structure activity relationships and concluded that, in the context of marine pollution, the use of triphenyltin and tributyltin incorporated into antifoulants represented the greatest potential threat to living resources in the sea. Therefore, the assessment document should focus on the environmental distribution and the physical, chemical and ecotoxicological properties of these two compounds, to form a scientific basis for possible control measures.

A general discussion followed on the general format required for a review of triorganotin compounds, and the Assessment of the State of Pollution of the Mediterranean Sea by Mercury and Mercury Compounds and Proposed Measures (UNEP/WG.160/8) was used as a model for guidance. However, the particular nature of the problems posed by triorganotin compounds required a specific format for the logical presentation of data, and an outline was prepared and subsequently expanded in an annotated form as shown in Annex III to give guidance to the consultant who will be ultimately commissioned to prepare a draft assessment.

## 7. DISCUSSION ON FUTURE WORK

The Working Group then turned its attention towards the actions required in the immediate future. The primary requirement was the provision of data on existing levels of triorganotin compounds in Mediterranean locations where "hot spots" were likely to be present, such as marinas, harbours, etc. Although it was recognised that there were disadvantages in limiting the survey to measurements of concentrations in sea water, there were analytical problems in measuring the levels of relevant organotin species in sediment and animal tissue. Also, much of the existing data on levels of organotin in areas outside the Mediterranean related to concentrations in water. Therefore, as a first step, two or more laboratories chosen for their geographical location and known analytical competence should undertake a survey of tributyltin and possibly triphenyltin in selected locations where "hot spots" could be predicted to occur. It was agreed that intercalibration between the laboratories would be difficult; therefore each laboratory would be free to use their analytical method of choice, provided that the limit of detection was not greater than 20 ng l<sup>-1</sup> TBT. A possible solution to determine the comparability of results would be to organise a Workshop at one laboratory where the different analytical techniques could be used on common water samples and the results compared.

When the results of this survey are available, decisions can be made on the need for further monitoring; for example, to measure trends of concentration in "hot spot" areas which may occur as result of regulatory measures to control triorganotin inputs.

In the meantime, it was important to develop appropriate analytical techniques to measure organotin compounds in sediments and biota. Also, there were several significant gaps in the information necessary to make an assessment of the risk which organotin compounds present, which required research. A number of possible research projects were discussed and the following subject areas were agreed by the Working Group as being the most important:

- (i) Evaluation of the existing analytical techniques, for sea-water analysis and their improvement to detect and quantify a wide range of organotin compounds and their degradation products in water, sediments, biota and eventually air. The development of a widely applicable reference method for TBT, TPT and derivatives in water, sediments and biota should be one important goal of this investigation.
- (ii) Improvement in the basic knowledge of the marine chemistry of organotin compounds. The suite of contaminant compounds, and the kinetics of transformation of one compound to another, should be determined (in simulated environmental conditions). The physico-chemical properties of the compounds, particularly TBT and derivatives, should be measured or calculated. Such properties include speciation (and relevant stability constants), solubility (and colligative properties) and partition coefficients (e.g. sediments/water).
- (iii) Evaluation of the tolerance of known sensitive marine organisms (e.g. molluscs) in Mediterranean polluted environments or in their absence, identification of other sensitive organisms in which sub-lethal effects can be produced by exposure to organotin compounds at the 10-50 ng l<sup>-1</sup> level in both laboratory and field conditions.
- (iv) Reviewing the knowledge available on the degradation mechanisms of TBT and TPT in water, sediment and biota, the Group recognized a lack of relevant information. It was noted that Mediterranean areas present a specific oceanographic condition in regard to the parameters which influence the persistence of the organotins in marine environment, such as water exchange, load of suspended solids, sun irradiation etc.

The Group felt that it was necessary to develop particular studies, both in the field and in the laboratory, in order to assess the degradability of TBT and TPT under specific Mediterranean conditions.

Apart from chemical surveys and monitoring, attention should be given to biological surveys of those areas where high concentrations of triorganotin are suspected or known. Although it might be difficult to show that an altered community structure was caused specifically by antifouling compounds, the absence of certain species which would be expected to be present, or abnormalities in individual organisms, will provide an indication of possible sensitive organisms. Such organisms can then be tested under laboratory conditions to confirm their sensitivity to triorganotin compounds. It should be emphasized that research such as that outlined in para 3 above should be fully supported by chemical analysis of triorganotin concentrations in the water used for exposing the test organisms, as well as measurement of organotin in the tissues.

## 8. RATIONALE FOR THE CONTROL OF TRIORGANOTIN COMPOUNDS

It was recognised that it would be very difficult to control the levels of triorganotin compounds in the marine environment by means of environmental quality standards. Also, because of the diffuse nature of the inputs, the use of fixed emission standards was impossible. Therefore, controls could only be set on the usage of these chemicals.

The Working Group agreed that, as a first step, the use of antifouling paints containing triorganotin biocides should be banned on boats of less than 25m in length. Also, such paints which are formulated for use on larger vessels should be formulated in such a way as to minimise the rate of release of TBT or TPT into the surrounding water; a ban may have to be imposed on the use of "free association" paints.

For those boats which are allowed to be painted with triorganotin antifouling paints, a code of practice should be prepared to minimise the risk of environmental contamination arising from the scraping of old paint, spillage of new paint and the disposal of paint containers.

The use of triorganotin compounds in antifouling coatings used in mariculture should not be allowed.

The extent to which organotin compounds are used as antifoulants in the cooling water systems of power stations needs further investigation; such usage should not be allowed if alternative, environmentally acceptable, biocides are available.

## 9. RECOMMENDATIONS

1. The assessment should be confined to tributyltin and triphenyltin, their derivatives and their breakdown products.
2. The form of the assessment should follow the guidelines given in Annex III.
3. A survey should be carried out on organotin concentrations in selected areas of the Mediterranean.
4. Research should be focused on analytical techniques, physicochemical properties and ecotoxicity for triorganotin compounds, their derivatives and their breakdown products.
5. The control of triorganotin compounds in the marine environment could be accomplished by:
  - a) a ban on the use of antifouling paints containing triorganotin on boats of less than 25 metres length,
  - b) a ban on the use of antifouling coatings containing triorganotin on structures associated with mariculture,
  - c) a ban on the use of free association paints containing triorganotin on boats greater than 25 metres in length,

- d) the issue of a code of practice to minimise the contamination of the marine environment in the vicinity of boat yards, dry docks etc. where ships are cleaned of old antifouling paint and subsequently repainted,
- e) the development of alternative, environmentally acceptable, antifouling paints and coatings.



ANNEX I

LIST OF PARTICIPANTS

1. C. ALZIEU  
IFREMER  
Centre de Nantes  
BP 1049  
Rue de l'Ile d'Yeu  
44037 Nantes Cedex 01  
FRANCE  
  
Tel. 40374100  
Telex 711196
  
2. E. BACCI  
Dipartimento di Biologia Ambientale  
University of Siena  
Via delle Cerchia 3  
53100 Siena  
ITALY  
  
Tel. 0577-288428  
Telex 572459 UNIV SI
  
3. T. BALKAS  
Chairman of the Department of  
Environmental Engineering  
Middle East Technical University  
Ankara  
TURKEY  
  
Tel. 2237100, ext. 2641  
Telex 42761
  
4. Jeanne CASTRITSI-CATHARIOS  
Zoological Laboratory  
University of Athens  
Panepistimiopolis  
157 84 Athens  
GREECE  
  
Tel. 7243244

6. R. LLOYD  
Ministry of Agriculture, Fisheries and Food  
Fisheries Laboratory  
Remembrance Avenue  
Burnham-on-Crouch  
Essex CM0 8HA  
UNITED KINGDOM

Tel. 621-782658  
Telex 995543 FSHBUR

7. V. MINGANTI  
Istituto di Chimica Generale  
Università di Genova  
Viale Benedetto XV-3  
16132 Genova  
ITALY

Tel. 515070  
Telex 271114 UNIVGE I

UN ORGANISATIONS

UNITED NATIONS  
ENVIRONMENT PROGRAMME

L. JEFTIC  
Senior Marine Scientist  
United Nations Environment Programme  
Co-ordinating Unit for the Mediterranean  
Action Plan  
P.O. Box 18019  
Vas. Konstantinou 48  
GR 116 10 Athens  
GREECE

Tel. 7244536  
Telex 222611 MEDU GR

S.F. CIVILI  
Marine Scientist  
United Nations Environment Programme  
Co-ordinating Unit for the Mediterranean  
Action Plan  
P.O. Box 18019  
Vas. Konstantinou 48  
GR 116 10 Athens  
GREECE

Tel. 7244536  
Telex 222611 MEDU GR

FOOD AND AGRICULTURE  
ORGANISATION OF THE  
UNITED NATIONS

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

Tel. 7244536  
Telex 222611 MEDU GR

WORLD HEALTH  
ORGANISATION

L.J. SALIBA  
Senior Scientist  
WHO/EURO Project Office  
Co-ordinating Unit for the Mediterranean  
Action Plan  
P.O. Box 18019  
Vas. Konstantinou 48  
GR 116 10 Athens  
GREECE

Tel. 7244536  
Telex 222611 MEDU GR

INTERNATIONAL ATOMIC  
ENERGY AGENCY

L.D. MEE  
Head-Marine Environmental Studies  
Laboratory  
International Atomic Energy Agency  
International Laboratory of Marine  
Radioactivity  
Musée Océanographique  
98000 MONACO

Tel. (93) 301514  
Telex 479378 ILMR

ANNEX II

AGENDA

1. Opening of the meeting
2. Background and scope
3. Election of officers
4. Adoption of the agenda
5. Organization of work
6. Status of present knowledge  
(methodology, levels, toxicology)
7. Scientific rationale for control measures
8. Recommendations for future work
9. Adoption of the report
10. Closure of the meeting

### ANNEX III

#### ANNOTATED OUTLINE OF THE ASSESSMENT DOCUMENT ON ORGANOTIN COMPOUNDS

##### 1) Introduction

Historical background

##### 2) Harmful organotin compounds

This section will provide the justification for the limitation of the assessment to tributyl (TBT) and triphenyltin (TPT). The use of these compounds in antifouling paints is considered to be the most harmful source of organotins in the marine environment.

The environmental behaviour, the use patterns, and the toxicological properties of the degradation products of TBT and TPT will be taken into consideration.

Comparisons with other organotin compounds will be given.

##### 3) Sources and inputs into the Mediterranean

General information should be given on the use of TBT and TPT as a wood preservative, as an antifoulant in power station cooling water, and as antifouling paints for boats and ships, and mariculture structures. Of these, the use as an antifouling paint is the major source of contamination of the marine environment.

Data should be given, if possible, on the quantity of antifouling paint (and its TBT and TPT content) used in the Mediterranean. Use on small boats and large ships lead to a generally diffuse input which can be localised in marinas, moorings and harbours.

Models should be described for calculating TBT diffusion from painted surfaces into the water. A distinction may be drawn between small boats which are repainted at frequent intervals, and large boats which are painted less frequently.

Other sources are local inputs where boats are cleaned before repainting, and dry docks, where old paint is removed in particulate form which can then contaminate sediments in the area. Also, disposal of unused or spilt paint, and old containers, may form localised inputs.

The use of TBT coatings on mariculture structures may form a minor input, which may be important if the cultivated species accumulate organotin compounds.

##### 4) Environmental distribution, pathways and fate

This section will describe the marine chemistry of TBT and TPT and their physico-chemical properties and will provide information on the environmental distribution, pathways and fate of selected organotin compounds (e.g. TBT and its derivatives).

A subsection will be devoted to quality assurance, data validation and intercalibration.

Levels of selected organotin compounds in the World Oceans in general, and in the Mediterranean Sea in particular, will be the subject of another subsection. In this subsection levels of selected organotin compounds found in estuarine water, sea water, marine biota and sediments will be compiled and discussed.

Persistence and fate of the selected organotin compounds will be dealt with, and special emphasis will be given to abiotic degradation.

Distribution and transformation of selected organotin compounds in marine biota will be discussed in relation to algae, fungi, bacteria and animals taking into consideration the uptake, metabolism and elimination processes.

If feasible, theoretical models describing biogeochemical cycles of selected organotin compounds will be given.

#### 5) Human exposure

The animal toxicity data base to assess potential human toxicity is highly deficient for all TBT compounds under review although there are some useful studies particularly with tributyltin oxide. The available information (obtained mostly with tributyltin oxide) indicates concerns over immunotoxicity, teratogenicity, dermal toxicity, inhalation toxicity, and endocrine effects.

#### 6) Effects on marine biota

The assessment document is expected to provide a general picture of the toxic potential of trialkyl tin compounds, particularly TBT homologues and their derivatives.

Lethal as well as sublethal data should be collected from experimental studies, both under laboratory and field conditions. Where possible, quantitative structure-activity relationships should be considered.

The particular sensitivity of aquatic organisms, mainly larval and juvenile stages, to TBT, TPT derivatives should be pointed out. Also, only in recent years has the actual measurement of exposure concentrations in the range 1-100 ng l<sup>-1</sup> been possible.

#### 7) Risk assessment to marine biota

Actual and predicted levels in different situations, including "hot-spots", should be used, together with the "effect-concentrations" obtained from sublethal ecotoxicological studies, to evaluate the risk (i.e. the probability that a given noxious effect will occur) for sensitive organisms.

The type of areas particularly at risk should be described.

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

National focal points will be requested to provide relevant information.

9) Rationale for establishing control measures in the Mediterranean region

The proposed rationale will take into consideration:

- (i) the toxicity levels of TBT and TPT and their degradation products for target organisms,
- (ii) the safe level of TBT, TPT and their degradation products, for the protection of the marine biota,
- (iii) the feasibility of monitoring "safe levels" in the marine environment,
- (iv) possible regulatory actions to limit organotin inputs into coastal waters where necessary.

10) Proposed measures

The Working Group on organotin compounds already made some suggestions.

11) References