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

FIR/MEDPOL/FUNG/2

31 May 1993

REPORT OF THE FAO/IAEA/UNEP CONSULTATION MEETING ON THE FUNGICIDES PILOT SURVEY

Ioannina, Greece, 27-29 May 1993

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

Convened jointly with:

IAEA UNEP

Athens, June 1993

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1. According to the decisions of the Contracting Parties, the Secretariat should prepare an assessment document on each one of the groups of substances listed in Annexes I and II of the Land-based Sources protocol to the Barcelona Convention. The assessment document should include inter alia a chapter on concentration levels of the substances in the marine environment. Such assessment documents have already been prepared for all the groups of substances included in Annex I and work has been initiated on substances, families and groups of substances listed in Annex II.

2. Item 2 of Annex II refers to biocides and their derivatives not covered in Annex I. Annex I lists organohalogen, organophosphorus organotin and carcinogenic compounds. It was considered appropriate to deal with herbicides and fungicides under item 2 of Annex II. The IAEA/FAO/UNEP Workshop on the assessment of pollution by herbicides and fungicides (Monaco, 30 October - 1 November 1990) recommended that herbicides and fungicides should be dealt with separately and in addition, that pilot surveys should be initiated to establish the levels of these compounds in selected Mediterranean areas. The pilot survey on herbicides has taken place during 1991 and the results are included in the Report of the FAO/IAEA/UNEP Review meeting on the herbicides pilot survey which took place in Athens from 7-9 April 1992.

3. The present meeting was organised mainly for the preparation of the pilot survey on fungicides. It was jointly convened by FAO, IAEA and UNEP in the framework of the MED POL activities and following the kind invitation of the Department of Chemistry, University of Ioannina, Greece, it took place in Ioannina from 27-29 May 1993. It was attended by the principal investigators of the pilot survey on herbicides and by representatives of FAO and IAEA. A list of participants appears as Annex I to this report.

Agenda item 1. Opening of the meeting

4. Mr. G.P. Gabrielides, FAO Senior Fishery Officer (Marine Pollution) at the Coordinating Unit of the Mediterranean Action Plan in Athens, welcomed the participants to the meeting on behalf of FAO and UNEP. He then gave the floor to Professor Ph. Pomonis, Head of the Chemistry Department, who welcomed the participants to Ioannina on behalf of the University and wished them every success and enjoyable stay in Ioannina. Mr. J.W. Readman welcomed the participants on behalf of IAEA.

Agenda item 2. Background and scope

5. Mr. G.P. Gabrielides explained the background and scope of the meeting. He mentioned that during this meeting he expected the participants to decide on an analytical protocol for the fungicides and prepare a programme for the pilot survey.

Agenda item 3. Election of Officers

6. The meeting unanimously elected Mr. Triadafillos Albanis, Assistant Professor at the University of Ioannina, as Chairperson, and Mr. Hesham Zaki Ibrahim, Associate Professor at the Institute of Graduate

Studies and Research, Alexandria, as Rapporteur. Mr. G.P. Gabrielides acted as Technical Secretary.

Agenda item 4. Adoption of the agenda

7. The provisional agenda prepared by the Secretariat was unanimously adopted and appears as Annex II to this report.

Agenda item 5. Organization of work

8. It was agreed to conclude agenda items 1-6 on Thursday, agenda items 7-9 on Friday and 10-11 on Saturday so that participants could travel back to Athens on Saturday afternoon.

Agenda item 6. Intercalibration exercise on herbicides

9. During 1992 an intercomparison exercise for the quantification of herbicides in water was organised within the framework of the MED POL pilot monitoring survey of herbicides in the Mediterranean. Samples of powder obtained from the freeze-drying of "spiked" natural water were distributed by Dr. D. Barceló, together with appropriate instructions and reporting forms. Results were returned to the IAEA-Marine Environment Laboratory, Monaco, for compilation and interpretation. Prior to the present meeting results were collected and distributed to the participants by IAEA-MEL.

10. Reporting sheets were returned by the following scientists/ institutes:

Dr. D. Barceló, CID-CSIC, Barcelona
Dr. J. Readman, IAEA-MEL, Monaco
Dr. J. Tronczynski, IFREMER, Nantes
Dr. S. Galassi, IRSA-CNR, Milan
Dr. T. Albanis, University of Ioannina

11. Concentrations were provided for three herbicides: atrazine, simazine and propanil. In general, results from analyses by the Mediterranean laboratories were comparable to those submitted by EEC laboratories (for whom the material was originally prepared). The addition of glycine to preserve pesticides during freeze-drying was in some instances found to affect herbicide recoveries through partitioning of the compounds into colloids formed by the glycine. Discrepancies relating to the individual compounds were as follows:

Atrazine:

Comparatively low concentrations reported by IRSA-CNR probably arose as a result of inappropriate storage during delivery. Low precision in results reported by the University of Ioannina was related to instability of their flame thermionic detector during the period of time when the analyses were performed.

Simazine:

A similar problem as described for atrazine was experienced by IRSA-CNR. Simazine was overestimated by the University of Ioannina probably owing to incomplete resolution of the compound from co-eluting peaks.

Propanil:

The good agreement obtained by laboratories measuring this compound probably relates to the stable nature of the compound.

12. This study has identified the need for further intercomparison exercises on herbicides and, as materials become available in the future, it was considered necessary by the participants that they be distributed to the Mediterranean laboratories.

Agenda item 7. Analytical protocol for fungicides

13. In 1992 a research contract was issued by the Mediterranean Action Plan (through IAEA-MEL) to Dr. D. Barceló to investigate analytical techniques suitable for quantifying fungicides in environmental waters. Under this agenda item, Dr. Barceló described results of his research and suggested an analytical protocol for consideration by the participants.

14. The compounds investigated through the research contract were derived from lists compiled at the IAEA/FAO/UNEP Workshop on the assessment of pollution by herbicides and fungicides (Monaco, 30 October - 1 November 1990). Based on a balance between usage in Mediterranean countries, reported persistence in environmental waters and potential compatibility with existing analytical systems within the Mediterranean laboratories, the following compounds were investigated: captan, captafol, folpet, chlorothalonil, metalaxyl, vinclozolin, carbendazim (which is marketed as an independent fungicide but is also the prime degradation product of the fungicide benomyl) and ethirimol.

15. The basis of the protocol suggested by Dr. Barceló is summarised in Fig. 1. It is based on the concentration of fungicides on C_{18}-bonded silica phases through which the environmental waters are passed. Trapped compounds are then eluted using solvents compatible with subsequent instrumental analyses (methanol/acetonitrile for HPLC or ethyl acetate for GC). Three instrumental techniques were shown to be necessary to quantify the compounds:

GC-ECD	GC-NPD	HPLC-UV
Captan	Chlorothalonil	Carbendazim
Captafol	Metalaxyl	Ethirimol
Folpet	Vinclozolin	
Chlorothalonil		
Vinclozolin		

16. Recovery experiments demonstrated that in excess of 85% of spiked compounds were recovered from distilled and tap water. Some problems were, however, encountered in recovery of the fungicides from riverine and estuarine waters containing natural organic materials. Recoveries of folpet and captafol substantially declined (to less than 60%)

possibly owing to hydrolysis of these compounds or saturation of C_{18} sites. It was strongly urged that laboratories conducting fungicide analyses should test recoveries from "blank" environmental waters to investigate matrix effects.

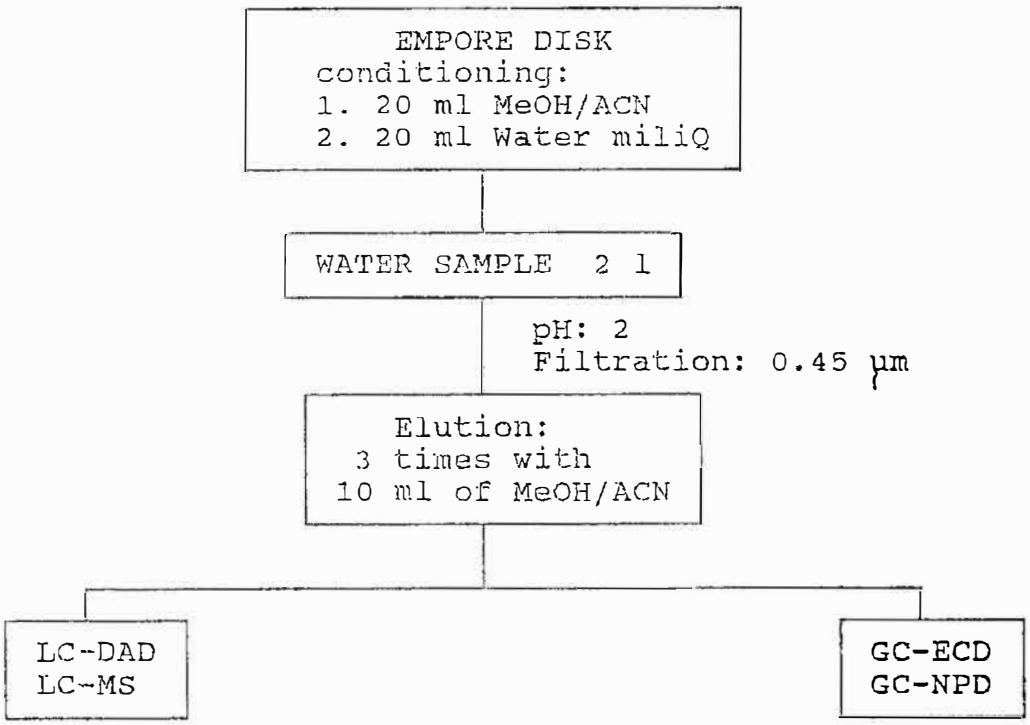


Fig. 1 Basis of the analytical protocol suggested

17. Suggested chromatographic conditions for quantification of the compounds are:

HPLC: Phenyl-bonded silica column (particle size 5 µm) (e.g. Zorbax or Waters Nova-Pack).
Column Length: 15 to 25 cm.
Gradient elution (approximately 20% to 90% acetonitrile in water in 30 minutes. Flow rate: 1 mL/min).
Detection: UV at 210 nm and preferably diode array detection.

GC: Capillary GC analyses can be achieved using fused silica 5% phenyl methylsilicone columns (more polar phases require evaluation). Temperature programmes should terminate at approximately 280°C.
Both split-splitless and on-column injection techniques are suitable.

18. Detection limits for the analytical protocols were estimated to be between 0.1 and 0.4 µg/L for HPLC-DAD analyses and approximately 0.005 to 0.01 µg/L for GC-ECD/NPD analyses.

19. Participants considered the protocols described by Dr. Barceló to be generally compatible with their existing laboratory facilities. Additional fungicides and their degradation products were, however, identified as being significant environmental contaminants. For example, some organo-metallic fungicides (eg. maneb, mancozeb, zineb) are used in very large quantities and it was suggested that these might be monitored using their common metabolite ETU which is more toxic to non-target organisms than the parent compounds. In addition, dicloran has been identified in water samples from French rivers. It was suggested by the participants that wherever possible the list of fungicides for quantification should be as large as possible and compatibility with the proposed analytical protocols should be tested accordingly.

Agenda item 8. Pilot survey for fungicides

20. As far as the number and actual fungicides to be included in the survey were concerned, the discussion described in the previous section (para. 14) was considered. However, the analytical feasibility was one of the main limiting factors. Fully equipped laboratories should include in the survey the fungicides suggested by Dr. Barceló as well as those pointed out in paragraph 16. If possible, additional fungicides should be sought for. Laboratories equipped with only GC-ECD and GC-NPD could not obviously include fungicides for which HPLC was necessary.

21. In the absence of any suitable reference materials, it was proposed that once developed, analytical protocols could be intercompared using a "blind" standard solution containing various fungicides at different concentrations. It was suggested that the solution should be prepared in methanol for spiking into water samples which could then be subject to the various analytical protocols. The representative of IAEA-MEL offered to distribute a suitable standard to the participating laboratories.

22. As described in paragraph 16, it has been demonstrated that substances present in natural waters can interfere with the analytical protocols. It was considered necessary that all participants investigate this problem by analysing spiked and unspiked samples of natural water samples to quantify recoveries.

23. As far as the areas to be monitored are concerned it was proposed that, as the likely route for these compounds to reach the marine environment was via rivers, it would be appropriate to concentrate monitoring in large rivers, their estuaries and adjacent coastal areas. The rivers mentioned were those of Ebro in Spain, Rhône in France, Axios and Louros in Greece, Po in Italy and Nile in Egypt.

24. Whilst it would be preferable to monitor different environmental matrices, the participants considered that analyses of water samples was most appropriate. This decision was based on (i) the physico-chemical properties of the fungicides which generally favour "soluble" species and (ii) the relative ease of analyses. (Sediments and biota require intricate clean-up protocols which would require development).

It was, however, suggested that for compounds with relatively high log K_{ow} values, analyses of sediments would be most useful and should be encouraged.

25. Sampling dates and frequency would be governed by the time applications take place. In general, however, it was considered that samples should at least be collected once a month during the period from May to October. The stations should preferably be placed along salinity gradients and salinity itself should be reported.

Agenda item 9. Any other matter

26. Under this agenda item, the Technical Secretary informed the participants that the fungicides pilot survey should be initiated as soon as possible. Those interested to participate should submit their programme to the FAO Project Office at the Coordinating Unit of the Mediterranean Action Plan giving the necessary details.

It was expected that, after the methods are set up in the laboratories, an intercalibration would be organised by IAEA-MEL (see para. 21).

Agenda item 10. Adoption of the report

27. The report of the meeting was adopted by the participants who affected the necessary amendments.

Agenda item 11. Closure of the meeting

28. The meeting was closed by the Chairperson who thanked the participants for their active participation. In his closing remarks the Technical Secretary expressed, on behalf of the collaborating UN Agencies and the participants, his deepest appreciation for the warm hospitality extended to all by the University of Ioannina (Chemistry Department) and especially by Dr. Albanis.

ANNEX I

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ANNEX II

AGENDA

1. Opening of the meeting
2. Background and scope
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4. Adoption of the agenda
5. Organisation of work
6. Intercalibration exercise on herbicides
7. Analytical protocol for fungicides
8. Pilot survey for fungicides
9. Any other matters
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11. Closure of the meeting