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MEDITERRANEAN ACTION PLAN

Expert meeting to revise the strategy for trend monitoring of pollutants in coastal water sediments

Anavissos, Greece, 14-15 April 2005

Report of the expert meeting to revise the strategy for trend monitoring of pollutants in coastal water sediments

UNEP

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1. Introduction

In accordance with the recommendations of the second review meeting of MED POL-Phase III monitoring activities held on 9-11 December 2003, an expert meeting to revise the strategy for trend monitoring of pollutants in coastal water sediments was organized in Anavissos (Attica, Greece) during 14-15 April 2005, at the Hellenic Centre for Marine Research .

Ten experts (Annex I) from the Mediterranean and outside the region and one international organization provided their expertise in coastal water sediment monitoring. The proposed agenda (Annex II) items were followed during the discussions and presentations. However, because of shortage of time, it was proposed and agreed to extend the meeting to finish at 18:00 hours on the second day.

The meeting was chaired by Mr Robert Precali who has been involved in setting up monitoring strategies in MED POL Phase III and also made a first evaluation of sediment database.

In the first day of the meeting, experts provided comprehensive presentations on the monitoring strategies they have experienced with sediments. They provided to MED POL copies of their contributions as well as a number of key reference materials (Annex III) which will be thoroughly used in future work.

In the second day of the meeting, experts discussed the difficulties in developing a common strategy for sediment monitoring and provided MED POL a set of recommendations for the process of revising the present strategy. The discussions also provided a scientific basis for the planning of the process of making the revision, in other words certain steps of the work has been identified.

2. Opening and Presentations

The meeting was opened by *Mr Evangelos Papathanassiou,* the director of the Institute of Oceanography of HCMR. He welcomed the participants and made a presentation on the activities of his institute.

Ms S Colpan Polat-Beken welcomed the participants on the behalf of the MED POL Coordinator and provided organizational details of the meeting. Later she highlighted the **objectives of the meeting** that are;

- Review different pollution monitoring strategies for coastal water sediments
- Propose a reliable spatial and temporal trend monitoring strategy to MED POL for Mediterranean coastal waters including pollution hot spots
- Recommend complementary tools or strategies to MED POL for monitoring the quality of coastal sediments

Later, she presented background information on the present **sediment monitoring programme as an integral part of MED POL Phase III monitoring activities**. For this part of her presentation, she also introduced the reference documents for the MED POL strategy presented in UNEP(DEC)/MED WG.273/Inf.1. In the second part of her presentation, she briefly introduced the database of MED POL Phase III and provided available information on the implementation status of the sediment component of the

overall monitoring activities and reference made to web version of the database accessible at http://195.97.36.231/medpol/ . She stressed the problems and gaps both in the strategy and the implementation phase which were basically concentrated on sampling strategies, normalization etc.

Mr Jean-Pierre Villeneuve presented the overall activities held for sediments by IAEA/MEL which is the organization for responsible of quality assurance activities of the MAP/MED POL programme. The activities concern are organization of training programmes, inter-laboratory comparison exercises, etc. He provided detailed information on sampling strategies as well as quality control and assessment.

Mr Barak Herut from Israel Oceanographic and Limnological Research presented how sediment monitoring could be used for assessing the marine environment quality providing evidences from the Israeli coastal area. He classified the coastal systems as erosive and sedimentary and stressed that only the later areas are convenient for monitoring purposes. He also mentioned the importance of quality assurance of sampling and analytical procedures and geochemical normalization of data for grain size and mineralogy.

Ms Nadia Mzoughi from Institut National des Sciences et Technologies de la Mer provided a comprehensive presentation on the monitoring of sediments at Tunisian coastal waters within the framework of different national programmes where sediment matrix has been considered as a core matrix for pollution monitoring. Grain size distribution of the sediments were properly done and <63 μm fraction was used for contaminant analysis.

Mr Daniel Cossa presented the sediment monitoring within the framework of French coastal monitoring programme that has been dealing with contaminant levels and spatio-temporal trends since late 70s. Depository sites were selected as appropriate monitoring sites where temporal trend of any contaminant was studied with deeper layer sediments and spatial trends with surface sediments. Site specific sedimentation rate information was used as a key tool to estimate the sampling frequencies.

Ms *Helen Kaberi* presented HCMR experience for the coastal waters of Greece where sediment has been included as a routine monitoring matrix. Normalization was used for grain size and for some lithogenic elements. A major problem was the sampling of coastal stations where sediments are very coarse and therefore their chemical anaysis is rather questionable. Biotests (microtox) were also used in parallel to the monitoring activities.

Mr *Esad Prohic* stressed the importance of the statistical set up for a reliable sediment monitoring station network as well as statistical treatment of data. He recommended as with the other experts the normalization of data. He also stressed the importance of quantification by using enrichment factors.

Mr Foppe Smedes presented the long run experience of OSPAR and ICES in sediment monitoring. It was stressed that provision of common guidelines for sediment monitoring for a whole region is rather a complicated task. However, recommendations based on science and experience could be made. A summary of his presentation and OSPAR/ICES recommendations could be found in Annex IV.

The last presentation was made by Mr *Damia Barcelo* on sediment quality and impact assessment of contaminants. He presented a conceptual model for sediment risk assessment and stressed that only with integrated scientific approach an ecological risk assessment of contaminated sediments could be performed. He provided information on the SedNet (European Sediment Research Network) Project where hazard, risk and impact were elaborated together with specified bridging tools. He provided important outputs of the project to the meeting and MED POL.

3. Discussions and recommendations for revision

3.1 Recommendations for a reliable spatial and temporal trend monitoring strategy for coastal water sediments including hot spots

A. What are the monitoring objectives?

The objectives of the monitoring activities in the framework of MAP/MED POL should at present be based on the requirements of LBS Protocol of Barcelona Convention. The Article 8 of the protocol stresses the following needs for designing monitoring activities :

- Systematic assessment of the levels of pollution along Mediterranean coastal waters
- Evaluation of the effectiveness of action plans, programmes and measures implemented under this Protocol to eliminate to the fullest possible extent pollution of the marine environment

To achieve the above, monitoring of sediments has been considered as an integral part of a monitoring system (MTS 120) of spatial and temporal trends for the assessment of pollution status of the Mediterranean coastal waters. Site-specific temporal trends were also introduced as an important tool for the evaluation of effectiveness of the control measures taken basically at identified hot spots.

By far the most important step in designing of the monitoring programmes is the strict definition of the objectives of the programme concerned where the objectives should be put as detailed, specific and quantifiable as possible. To do that, a number of important factors should be taken into account, including the nature of the control measure, the contaminant concerned, the nature and location of the inputs, statistical aspects of sampling and analysis etc. Regarding the statistical objectives

The monitoring has to permit a statistical comparison of the concentration of contaminants between sites (spatial distribution), highlighting areas with high concentrations of contaminants that are of concern and merit a trend survey.

It is anticipated that the metals programme will at worst have 90% power to detect a 5% per year change over a period of between 15 and 20 years.

Sampling strategy of a monitoring programme should always be designed with certain statistical objectives.

B. Where to recommend sediment monitoring?

Within MED POL monitoring programmes basically two site typologies are considered:
Hot spots and coastal areas (MTS 120).

1. From the sediments monitoring point of view the definition of hot spots and coastal areas might be stated as
    - *Hotspots are the most polluted sites as recorded with sediments* (not necessarily be the same with anthropogenic input areas) and all such sites should be monitored
    - *Coastal sites are sites mainly located in the near shore coastal waters* and a limited representative stations should be selected for state assessments
2. Both hotspot and coastal areas are suitable for monitoring contaminants content in sediments, however, only sedimentary basins with positive accumulation can be considered for monitoring. Basins having sedimentation rates >1cm/year might be favourable monitoring sites. Local experts may also take into consideration the sedimentation rate at each monitoring area while designing the frequency of the sediment sampling.
3. Sensitive areas for biological life and protected areas within the near shore coastal waters should be included in the monitoring network.

C. What is the correct sampling strategy?

The sampling strategy is controlled by the objectives of monitoring programme. The right sampling strategy will allow us to fulfil the objectives and to minimize the financial effort. The sampling strategy design is a scientific effort, in which expertise in the field of geology, biology, environmental and analytical chemistry, statistics, and hydrography must be combined, utilising specific information in the area to be monitored.

In the initial phase of monitoring, it is recommended to over-sample if the variance introduced through sampling and analytical part is unknown. This first phase of the monitoring is considered as the pilot phase (usually the first 5 years) and after that an optimization of the sampling strategy is suggested.

The next are recommended to be considered when the sampling strategy is decided:

<u>Station network</u>

Sites defined in Section B should be taken into account while setting up a monitoring station network.

At least **three** stations are recommended to be chosen along the sediment distribution gradient of a selected site to include hot spot and the near-shore coastal area. While doing so, nearby sensitive areas for biological life should also be included in the network.

It is also recommended to limit the number of stations for data quality assurance purposes, however, the selected station(s) should be representative for the hot spot and the other area of interest.

It is also recommended to examine the selected site for sedimentary purposes as an initial step of the work in order to identify the sediment structure of the whole area as well as the sedimentation rates. Fine and regular sedimentation sites are experienced as more favourable for monitoring purposes.

Sampling layer

For a spatial trend monitoring at a distribution gradient, surface sediments (uppermost 1 cm) should be sampled both at hot spots and near-shore waters.

For temporal trends, consensus was achieved by the meeting to recommend the sampling of the upper 1 cm at hot spot stations whereas at coastal near-shore sediments deeper layers could be used. However, this will be depending on the specific situations.

Sieving

For spatial trend monitoring sieving is not a critical issue however sieving from <1mm or <2 mm in the field could be recommended directly after sampling. However, on board sieving may cause contamination problems basically for organics. Therefore, it must be ensured that contamination is avoided or else on-board sieving from <1 or 2 mm should not be performed.

For temporal studies sieving could be recommended over 63 μm. However, it is important to achieve the programme consistency, therefore, if all set criteria in terms of sufficient trend detection are met by a laboratory that is using a whole fraction (e.g less than 1 or 2 mm) for temporal studies, at present it is not recommended to switch to any other fraction.

For any normalization procedure further sieving could be performed at the laboratory (see below).

Sampling frequency

As a basis and general rule, it was recommended that the sampling frequency has to be adapted considering the sedimentation rate.

It is generally accepted that for monitoring temporal trends at hotspot stations with high sedimentation rates (>1 cm/y), the sampling frequency can be initially set to **yearly** If the sedimentation conditions are very variable at selected hot spots other frequencies could be adapted.

On the other hand, if sampling of deeper layers at near-shore coastal waters was adopted for temporal trends then sampling frequency could be reduced according to the accumulation rate at the site. However, it should also be kept in mind that near shore waters are generally dynamic, therefore, laminated layers may not always exist in deeper layers and it might be considered as mixing layer. In such cases, sampling frequencies should be re-examined. Sampling frequency can also be reduced when parameters are close or below the quality targets.

For the spatial trends, it was agreed to propose surface sampling with a frequency that will be adapted according to the sedimentation rate. Therefore, it is critical first to obtain this information for each sampling site.

Sampling has to be performed in the season with highest accumulation rate. However, it was also mentioned that at the periods of highest accumulation, biological activity within the sediment is also increased which cause unstable conditions. Therefore, a period with high accumulation rate and minimum biological activity could be decided by the local expert for the yearly samplings. On the other hand, the integrity among the different components of the monitoring programme is also important and recommended as a general rule to be realized in all monitoring programmes, therefore, sampling time should preferably be the same for biota and sediment.

Number of samples

Multiple samples have to be collected at each station in order to achieve the statistical sensitivity of sampling. It was recommended to take at least **three** samples at each station area (ex: for an area with app. 10 m depth and 10 m radius). However, it was also suggested to have a larger area to increase the representativeness of the samples of the area. In the pilot phase (first five years) **five** samples for each station is recommended to better understand the sampling variability if it is not known from previous monitoring efforts. Pooling of individual samples is not recommended especially in the pilot phase in order to achieve the field variability which is an essential parameter for power analysis and trend tests.

Sampling instruments

For both surface layer and sub-surface samplings it is recommended to use corers (box corer etc.). Multi-corers are also good options. If Van Veen grabs are preferred for surface samplings, then, they should be equipped with a trap at the top to collect the surface of the sediment.

D. What are the general and pollutant specific rules recommended for normalization?

Normalisation is defined here as a procedure to correct contaminant concentrations for the influence of the natural variability in sediment composition (grain size, organic matter and mineralogy). Most natural and anthropogenic substances (metals and organic contaminants) show a much higher affinity to fine particulate matter compared to the coarse fraction. Constituents such as organic matter and clay minerals contribute to the affinity to contaminants in this fine material.

Two different approaches to correct for variable sediment compositions are widely used:

a. Isolation of the fine fraction by sieving (e.g. <20 µm, <63 µm) can be regarded as a physical normalisation to reduce the differences in sediment granulometric compositions and is applicable to both metals and organic contaminants. Thus, sieving is a first powerful step in normalisation.
b. Normalisation can be performed by relating the contaminant concentration with components of the sediment that represents its affinity for contaminants, i.e. binding capacity. Such co-factors are called normalisers. Normalisation can be performed by simple contaminant/normaliser ratios or linear regression. Another procedure takes into account that the coarse sediment fraction contains natural metal concentrations in the crystal structure before the normalisation is performed. Combinations of co-factors, possibly identified from multiple regression analysis, can be used as normalisers.

At the moment only suggestion for normalization of trace metal content in sediments is provided. It is recommended to analyse the fraction below 63 µm, although if in the area significant amount of contaminant is bonded to the fraction above 63 µm the analysis of that fraction could also be considered.

It was stressed by the meeting that an additional investigation for obtaining the normalization error has to be done by an expert before sieving <63 µm is recommended as an overall strategy for Mediterranean countries.

Apart from normalization according to grain size, it was widely accepted that organic-C, lipid content, carbonates and Al, Li could be used as normalisers respectively for organic and inorganic contaminants.

E. How to reach background values of specified pollutants in the sediments?

Background levels are very important in tracing anthropogenic contamination. It is suggested to follow the experience of OSPAR/ICES in that field (ICES ACME 2004, Annex 3). A collection of already existing data has to be performed and a Workshop on background concentrations of trace metals and PAHs has then to be organized.

It is also suggested the introduction of the term Background Assessment Concentrations (BAC). The term is associated to the problem how to test statistically whether areas are at, or near, background values.

F. Initiative for a baseline study of the Mediterranean area

Reviving the initiative for a baseline study of the Mediterranean area it is suggested to consider the organisation of multi-national cruise(s) mainly in the areas where such data is missing. It was also proposed that such an activity could be joined with an on-board training activity as part of Data Quality Assurance.

Such an effort would also serve for assessing the region-wide status of pollution and identification of hot spot areas. An expert could help to evaluate each location with locals for application of proposed guidelines for sampling.

3.2 Complementary strategies for monitoring sediment quality

When the quality of sediments are concerned, biological component should be integrated with any monitoring efforts for levels and/or trends of contaminants. Studies for ecological risk assessments have to be made for impact of contaminants on aquatic biological life. As part of the process, sediment toxicity tests could be included within the routine monitoring activities.

The appropriate Quality Criteria for sediments (certainly including dredged material) should be developed in parallel. The inventory of sediment quality criteria presented in Annex VI of 2003 report of the ICES WGMS can be considered as a very useful reference study for the Mediterranean community.

4. Conclusions

A two-day meeting was not enough to come to certain conclusions for common views/guidelines for sediment monitoring. It was stressed that the meeting could only be considered as an initial step for revising the present strategy of trend monitoring of pollutants in coastal water sediments. In spite of the fact, the presentations and the discussions provided valuable inputs to prepare a first version of the revised strategy where recommendations and advise might be provided. Effort should be made to

continue the work initiated with this expert meeting and the following steps could be proposed to be achieved in *short-term*:

- MED POL Secretariat will prepare a first version of the revised monitoring strategy for coastal water sediments based on the discussions and the material of the expert meeting held.
- Studies at the expert level will be launched for obtaining normalization errors
- Studies on background levels of pollutants at the Mediterraenan sub-regions will be followed and promoted.

And in *mid-term*:

- Look for the possibilities of organizing baseline surveys in cooperation with other such initiatives
- MED POL will consider how its monitoring and assessment component can be extended to cover the status of quality of coastal environment (e.g water, sediment)

Finally, the MED POL Secretariat wish to thank all the experts for their contribution to this work during and after the meeting. It is believed that the group will continue to cooperate with future activities.

Annex I

List of Participants

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Annex II

Agenda

14 April 2005

09:30-10:00	Opening and objectives of the meeting
10:00-10:40	Review of the MED POL monitoring activities on sediments
10:40-11:00	Coffee Break
11:00-13:00	Presentations of Experts - Experiences of sediments monitoring in the Mediterranean
13:00-14:30	Lunch Break
14:30-15:30	Presentations of Experts - Experiences of sediments monitoring in the Mediterranean (cont'd)
15:30-15:50	Coffee Break
15:50-17:00	Presentation of the work of the ICES WG on marine sediments in relation to pollution

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09:30-10:00	Sum up of presentations and general discussion
10:00-11:00	Preparation of an outline of a reliable trend monitoring strategy for sediments of coastal waters including hot spot areas
11:00-11:30	Coffee Break
11:30-13:00	Alternative strategies for monitoring sediments quality and recommendations

Detailed Programme (as amended by the meeting)

14 April 2005

Opening by HCMR and MAP/MED POL (welcome and organization of two days)
Introduction by participants
Organization of the meeting (agenda, programme, documents, outputs)
Objectives of the meeting

MED POL Experience in Monitoring with sediments, MED POL Colpan Beken

Coffee Break (10:40-11:00)

Sediment sampling strategy and quality control *by J.-P. Villeneuve*, IAEA/MEL

The use of sediment monitoring for assessing the marine environment quality, The case of Israeli Mediterranean Coast *by B. Herut*, IOLR

Strategy for trend monitoring of pollutants in Tunisian coastal water sediments *by N. M'Zoughi*, INSTM

The French Coastal Monitoring Programme / Sediment monitoring : French experience and strategy *by D. Cossa*, IFREMER

Presentation *by H. Kaberi*, HCMR

Lunch (13:00-14:30)

Some problems concerning the interpretation of sediment analysis data - sampling, analytics, statistics *by E. Prohic*, UoZ

Sediment Quality and impact assessment of contaminants *by* D. Barcelo, CID-CSIC
Coffee Break (15:40-16:00)

Experience of ICES WG on sediments *by F. Smedes*, RWS-RIKZ

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Working session 1: Preparation of a detailed outline of trend monitoring strategy for Mediterranean coastal waters including hot spots, recommendations (9:30-)

Coffee Break (11:00-11:30)
Working session 1 (cont'd.)

Break (13:00-15:30)
Working session 1 (cont'd.) ,

Working session 2: Propose complementary strategies for monitoring sediments quality (-18:00)

Annex III

List of reference documents collected by the meeting for future work in MED POL

Report of the meeting of MED POL-Phase III Monitoring Activities, UNEP(DEC)MED WG.243/4, 3/3/2003.

MAP Technical Reports Series No. 120, UNEP, Athens 1999. UNEP/MAP. MED POL Phase III Programme for the assessment and control of pollution in the Mediterranean region.

Reference Methods for Marine Pollution Series No.63, UNEP, 1995. Manual for the geochemical analyses of marine sediments and suspended particulate matter

Reference Methods for Marine Pollution Series No.20, UNEP, 1992. Determination of petroleum hydrocarbons in sediments

OSPAR/JAMP Guidelines for Monitoring Contaminants in Sediments…Ref.No :2002-16

ICES Advise 2004, ACME Report

Report(s) of the Working Group on Marine Sediments in Relation to Pollution (WGMS) ICES Marine Habitat Committee CM Ref. ACME For 2000-2004.

Report(s) of the Working Group on Statistical aspects of Environmental Monitoring (WGSAEM) ICES Marine Habitat Committee CM Ref. ACME For 2001-2004.

UK National Marine Monitoring Programme-Green Book, 10/11/2003.

Michael Kersten and Foppe Smedes, 2002. Normalization procedures for sediment contaminants in spatial and temporal trend monitoring. *J.Environ.Monit.,* 4, 109-115.

Birger Larsen and Anders Jensen, 1989. Evaluation of the sensitivity of sediment stations in pollution monitoring. *Marine Pollution Bulletin*, 20 (11), 556-560.

Annex IV

OSPAR/ICES recommendations and presentation of Foppe Smedes (summary)