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Long-Term Programme for Pollution Monitoring and Research
in the Mediterranean Sea (MED POL - PHASE II)

REPORT ON THE ACTIVITIES OF THE GESAMP WORKING GROUP ON THE INTERCHANGE
OF POLLUTANTS BETWEEN THE ATMOSPHERE AND THE OCEANS AS RELATED TO
MED POL - PHASE II

In Co-operation with:



WORLD METEOROLOGICAL ORGANIZATION
INTERNATIONAL ATOMIC ENERGY AGENCY

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INTRODUCTION

The Long-term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL - PHASE II), adopted by the Contracting Parties to the Barcelona Convention at their Second Meeting in Cannes, 2 - 7 March 1981, includes the monitoring of the transport of pollutants into the Mediterranean Sea through the atmosphere.

At that same meeting, the Contracting Parties decided that, until a more thorough knowledge of the matter was achieved, this component of the monitoring should be treated as a research activity.

Following this, and the advice of the Working Group for Scientific and Technical Co-operation at its first meeting (UNEP/WG.62/7), the secretariat, in close co-operation with WMO and IAEA, undertook a number of activities closely linked to the work of GESAMP in this field.

The present document summarizes the activities undertaken and planned by the WMO-led GESAMP Working Group as related to the relevant activities of the Long-term Programme for Pollution Monitoring and Research in the Mediterranean (MED POL - PHASE II).

BACK GROUND

Art 4 of the Protocol for the protection of the Mediterranean Sea against pollution from land-based sources, foresees the establishment of measures to control the input of pollutants into the Mediterranean Sea through the atmosphere.

It is well known that a noticeable part of the pollution entering the Mediterranean Sea derives from sources located on land via atmospheric transport. This is particularly true for pollutants having a gaseous phase, such as organohalogens, volatile elements such as Hg, or elements having a solid phase in the aerosol size range, such as Cd.

Monitoring the transport of pollutants via the atmosphere requires that distinction be made between naturally occurring substances and anthropogenic substances. This is often done by use of normal elemental ratios found in crustal materials as compared to actual ratios measured.

Another requirement is a good knowledge of the physical and physico-chemical processes affecting, on one hand, the general movement of air masses, and on the other, the behaviour of specific pollutants considered.

Owing to the great difficulties arising in the establishment of sampling stations there is a need to develop regional computational models which, on the basis of emission inventories, allow the forecast of the net flux of pollutants across the air/sea interface.

A few properly selected sampling sites or sampling cruises should then allow validation of the model and assessment of flux computations.

In the framework of the MED POL - PHASE II programme, an attempt is being made by the secretariat, in close co-operation with WMO and IAEA, to collect the information and expertise available in the Mediterranean Region (see documents UNEP/WG.91/3 and UNEP/WG.91/4). In addition, through the UNEP-sponsored Working Group of GESAMP (V. Pravidic, 1981), worldwide knowledge is complementing the actions taken through the MED POL programme.

GESAMP Activities

The general processes controlling the transport between the ocean and the atmosphere have been analysed by the GESAMP Working Group on the Interchange of pollutants between the atmosphere and the oceans at its first and second sessions held in 1977 and 1978. The results of this analysis were reviewed by the eleventh session of GESAMP (1980) and published (GESAMP, 1980a).

Since the eleventh session of GESAMP, at the request of UNEP, the Working Group focused its terms of reference on the description of transport processes towards and into specific regions, using the Mediterranean as a model of a semi-enclosed sea, including horizontal atmospheric transport, vertical atmospheric transport to the air/water interface, and the interchange at this boundary, and also to review the scientific literature and assess the pathways and fluxes of important pollutants into the Region, differentiating between natural and pollutant sources (GESAMP, 1981).

The fourth session of the GESAMP Working Group undertook the discussion of the specific requirements of the MED POL programme, and made relevant recommendations. The report on the session as prepared by WMO and submitted to the thirteenth session of GESAMP is reproduced as Annex I to this document.

The fifth session of the GESAMP Working Group is scheduled to take place in Athens, in the Co-ordinating Unit for the Mediterranean Action Plan, on 28 November - 2 December 1983.

REFERENCES

- GESAMP 1980, Report of the Eleventh Session. Rep. Stud. GESAMP (10), UNEP.
- GESAMP 1980a, Interchange of Pollutants between the Atmosphere and the Oceans Rep.Stud. GESAMP (13), WMO.
- GESAMP 1981, Report of the Twelfth Session. Rep. Stud. GESAMP (14), WMO.
- V. Pravidic 1981, GESAMP, The First Dozen Years, UNEP.

Thirteenth Session
28 February - 4 March 1983
Agenda item 6

A N N E X I

REPORT OF THE FOURTH SESSION OF THE GESAMP WORKING GROUP
ON THE INTERCHANGE OF POLLUTANTS BETWEEN THE
ATMOSPHERE AND THE OCEANS

(Villa Girasole, Monte Carlo, Monaco,
25-29 October 1982)

1. OPENING OF THE MEETING

The fourth session of the GESAMP Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans was held at the Villa Girasole, Monte Carlo, Monaco, from 25 to 29 October 1982. The meeting was opened by Mr. W. D. Garrett, the Chairman.

A period of silence was observed out of respect for the late Princess Grace of Monaco.

Appreciation was expressed to His Excellency, Ambassador Solamito, President of the Centre Scientifique de Monaco for providing the conference facilities and Mr. R. Fukai, Director of the International Laboratory of Marine Radioactivity, for his assistance in arranging the meeting, facilities and support services.

On behalf of the sponsoring agencies (WMO, UNEP and IAEA) Mr. V. Smagin, the Technical Secretary of the Working Group welcomed the participants of the session. Mr. John Miller was elected rapporteur of the meeting. A list of participants is given in Annex I.

2. ADOPTION OF THE AGENDA

The Group adopted the agenda as circulated by the Technical Secretary with some amendments suggested by the participants (see Annex II).

3. PROCEDURAL PLAN OF MEETING WITH SUB-GROUP AND ASSIGNMENTS

A sub-group was established to draft recommendations on development of conceptual models for monitoring the transport of pollutants to the Mediterranean Sea via the atmosphere.

4. REVIEW OF GESAMP-XII AND RATIONALE FOR FUTURE ACTIVITIES OF THE WORKING GROUP UNDER MODIFIED TERMS OF REFERENCE

The Chairman informed the Working Group of GESAMP-XII's discussion regarding future activities of the Working Group on the Interchange of Pollutants. He noted that GESAMP-XII decided that the Working Group should continue its activities under modified terms of reference. Emphasis has now shifted to include describing atmospheric transport processes towards and into specific marine regions, using the Mediterranean as a first example. This change in emphasis was made bearing in mind the work accomplished until now by the Working Group and at the request of the Contracting Parties to the Barcelona Convention addressed to UNEP. It was noted that a similar request might be expected to also be addressed to the UN system from the Governments of other regions.

The terms of reference are given in Annex III.

5. ATMOSPHERIC POLLUTANT TRANSPORT PROCESSES INTO REGIONAL SEAS

To begin the scientific discussions of atmospheric transport of pollutants to the sea, the chairman called upon the members of the Working Group to present their prepared assignments. The summaries of these papers are presented in Annex IV.

After completion of these presentations, the Working Group considered and discussed the possibilities and potentialities of modelling atmospheric pollution in order to estimate the flux of pollutants from the atmosphere into the Mediterranean Sea. A general strategy of such activities should include:

- (a) Establishment of reliable emission inventories of the pertinent pollutants.
- (b) Defining the important atmospheric mechanisms of physical transport by the winds, chemical transformation during transit and removal processes both wet and dry.
- (c) Measurement of deposition and determination of the net flux of the material at the sea surface.

From this discussion the following conclusions and recommendations evolved:

- (i) Estimates of atmospheric input of pollutants to the Mediterranean Sea are needed for many different pollutants in order to assess the pollution loading into the sea and its possible effect on the marine environment. Such pollutants include trace metals (Pb, Hg, Cd, etc.), petroleum hydrocarbons, chlorinated hydrocarbons and pathogenic micro-organisms.
- (ii) Deposition estimates could be obtained by the application of meteorological dispersion models, which have been used successfully in other geographical areas for certain compounds and other pollutants. Model results have to be checked against measured concentration and deposition data. It is therefore recommended that about five monitoring stations be established or identified at already existing BAPMON and other stations at various suitable sites in the Mediterranean area. These stations should be located in remote areas on platforms or small islands, and as far as possible avoid contaminations by local sources. In addition to fixed stations, complementary sampling should be performed aboard research ships. At these stations the pollutants of interest along with the meteorological parameters such as wind speed and direction, precipitation, solar radiation, etc., should be measured.

- (iii) Evidence already available shows that concentrations of many of the pollutants of interest, measured over the seas, exhibit significant variations on the time scale of a few hours or one day. This means that the measurements should have a time resolution of 24 hours or better. In order to study the behaviour of pollutants in the atmosphere, back trajectories arriving every 6 hours at the measurement stations should be constructed. These back trajectories could also be used as a basis for modelling the day-to-day variations of concentrations and deposition patterns. At the same time, the history of the air parcel movements, as revealed by the trajectory together with other available meteorological and chemical data would allow for case studies of selected special situations. In the first phase of the programme, these procedures should be conducted at one of the stations for a minimum period of one year.
- (iv) These studies should then lead to the application of dispersion model(s) mentioned before in order to estimate long-term (annual or seasonal) deposition patterns covering all of the Mediterranean Sea. An absolutely necessary prerequisite for quantitative modelling is the availability of an emission inventory of the pollutant(s) concerned. The emission inventory should contain information on the sources including particle size, and should give the geographical position of the sources on a scale in the order of 50-100 km. Furthermore, a survey should be made on the availability of meteorological input data to the model. Since meteorological data over the sea are scarce, interpolation schemes in time and space have to be refined and utilized. Satellite data and radar information might be used to supplement the meteorological data base for precipitation.
- (v) For many pollutants their physical and chemical behaviour in the atmosphere is not known. Deposition velocities and scavenging rates are needed in order to arrive at reliable model results. Early studies to obtain these parameters are recommended.
- (vi) Considering the difficulties connected with some of the pollutants (e.g. the presence of Hg in both vapour and particulate form), it is recommended that one pollutant should be used as a pilot substance. The Working Group is proposing to take Cd as a first model pollutant. Other pollutants could follow if the modelling of this substance proves reasonably successful.
- (vii) It is recommended that all data be collected, quality controlled and evaluated in a leading centre to be identified for this programme, in order that efficient data handling, processing and interpretation can be accomplished. It is further recommended that scientists working at this centre draw on the wealth of experience accumulated at the Synthesizing Centres within the EMEP Programme and establish close co-operative interactions.
- (viii) Special meteorological effects influencing pollutant distributions in coastal areas (e.g. land/sea breeze and sea spray effects, etc.) should be studied in the framework of this programme. The application of sophisticated and detailed meteorological models in such areas should also be encouraged.

6. ACTION PLAN FOR A MEETING OF EXPERTS TO ADVISE ON THE STUDY OF THE ATMOSPHERIC TRANSPORT OF POLLUTANTS INTO THE MEDITERRANEAN SEA

The Working Group discussed the terms of reference for a meeting of experts to advise on the planning and implementation of the monitoring activities to assess the airborne transport of pollutants into the Mediterranean Sea.

The meeting should be attended by representatives of participating laboratories of the region, experts from laboratories with previous experience in atmospheric pollution research and long-range transport of pollutants, and by representatives of co-ordinating and sponsoring agencies.

The meeting should take into account the problems solved during the execution of such programmes as SEAREX (USA) and PHYCEMED (France), as well as other studies carried out in the Mediterranean Sea.

The following guidelines are recommended to be considered:

6.1 Choice of model pollutant(s)

Realistically, only one or a few pollutants should be chosen to fulfil the following prerequisites:

- (a) Its land-based sources should be identifiable and quantifiable.
- (b) Its distribution ratio between the gaseous (vapour) and particulate form should be known. It would be preferable if the chosen pollutant did not have a significant gas (vapour) component.
- (c) Its known or anticipated concentration in the atmosphere and in the surface waters should be within the sensitivity of analytical techniques, discussed in 6.3 overleaf.
- (d) The pollutant should be one from "ANNEX I" of the Protocol for the Protection of the Mediterranean Sea Against Pollution from Land Based Sources.
- (e) The concentration of the pollutant chosen for measurement should be refined to the concentration of a conservative element of crusted origin.

6.2 Choice of sampling techniques, methodology and selection of sites

The Working Group has identified the sampling procedures as the most involved part of the whole exercise. It is in the sampling procedure where errors are most likely to occur, endangering the success of the whole exercise.

6.2.1 Sampling techniques

Based on the experience of the above mentioned programmes one aerosol collecting technique should be chosen in order to estimate dry deposition. The wet-only (rain) sampler has to be chosen in the same way, with particular attention paid to the turn-on/shut-off procedure (manual, semi or fully automatic). The selected sampler systems should be standardized. If a decision is made that the sampling of the sea surface layer is to be performed simultaneously, standardization of suitable surface sampling techniques is mandatory.

6.2.2 Methodology of sampling

A decision should be made on the regime of sampling (time series, number of repetitive or parallel samples). In wet sampling a decision should be taken whether the sampling be done strictly on an event basis or in a composite mode.

The standardization of the methodology should also include removal of sample from the sampler, its storage and transfer to a clean laboratory whether on site (ship or platform) or to a remote unit.

6.2.3 Site selection

The selection of the site (or sites) for sampling should be made in conjunction with several considerations. Foremost are the requirements of absence of any identifiable source of local contamination. In addition the site selection should be made in full consideration of the air mass trajectories, and of other components required in a numerical model of long-range atmospheric transport of pollutants. The last requirement would also mandate the minimum number of sampling sites and of independent samples to ensure the required statistical significance of the whole exercise.

6.3 Analytical methodology

The choice of analytical techniques is the final important component of the exercise.

6.3.1 For the analysis of trace metals, it is recommended that either the flameless atomic absorption spectrometer (FLAAS) or the electrochemical technique of anodic stripping voltametry (ASV) be used. Both techniques have been developed, each for a host of elements, to high degrees of sensitivity, precision, accuracy and yet simplicity of operation.

6.3.2 For the analysis of organics, choice should be made of either high pressure liquid chromatography (HPLC), or gas chromatography (GC) or of gas chromatography - mass spectrometry (GCMS) considering the pollutant(s) chosen, the specificity and sensitivity of analysis required, and whether "finger printing" identification data are required.

Whatever techniques are chosen, if several laboratories participate in the exercise, intercalibration of procedures should be made mandatory.

Once a programme has been decided upon, strict observance of standardized techniques is also mandatory.

6.4 Data handling and information processing

A decision should be made on data handling using standardized computational methodology, concentration units, and reporting formats. Data should be made available for use in computational models and other forms of information processing. It is therefore necessary that an unrestricted information flow be assured between all the participants in such an exercise.

6.5 Recommendations

On the basis of the above discussions and information contained in Annex IV, criteria for selection of man-made pollutants, the Working Group has identified cadmium as the most suitable pollutant for the initial phase of the exercise.

The Working Group also identified aluminium as the most suitable tracer of crustal origin.

While making this recommendation the Working Group was aware that other pollutants (Zn, Cu, etc., or high-molecular-weight chlorinated hydrocarbons) might also fulfil the requirements.

7. DISCUSSION AND ADOPTION OF REPORT OF THE AD HOC MEETING, TALLINN, ESTONIAN SSR, MAY 1981

The Working Group received the report of the ad hoc meeting in Tallinn, Estonian SSR, and adopted it after the following clarifying discussion. It was noted that the paper by Andryukov and Nazarov at the ad hoc meeting estimated the global atmospheric input of petroleum hydrocarbons which was greater than five times that estimated by a workshop sponsored by the US National Academy of Sciences held in 1975.

With regard to the section entitled Distribution and Forms of Petroleum Hydrocarbons at the Surface of the Sea, (annex V, p. 15, of the report of the ad hoc meeting), the Working Group discussed the reported effects of oil pollution on surface tension, viscosity and freezing point of seawater. It was reported that these data were determined on surface microlayer samples which had been placed into a container prior to measurement and were not performed in situ. There was no information available as to whether these samples were collected primarily in areas heavily polluted by oil films.

The Working Group considered the information contained in the annex of the ad hoc Working Group is the opinion of the authors and not necessarily the concensus of the ad hoc group.

8. ADDITIONAL WORKING GROUP BUSINESS

The Working Group discussed the WMO proposal to amend the GESAMP working definition of marine pollution. While one member of the Working Group expressed his reservation to such an amendment, the Working Group felt that the present GESAMP definition does not reflect pollutant modification of the physical properties of the air-sea interface. The majority of the Working Group suggested to add to the marine pollution definition the following wording: "and altering ocean-related physical processes especially pertinent to climate".

The Working Group noted information presented by Mrs. A. Tsyban on an international symposium on Integrated Global Monitoring of the Ocean sponsored by UNEP, IOC of Unesco and WMO to be held in Tallinn, USSR, from 2 to 10 October 1983.

The representative of the Operational Unit for the Mediterranean presented the International Bathymetric Charts for the Mediterranean (IBCM) as an example of cartographic works that have been carried out under the aegis of IOC. He also informed the Working Group that IBCM sea bottom sedimentology sheets are now under preparation.

The Working Group noted that IBCM may provide useful input to marine pollution research in the Mediterranean Sea. The Working Group was of the opinion that the creation of the overlay sheets in marine biology, chemistry, physics would have more important significance for this purpose.

9. PREPARATION AND APPROVAL OF AN INTERIM REPORT FOR GESAMP-XIII

The report of the fourth session of the GESAMP Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans was considered and approved by the Working Group on the final day of the session. The Working Group expressed its deep appreciation to Mr. W. D. Garrett, the Chairman of the Working Group, for his most able guidance during the session.

10. FUTURE PLANS, ASSIGNMENTS AND ORGANIZATION OF THE WORKING GROUP

The Chairman opened the discussion by noting the importance of the present activity of the Working Group with regard to the atmospheric transport of pollutants into the Mediterranean Sea. He expressed the thought that in the future it would also be useful for the Working Group to continue to contribute scientific knowledge on global problems involving pollutant interchange between the atmosphere and the oceans.

The Working Group stated that there are a number of present and future problems in this area which require careful scientific attention. These include microbiological, photochemical and physical processes in the air-sea boundary layer which are affected by various pollutants. It was suggested that this Working Group could assume a predictive role toward the determination of air-sea effects of pollutants ten or more years into the future when, for example, the use of coal as an energy source will significantly increase. This situation could increase the transport of trace metals, radionuclides and CO₂ to the oceans.

The Working Group was informed by Mr. Chesselet that the SCOR Working Group 44 (Ocean-Atmosphere Material Exchange) has been reconstituted as WG 72 entitled "The Ocean as a Source and Sink for Atmospheric Constituents". This new SCOR group will review existing knowledge on the flux of gases and particles, the photochemical processes and microbiological processes at the air-sea interface.

The GESAMP Working Group concluded that it had future roles in the area of ocean-atmosphere pollutant exchange on both a regional and global scale and that it could benefit from liaison with the SCOR group.

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AGENDA

1. OPENING OF THE MEETING
 2. ADOPTION OF THE AGENDA
 3. PROCEDURAL PLAN OF MEETING WITH SUB-GROUP AND ASSIGNMENTS
 4. REVIEW OF GESAMP-XII AND RATIONALE FOR FUTURE ACTIVITIES OF THE WORKING GROUP UNDER MODIFIED TERMS OF REFERENCE
 5. ATMOSPHERIC POLLUTANT TRANSPORT PROCESSES INTO REGIONAL SEAS
(Discussion of Working Papers prepared for this session)
 - (a) Horizontal atmospheric transport into the region
 - (b) Vertical atmospheric transport to the air-water interface
 - (c) Air-water interchange
 6. ACTION PLAN FOR A MEETING OF EXPERTS TO ADVISE ON THE STUDY OF THE ATMOSPHERIC TRANSPORT OF POLLUTANTS INTO THE MEDITERRANEAN SEA
 7. DISCUSSION AND ADOPTION OF REPORT OF THE AD HOC MEETING, TALLINN, ESTONIAN SSR, MAY 1981
 8. ADDITIONAL WORKING GROUP BUSINESS
 9. PREPARATION AND APPROVAL OF AN INTERIM REPORT FOR GESAMP-XIII
 10. FUTURE PLANS, ASSIGNMENTS AND ORGANIZATION OF THE WORKING GROUP
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TERMS OF REFERENCE OF THE WORKING GROUP
(as defined by GESAMP-XII)

- (i) to describe transport processes towards and into specific regions, using the Mediterranean as the first example, including:
- horizontal atmospheric transport affecting the region;
 - vertical atmospheric transport to the air-water interface;
 - air-water interchange, and
- (ii) to review the scientific literature and assess the pathways and fluxes of important pollutants into particular regions, using the Mediterranean as the first example, and to differentiate between natural and pollutant sources.
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SUMMARIES OF THE WORKING PAPERS PRESENTED BY PARTICIPANTS

UNITED NATIONS ENVIRONMENT PROGRAMME (UNEP)

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

The Long-term Programme for Pollution Monitoring and Research (MED POL - Phase II) of UNEP's Mediterranean Action Plan was endorsed at the second meeting of the contracting parties to the Convention for the Protection of the Mediterranean Sea against Pollution. This programme includes monitoring of the transport of pollutants into the Mediterranean Sea through the atmosphere.

The purpose of this monitoring is to establish the atmospheric input (flux) of pollutants into the Mediterranean Sea and thus to provide additional information on the pollution load reaching the Mediterranean Sea. This activity should contribute to the enforcement of Article 4 of the Protocol for the Protection of the Mediterranean Sea Against Pollution from Land-Based Sources. This monitoring should include:

- (i) areas directly influenced by identifiable sources of air pollution.
- (ii) reference areas not directly influenced by identifiable sources of air pollution.

In its developmental phase, this monitoring programme should be considered concurrently with another research topic, i.e. pollutant transfer processes at the air/sea interface, which is also included in MED POL - Phase II. Selection of the most suitable parameters on the basis of their relevance to ANNEX I and ANNEX II of the Land-Based Sources Protocol should be made, along with identification of adequate sampling, analytical and computational techniques and of adequate locations for monitoring stations.

WORLD METEOROLOGICAL ORGANIZATION (WMO)

Report on WMO's work in relation to UNEP MED POL - Phase II

The atmosphere acts as one of the major means of transport for pollutants ultimately deposited in water bodies, particularly in regional seas which are surrounded by potential man-made pollution sources. For example, it was estimated that between one tenth and a few per cent of the total content of certain pollutants present in the Baltic Sea are annually deposited from the atmosphere. It was also estimated that the amount of atmospheric input of many trace metals to the Mediterranean Sea is comparable to that of the discharge of metals from rivers.

When considering how such investigations could be carried out it should be noted that monitoring of the atmosphere and in particular of wet precipitation in areas of open sea is technically difficult if not impossible. Therefore, it is necessary to develop a basis to describe and quantify the deposition processes by employing models using meteorological parameters. This has been done within the existing ECE/UNEP/WMO Co-operative Programme for the Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP) for which two Meteorological Synthesizing Centres (MSCs), organized by WMO, are operated which estimate, four times daily, the long-range transport and deposition for about 700 locations in Europe thereby using the data from about 70 monitoring stations, mathematical models and meteorological data. A part of the Mediterranean area is also covered in EMEP.

Transport, transformation and deposition is computed so far for sulphur compounds. Hence, the models used in EMEP would also need to be adjusted to take into account other substances of particular interest to the Mediterranean Sea, including trace metals, organohalogen, organophosphorus and radioactive substances.

All work on modelling remains rather academic as long as the results cannot be verified. Therefore, a number of monitoring stations are required and their data can be used to both verify and calibrate the model. There are already a number of WMO Background Air Pollution Monitoring Network (BAPMON) stations, operating on a monthly basis, and as far as suspended particular matter (SPM; aerosols) is concerned on a 24-hour basis (see Appendix). Their number, however, is insufficient and not all sites are appropriate for checking a transport model. The stations Sidi Barrani (Egypt), Carpentras (France), Methoni (Greece), all stations in Italy, Thala (Tunisia), and Ivan Sedlo (Yugoslavia) are suitably located and are operational at the present time or will be very soon. As soon as a first version of an extended transport model is available, proposals for additional locations can be made. It should also be noted that satisfactory emission data for the pollutants in question and for the wider Mediterranean area are an absolutely essential requirement for good model estimates. To this end, the Contracting Parties should make serious efforts to provide such emission data as model input. Regarding ground observations, in addition to the BAPMON stations located around the Mediterranean Sea, the few EMEP stations in the area and furthermore, research vessels could be considered as possible monitoring sites.

With regard to the modelling of air flow and orographic precipitation in the northern part of the Mediterranean area, the results emerging from the WMO Alpine Experiment (ALPEX) will constitute a valuable contribution since during ALPEX aircraft soundings were made at different levels.

W. D. GARRETT

Residence times of pollutants in the sea surface microlayer

In comparison with other marine interfaces, the transit time for most pollutants across the air-sea boundary is relatively short. The estimated residence time for water wettable particulate trace metals is about 2 seconds. When the trace metals particulates are surface stabilized by less wettables organic coatings, the particles have estimated residence times in the surface microlayer of from 1 to 30 minutes.

Lipophilic pollutants (e.g. PCBs, chlorinated pesticides, organic forms of heavy metals, etc.) may be accumulated by natural or pollutant organic surface films. Lifetimes of pollutants in natural slicks are probably measured in hours, but under extended periods of calm marine weather, a lifetime of a day or two may occur. The persistence of organic sea surface films is governed by the dynamics of the air-sea interface, and when winds exceed $4-5 \text{ sec}^{-1}$ natural slicks usually disappear. When calm conditions recur there is a potential for lipophilic pollutants to return to the sea surface.

Oil spills may survive as continuous films and emulsions at the air-sea interface for hours or days depending upon environmental conditions and the nature of the petroleum product spilled.

It is essential to predict the frequency, distribution and longevity of natural and petroleum slicks, in order to ascertain the importance of organic films as collectors of oleophilic pollutants at the sea surface. The most influential factors limiting the existence of organic surface films are air-sea dynamics; breaking waves, bursting bubbles, sea spray, and wave processes which disperse the films by entrainment, turbulent transport, etc. In addition, constituents of a surface film are selectively removed by dissolution, evaporation, biological degradation, spreading and photocatalytic oxidation. The lifetime and fate of natural and petroleum slicks in the marine environment has been related to such dispersive processes. Because of the great influence of wind and waves, the probability of encountering slicks or persistent oil films in the open ocean may be related to average wind conditions. Data on visual observation of oil slicks on the Mediterranean derived from the IGOSS Pilot Project on Marine Pollution (Petroleum) Monitoring show that greater than 10% of visual observations indicated the presence of oil over most of the sea surface. This rate of positive observations is considerably higher than the corresponding rate generally found for the open ocean. Consequently, there is a corresponding potential for the incorporation and concentration of other oil-soluble pollutants into the petroleum films on the Mediterranean, a condition which can lead to an increased sea surface lifetime for the solubilized pollutants.

R. P. CHESSELET

Basis for the selection of a pilot pollutant for the study of the atmospheric transfer of harmful substances into the Mediterranean Sea

In the marine aerosols collected over the global ocean, cadmium (Cd) is shown to belong to the "anomalously enriched elements" (AEE)* group which encompasses almost all the heavy metals. This means that the concentrations of these elements are enriched relative to either bulk seawater or average coastal material. This enrichment was also found for Cd recently collected over the Western Mediterranean during ETNA 80 and PHYCEMED 81 cruises. Over the Western Mediterranean in about 30 samples of 24 hours duration, the average concentration of Cd is 0.50 ng/m^3 , while for the North Atlantic, its average concentration from a 2 year survey is 0.10 ng/m^3 .

The Cd enrichment factor (EF/crust)*, over the Western Mediterranean is shown to be about 1,000, while over the North Atlantic it is around 400. This factor of 2 in the Cd EF/crust is greater than statistical uncertainties in the calculation. A crude approximation of Cd delivery to the Western Mediterranean from the atmosphere is about $150 \text{ tons/year}/10^6 \text{ km}^2$, which is between 1 and 5 per cent of the total delivery of Cd to the atmosphere by man's global activities. It has been shown that man's activities in nations bordering the Western Mediterranean is introducing about 1 per cent of the global Cd delivered to the atmosphere. Thus from a crude mass balance approach it appears that the Cd geochemistry over the Western Mediterranean is mostly controlled by man's activities. At this point, it is interesting to note that the Cd input of Mount Etna's volcanic activity is 10 tons per year which constitutes only a small percentage of the Cd atmospheric burden over the entire Mediterranean.

Methodology

- (a) By flameless atomic absorption it has been shown that the absolute detection limit for Cd is 10^{-11} g . For a filtration of air over the sea of about 100 m^3 , the operational sensitivity of the method is: 0.1 ng/m^3 , which provides good precision in the Cd concentration measurements. The real problem is to maintain a strong control over the "filter blank" before sampling.
- (b) The samples, inland or on board ships, should be collected on the only appropriate filter which is the Whatman 41 filter of 7 cm diameter. For remote platforms, sample holders should be placed on the top of a tower at about 10m above the sea surface. Wind direction and speed during sampling should be continuously monitored for both inland and ship board collection of aerosols.

* See previous INTERPOLL reports.

V. PRAVDIC

Comments on the research components of future international programmes on the air-sea interchange and atmospheric transport of pollutants

The task of developing a scientific rationale for future international research and monitoring programmes of airborne transport of pollutants has been on the agenda of the present Working Group ever since the first meeting in Dubrovnik, 1977. At the second session of the INTERPOLL Working Group, Vancouver, Canada, 1978, the same problem of international research and monitoring programmes was discussed.

The Working Group recommended such international programmes which would lead to a better understanding of transport of airborne pollutants through careful measurements carried out at selected locations. Indeed, the report suggested that measurements be made at sampling stations at least 100 km in all directions away from population centres, highways, and similar airborne pollution sources. For the reason of future reliability the Working Group recommended adoption of procedures described in WMO Publication No. 491 (WMO, 1978). This recommendation also requires a forecast of at least 50 years (!) of no anticipated change in land use. Furthermore, sampling sites should experience only infrequent effects from local natural phenomena, such as volcanic eruptions, forest fires, dust and sandstorms.

While such requirements can be met in several parts of the world, particularly in the Pacific, Indian and probably Atlantic Oceans, they are virtually non-existent in semi-enclosed seas such as the Baltic, the Mediterranean and the Gulf.

In its latter part the same Working Group report elaborated gas exchange, particle dry deposition research, and precipitation.

At the third session of the INTERPOLL Working Group, Miami, Florida, USA, a discussion was held on the methodology and strategy of an international project, termed INTERPASES (Interchange of Pollutants between the Atmosphere and Semi-Enclosed Seas). The conclusion of the Working Group was summarized in a few short paragraphs highlighting the main problems of such an exercise. These were (i) the choice of representative pollutants, (ii) selection of sites for measurements, (iii) measurement techniques and intercalibration among participating laboratories, and (iv) data processing and analysis.

With respect to INTERPASES and its possible first application in the Mediterranean region, it was considered advisable to use the framework of the MED POL XII (Phase I) Project, led by WMO. The Working Group concluded that all the necessary techniques of sampling, sample treatment and analysis are already available. It would depend on the participating laboratories to assess the feasibility of such a programme, i.e. availability of techniques, funding and collaboration goodwill to start such a programme. Since that time, the Protocol for the Protection of the Mediterranean Sea Against

Pollution from Land-Based Sources was signed, following a similar Protocol for the Baltic Sea. The research and monitoring of airborne pollution resulting from land-based emissions has thus become an obligation for Member States.

During INTERPOLL III progress in the SEAREX programme was also reported. It was indicated that the geochemical cycles of some heavy metals (Pb, Cu, Zn, Cd, Hg, and Se) are very sensitive to atmospheric inputs. Some 90% of all Hg has been found to be in the vapour phase, but only 10 to 60% of Se. These data have stimulated much research into the mechanism of interfacial transport of these metals, without which many previous calculations of fluxes in the geochemical cycle cannot be properly interpreted.

The ad hoc meeting of INTERPOLL, held in Tallinn, Estonian SSR, in 1981 displayed some of the most important pieces of work done by Soviet researchers in the domain of atmospheric transport of some pollutants, including sulphur and petroleum hydrocarbons and of the distribution of some low molecular weight chlorinated hydrocarbons and chlorofluorocarbons.

In the framework of MED POL - Phase II, a research exercise has been suggested, termed "Activity L: Pollutants transfer processes". Of this exercise one part concerns the air-sea interface. Within the long-term MED POL pollution monitoring programme, the so-called "Strategy D" was intended to assess the transport of pollutants mainly from diffuse, land-based sources through the atmosphere into the sea, and quite possibly vice versa. However, it was strongly stated that this strategy, although considered highly important will not be implemented before completing some preparatory activities, specifically through the research topics mentioned in "Activity L" of the MED POL - Phase II Research Programme.

Techniques, methodologies for investigation, and the proof of existence of atmospheric input paths of pollutants has all reached a level in which large scale international programmes are feasible. Major efforts should be made towards establishing agreements on standardization of techniques and methodologies of sampling and analysis. If such prerequisites are met, large scale programmes relating to semi-enclosed seas warrant significant results.

A proper understanding of the pathways of pollutants would enable the most economical solution to be found for emission control, and accordingly, a proper balance between the mandatory maximum levels of permissible concentrations of pollutants in aqueous and gaseous emissions could be established.

G. CLERICI

Computational method for monitoring the atmospheric transport of pollutants to the Mediterranean Sea

The aim of the paper is to develop a model capable to describe the impact of air pollution on the Mediterranean Sea, due to LRT. Between the two possible approaches, i.e. to start with a new model or use an existing one, a compromise solution was chosen. The starting point is the model of Jacob and Pandolfo, developed in 1971 and revised in 1979. Several modifications have been introduced in the original model, regarding:

- the adoption of a new "finite-differencing" technique
- the topographic effects
- the initialization problems
- the thermal radiation due to the atmospheric pollutant
- the vertical diffusion coefficients

So practically a new code is derived whose performance has been tested, by comparing its results with those of Jacob for the Eastern USA. A good agreement both from qualitative and quantitative points view is obtained. Afterwards the model has been applied to some Italian regions: Po Valley and the Tiber Valley district. By comparing the numerical predictions with the available experimental data of these regions, the flexibility of the model is worked out in describing different geographic and meteorological situations. At present the model has been applied to restricted regions. The extension to all the Mediterranean region is under development.

A. ELIASSEN

Modelling of long-range transport of sulphur over Europe : a two year model run and some model experiments

The "ECE/UNEP/WMO Co-operative Programme for the Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe" (hereafter referred to as EMEP) was initiated in 1977. The main objective of EMEP is to provide governments with information on the deposition and concentration of air pollutants, as well as on the quantity and significance of pollutant fluxes across national boundaries. EMEP is supervised by a Steering Body under the ECE, where participating countries, as well as ECE, WMO and UNEP are represented.

The activities of EMEP are divided into a chemical and a meteorological part. A Chemical Co-ordinating Centre (CCC), located at the Norwegian Institute for Air Research (NILU), is responsible for the chemical part of the programme. The main tasks of the CCC during the first phase of EMEP have been to collect data from national measurement programmes in the participating countries, to check and store these data and issue semi-annual data reports, and to organize interlaboratory tests of the quality of chemical analyses.

The meteorological part of EMEP is co-ordinated by WMO, and two Meteorological Synthesizing Centres (MSCs) have been designated. The Meteorological Synthesizing Centre, East (MSC-E) is situated in Moscow, and the Meteorological Synthesizing Centre, West (MSC-W) is situated at the Norwegian Meteorological Institute (NMI). In accordance with its terms of reference, MSC-W co-operates with the UK Meteorological Office.

The main tasks of the MSCs are to design, operate and using the measured chemical data, verify meteorological dispersion models which provide estimates of the quantity of sulphur pollution crossing national boundaries between European countries.

The long-range transport of sulphur over Europe is quantified using a simple trajectory model with constant mixing height. Results from a model run covering a two year period show that average concentrations of sulphur dioxide and particulate sulphate are predicted reasonably well. The calculations confirm that, in most countries in Europe, the deposition of sulphur due to foreign sources represents an important contribution to the total deposition. Seasonal concentration variations are not well predicted with this simple model. The model experiments show that improvements are gained in this respect when a variable mixing height is introduced together with an increased transformation rate to sulphate in summer and a mechanism for exchange of air between the boundary layer and the free troposphere.

S. M. SIAHMED

Before monitoring for a continuous control of air pollution, four obvious questions arise : WHAT? - WHERE? - HOW? - FOR WHAT PURPOSE?

For the first question, a provisional list of pollutants particularly heavy metals with biological effects must be discussed and agreed upon - bearing in mind the availability of information from the Mediterranean countries or other concerned (referring to the Protocol for the Protection of the Mediterranean Sea Against Pollution from Land-Based Sources) in order to give top priority to certain pollutants.

As to the second question, it is suitable in a first step to utilize in the best possible way, the existing monitoring stations, i.e. the BAPMON network already operating, and stations under national authorities. It would be understood that there would be a need for the standardization of sampling methodology. In a second step, one would be required to establish a site selection criteria for new stations, but here again there might be two possible approaches, (1) take into account the Mediterranean Sea as a whole, and if so, for a limited number of stations general trends for the entire region or (2) a defined local area and obtain a relatively higher precision and possibly try to extrapolate results to other areas in the Mediterranean with similar patterns.

Furthermore, if ship board sampling is to be undertaken, special care should be taken as pointed out in the document produced by GESAMP (Reports and Studies No. 13). Regarding the methodology and techniques sampling procedures, they must be defined for air and airborne pollutants. In that sense, recommendations should be made for unified construction and use of impactors, filters, air pumps and collectors. As far as analysis is concerned, techniques already used in MED POL projects for heavy metals should be continued and for other pollutants choosing the most reliable sampling methods as it has been stressed in the report of the first Unesco workshop on marine ecosystem modelling.

Finally, the purposes of monitoring are to describe transport processes towards and into a specific region (horizontal and vertical atmospheric transport), to better evaluate the ultimate fate of pollutants introduced into the Mediterranean, to understand the nature of the ecosystem modification resulting from exposure to these pollutants, to assess the environmental threat caused in cases of irreversible ecosystem modification and to provide the necessary information for a model calibration.

A few of the concepts related to monitoring problems in the Mediterranean have been sketched in this paper. Much remains to be discussed. And my sincere hope, is that, through wider experience of the members of the group, this work will be fully completed so that it will be of some use for the Mediterranean community.

A. TSYBAN

Atmosphere to ocean - Transport of pollutants and their influence upon geochemical and biological processes in the sea surface ecosystem

The air-sea exchange processes play an important role in the global biogeochemical cycle of carbon, phosphorus, nitrogen and sulphur. This paper contains a brief discussion of recent achievements in the study of atmospheric deposition of pollutants on the sea and their influence upon biological and geochemical processes. In terms of the aim of our work here, my short report deals with the fate of pollutants entered into the sea from the atmosphere and their pressure on marine organisms. Present investigation shows that atmospheric input of pollutants may be comparable with the river input especially in the areas of internal seas such as the Mediterranean and the Baltic, etc. It has been estimated that every year about 200 million tons of organic-carbon and about 1 million tons of phosphorus (and other nutrients) enter the ocean from the atmosphere. They provide favourable conditions for development of life in the ocean-atmosphere border line. At the same time many pollutants and pathogenic micro-organisms release into the ocean also from the atmosphere: 30.000 tons of arsenic, 60.000 tons of oil hydrocarbon, 2.000 tons of PCB, and 2.000 tons of DDT. They have an influence on important geochemical processes: temperature, surface tension, exchange of aerosols and gases, and oxidation of organic matter. They produce hazardous effects upon biological processes in this specific micro-ecosystem.

The surface microlayer is a specific zone of life with its peculiar characteristics:

1. Enrichment of organics due to foam formation and precipitation from the atmosphere.
2. Concentration of particulate matter.
3. Concentration of nutrients.
4. Concentration of toxic matters from both sources: water column and atmosphere.

The rate of organic bio-oxidation is governed by micro-organisms, including bacteria, fungi (coastal areas), Protozoa.

The importance of neuston and bacterianeuston has been discussed in many papers. Chemical compounds deposited on the surface of the ocean are accumulated in organic slicks, suspended aggregates and oil films. They affect the neuston community which plays an important part in the larval stage of many valuable food fishes.

Summarizing all the aforementioned in terms of our task here, I would like to mention the following:

1. The station for monitoring should be located in areas reflecting main water masses of the sea. At the same time all the links of the biological chain of the organisms are to be represented there.
2. The sampling and analyzing procedure should be carefully examined and correspond to contemporary scientific requirements.
3. The pollutants to be measured: molecular stable organisms and toxic metal - lead, etc.
4. The marine organisms to be monitored: micro-organisms including pathogenic forms typical for this region, and neustan organisms, mainly copepods at different stages of their ontogenesis.
5. Collection of all necessary data for budget of the pollutants in the region of the Mediterranean Sea.

J. M. MILLER

Long-range transport in North America

In the last ten years, it was recognized that acid-forming pollutants could be transported long distances. Specifically such substances as sulphate, sulphur-dioxide, nitrogen oxides and others, are carried from their sources in large industrial areas to remote areas of North America. Wet or dry depositions of these acidic materials may cause ecological damage. Because of this problem Canadian and United States' scientists under a Memorandum of Intent, have begun to study all aspects of acid rain. Two working groups were formed to investigate ecological effects and atmospheric processes respectively. The atmospheric group has written four technical reports: Local and mesoscale transport, regional transport, atmospheric chemistry and deposition modelling. From these reports, the one most relevant to the MED POL - Phase II planning is the report on the regional models.

This report was reviewed at the meeting. It covers the major regional modelling activity in North America and describes the intercomparisons of the models. The important conclusions can be summarized as follows:

While differing opinions remain within the modelling community as to the proper method and the statistics to be used for evaluation and intercomparison of model results, the US-CANADIAN REGIONAL MODELLING SUBGROUP has designated common evaluation criteria for performing this task for the eight selected models used in this application.

It is generally accepted that one should expect model predictions to deviate from measurements because a practical model cannot incorporate even our current understanding of the relevant chemical and physical processes, and because our available emissions and monitoring data bases contain inaccuracies and are insufficient to estimate the ensemble average which the model is designed to predict. Due to these deficiencies, it is not possible to quantify the uncertainties in model predictions based on the differences between model predictions and observations (residuals). Furthermore, the assumption of linearity by the models provides for rate constants that are independent of emissions and co-pollutant concentrations. The question is raised as to whether the linear models of sulphur transport represent reasonable first approximations in the absence of operational non-linear models. It thus becomes subject to individual scientific judgement whether or not non-linear effects would invalidate the general seasonal and annual results of these linear models.

V. KOROPALOV

Organic pollutants in the atmosphere over the ocean

Organic compounds (freons and some others), belong to the group of minor atmospheric pollutants which can deplete stratospheric OZONE. To obtain data on large scale processes of minor pollutants spreading in the troposphere, the concentrations of F-11, F-113, CH₃Cl, CHCl₃, CH₃CCl₃, in the near-water atmospheric layer were measured during the XXXI cruise of the research vessel "Academic Korolev" (January-April 1982) in the Pacific and Indian Oceans.

Using the preliminary analysis of the obtained results on the base, one can make the following conclusions:

- Atmospheric concentrations of F-11, F-113, CHCl₃, and CH₃CCl₃ are not uniformly distributed between the northern and southern hemispheres.
 - Considerable variability of CHCl₃ and CH₃CCl₃ atmospheric concentrations over the ocean observed at the meridional cross-section in the Pacific makes it possible to assume presence of significant tropospheric sources and sinks for the pollutants.
 - A rather uniform distribution of CH₃Cl atmospheric concentrations over the ocean and their slight increase at sub-tropical latitudes confirms the hypothesis according to which the ocean is the basic source of CH₃Cl.
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EXPLANATORY REMARKS TO LIST OF STATIONS

- x generally refers to an existing situation, while
+ generally refers to an action which is being prepared or envisaged

- Column 1 Indicates the country operating the station
- regional stations are not underlined
 - regional stations with extended programme are dashed
 - baseline stations are fully underlined
- Column 2 Indicates the WMO Regional Association to which the Member operating the station belongs
- Columns 3-6 Indicate the status of implementation of the station
- Columns 7-9 Indicate longitude, latitude and elevation above mean sea level of the station
- Columns 10-15 Indicate the observation programme carried out at the station
- wet precipitation (10) indicates that precipitation collection is carried out by means of a gauge which is only open during a precipitation event, either automatically or manually operated
 - bulk precipitation (11) indicates that precipitation collection is carried out using a continuously open gauge
 - turbidity (12) observations are made with sunphotometers at several wavelengths and under clear sky conditions. At some stations actinometers are still used
 - SPM (13) = Suspended Particulate Matter, sampled by means of high volume air samplers supposed only to collect particles smaller than 15-30 m
 - CO₂ (14) carbon dioxide monitored by continuously operated nondispersive infrared (NDIR) analyzers. Under certain circumstances grab sampling (usually by flask) is carried out
 - "other" (15) refers to additional activities exceeding the minimum monitoring programme, including, e.g. gaseous parameters. Details, if available, are given in Column 27
- Columns 16-19 Give the type of data reported by the station

- Column 20 Shows whether the country is participating in the laboratory intercalibration exercises organized by the WMO Precipitation Chemistry Reference Laboratory
- Columns 21-25 Indicate the type of equipment provided, either from UNEP funds, VCP or, in some cases, through bilateral co-operation
- Column 26 x indicates that one and xx indicates that two or more visits have been made by consultants appointed for this purpose or by WMO staff members. Objectives of such visits were to give special advice and assistance required or to discuss the possible establishment of BAPMON stations
- Column 27 Remarks, gives additional information as appropriate
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