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Atmospheric transport of contaminants into the Mediterranean region

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PREFACE

GESAMP, the Joint Group of Experts on the Scientific Aspects of Marine Pollution, was established in 1969 and is today co-sponsored by the International Maritime Organization (IMO), Food and Agriculture Organization of the United Nations (FAO), United Nations Educational, Scientific and Cultural Organization (UNESCO), World Meteorological Organization (WMO), World Health Organization (WHO), International Atomic Energy Agency (IAEA), United Nations and United Nations Environment Programme (UNEP). According to its present terms of reference, the functions of GESAMP are:

- to provide advice relating to the scientific aspects of marine pollution [1/]; and
- to prepare periodic reviews of the state of the marine environment as regards marine pollution and to identify problem areas requiring special attention.

Since its beginning GESAMP involved a large number of experts as members of GESAMP or GESAMP Working Groups and produced, at the request of the sponsoring organizations, numerous reports [2/].

This document reproduces the substantive part of the report of the GESAMP Working Group on Interchange of Pollutants between the Atmosphere and the Oceans, approved by the fifteenth session of GESAMP (New York, 25 - 29 March 1985).

At the request of the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona, 1976) the WMO-led GESAMP Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans in 1981 was invited to describe air pollutant transport processes towards and into the Mediterranean Sea (including horizontal atmospheric transport affecting the region, vertical atmospheric transport to the air-water interface and air-water interchange) and to review the scientific literature and assess the pathways and fluxes of important contaminants into the Mediterranean region.

To tackle these tasks the Working Group held three meetings in 1982 in Monte Carlo, in 1983 and in 1985 in Athens. At the Monte Carlo meeting a conceptual model was developed as regards atmospheric transport processes towards the Mediterranean Sea which included a general strategy of relevant activities, recommendations on suitable monitoring sites, model approaches and a pilot contaminant - cadmium, on sampling and analytical methodologies and data handling.

1/ GESAMP defined marine pollution as "introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea-water, and reduction of amenities."

2/ V. Pravdic: GESAMP, The First Dozen Years. UNEP, 1981.

At the Athens meeting in 1983, model approaches and the data requirements for the applications of dispersion models enabling to estimate the flux of contaminants (heavy metals) from the atmosphere into the sea were discussed in detail and a general framework was formulated of a pilot project for the study of the atmospheric transport of contaminants into the Mediterranean.

A review of the knowledge of the physical, chemical and biological processes, which control the air-sea exchange of contaminants, and of the results of relevant research conducted in the Mediterranean along with a brief description of existing programmes in other regions were made at the expert consultation held in Athens in 1985. At that meeting the outcomes of two previous meetings were also generalized and the present report entitled "The Atmospheric Transport of Contaminants into the Mediterranean Region" was prepared.

The Third Meeting of the Working Group for Scientific and Technical Co-operation for MED POL (Athens, May 1985) recommended to initiate in 1986 a pilot-project on "studying air pollutant deposition into the Mediterranean region and pollutant concentrations in air" using this report as a basis for such a pilot project.

The activities of the GESAMP Working Group on Interchange of Pollutants between the Atmosphere and the Oceans were organized by the World Meteorological Organisation (WMO), acting as the "lead agency". Financial support for the Working Group was provided by WMO and UNEP.

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1. EXECUTIVE SUMMARY

Since the eleventh session of GESAMP, at the request of UNEP, the Working Group on the Interchange of Pollutants Between the Atmosphere and The Oceans (INTERPOLL) 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, the Group examined horizontal atmospheric transport, vertical atmospheric transport to the air/water interface, and the interchange at this boundary. The Working Group also reviewed the scientific literature pertinent to this problem. During its fourth and fifth sessions which took place in Monaco in 1982 and in Athens in 1983, the Working Group discussed the specific requirements of the MED POL programme and made relevant recommendations. The reports of these two sessions were analyzed during the present meeting and used, along with more recent data, to produce the present interim report on atmospheric transport of contaminants into the Mediterranean Region.

The first part of this report provides a review of the knowledge of the physical, chemical and biological processes, which control the air-sea exchange of contaminants, along with a brief description of existing programmes in the Pacific Ocean, the North Atlantic, the Baltic Sea, the North Sea and the Mediterranean Sea. The second part of the report discusses existing works relevant to the Mediterranean area. A limited data base exists for contamination of marine concern, with most information on air concentrations of heavy metals (particularly Cd and Pb), PCB's and n-alkanes, and very little information on concentrations in precipitation. The available data indicate that levels of atmospheric contamination over the Mediteranean are comparable to those over other European regional seas. Indirect evidence, based on the association of some metals (eg. Cd, Pb) with submicrometer-sized particles, and direct evidence based on the transuranic content of Mediterranean rains, suggest that the sources for some atmospheric contaminants transported into the Mediterranean Sea are quite distant. Natural inputs of some metals (on a regional or episodic basis) into the Mediterranean atmosphere were also considered to be important. These include volcanic activity and soil erosion particularly from the Sahara. Flux estimates for some elements, such as Hg, Cd, Pb, Cr, and transuranic elements, indicate that the atmospheric transport of contaminants is at least comparable in magnitude to riverine inputs into the Mediterranean.

Evaluating the pathways of contaminants to the region requires a comprehensive understanding of climatology and meteorology of the region. An analysis of nine years of back trajectories to the western Mediterranean showed that northerly flow took place 30% of the time with relatively large changes from year to year and with no significant seasonal variation. Also the number of the trajectories from the south was greater in the early summer and this transport would be expected to bring desert dust particles during this period. In the eastern part of the basin, the trajectories climatology shows that flow from the north and northwest is predominant.

To assess the contributions of different source regions to the concentrations and deposition in the Mediterranean area, the application of a mathematical model is strongly advised. Detailed suggestions with regard to one type of model for long range transport and its application are given.

The Working Group recognized the problems in assessing atmospheric pollutant input into the Mediterranean, identifying in particular the need for more quantitative information on emission sources of pollutants in the region, local climatological data, transport pathways and air-sea exchange rates of pollutants. A strategy for such an assessment was developed in which Cd, was recommended as an appropriate substance for study in a pilot project. For such a pilot project, sampling sites, sampling methodology and analytical techniquss have been suggested.

2. INTRODUCTION

The fields of marine chemistry and marine contamination have long been concerned with understanding the budgets of chemical species in the oceans and the geochemical cycles of these elements. Initially, research focused on the most obvious input flux to the oceans - that borne by rivers. However, it is now recognized that a substantial fraction of the contamination entering the ocean derives from sources located on land via atmospheric input (NAS, 1978; Waldichuk, 1982). Contaminants of major concern are heavy metals and matalloids such as Pb, Cd, Hg, As, and Sn, petroleum hydrocarbons, chlorinated hydrocarbons and pathogenic microorganisms. Such elements or substances are present in the air in the particulate form and/or in the gaseous form. The atmospheric lifetime of such materials is generally long enough (greater than 1 day) to allow them to be transported far from their sources (greater than 1000 km). On the other hand, these lifetimes are often too short (less than 1 year) to allow uniform horizontal and vertical mixing of contaminant material in the global atmosphere.

The study of atmospheric transport to the sea is in many ways analogous to the study of river transport. In both cases there is a common objective, that of defining the temporal variability of the flux - how does the source output vary with climate and human activity? An understanding of this variability is essential if we are to characterize the present day flux. The characterization of the temporal and areal variability of the continent-to-ocean wind-borne flux is a difficult task. In contrast to rivers, which have well-defined channels and are relatively shallow, the winds are global in scope and they have significant vertical structure. Thus, in order to quantify atmospheric transport, it is necessary to develop a comprehensive understanding of the governing meteorological processes, such as wind flow and precipitation patterns, and to evaluate their effects on the chemical fluxes.

2.1 Transport Processes

2.1.1. Horizontal Transport

In the simplest sense, atmospheric transport to the ocean, as seen from a meteorological perspective, can be regarded as occurring in two different scales: off-shore and long range (NAS, 1978).

In the off-shore transport mode, it may be assumed that a considerable fraction of contaminant deposition will occur on waters relatively close to the major coastal sources (less than 100 km). In this mode, the transport of contaminated air parcels takes place in the turbulent, relatively shallow boundary layer which is well-mixed in the vertical plane (height less than 1000m). This flow is essentially two-dimensional in the horizontal plane and the resulting deposition pattern extends directly from the source. In many cases, the problem here is similar to atmospheric deposition of contaminants around urban areas. On such a scale, the well known Gaussian plume model dominates most practical applications since assumptions that the wind field is uniform and that the turbulence is homogeneous are approximately valid

within the boundary layer and therefore lead to a considerable simplification in the prediction of contaminant dispersion. Various models of this kind are available in the literature (Atmospheric Environment, 1984; Ritchie et al., 1983; Van Egmond and Kesseboom, 1983). They all include transport, transformation, and removal (dry deposition and precipitation) processes. Provided that detailed local meteorological information and source emission strengths are continuously available, such models can predict reasonable well, within a factor of 2 or 3, deposition rates of contaminants on a monthly or yearly basis.

In contrast to offshore transport, long range transport (100-1000km and greater) involves mechanisms that incorporate chemical substances into the upper troposphere. The air parcel eventually undergoes large-scale descent and again becomes incorporated into the boundary layer. During ascent, interactions with cloud and rain droplets can chemically and physically alter, effectively remove and vertically displace some of the trace constituents. Such interactions are extremely complex and still little understood, and models capable of describing the complete three-dimensional picture of emission/deposition have not been developed. Nevertheless, recent advances in computer techniques have allowed the development of a number of methods which can be applied in evaluating transport to the ocean (Eliassen, 1978).

A recent promising method for interpreting long-range transport is the use of air trajectory models. The construction of atmospheric trajectories has been a useful tool in meteorology for decades. Computer techniques now permit the routine computation of numerous trajectories to relate pollution movement forward in time from sources of emissions and also backward in time from sampling arrays. They can be constructed using several techniques based on pressure and temperature fields and observed wind fields (Miller 1981; Wilson et al 1982: Miller and Harris 1985; Merrill et al, 1985). When calculated over a period of a number of years, trajectories are extremely useful to describe long-range flow climatology and to characterize year to year variations.

When combined with chemical measurements, the use of trajectories provides a means to identify the source region of materials being investigated. For example, together with daily chemical measurements from ships, backward trajectories have been recently used over the Mediterranean Sea (Arnold et al., 1982; Chester et al., 1984). Such an approach has resulted in a qualitative evaluation of the transport and has helped to understand the observed day-to-day variations of concentrations and deposition which appear to be significant over the Mediterranean Sea. For example, during the PHYCEMED I cruise (1981), high atmospheric concentrations of metals associated with silicate dust from soil erosion have been related to an episode of fast transport, less than three days, of soil-derived aerosols from North Africa. During that period, the first day showed the highest concentrations of metals such as lead, likely due to the passage of the air parcel over the Barcelona region (Arnold et al., 1982).

In recent years, simplified linear dispersion models have been developed in order to estimate long term (annual or seasonal) deposition patterns of sulfur in Europe (Eliassen, 1978) and in North America (Young, 1982). For example, the EMEP study in Europe used a simple trajectory model with constant mixing height. The results from model runs covering a two year period showed that average concentrations of sulfur dioxide and particulate sulfate are predicted reasonably well (Eliassen and Saltbones, 1982). The calculations are based on emission data for 150 by 150 km squares and air trajectories followed for 96 h arriving at the center of all grid elements every 6 h. Results of such calculations were then compared with measurements at 70 stations throughout Europe. Such calculations have confirmed that, in most countries in Europe, the deposition of sulfur due to foreign sources represents an important contribution to the total deposition. This model has been applied recently with some success to understand the transport of trace metals to southern Norway (Pacyna et al., 1984).

2.1.2 Deposition

There are two basic processes by which contaminants enter the ocean from the atmosphere: dry deposition and wet deposition. Both processes are poorly understood (NAS, 1978; Liss and Slinn, 1983).

a. Wet Deposition

Collection of precipitation samples which are representative of trace quantities of contaminants over the ocean is often quite difficult. To distinguish wet from dry deposition, wet-only sampling is required, i.e. sampling only when rain is actually falling. Wet only sampling includes both the rainout (within-cloud scavenging) and washout (below-cloud scavenging) components of wet deposition. In recent years, specific protocols have been developed to insure that samples are not contaminated during the collection process. In fact the type of collector, period of sampling, and handling procedures may have a significant impact on the quality of the data (WMO 1983).

Washout factors, or scavenging ratios, are often used to relate atmospheric concentrations of substances present in aerosols or in the gas phase to their concentrations in rain. Washout factors have been defined in several ways, but all involve a ratio of the rain concentration to the atmospheric concentration of the substance of interest. A detailed review of washout factors and precipitation scavenging is presented by Slinn (1983). Once the relationship between the concentration of substance M in the air and in the precipitation has been established, one can utilize its atmospheric concentration of M, which can usually be more easily and accurately determined, to predict the concentration in precipitation.

The use of washout factors to calculate deposition rates of substances implicitly assumes that the concentrations in rain and air are linearly related. However, it is very difficult, if not impossible, to rigorously test the significance of this relationship. Problems arise because of possible differences in the removal efficiency of particles as a function of chemical composition and rain droplet size. Rain concentrations represent an integrated removal

thoughout the atmospheric column through which the rain is falling, while the air concentration is determined only at the surface. Thus substances with different vertical concentration profiles but similar surface air concentrations might have very different washout factors. For gases, it must be assumed that vapor phase equilibrium with the rain is attained rapidly.

An additional problem faced in truly remote regions is that it may take many hours, occasionally even days, to collect an aerosol particle or gas sample large enough to analyze for many substances, whereas the rain sample may be collected over a period of minutes to hours. Thus the true atmospheric concentration, even at the surface, appropriate to the washout factor calculation may not really be known. Washout factors for gases vary greatly depending on the Henry's Law Constant for the gas, since

$$C_R = C_A H \qquad (1)$$

where C_R is the concentration in rain

C_A is the vapor concentration in air, and

H is the Henry's Law Constant.

Only a set of carefully collected rain and air samples should be utilized to determine appropriate values for washout factors for contaminants of interest at each sampling site.

b. Dry Deposition

(i) Aerosols

The dry deposition of aerosol particles to the ocean surface refers to all deposition processes except precipitation. It is often estimated by utilizing the dry deposition velocity, v_d, given by

$$v_d = F/M \qquad (2)$$

where v_d is the dry deposition velocity

F is the flux of particles to the surface, and

M is the atmospheric concentration.

Direct measurements of the dry deposition of trace substances on aerosol particles to the ocean surface are not technically feasible at present. One method for obtaining reasonably accurate estimates of dry deposition is the use of available models of dry deposition to a water surface as a function of particle size (Slinn 1980 and 1981; Williams, 1982; Slinn, 1983). However, the use of such models requires an accurate measurement of the mass-size distribution of the trace metals. In addition, dry deposition velocities depend markedly upon particle size, relative humidity and wind speed.

Model calculations of dry deposition have been rather successful for sea-salt aerosol particles, provided extreme care was taken to obtain air samples that represent the true sea-salt particle mass and size distributions (McDonald et al., 1982). Acceptably accurate size distributions for sea-salt aerosol particles can be deduced from the use of high-volume cascade impactors, when proper corrections are made for particle loss in the largest size range. The situation is even worse for trace elements such as Pb, As and Cd because a major fraction of the mass of these elements occurs on particles less than 0.25 um radius, and cascade impactors currently in use do not separate particles below that size range.

(ii) Gases

Unfortunately techniques are not yet available to measure directly gas fluxes across the air/sea interface. Fluxes must be estimated by use of gas exchange models. Liss (1973) has reviewed the process of gas exchange across the air/sea interface. In a two-layer boundary system at an air/water interface the flux of any gas through each boundary layer is given by:

$$F = k\,c \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where F is the flux

c is the concentration difference across the particular layer

k is the corresponding transfer velocity.

As Liss (1973) points out, k depends on many factors, including the degree of mixing of the water and air and the chemical reactivity of the gas. The reciprocal of k is often called the resistance, r, and is a measure of the "resistance" of the gas to transfer. It has units of sec/cm. The total resistance to the exchange of any gas will be the sum of the resistance in the gas and liquid phase laminar layers. Surface contamination, such as an oil film, would contribute to the resistance in the liquid phase.

The exchange of gases which are not particularly soluble in water, e.g. N_2, O_2, CO_2, and the inert gases is largely controlled by the resistance in the liquid phase. This group includes a number of synthetic organic compounds. On the other hand, the exchange of such very soluble gases as H_2O, SO_2, HNO_3, HCl, etc. is controlled by resistance in the gas-phase laminar layer. This class of compound is often quite reactive in the aqueous phase.

c. Complications in Wet and Dry Flux Determinations

While an accurate measurement of the concentration in rain and dry deposition is a necessary first step in evaluating fluxes of substances to the ocean, it is not sufficient in itself. Let us take trace metals as an example. The total amount of rainfall in the period of interest, per year for example, must be known. Potential problems arise concerning variability of rainfall amount and intensity with season and how this will affect the metal concentrations, as well as

how seasonal changes in wind flow patterns or particle production processes will affect atmospheric metal concentrations at the marine location. Even taking these factors into consideration, significant problems remain. In the marine environment, the gross deposition of a metal to the ocean is composed of a net input as well as a component associated with recycled sea spray. The importance of the atmosphere as a transport path for material from the continents to the ocean can only be assessed accurately if the relative contributions of the net and recycled components can be distinguished (Arimoto et al., 1985; Jickels et al., 1984; Settle and Patterson, 1982). There is strong evidence that atmospheric sea salt particles produced by bubbles bursting at the sea surface contain many metals in concentrations considerably higher than would be expected on the basis of the metal-to-sodium ratio of near-surface water. It is apparent that some fraction of these metals is associated with surface active organic material and is scavenged by the raising bubbles and concentrated on the sea salt particles produced from a very thin layer of the air/sea interface when the bubbles burst (Weisel et al., 1984). If this fractionation is not taken into account, the calculated net deposition to the ocean will be anomalously high.

More sophisticated techniques for accurately evaluating this recycled fraction must be developed. Future work should focus in two areas: a) the use of adequate tracers (stable or radioactive) during field measurements; and b) an improvement of our knowledge of metal/Na ratios as a function of sea-salt particle size through carefully designed in situ or laboratory experiments.

2.2 Sea-Surface Microlayer

The sea-surface microlayer represents the thin water layer at the air-sea interface, where accumulations of material, living and dead, can occur. A detailed description of processes occurring in the microlayer is given in GESAMP Reports and Studies No. 13 (GESAMP, 1980). The thickness of the microlayer is usually defined operationally, i.e., it is dependent on the technique used to sample the microlayer and may range from 1 um to 1000 um. Therefore, it is important to compare concentrations of materials in the microlayer from one set of observations with another only when the same technique of sampling has been used. The microlayer is the site of accumulation of oil films, both natural and man-made. Secretions of organisms contribute to the natural films, while introduction of petroleum hydrocarbons from deliberate or accidental spills usually contribute to the man-made films. Oil films are capable of concentrating various lipophilic organic substances, such as organohalogen compounds, as well as concentrating metals (see Table 1). Thus, in the context of air-sea exchange of contaminants, the microlayer represents the location where there is a holdup, or discontinuity, in the transfer process. The extent of this holdup is determined by the residence time of a particular material in the microlayer.

In comparison with the other marine interfaces, the transit time for most contaminants across the air-sea boundary is relatively short. The estimated residence time for water wettable particulate trace metals is about 2 seconds. On the other hand, when the trace metal particulates are surface stabilized by less wettable organic coatings, the particles have estimated residence times in a 50-micrometer thick sea surface layer of from 1 to 30 minutes (Hunter, 1979). Pattenden et al. (1981) postulated that the residence time for most heavy metals was 5-20 minutes in a microlayer of 1 micrometer thickness. Hardy (1985) predicts residence times in a calm sea surface layer (50 micrometers) of from 3.5 to 15 hours, increasing through the series Ag, Zn, Mn, Pb, Cu and Ni, while with a 4 $m.s^{-1}$ wind the residence time varied from 1.5 to 8.5 hours.

Various forms of microorganisms, plants and animals, are associated with the microlayer and are collectively termed neuston. They consist of bacterioneuston, phytoneuston and zooneuston. Like the non-living organic and inorganic matter, neuston organisms concentrate in and near the microlayer. These organisms are enriched in the microlayer, compared to the seawater only a few cm below, by factors of $10^2 - 10^4$ for bacterioneuston, $1 - 10^2$ for phytoneuston and 1 - 10 for zooneuston (Hardy, 1982). Neuston organisms engage in various processes, which undoubtedly affect the transfer of substances between the atmosphere and the sea. These include biodegradation, biotransformation, bioaccumulation, exudate release, defecation, photosynthesis, predation and diurnal vertical migration. There are few quantitative data on the effects of the foregoing processes on air-sea exchange of pollutants and other substances. These effects probably vary with the physical and chemical characteristics of a particular marine area.

How the sea-surface microlayer affects air-sea transfer of pollutants in the Mediterranean is unknown, but it is expected to be rather small in relation to other processes involved in air-sea exchange for water-wettable species. Under quiescent conditions, however, oleophilic pollutants may have a sufficient residence time in organic films at the air-sea boundary for bioaccumulation by neustonic organisms.

2.3 Aerobiological Involvement in Atmospheric Contaminant Transport

A general review of biological involvement in air-sea exchange was given in GESAMP Reports and Studies No. 13, Section 4 (GESAMP, 1980). The introductory paragraph to that section bears repeating here:

"Marine plants and animals may be involved in the exchange of pollutants between the atmosphere and the sea in a number of significant ways: (a) excrete oily substances, which form a film on the sea surface and alter air-sea exchange; (b) release substances that enter the atmosphere; (c) bioconcentrate certain substances entering the sea from the atmosphere and *biomagnify these through the food chain; (d) *acute toxicity or sub-lethal effect to organisms in the

(* The present group considered these statements questionable for certain contaminants)

Table 1. Concentrations of different constituents and enrichment factors in the microlayer

Pollutant	Microlayer Concentration[a]	Enrichment Factor[b]	Region	Reference
Metals				
Ni	0.4 - 36 ug l^{-1}	(-0.6)- 12.3	North Sea	Hunter, 1980
Cu	0.4 - 5.3 ug l^{-1}	(-0.1)- 4.3	North Sea	Hunter, 1980
	0.1 - 0.5 ug l^{-1}	(-0.5)- 48	North Atlantic	Piotrowicz et al, 1972
Zn	2 - 13.2 ug l^{-1}	0.4 - 2.2	North Sea	Hunter, 1980
Cd	60 - 920 ng l^{-1}	(-0.6)- 6	North Sea	Hunter, 1980
Hg	16 - 93 ng l^{-1}	(-0.6)- 3.4	NE Pacific	Williams et al., 1974
Pb	1.5 - 10.7 ug l^{-1}	0.1 - 2.4	North Sea	Hunter, 1980
^{210}Pb	43 - 169 fCi l^{-1}	1.3 - 4.8	Mediterranean	Heyraud & Cherry, 1983
	27 - 188 fCi l^{-1}	0.9 - 7.3	Vineyard Sound, USA	Bacon & Elzerman, 1980
^{210}Po	38 - 225 fCi l^{-1}	1.7 - 7.4	Mediterranean	Heyraud & Cherry, 1983
	45 - 234 fCi l^{-1}	0.4 - 6.4	Vineyard Sound, USA	Bacon & Elzerman, 1980
Organics				
PCB	31 - 42 ng l^{-1}	23 - 43	Mediterranean	Burns & Villeneuve, 1983
	3.8 - 26 ng l^{-1}	3 - 463	Sargasso Sea	Bidleman & Olney, 1974
	5.2 - 6.2 ng l^{-1}	(-0.1)- 0.3	N. Pacific	Williams & Robertson, 1975
p,p' DDT	0.2 - 2.1 ng l^{-1}	8.3 - 13	Sargasso Sea	Bidleman & Olney, 1974
o,p DDT	0 - 0.3 ng l^{-1}	0 - 5	Sargasso Sea	Bidleman & Olney, 1974
HCB	2.5 - 3.2 ng l^{-1}	2.7 - 4.4	Mediterranean	Burns & Villeneuve, 1983
Lindane	2 - 4.4 ng l^{-1}	3.1 - 6.7	Mediterranean	Burns & Villeneuve, 1983
Hydrocarbons				
n-Alkanes	0.2 - 13.3 ugl^{-1}	(-1)- 266	Mediterranean	Saliot & Marty, in press
non-aromatic	1.9 - 34.2 ug l^{-1}		Mediterranean	Saliot & Marty, in press
aromatic	49 - 165 ng l^{-1}	(-0.56)-3.59	Mediterranean	Saliot & Marty, in press

a. All samples were collected with a screen.
Numbers listed are rounded for uniformity, whereas the original data are often given to greater precision.

b. The Enrichment Factor is calculated from $\frac{\text{(concentration in the microlayer)}}{\text{(conc. in the subsurface water)}} - 1$

Negative values mean that depletions in the microlayer have occurred.

surface microlayer from substances introduced through the sea to the atmosphere; (e) microorganisms may be concentrated in the surface microlayer and projected into the atmosphere by bursting bubbles, or transferred from the sea surface to the overlying air by wind spray".

With respect to atmospheric contaminant transport, the most significant biological involvement stems from the injection of microorganisms into the atmosphere from the sea. The greatest concern arises from the potential wind transport of pathogenic bacteria and viruses from sewage-polluted sea areas to humans on the seashore or even further inland. Data on concentrations of different organisms in the microlayer and enrichment factors therein for various regions in the world are given in Table 2. There are comparatively few data on concentrations of microorganisms in the microlayer of the Mediterranean, and no known data are available on the concentrations of such organisms or their metabolites in the atmosphere over the Mediterranean or over adjacent land.

2.4 Review of some Existing Programs on Air-Sea Chemical Exchange

The growing awareness of the importance of the atmosphere as a transport path for both natural and pollution derived substances to the ocean has led to considerably increased research efforts in the past 5-10 years. Of particular importance have been several large scale interdisciplinary, and often international, efforts to evaluate air/sea exchange rates and processes. Geographical areas covered by these research programmes range from the open Pacific Ocean to the western Atlantic and the North and Baltic Seas. Techniques of sampling, analysis and quality control for each programme are reviewed in relevant documents reporting results of each (e.g. Arimoto et al, 1985, for the SEAREX programme). Brief descriptions of some of these programmes follow:

2.4.1 The Sea/Air Exchange Program (SEAREX)

The objectives of SEAREX are as follows:

Sources: To identify the sources of the substances found in the marine atmosphere over the Pacific Ocean.

Transport: To investigate the meteorological processes that control the transport of materials from continental sources to the ocean and to model these processes.

Fluxes: To investigate the mechanisms of exchange of these substances across the sea/air interface, to measure the net deposition of these substances to the ocean, and to assess the impact of atmospheric fluxes on marine chemical cycles.

To accomplish these objectives quantitative measurements have been made for selected species in the atmosphere and precipitation: trace elements (e.g., Pb, Cd, Zn, Se, Sb, Cu, Fe, Mn, Hg, Ag, V, B, etc.); alkali and alkaline earth metals; soil dust and mineral aerosol; ^{210}Pb and its daughter ^{210}Po; $SO_4^=$; NO_3^-; the halogens; sea salt; ozone; particulate organic carbon; a number of organic compounds, particularly PCB's, DDT, HCB, and other heavy chlorinated hydrocarbons; aliphatic hydrocarbons; phthalate plasticizers; fatty acids; fatty and steroidal alcohols; and wax esters. Standard meterological variables

Table 2. Concentrations of various organisms in the microlayer and enrichment factors therein for various parts of the world oceans

Material	Collection Method	Microlayer Conc.[a]	Enrichment Factor[b]	Region Sampled	Reference
Bacteria	Screen	1.4×10^{1} to 5.9×10^{2} ml^{-1}	3.4 to 37.4	San Francisco Area	Lion et al., 1979
	Screen	0 to 2.5×10^{2} ml^{-1}	0. to 250.	Alaskan Coast	Taiban & Teplinskaya, 1972
	Screen	--- 2.4×10^{3} ml^{-1}	--- 299.	California to Panama	Gieburth, 1961
	Teflon	1.4×10^{4} to 1.4×10^{5} ml^{-1}	10. to 386.	Swedish Coast	Kjelleberg & Hakansson, 1981
	Adsorption	10^{5} to 10^{8} ml^{-1}	0.1 to 1×10^{6}	Gulf Coast	Crow et al., 1975
	Bubbling	2.6×10^{6} to 3.5×10^{7} ml^{-1}	32. to 249.	Scripps Pier, Calif.	Dezdak & Carlucci, 1972
Yeasts	Adsorption	10^{3} to 10^{4} ml^{-1}	10. to 100.	Gulf Coast	Crow et al., 1975
Molds	Adsorption	10^{3} to 10^{4} ml^{-1}	10. to 100.	Gulf Coast	Crow et al., 1975
Fungi	Adsorption	10^{4} to 10^{5} ml^{-1}	10. to 100.	Gulf Coast	Crow et al., 1975
Flagellates	Drum	4.5×10^{3} ml^{-1}	--- ---	La Jolla, California	Harvey, 1965
	Drum	1.7×10^{3} ml^{-1}	--- 4.7	Hawaii Lab Tank	Harvey & Burzell, 1972
Dinoflagellates	Drum	3.1×10^{4} ml^{-1}	--- 27.4	La Jolla	Harvey, 1966
Ciliates	Drum	3.3×10^{2} ml^{-1}	--- 2.3	La Jolla	Harvey, 1966
	Drum	2.2×10^{3} ml^{-1}	--- 5.9	Hawaii Lab Tank	Harvey & Burzell, 1972
Diatoms	Drum	9.3×10^{2} ml^{-1}	--- -0.9	La Jolla	Harvey, 1966
	Drum	5.7×10^{2} ml^{-1}	--- 4.1	Hawaii Lab Tank	Harvey & Burzell, 1972
Detritus	Drum	5.4×10^{4} ml^{-1}	--- 13.9	Hawaii Lab Tank	Harvey & Burzell, 1972
Seston	Drum	7.2 to 92.8 mgl^{-1}	0.6 to 8.0	Mediterranean	Daumas et al., 1976
	Screen	6.4 to 29.2 mgl^{-1}	0.4 to 1.8	Mediterranean	Daumas et al., 1976
Phytoplankton	Screen	2.5×10^{2} to 8.3×10^{3} l^{-1}	-0.2 to 4.3	Chesapeake Bay	Roy et al., 1970

a. Numbers listed are rounded for uniformity, whereas the original data are often given to greater precision. No adjustments have been made to compensate for different sampling techniques, such as "drum and screen", to make them more directly comparable.

b. The Enrichment Factor is calculated from $\frac{\text{(concentration in the microlayer)}}{\text{(conc. in the subsurface water)}} - 1$. Negative values indicate depletion in the microlayer.

are measured. Both particulate and vapor phase samples are collected for all organic substances, halogens, boron, mercury, and selemium. Bulk filtration and size separation by cascade impactors are used for particulate matter.

Several institutions in the United States, France and Great Britain have been involved in a series of closely coordinated field experiments and individual laboratory studies since 1977.

The coordinated field experiments fall basically into two categories: (a) Flux experiments, where estimates of the atmospheric dry and wet deposition of the various chemical substances to the ocean surface are made from measurement of atmospheric concentrations, and concentrations in rain and dry deposition samples and (b) Source experiments, where the ocean is investigated as a source for these substances through the bubble breaking process. Vegetation, soil emissions, pollution, etc., have also been investigated as sources for these substances in the remote marine atmosphere.

SEAREX was designed to investigate air/sea exchange of chemical substances in the Pacific Ocean region: experiments were planned for each of the four major tropical and temperate surface-level wind regimes i.e., the North Pacific tradewinds (Enewetak Atoll, 1979), the South Pacific tradewinds (American Samoa, 1981), the South Pacific westerlies (New Zealand, 1983), and the North Pacific westerlies (research cruise at 35°-40°N, 170°W, 1986).

The atmospheric sampling towers (14-20 m high) are located on the windward coasts and are necessary to get above any local contamination from natural erosion products and surf spray generated when waves strike the shoreline.

SEAREX has a continuously operating network of 13 island stations in the North and South Pacific which are manned by local personnel. Samples are analyzed for mineral aerosol, sulfate, nitrate, sea salt, ^{210}Pb, and selenium.

2.4.2 The Western Atlantic Ocean Experiment (WATOX)

The Western Atlantic Ocean Experiment (WATOX) is designed to determine the magnitude and fate of selected sulfur, nitrogen, metal and organic compounds that are advected eastward from North America. This program has two phases: long-term and intensive. The long-term phase began collecting data in 1980 on the composition of wet deposition at Lewes, Delaware and Bermuda. These data are used to calculate rates of wet deposition and to track air masses from North America. As a supplement to the long-term program, intensives are held during selected periods to investigate the processes that control the transport, transformation and deposition of materials to the Western Atlantic Ocean. During intensives, which last 1-4 weeks, instrumentation to determine atmospheric concentrations of gas and aerosol species is used at the two long-term sites and on mobile sampling platforms (ships, aircraft). For the intensives, scientists from other institutions and countries are invited to participate in such a way as to complement the skills and research abilities of the permanent WATOX scientists. To date, there have been three intensives.

The first two intensives occurred in October 1982 and February 1983. Their objectives were to investigate the changes that occurred in the composition of air parcels during transit from North America to Bermuda. In addition to the long-term measurements of wet deposition, scientists measured the concentrations of trace gas and aerosol species at Lewes, Delaware and High Point, Bermuda. The third intensive used a ship (MV Oceanic) to sample gases and aerosols between North America and Bermuda in support of the above objective and to test new shipboard precipitation-collection devices.

The above intensives sampled air in the marine boundary layer during transport from North America to Bermuda. Obvious limitations of this approach were that Lewes, Delaware and Bermuda may not be representative of the North American East Coast and the Western Atlantic Ocean respectively, and that measurements at sea level give no information about upper-air transport. Therefore, the fourth intensive was designed with these limitations in mind. In addition to the ground-level sampling of gases and aerosols at Lewes, Delaware and High Point, Bermuda, the NOAA research aircraft will be used to sample atmospheric gases and aerosols as a function of altitude and latitude during frontal passages between North America and Bermuda.

Future studies under WATOX will include continued measurements at the two sites, a special field study employing aircraft in 1985 and 1986 and an analysis of all the data using an atmospheric transport model.

2.4.3 Studies in the Baltic Sea Area

Preliminary studies and estimates of atmospheric input of contaminants to the Baltic Sea made in the 1970s by some national institutions of the Baltic Sea area showed that this input was comparable to the contaminant input by rivers or with domestic and industrial waste discharges. This referred especially to many heavy metals, some inorganic non-metals (e.g. nitrogen compounds), organochlorines (DDT, PCB) and some radionuclides.

To initiate joint studies in this field, the Baltic Marine Environment Protection Commission (Helsinki Commission = HELCOM) established an Ad Hoc group of experts nominated by countries to review, plan and coordinate the activities on air-borne pollution research and monitoring. In 1982 the group prepared a status report and preliminary proposals for a future monitoring programme, based on information provided by countries. About 20 stations were reported as operational or planned for air pollution monitoring.

The outcome of the Seminar on the Investigation of Airborne Pollution of the Baltic Sea (Tallinn, USSR, 21-25 September 1983) served as a basis for the first meeting of the Ad Hoc group of Experts on Airborne Pollution (EGAP) held in September 1984, which considered the status report on national monitoring and research activities and a compilation of atmospheric and precipitation concentration data and estimation of wet and dry depositions to the Baltic Sea prepared on the basis of data submitted by the countries.

The proposals for the airborne pollution monitoring programme within the Baltic Sea area developed by EGAP included the following recommendations:

- to initiate the programme in January 1985 in all Baltic countries;
- to include in the national measurement programmes the following parameters: NO_3^-, NH_4^+, Pb, Cd, Cu, Zn, SO_4^{2-}, Na and Mg in precipitation; NO_2 and SO_2 in the air and HNO_3, NO_3^-, NH_3, NH_4^+, Pb, Cu, Zn, SO_4^{2-}, Na and Mg in aerosols;
- to prepare (by January 1985) a list of institutes, laboratories and monitoring stations participating in the programme;
- to use as far as reasonable the existing WMO-BAPMoN and ECE-EMEP stations in coastal areas;
- to use research vessels and submit the information on such cruises to the Secretariat;
- to report data on a monthly basis in accordance with a special data reporting format which includes information on the results of concentration measurements, sampling time, monitoring site characteristics, meteorological conditions (precipitation amount, temperature, wind speed and direction etc.), brief description of sampling and analytical methods.

As far as intercomparisons and intercalibrations of sampling and analytical methods are concerned, it was recommended that such exercises be carried out in a host country (starting with Sweden in 1985). The different sampling equipment should be installed at one station in the host country and each participating laboratory would analyse samples using its own equipment. The sampling time and equipment would be analogous to those used in the monitoring programme. The priority should be given to the sampling procedures for heavy metals. For the intercalibration of analytical procedures artificial rain samples prepared by WMO, IAEA or by a lead country should be used. The information on airborne pollution would be derived from national annual data reports, including monthly mean values. The information would be used for constructing annual deposition fields for the Baltic Sea area and for assessing the total airborne load of pollutants (in tons/year) for different sub-areas of the Baltic Sea.

The annual data reports would be sent to the Secretariat not later than 1 May of the following year. The generalized annual reports, as well as additional information on monitoring and research activities, would be regularly considered by the Scientific-Technological Committee and presented to the contracting parties.

It is also envisaged that backward trajectories would be constructed for some monitoring stations by the Meteorological Synthesizing Centres of the Co-operative Programme for the Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP).

2.4.4 Studies in the North Sea Area

A number of research programmes on atmospheric input of pollutants into the North Sea were carried out in the 1970s. For compiling pollutant input data, the Working Group on Pollution Baseline and Monitoring Studies of the International Council for the Exploration of the Sea (ICES) developed an Inputs Questionnaire in which countries bordering the North Sea were asked to provide information on inputs of major pollutants including domestic sewage, industrial effluents, and those from river run-off, ocean dumping and the atmosphere. Summaries of the results of these investigations were published by ICES (1978).

At the present time, ICES does not have a co-ordinated international programme on air-borne pollution of the North Sea, although some work in this field is carried out by the ICES Marine Chemistry Working Group.

Some co-ordination of national programmes on monitoring of airborne pollution of the North Sea was organized by the Paris Commission through its Working Group on the Atmospheric Input of Pollutants to Convention Waters.

The most comprehensive and up-to-date assessments of the pollution of the North Sea from the atmosphere were prepared by the Netherlands Organization for Applied Scientific Research - TNO (van Aalst, et al 1982).

The recommendations for further research made in the report include the following:

- measurements of the concentrations of relevant compounds in the air and the flux of dry deposition over the North Sea depending on meteorological conditions;
- determination of the distribution coefficient of organic compounds between air and North Sea water;
- measurements of the concentrations in rainwater collected in wet-only collectors in the North Sea area;
- calculations of contributions of source categories and source areas to the concentration and deposition over the North Sea, by means of dispersion modelling;
- implementation of a feasibility study for the application of models for similar calculations for the wet deposition; and
- further study of the pollution via non-atmospheric routes.

2.4.5 Studies in the Mediterranean Area

The Long-term Programme for Pollution Monitoring and Research (MED POL - Phase II) of UNEP's Mediterranean Action Plan endorsed at the Second meeting of the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against Pollution (Cannes, 1981) includes monitoring of the transport of pollutants into the

Mediterranean Sea through the atmosphere and research and studies on pollutant-transfer processes at air/sea interface. The purpose of the monitoring is to establish the input (flux) of pollutants into the Mediterranean Sea through the atmosphere and thus to provide additional information on the pollution load reaching the Mediterranean Sea. The monitoring should be based on the work of national research centres and include:

- areas directly influenced by identifiable sources of air pollution and
- reference areas not directly influenced by identifiable sources of air pollution.

The Contracting Parties decided to consider the first phase of this monitoring as research activity and to assess the possibility of using the existing WMO's Background Air Pollution Monitoring Network (BAPMoN) stations as the basis on which to begin the monitoring.

The research activities are aimed at investigating the role and importance of the atmospheric transport in the cycles of pollutants, elucidating the transport mechanisms and the flow of pollutants across the air/sea interface, at developing models of transport processes towards and into the Mediterranean Sea, sampling and analytical techniques and at establishing an operational core network of monitoring stations.

Apart from the work carried out by the INTERPOLL W.G. and as a part of research activities on pollutant-transfer processes at air/sea interface (reports of IV and V meetings of the Working Group), several projects were implemented by Mediterranean research centres and outside consultants.

The Meteorological Observatory, Milan, Italy, developed a computational method for monitoring the atmospheric transport of pollutants to the Mediterranean Sea. The method was applied to the Po and Tiber valleys and showed good agreement with the available experimental data. Later on, this observatory developed an evaluation model of the transport of heavy metals: deposition and net flux of cadmium across the Italian coasts and calculated Cd emissions, concentrations in air, depositions and fluxes crossing the Italian coasts from domestic sources (Clerici, in press). An extension of this model to take into consideration fluxes of Pb, Al, Hg across the Italian coasts and an inventory of sources of these pollutants in Italy is being considered.

The Institute of Geology and Geophysics, Naples, Italy, estimated the atmospheric input of some heavy metals to the Bay of Naples and diffusive models were set up in order to evaluate the surface distribution of these substances over the whole bay on the basis of observations made along the coast. The experimental data showed the highest values for Fe, followed by Zn, Pb, Cu and Cd (Palumbo et al., 1985).

The Federal Hydrometeorological Institute, Belgrade, Yugoslavia, is implementing a preliminary study of potential long-range cadmium transport from major identified sources in Europe into the Mediterranean region.

A draft of the reference method "Sampling of aerosols and wet precipitation for analysis of chemical pollutants" was prepared by IAEA on the basis of the "WMO International Operations Handbook for Measurement of Background Atmospheric Pollution" (WMO, 1978). The method is under review for its publication in the UNEP series on Reference Methods for Marine Pollution Studies.

Negotiations with countries participating in BAPMoN have resulted in identifying three stations to serve also MED POL purposes: Carpentras (France), Messina (Italy) and Zavizan (Yugoslavia), the latter having been integrated in the Yugoslav National Monitoring Programme. An agreement was reached between WMO and IAEA that IAEA's laboratories in Vienna will analyze filter and precipitation samples for cadmium and mercury from all MED POL stations. Two of the stations mentioned above are now operational and it is expected that in the near future Greece, Turkey and Algeria will also join in the monitoring network through WMO.

Programme on Physics and Chemistry of the Mediterranean Sea (PHYCEMED)

The PHYCEMED is a joint Research Programme organized by IFREMER, FRANCE in collaboration with CNRS, France and French Universities. The major goal of this programme is the understanding of the physical, chemical and biological processes which control the air-sea exchange of contaminants and their transfer in the water column and to the sediments of the Mediterranean Sea. Scientists from France, Spain, Tunisia, Yugoslavia and the United Kingdom have already participated in this program. Two cruises have taken place, mostly in the Western Basin, in 1981 and 1983. Eight pre-selected water-sampling stations have been visited twice and will be visited in the future. Contaminents being investigated include heavy metals (Pb, Cd, As, Hg, Cu, Tn) and organic compounds. Work related to the evaluation of the atmospheric input of these substances has been undertaken by Université Pierre et Marie Curie (Organic Compounds) and the Centre des Faibles Radioactivités (Heavy Metals) and is summarized in section 3.1. The programme of the latter institute is also a part of the MED POL - Phase II Research Activities and a detailed report of the results will be available in 1986.

Eastern Atlantic and Mediterranean Transport Experiment

An expert meeting was organized by WMO, UNEP and some Spanish agencies in Madrid, Spain, in December 1984, to elaborate the programme of the "Eastern Atlantic and Mediterranean Transport Experiment" (EAMTEAX) aimed at in situ measuring the background composition of the atmosphere which will be used for assessing the long-range atmospheric transport of trace substances to the Mediterranean Sea. Aircraft provided by the Spanish Government and the BAPMoN baseline station Izana, Tenerife, will be used in the experiment which should start in 1985.

3. PRESENT UNDERSTANDING OF TRANSPORT IN THE MEDITERRANEAN

3.1 Levels of Atmospheric Contaminants over the Mediterranean

The Working Group reviewed the available data base on atmospheric concentrations of contaminants over the Mediterranean. One very striking feature of this data base is that there is currently an insufficient number of measurements over time and space to allow for a comprehensive assessment of atmospheric contaminant concentrations in this region. Most of these data derive from recent oceanographic cruises, predominantly in the Western Mediterranean Basin during the PHYCEMED program. The most studied contaminants to date have been the heavy metals and metalloids, such as V, Cr, Mn, Cu, Zn, As, Se, Ag, Cd, Sb, Hg, Au and Pb. An even more limited data base exists for organic substances (eg., PCBs) and artificial radionuclides (eg., $^{239+240}$Pu).

Given the available data, the Working Group focused on the two best studied elements (Pb and Cd) which originate in large part from anthropogenic sources. Table 3 presents a summary of atmospheric Pb and Cd concentrations over various regions of the Mediterranean. Atmospheric concentrations span 2 orders of magnitude, with extreme variability being noted over very short time periods (hours to days) (Arnold et al., 1982). Within the Mediterranean, it is apparent that Pb & Cd concentration in air are 5 - 10 times higher in densely populated coastal regions than over open waters (Table 3). Recognizing that the data from different regions were probably collected by different techniques, with different levels of quality control in sampling and analysis, the Working Group noted, nevertheless, that the range of mean atmospheric and rain concentrations of Pb and Cd over the Mediterranean are comparable with those over other regional seas such as the Baltic and North Seas (Table 4). These concentrations are an order of magnitude greater than levels over the North Atlantic and up to four orders of magnitude greater than concentrations in remote regions of the South Pacific (Table 4). Direct assessments of total atmospheric deposition (wet and dry) of contaminants into the Mediterranean are not possible, as there have been very few reliable measurements of contaminant levels in rain. Table 4 presents a rough estimate of total atmospheric deposition into the Mediterranean based on a total deposition velocity of 1 cm sec^{-1} (Buat-Ménard and Chesselet, 1979). Again it can be seen that the atmospheric flux of contaminants does not differ appreciably between the Mediterranean and other regional seas around Europe, while Atlantic and Pacific deposition are lower. As demonstrated in other oceanic regions (Buat-Menard and Duce, 1985), rain can be expected to account for most of the atmospheric deposition into the Mediterranean. Thus, seasonal variation in flux of contaminants into the Mediterranean should occur, with greater deposition occurring during rainy periods.

The few measurements of organic substances in Mediterranean air that have been made suggest that the PCBs (chlorinated hydrocarbons) are lower than in North Sea air and comparable with open ocean regions of the Atlantic and Pacific (Table 5). By contrast, concentrations of

Table 3. Atmospheric Concentrations of Pb and Cd over the Mediterranean Basin (ng m^{-3})

	Pb		Cd		n of samples	References
	range	mean	range	mean		
- Eastern and Central (1979)	2-26	14	--	--	5	Chester et al., (1981)
- Tyrrhenian Sea (1979)	3-16	10	0.07-1.6	0.48	9	Chester et al., (1984)
- Central and Tyrrhenian Sea						
(1980) -	10-98	50	0.2-6.0	2.10	19	Seghaier (1984)
(1982) -	3-39	15	0.2-2.4	0.9	16	Buat-Menard et al., unpubl. data
- Western Basin						
Phycemed 1 Cruise (1981)	3-58	33	0.1-5.5	1.4	13	Seghaier (1984)
Phycemed 2 Cruise (1983)	4-54	27	0.4-3.2	1.6	15	Buat-Menard et al., unpubl. data
- Alboran Sea (1981)	5-28	49	0.1-7	1.5	7	Seghaier (1984)
- Coastal Regions						
Marseille (1977-1979)		305		5.9	200	Viala et al., (1979)
Monaco (1978)		171		4.6	30	Seghaier (1984)

Table 4. Atmospheric and precipitation concentrations of, and flux data for, Pb and Cd in different regions

	Pb	Cd	References
AIR	ng m^{-3}		
Samoa area			
Tropical South Pacific	0.02	<0.002	Duce, unpublished data Patterson, unpublished data
Enewetak			
Tropical North Pacific	0.12	0.003	Duce et al., (1983)
Hawaii	2	0.02	Settle and Patterson (1982) and Hoffman et al., (1982)
North Atlantic	10	0.13	Buat-Menard (1983)
Bermuda Area	3	0.2	Duce et al., (1976)
Baltic Sea	10–60	0.1–0.5	Rodhe et al., (1983)
North Sea	20–200	0.5–2.5	Van Aalst et al. (1983) Chester et al., (1981, 1984)
Mediterranean Sea	10–60	0.4–2.1	Arnold et al., (1982) Seghaier (1984) Buat-Menard et al., unpub.
PRECIPITATION	$\mu g.l^{-1}$		
Samoa	0.007	—	Duce et al., unpub. data Settle et al., (1982)
Enewetak	0.023	0.0041	Arimoto et al., (1985) Settle et al., 1982)
Bermuda	0.77	0.006	Jickells et al., (1984)
Baltic Sea	10–30	0.3	Rodhe et al., (1980)
North Sea	10–35	0.3–1.2	Van Aalst et al., (1982)
Mediterranean Sea	6–12	—	Buat-Menard et al., unpub.
TOTAL DEPOSITION	$ng.cm^{-2}.yr^{-1}$		
Enewetak	7	0.35	Arimoto et al., (1985) and
North Atlantic	310	5	Buat-Menard (1983)
Baltic Sea	400–1750	13–20	Rodhe et al., (1980)
North Sea	700–2600	20–85	Van Aalst et al., (1983)
Mediterranean Sea	300–1800	10–50	Calculated from Chester et al., (1981, 1984), Arnold et al., (1982), Buat-Menard et al., unpub. data.

Table 5. Concentrations in Air (ng m^{-3}) of Organic Compounds in Different Regions

Region	PCB	n Alkanes (Vapor)	n-Alkanes (Particulate)
Mediterranean	0.04-0.3 (Villeneuve, in press)	65-147 (Ho et al., 1982)*	10.8-43.7 (Ho et al., 1982)*
North Sea	0.96 (Diederen et al., 1981)		-
Central Pacific	0.19-0.32 (Tanabe et al., 1982)		-
N. Pacific Trades	0.049 (Giam & Atlas, 1982)	2.6** (Duce & Gagosian, 1982)	0.044*** (Duce & Gagosian, 1982)
S. Pacific Trades	0.012 (Giam & Atlas, 1982)	1.4 - 3.9+ (Giam & Atlas, 1982)	-
W. Ireland	-	263++ (Eichmann et al., 1979)	3.3+ (Eichmann et al., 1979)
Equatorial Atlantic	-	30-281* (Marty & Saliot, 1982)	1.5 - 14* (Marty, 1981)
Tropical N. Atlantic	0.21-0.65 (Eidleman & Olney, 1974)		4-50* (Marty, 1981)
N. Atlantic	-	66** (Duce & Gagosian, 1982)	3.3+ (Duce & Gagosian, 1982)

* C_{14} - ?
** C_{13} - C_{30}
*** C_{21} - C_{33}
\+ C_{15} - C_{24}
++ C_{16} - C_{21}

n-alkanes, both in particulate and vapour phases, are substantially higher than over the Pacific (Table 5). The Working Group was not aware of any measurements of organic contaminants in rain over the Mediterranean.

In comparing total atmospheric input of metals into the Mediterranean with riverine input, it is clear that the former is a significant and major source of contaminants (Table 6). This is not to say that the local impacts of riverine and atmospheric inputs are comparable. Similar conclusions on atmospheric input were drawn from studies in other regional seas (Rodhe et al., 1980; van Aalst et al., 1982). It is noteworthy that deposition of the transuranic elements derived from atmospheric weapons tests over the Pacific is detectable over the Mediterranean. Thus, very long range atmospheric transport of contaminants clearly occurs over the Mediterranean. The association of metals and other contaminants with very fine aerosol particles (< 1 um), demonstrated in the Mediterranean (Seghaier, 1984) and elsewhere (Duce et al., 1976, 1983), clearly indicates that these contaminants have been transported over very long distances.

The Working Group also considered the question of short range atmospheric transport of contaminants from local sources into coastal regions. Certainly, the observation that air over coastal regions has greater contaminant concentrations than open-ocean air (Table 3), even though the data were collected by different investigators by possibly different techniques, suggests the possibility of enhanced atmospheric deposition of these contaminants in coastal areas. Only three studies in the Mediterranean region are known to focus on this problem. Clerici (1983) calculated deposition of Cd around some large industrial centers in Italy, and Palumbo and Iannibelli (1985) showed that atmospheric deposition of Fe, Cu, Zn, Cd, and Pb was a major contribution to contamination in the Bay of Naples. A third study on the off-shore transport of heavy metals emitted by the industrial area of Fos sur Mer, France, is presently underway (Gamez and Berganetti, personal communication).

3.2 Emissions

The Working Group reviewed the available data base on emissions of atmospheric contaminants in the Mediterranean region and nearby countries. This data base is non-existent for any kind of contaminant from the North African region, while for Europe, only a study applying to metal emissions by country from the year 1979 (Pacyna et al, 1984) was available (Tables 7 and 8). Inventories of organic substance emissions into the atmosphere from European sources were unknown. The values presented in Tables 7 and 8 represent indirect estimates of metal emissions based on consumption data, evaluation of metal content of raw materials, the physical/chemical properties of the metals, technology of production, and the efficiency of emission control devices (Pacyna et al, 1984). It should be noted that the most accurate estimates are probably for Pb, Cd and As, while data for the other metals warrant much further study. It is also noteworthy that, in the context of modeling long-range atmospheric transport of these contaminants, there is almost no available information on single large sources. The estimated atmospheric deposition of Pb, Zn and Cr over the Mediterranean (Table 6) represents about 5-20% of total European emissions of these metals.

Table 6. Comparison of Atmospheric and Riverine Inputs into the Mediterranean Sea

	Atmospheric Input y^{-1}	Riverine Input y^{-1}****
Pb	5000-30000 tons*	2200- 3100 tons***
Zn	4000-25000 tons*	11000-17000 tons***
Cr	200- 1000 tons*	350- 1900 tons***
Hg	20- 100 tons*	30- 150 tons***
^{137}Cs	980 Ci**	32 Ci**
^{238}Pu	0.45 Ci**	0.12 Ci**
$^{239+240}Pu$	20 Ci**	0.46 Ci**
^{241}Am	1.5 Ci**	0.19 Ci**

* Based on data from Arnold et al. (1982); Buat-Menard et al (unpub. data); Chester et al (1981, 1984)
** Fukai et al, (1981)
*** UNEP Rept No 32 (1984)
****The riverine inputs are based on measurements of the dissolved-phase transport only.

Note: It should be noted that fallout nuclides can have long residence times in drainage basins and therefore the riverine input may be more sustained in the long term than the atmospheric input.

Table 7. *Emission of trace elements in 1979 (t · year⁻¹)* (from Pacyna et al, 1984)

Europe	As	Be	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Se*	V	Zn
coal combustion	460	50	146	851	2,190	1,870	2,030	595	2,970	1,670	276	208	1,300	2,350
oil combustion	218		110	1,150	384	1,550	363	250	9,080	1,120		165	32,900	790
wood combustion	40		25			1,500			375	562				4,590
gasoline combustion			31				92		1,330	74,300				
mining			1			192	275		1,640	1,090		0.2		460
primary non-ferrous metal production														
copper-nickel smelters	4,490		595			7,850				9,250				2,500
zinc-cadmium smelters	910		1,550			440	13			7,880		13		48,800
lead smelters	300		8			120	3		140	10,450				480
secondary non-ferrous metal production														
copper			2			61				55	1			660
zinc														2,630
lead			1							387				150
iron, steel and ferro-alloy manufacturing			58		15,400	1,710	14,770		340	14,660				10,250
refuse incinerators	11		84	4	53	260	114		10	804	100	32	19	5,880
phosphate fertilizers			27			77			77	6		v.s.		230
cement production			15		663					746				
industrial applications	136													
TOTAL	6,500	50	2,700	2,000	18,900	15,500	17,600	850	16,000	123,000	380	420	34,500	80,000

* The Se emission with particles. An additional amount of 560 t year⁻¹ of selenium emitted in the vapor phase should also be considered when calculating the long-range transport of this element.

v.s. = very small.

Table 8. *Emissions of trace elements for all sources in Europe in 1979 (t·year⁻¹)* (from Pacyna et al, 1984)

Country	Element ... As	Be	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Albania	31	0.1	1	3	5	71	1	1	92	134	0.4	0.5	43	72
Austria	103	0.2	137	22	200	134	182	6	184	1,933	1.1	4.5	552	4,370
Belgium	360	0.5	171	55	642	613	613	25	381	3,986	10.9	11.4	908	4,736
Bulgaria	152	1.4	67	47	181	208	218	22	291	2,234	7.5	9.7	701	1,722
Czechoslovakia	86	3.1	23	86	791	323	712	44	472	1,726	16.8	18.0	943	635
Denmark	7	0.1	9	23	50	38	37	6	185	753	12.2	3.8	596	706
Finland	127	0.2	84	23	115	246	109	7	237	1,621	1.2	4.1	565	2,460
France	228	1.4	170	103	1,095	450	1,192	34	903	10,545	30.3	18.0	2,338	6,127
German Dem. Rep.	133	4.7	37	108	528	376	432	61	549	2,084	25.1	24.1	965	746
German Fed. Rep.	782	3.9	328	136	2,153	1,552	2,054	60	1,013	9,308	49.5	46.6	2,222	11,689
Greece	10	0.2	4	17	77	55	45	6	273	1,303	1.6	3.1	372	121
Hungary	34	0.6	8	24	198	509	160	10	163	888	3.4	4.6	389	280
Iceland*	73	...	81	378	336	514	—	84	4,130	36,100	—	53	10,900	264
Ireland	2	0.1	1	8	11	13	8	2	65	456	0.4	1	199	33
Italy	93	0.8	124	150	1,055	385	935	38	1,080	9,365	16	24	3,952	4,420
Netherlands	58	0.3	88	38	255	105	253	10	321	2,427	9.3	7.9	979	3,067
Norway	36	v.s.	39	6	40	56	45	2	66	803	0.2	1.2	160	1,188
Poland	656	8.2	207	151	1,161	1,113	1,009	97	653	4,568	43.0	37.0	672	4,725
Portugal	9	v.s.	3	10	27	29	20	2	97	525	0.1	1.4	268	39
Romania	35	2.4	13	61	619	228	554	33	338	1,827	12.7	13.1	660	614
Spain	302	0.9	126	61	571	565	427	20	510	5,534	4.8	10.9	1,373	3,255
Sweden	147	0.4	16	36	195	237	172	9	323	2,270	0.4	5.4	1,003	346
Switzerland	1	v.s.	1	5	40	18	25	1	51	1,083	0.03	0.6	130	50
Turkey	62	1.1	11	30	147	427	126	15	277	1,180	6.0	5.1	419	994
USSR	2,812	15.0	816	631	7,147	6,515	6,874	257	6,014	43,842	80.0	120.0	11,262	21,281
United Kingdom	164	4	99	130	1,134	580	1,032	60	899	10,098	40.0	36.0	2,074	3,488
Yugoslavia	134	0.8	65	40	205	287	177	16	284	2,423	5.3	7.6	718	2,013
Luxemburg	0.4	v.s.	1.1	1.3	196	24	192	0.4	15	301	0.6	0.2	30	158
Total	6,500	50	2,700	2,000	18,900	15,500	17,700	850	16,000	123,000	380	420	34,500	80,000

* kg year⁻¹

v.s. = very small.

Since some contaminants can originate from natural as well as anthropogenic sources, the Working Group considered such natural sources as volcanic activity, soil erosion, and the ocean surface. Studies of emissions from Mt. Etna indicate that volcanic activity may be an important source of Se, Hg, As, and Cd for central and eastern basins of the Mediterranean (Buat-Menard & Arnold, 1978; Martin et al., 1984). Soil erosion can be a major source of metals in the atmosphere, but is very episodic in nature.

The annual input from soil erosion, including the periodic but pronounced dust storms bringing in Saharan dust, has not yet been quantified. It is thought too that aerosol production from the ocean surface may result in the recycling of certain pollutants (heavy metals, radionuclides, bacteria, organic compounds); the importance of this phenomenon has not been assessed for the Mediterranean. It should be pointed out that in coastal areas this phenomenon might contribute significantly to the atmospheric concentrations of these contaminants under sea-breeze conditions.

3.3 Evaluation of pathways

3.3.1 Climatological studies

The Mediterranean region is known throughout the world for its distinctive climate. It is used as the arch-typical example of the subtropical summer-dry weather regime. Though parts of the region do represent this type of climate, other areas in the north and west can only be described as transitional zones between Mediterranean and continental weather systems. In order to understand the transport of chemical substances to the area from the anthropogenic and natural sources, the climatology and meteorology of the Mediterranean basin must be well understood.

European weather is generally dominated by two pressure systems - the Icelandic low and the Azores high. The intensity and movement of these systems northward and southward regulate the meteorology of the continent. This produces an almost straight westerly flow of moist air off the Atlantic Ocean. At times such as the winter of 1985, the Siberian anticyclone can move west and advect cold continental air all the way to the Atlantic. The Mediterranean Sea is on the southern border area of this westerly flow and, because of its warm waters and surrounding topography, causes a complex interaction that complicates the meteorology in the area. This can be seen from the rainfall patterns shown in Figures 1a and 1b. Additionally local winds affect the transport of contaminants into the Mediterranean Sea and they have to be considered in relation to the long- range transport. The western part is also a major source area of cyclogenesis, particularly in the winter (Figure 2).

Despite this complex situation, it is possible to point out two areas mainly characterized by their precipitation patterns. These regions are roughly: (1) The northern part of the western basin, (2) the southern part of the western basin, and (3) the eastern part of the Mediterranean sea. The question then arises as to how can we describe atmospheric transport of contaminants under such complex conditions. There are several ways to approach this problem, some of which are discussed in the next sections.

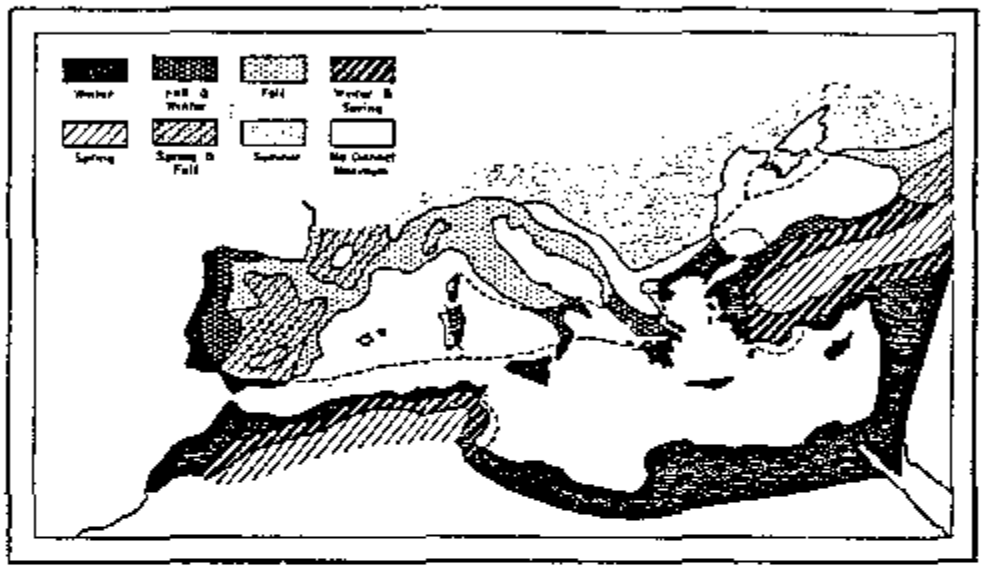

Fig. 1a Showing seasons of maximum rainfall in the Mediterranean Basin. Much of the northern basin does not have a simple winter maximum typical of the Mediterranean type of climate (Huttary, 1950)

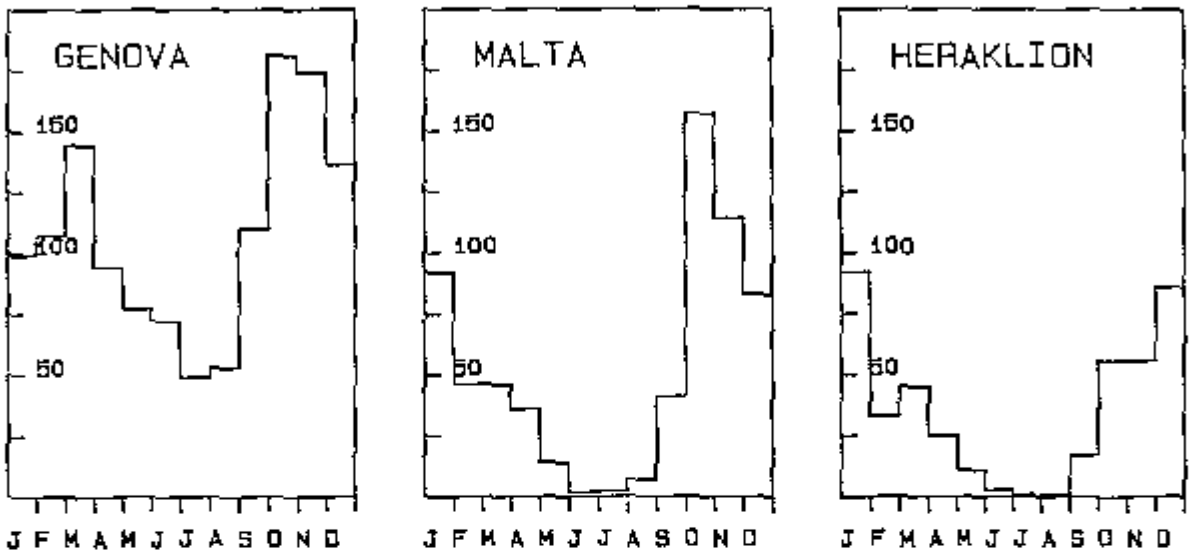

Fig. 1b. Mean monthly precipitation (mm) at Mediterranean Stations

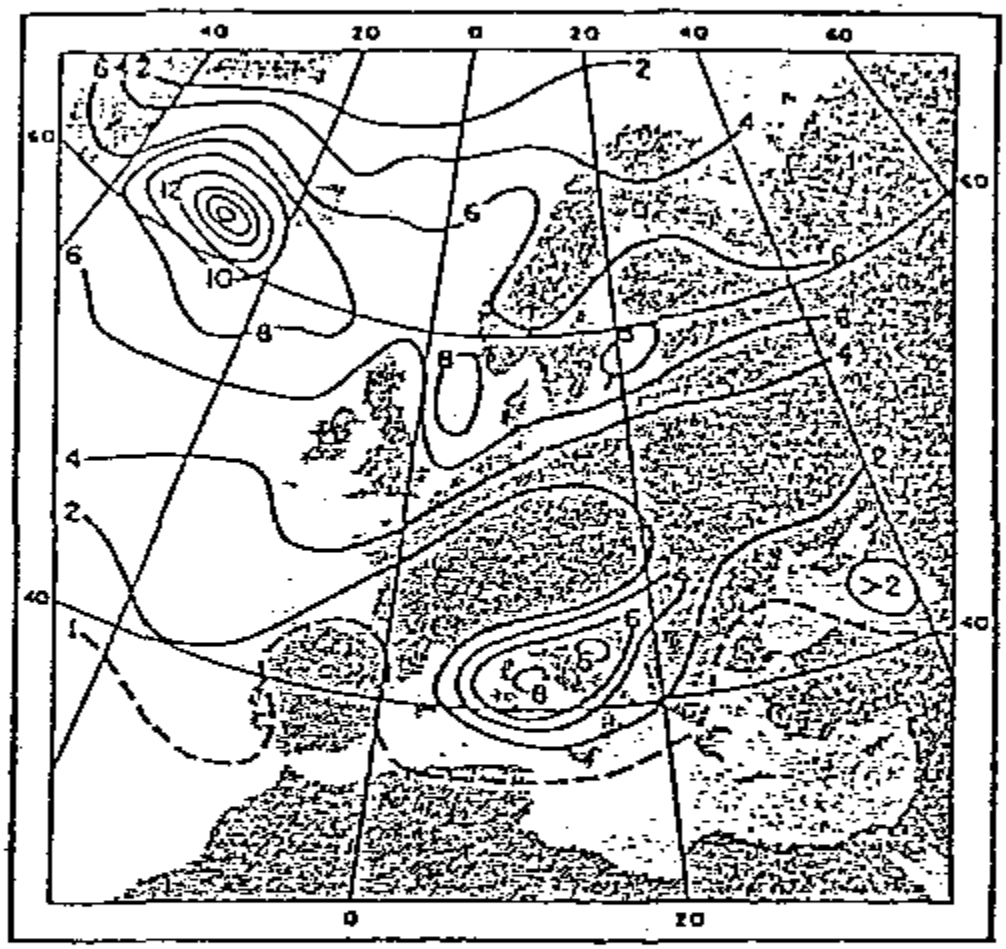

Fig. 2 . Annual frequency of deep cyclones with central pressure less than 1000 mb.
(Schedler, 1924)

3.3.2 A comparison of Back Trajectories Climatologies

The possibility of using back trajectories in the Mediterranean area was first discussed at the GESAMP Working Group meeting in Monaco in 1982. Since that time, trajectories, using different methods, have been calculated for the eastern and western part of the region. A comparison between two of these methods has been done for the western part of the Mediterranean Sea. This section will report the preliminary results of the comparison. The two methods are fundamentally different.

The details of the ARL (Air Resources Laboratory, NOAA, Silver Spring, Md., USA) model have been described elsewhere (Harris, 1982). Briefly, this model calculates back trajectories twice a day from any place on the globe. The input winds are taken from the US National Meteorological Center's gridded fields at 0000 and 1200 UT (UT = Universal Time) for standard pressure levels. For this study, trajectories of 10 days' duration are calculated at the 850-h Pa and 700-h Pa levels of the atmospheric pressure from January 1975 to December 1983. To characterize the western Mediterrnean, a point (40°N, 6°E) which will be referred to as the MED point was chosen as the starting place for the back trajectories; it was also the location of measurements made during the PHYCEMED 81 project.

The second method, described by Martin et al. (1984), uses geopotential fields to calculate the winds using the geostrophic approximation. The classification is made by counting the number of starting points whose origins are from a selected sector and for a chosen day's duration.

The preliminary results show a good agreement between annual percentages of occurrence for given sectors of both methods. Slight differences were noted for the monthly variations, however considering the two types of data, the two types of classification methods and the slightly different sectorisation these were rather small. The following analyses and conclusions were derived from the use of both methods.

3.3.3 Analysis of back trajectories from the western Mediterranean

Trajectories for the nine-year period were classified using the method shown in the lower portion of Figure 3. There were six different categories: 1. North, flows coming from this area would carry polluted air with them; 2. East, trajectories rarely come from this direction; 3. South, this flow pattern brings air from the Sahara with accompanying desert dust; 4. West, air from the west could be expected to be the cleaner; 5. Miscellaneous, this case includes times when the trajectories show strong cyclonic motion, or very weak flow. At these times, categorization is impossible; 6. Missing data. A summary of the number of cases for each category is shown in Figure 3. One can see the prevailing westerly and northerly flow patterns. The year-to-year variations are shown in Figure 4; it should be noted that there can be large differences between years. This may have implications to the quantities of a given pollutant which will be transported to the region in a certain year.

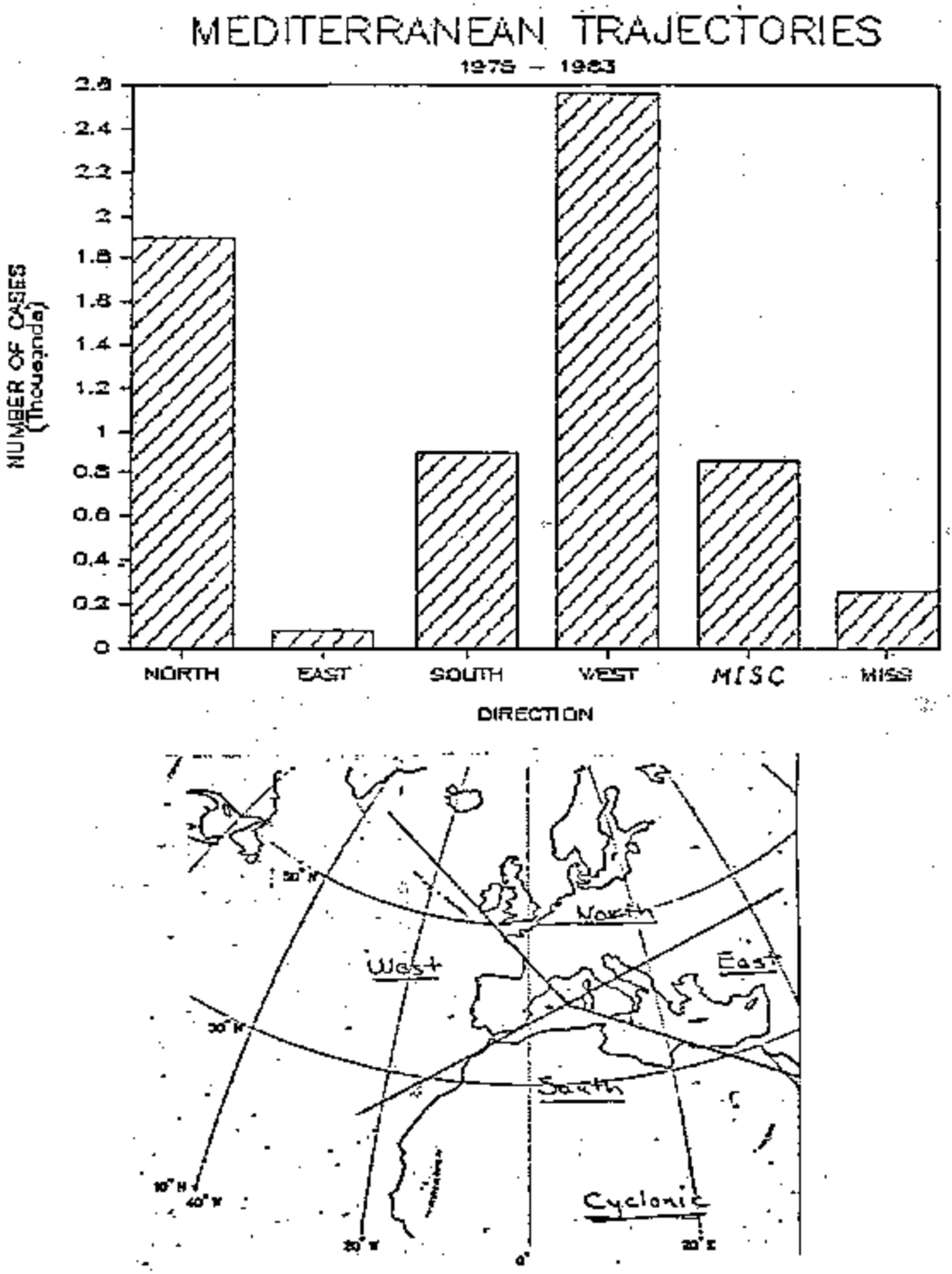

Fig. 3. Mean nine-year trajectories for the western Mediterranean (1975-1983) based on the sectors shown in the lower figure.

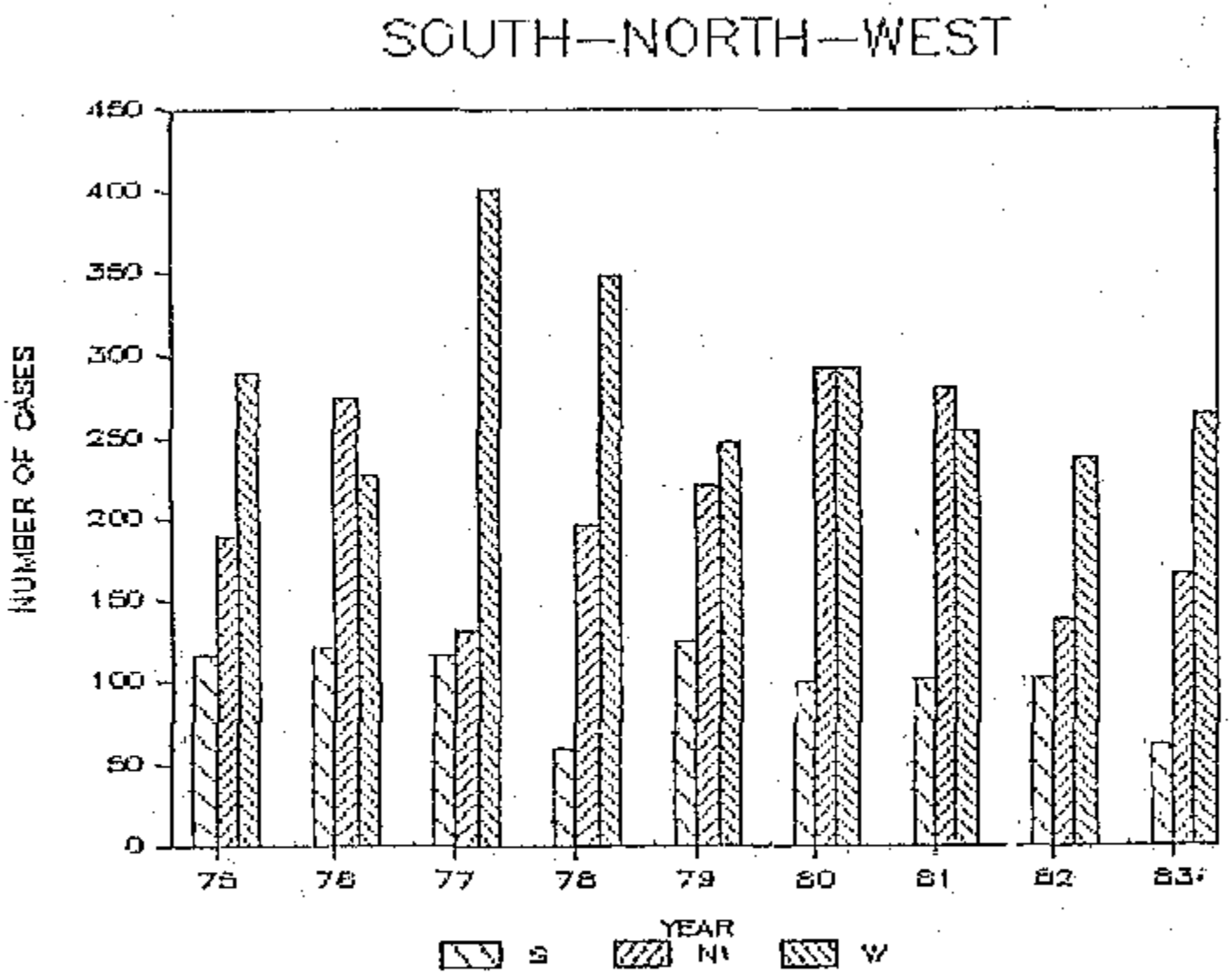

Fig. 4. Year-to-year variations in trajectories for the western Mediterranean.

Initially, one would expect a seasonal variation in the trajectories however this is the western part of the region which, as it was explained earlier, is an area of transition. Figure 5 shows the West, North and South categories on a seasonal basis over the nine year period. There is no obvious change from season to season. In Figure 5, an increase in the number of southerly trajectories is detectable in summer. With no seasonal variation of northerly flow, pollutants can reach the western Mediterranean at all times of the year, while the summer is the time when Saharian dust is transported to the sea.

3.3.4 Analysis of back trajectories from the eastern Mediterranean

To characterize the transport to the eastern Mediterranean Basin, a point (MED Point) at PLATANOS (Crete) has been chosen to compute back trajectories climatology using the geopotential technique (Martin et al 1984). This location was also the site of a field experiment conducted during September 1983. Trajectories are classified using a sectoring technique shown in Figure 6. There were four different categories: 1. North: 39% of trajectories fall into this category. It is the prevailing sector on an annual basis, and represents the potential contributions coming from Greece, eastern European countries including European part of the USSR. 2. West/Northwest: 27% of the trajectories have this origin (Italy, France, Britain and Spain). 3. East: 17% of the trajectories have an origin to the east of the MED Point. 4. South: 16% of trajectories can represent Saharan and North Africa contributions. Compared to the western area, one can see marked seasonal variations (Figure 7): the south sector has its maximum in March while the north sector has its maximum (60%) during the summer months.

A more detailed analysis of the results is planned in the future.

3.4 Modelling the Fluxes of Air Contaminants into the Mediterranean Sea

The simulation of the fluxes of air contaminants into the Mediterranean Sea by means of a mathematical model is considered to be an essential part of the study. This method makes it possible to assess quantitatively the origin of a contaminant and to devise abatement strategies for reducing the contamination of the sea.

At its fifth meeting (Athens, 1983) the Working Group discussed the available model types, and their advantages and drawbacks relative to the requirements posed by the present program. It was recommended that for long-range transport (distances on the order of a few thousand kilometers) a Lagrangian, one layer, backward trajectory model should be used. The use of smaller scale models in certain coastal regions, where the contamination is likely to be high, was enco[illegible]. Following the Working Group discussions, more detailed suggestions were made on the long-range transport models (Klug, 1984) and they are summarized here.

The model to be used for assessing air contamination fluxes into the Mediterranean Sea must simulate quantitatively, on the basis of an emission inventory and the pertinent meteorological data, concentrations, wet and dry deposition values of a given contaminant at

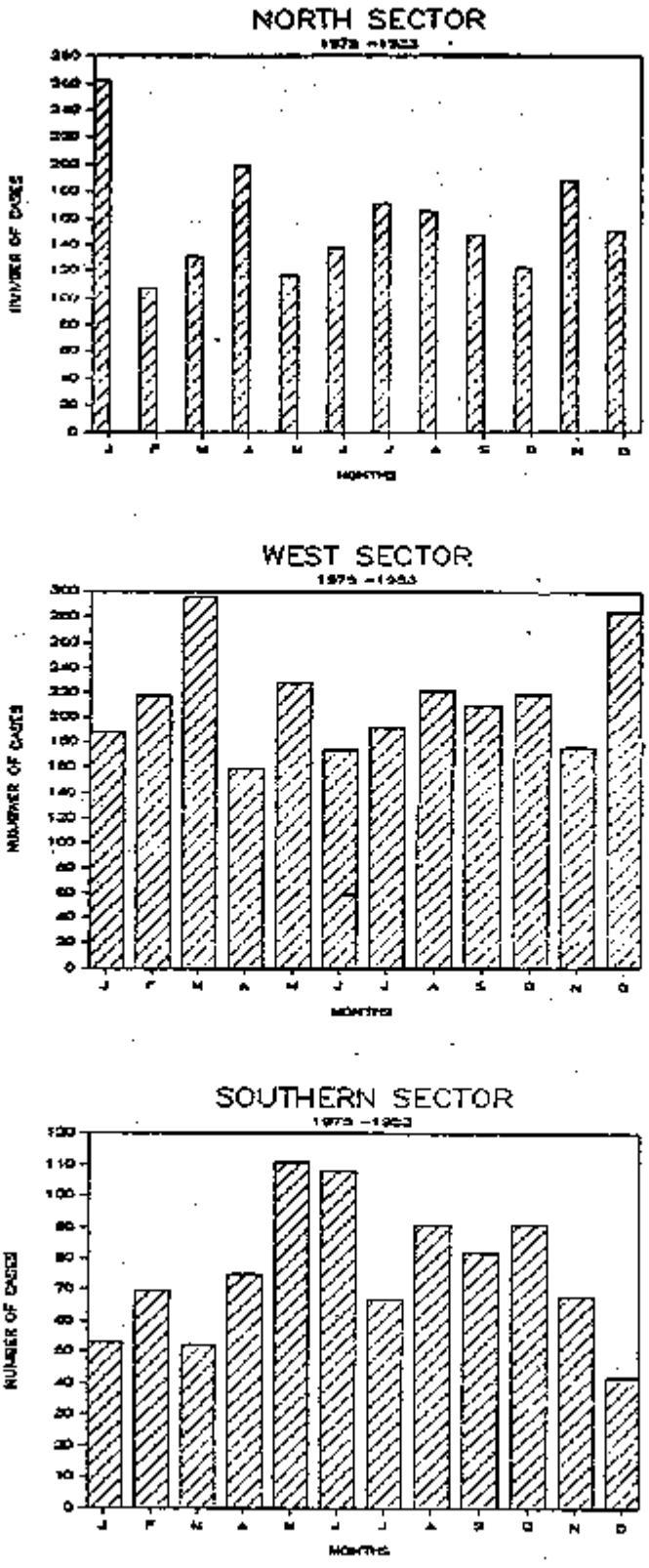

Fig. 5. Trajectories for North, West and South sectors on a seasonal basis for the nine-year period (1975-1983)

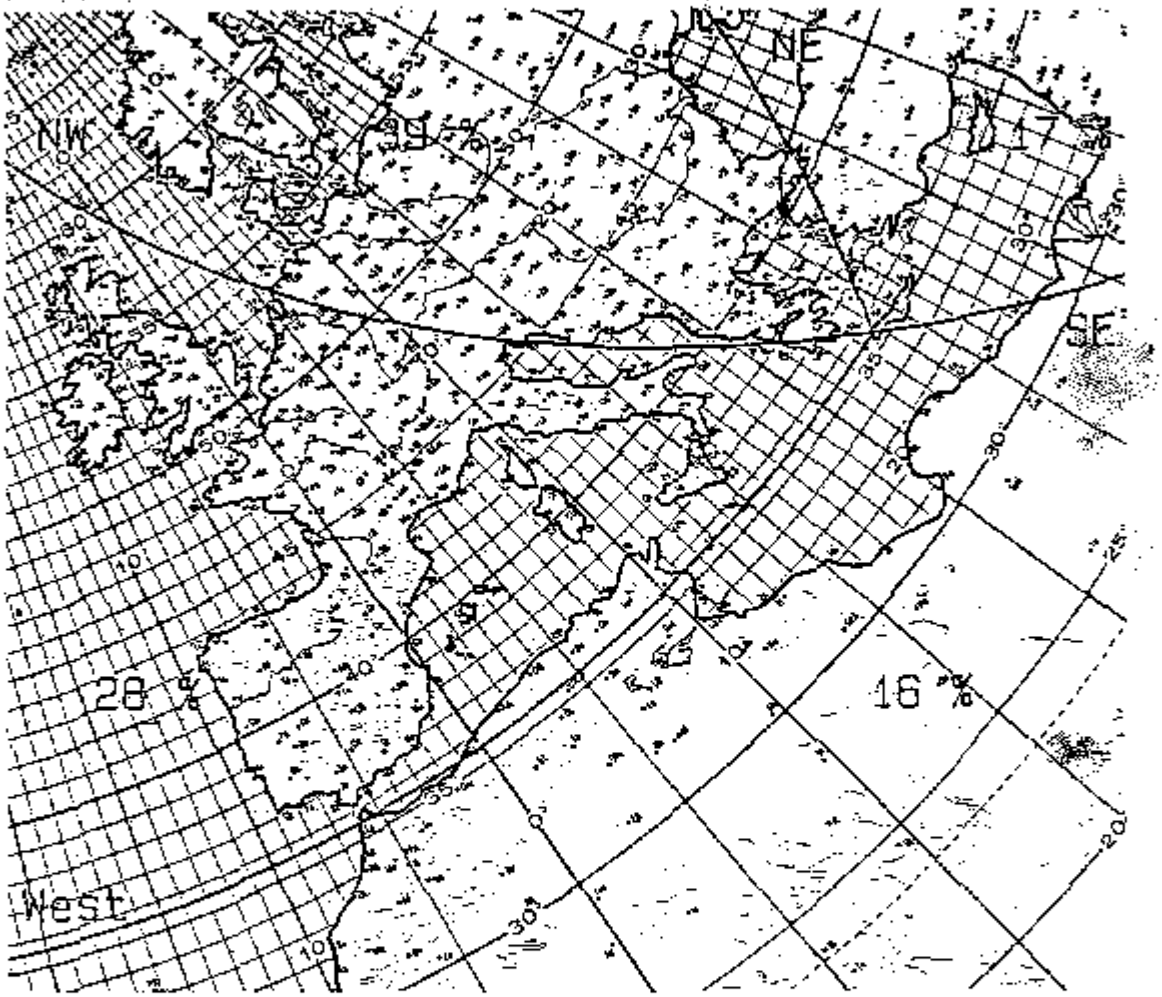

Fig. 6. CRETE trajectories shown on an annual percentage basis for West, Northwest, Northeast and Southeast sectors.

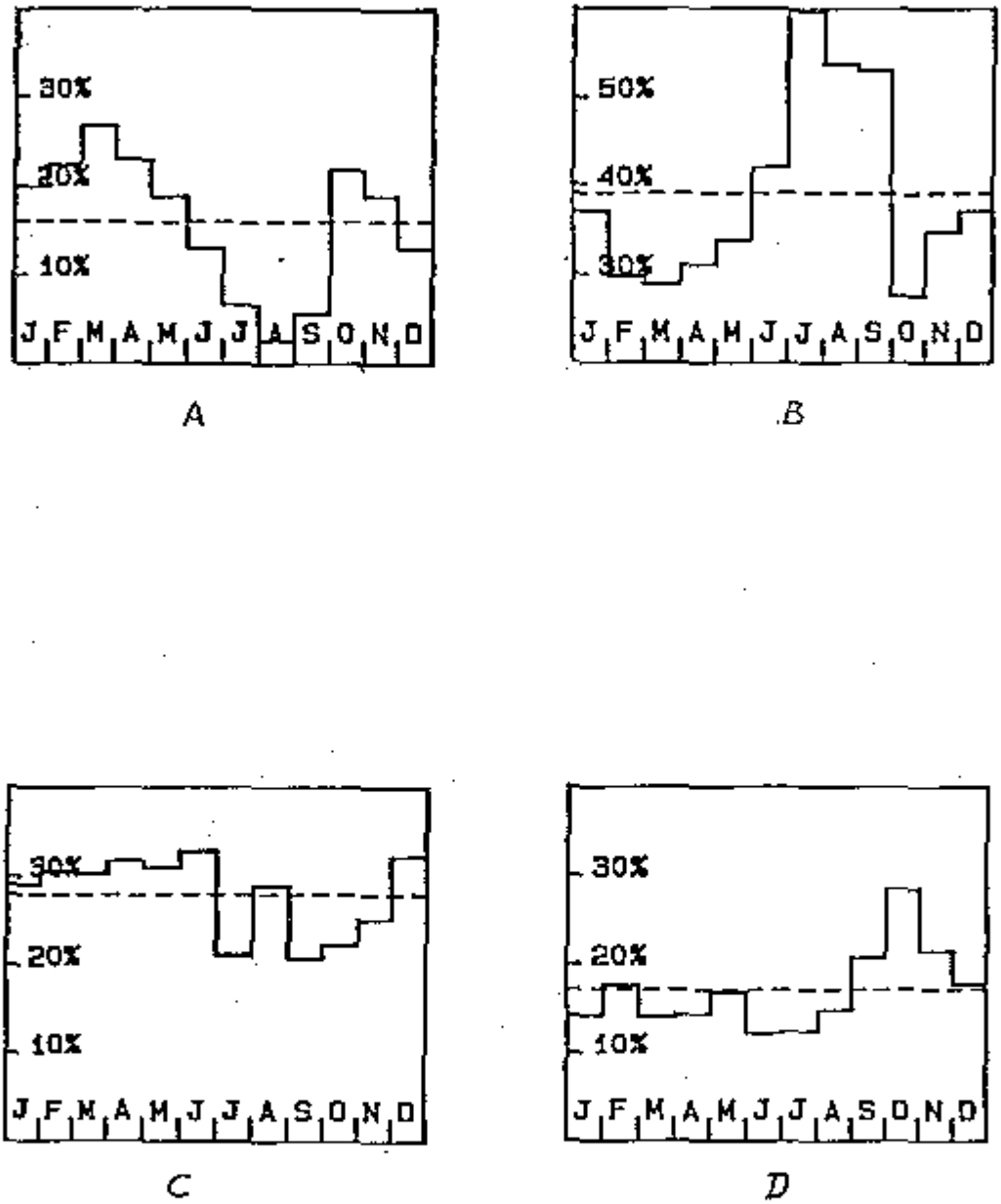

Figure 7. Mounthly variations of CRETE trajectories

A : WSW, SSW, SSE directions (Africa)
B : NNW, NNE directions (Greece, Eastern Europe)
C : WNW direction (Western Europe)
D : ENE, ESE directions (Turkey, Middle East)

a specified receptor point as average values over a year or a season. The output of the model will be and must be verified with measurements at the same site.

Models differ in their structure according to the purpose of their application. A model for long-term averages - for a year or a season - has very often a different and usually a simpler structure than a model which is constructed to give hourly values of air quality data. The latter is often called an episode model. Since it was agreed that long-term averages are needed in this program, it was suggested that the Langrangian form of a box model be used where the box is moved with a representative wind (Eliassen, 1980). It is assumed that the contaminant is completely mixed within the box and that the removal processes, dry and wet deposition, can be parameterized by a dry deposition velocity and a wet scavenging coefficient.

The Lagrangian models have the advantage of being easy to understand in the physical properties and in the computing algorithm. Also, with Lagrangian models the contribution of a certain emission area to the concentrations and depositions at a specified receptor point can easily be evaluated by constructing only those trajectories arriving at this point. There is no need then to calculate transport and diffusion over the whole region as it is done with an Eulerian type (grid) model.

It is therefore suggested that a one-layer Lagrangian backward trajectory model be used. This model implies that for each of the defined receptor points in the Mediterranean Sea and for each time interval (say, 6 hrs) a trajectory is started from the receptor point and followed backward in time until it has reached the boundary of the emission inventory area. Then the calculation of the concentration starts by picking up the emissions along the trajectory until the receptor point is reached again. There exist a number of algorithms to calculate the trajectories which are more or less straightforward.

Three sets of meteorological data are needed as model input: (1) the wind field at a specified height; (2) the mixing height, which is the height of the box; and (3) precipitation. Suggestions were made by Klug (1984) on how these sets can be obtained in a region which is as data sparse as the Mediterranean Sea. A combination of observed data with data obtained from a weather forecasting model seems most appropriate.

As was mentioned earlier in this report, the values of the parameters describing the removal processes of dry and wet deposition are uncertain, even under ideal conditions. Furthermore, they were derived as average values and cannot be applied to single events, where they will vary over one order of magnitudes. The calculated values of dry deposition at a fixed distance are not sensitive to the value of the deposition velocity. If there is rapid deposition, then little material reaches the site and is available to be deposited. On the other hand, with slow deposition more material reaches the site, but only a small part is deposited.

Before the model is used for regulatory decisions, it should be verified at a number of observation stations.

3.5 Summary of understanding of atmospheric contamination transport to the Mediterranean Sea

There is no question that contaminants are being transported via the atmosphere to the Mediterranean Sea. Both local sources near the basin and source areas up to thousands of kilometers away contribute to the contamination of the atmosphere and the sea. At certain times, natural materials such as Saharan dust and volcanic emissions can be important sources for some trace substances to the Mediterranean region. With the realization that atmospheric transport may be a major pathway for many marine contaminants, it has become extremely important for the countries that ring the Mediterranean to understand the possible seriousness of the problem. To this end, the Working Group reviewed current knowledge in the field of atmosperic transport, with special emphasis on the Mediterranean area. Much of the work in this area is just beginning. The problem can be summarized by three questions:

1. What is the present status of our understanding of atmospheric contamination transport to the Mediterranean?

2. Where are the important contamination sources; are they close to the Mediterranean or long distances away?

3. What are the major atmospheric pathways for contaminants reaching the Mediterranean?

In answering the first question it has been shown that the concentrations and depostion of certain atmospheric contaminants (e.g. Pb and Cd) over the Mediterranean are comparable to those over the Baltic and the North seas. For Pb, Zn, Cu and Hg the atmospheric input to the Mediterranean appears to be of the same order of magnitude as the input from rivers. Though many more contaminants must be measured, the initial evaluation leads to the conclusion that the Mediterranean basin is being contaminated by atmospheric input.

The answer to the second question is less certain. It is recognized how poorly the overall contamination sources are known, especially in the North African area. The pioneering work of Pacyna et al (1984) needs to be continued and improved. The relative importance of local versus long-distant sources is also still largely unknown. The episodic emissions of natural sources such as soil dust and volcanic material complicate the evaluation of sources. Determination of the type, magnitude, and location of the atmospheric sources is a very critical aspect of evaluating the impact of the atmosphere on Mediterranean marine contamination.

The last question bears on how well we understand the meteorology of the Mediterranean region. As described above, the Mediterranean area has a very complex weather regime. Based on the trajectory climatology, however, the following can be stated:

- Long-range contaminant flow from the north to the western Mediterranean takes place at least 30% of the time, with no detectable seasonal variation.

- Transport to the eastern Mediterranean is mainly from the north and north west, where industrial sources could contribute to contamination loadings.

- Flow patterns vary significantly from year to year. From this one can conclude that contaminant transport will change from year to year.

Though some preliminary statements can be made about atmospheric transport to the Mediterranean basin, considerable work is needed to understand completely this major environmental problem. The following section presents the Working Group's recommendations for future work.

4. RECOMMENDATIONS FOR FUTURE WORK

4.1 Introduction

The Working Group discussed how to approach the assessment of the contribution of atmospheric transport to the total contamination load of the Mediterranean Sea. The input of contaminants originating from land-based runoff has been documented for a number of substances. At least in principle, this contaminant load is under the direct control of the riparian states. This is not the case for the airborne input of contaminants. Measurements in the Mediterranean region have already shown some evidence for long-range atmospheric transport of metals from diverse sources. Any strategy for abating contamination in the Mediterranean region must take into account this contribution.

4.2 Choice of Pilot Contaminant

The Working Group concurred with the choice of cadmium as a pilot contaminant for the study of the atmospheric transfer of harmful substances into the Mediterranean Sea (Reports of the 4th and 5th sessions of the Working Group, Monaco, 1982 and Athens, 1983). The Working Group considered recent research data and the desirability of including other metals (Cu, Pb, Hg) and select organic contaminants in future studies. The criteria for the selection of a pilot contaminant are outlined below:

(a) It should have land-based sources which ultimately should be identifiable and quantifiable.

(b) Its distribution ratio between the gaseous (vapor) and particulate form should be known. It would be preferable if the chosen contaminant did not have a significant gas (vapor) phase.

(c) Its known or anticipated concentration in the atmosphere and in the surface waters should be within the sensitivity of analytical techniques.

(d) Ideally, the substance chosen should be from ANNEX I of the Protocol for the Protection of the Mediterranean Sea Against Pollution from Land Based Sources.

(e) The concentration of the contaminant chosen for measurement should be referenced to the concentration of a conservative element of crustal origin and one of marine origin. (The Working Group recommends Al as the most suitable element for assessing crustal sources and Na for assessing the contribution of sea-source aerosols to Cd recycling.)

4.3 Site Selection

The Working Group concurred with the criteria for choosing sites for sampling discussed at the 4th session of the Working Group. The foremost consideration is the need for representative estimates of the downward flux of a given atmospheric contaminant. Based upon the logistics of sampling, the Working Group concluded that a fixed land-based sampling station is required to provide long-term sampling, maintenance, and servicing. The Working Group reached this recommendation in light of the fact that weatherships are not available and oceanographic research vessels are not suitable for the required long-term sampling at a given site. It is envisaged that the data simulated by a synoptic-scale atmospheric model should be used as a guide for specifying areas with increased contamination from identifiable sources.

The Working Group considered that the following criteria are essential in site selection:

(a) Absence of local contamination sources (industrial plants, mining activities, automobile traffic, major shipping lanes),

(b) Full exposure to maritime air most of the time,

(c) Availability of power sources,

(d) Proximity of weather stations providing basic meteorological data,

(e) The number of locations of sites should conform with the requirements of the transport models used.

The Working Group concluded that the following locations might meet these criteria and thus warrant further investigation:

Eastern Menorca Island

Western Sardinia

Western Corsica

Western Sicily

Malta

Zakinthos Island

Western Crete

Kasos Island

The project could be started on two or three operating stations located among the above-mentioned possibilities. The Working Group was made aware of the initiation by France of a permanent sampling program in northwestern Corsica (automatic aerosol sampler and precipitation collector).

The Working Group also recognized the usefulness of additional information on concentrations of contaminants in precipitation and aerosols which could be obtained by use of some WMO Background Air Pollution Monitoring Network (BAPMoN) stations in the region.

4.4 Sampling

The Working Group considered the experience acquired during international sampling programs such as SEAREX and PHYCEMED as the basis for a sampling protocol. Considering the nature of the proposed project, some simplifications of the sampling procedures have been recommended:

(a) Dry Deposition: Owing to its complexity, direct measurements of dry deposition should be eliminated. However, dry deposition fluxes can be estimated using aerosol-collecting techniques with size-separated aerosol collectors (cascade impactors) and relevant deposition models. Since Cd concentrations in the Mediterranean atmosphere appear to be in the range of 0.1 to 1 ng/m^3, the sampling duration with such a collection system should be of the order of a week.

(b) Wet Deposition: The rain sampling should be on an event basis. Owing to recent improvements in instrumentation, it is suggested that a fully automatic device be employed.

(c) Air Filtration: It is also recommended that bulk air filtration sampling on a short time scale (12-24 hours) should be undertaken. This might enable the establishment of relationships between atmospheric Cd concentrations and air mass movements. Supplemental information of this kind should also be obtained from shipboard air samples collected during oceanographic cruises.

During sampling it is necessary that standard meteorological data, such as wind speed and direction, air temperature and humidity, sea state, and cloud cover be recorded.

On the basis of the SEAREX experience, it is recommended that the samplers be installed at least 10 m above ground level and as close as possible to the shoreline. It is stressed that reliable data can only be obtained if stringent precautions are taken against local contamination during sampling and sample handling (WMO, 1978).

It is envisaged that such a project should be run continuously for at least 2 years. The estimated number of samples could be about 400 per site and per year. This would necessitate cooperation among laboratories capable of handling such a large number of samples. Intercalibration exercises would be mandatory.

4.5 Analysis

For the analysis of trace metals, it is recommended that either flameless atomic absorption spectrophotometry (FLAAS) or the electrochemical technique of anodic stripping voltammetry (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. For the analysis of organics, choice could be made from high pressure liquid chromatography (HPLC), gas chromatography (GC), or gas chromatography-mass spectrometry (GCMS), considering the contaminants chosen, the specificity and sensitivity of analysis required, and whether "finger printing" identification data are required. The method selected should be proven reliable and intercomparable.

Whatever techniques are chosen, if several laboratories participate in the exercise, intercalibration of procedures and standardized techniques should be mandatory. The Working Group emphasizes again the need for the most stringent precautions against contamination during collection and analysis.

4.6 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.

4.7 Climatological Studies

The Working Group encourages the meteorological investigations of the Mediterranean region. It pointed out the need for more detailed climatology (precipitation, height of the mixing layer) over the sea. In addition the usefulness of back trajectories climatology was pointed out. It recommended the further applications of trajectory classification techniques which associate geochemical, diffusion, and meteorological parameters.

Back trajectories associated with geochemical analysis have an important role to play in evaluating transport, and their use is encouraged. However, great care must be taken in interpreting these data because of limitations of the back trajectory methods.

4.8 Modelling Transport Processes Toward and Into the Mediterranean Sea

The Working Group discussed the necessity of modelling atmospheric pollution in order to estimate the flux of contaminants from the atmosphere into the Mediterranean Sea. It is recognized that estimates of deposition are needed for many different contaminants, including trace metals (such as Pb, Hg, Cd, Cu, etc.), petroleum hydrocarbons, chlorinated hydrocarbons, and pathogenic microorganisms. Such deposition estimates could be obtained by the application of a dispersion model. However, such results have to be checked against measured data.

When the Working Group discussed the available model approaches and the data requirements for the application of a dispersion model, there was a general consensus that attempts should not be made to model concentrations and deposition on a fine-grid scale (e.g. on the order of 50 km x 50 km or 100 km x 100 km), but rather define a number (3-10) of receptor points distributed over the area of the Mediterranean Sea. Furthermore, it was agreed that long-term seasonal or annual averages

of concentrations and deposition would serve the purpose of the study. Since Cd was chosen as a pilot contaminant, the model applications should also begin with this substance. At the same time the Working Group also endorsed the application of smaller scale (10-100 km) models in order to study coastal effects or special situations.

Considering the above conclusions, the Working Group recommended the application of a one layer, Lagrangian backward trajectory model, since such a model has been applied successfully for similar purposes and experience with the model's performance is available. However, before such a model can be applied on a routine basis several requirements have to be met. It is obvious that the first requirement for the calculation of concentrations is an emission inventory of the contaminant under consideration. The Working Group recommends that an independent consultant or organization should be contracted to establish such emission inventories. If it is not possible to obtain an emission inventory from certain countries, the flux of contaminants across their boundaries should be obtained. Furthermore, the meteorological input data into the model must be supplied. This is not a simple task for the Mediterranean area, where only a few radiosonde stations exist which can measure upper air data. A combined usage of such measured data and data as observed from a meteorological forecasting model on the synoptic or meso-scale is advisable, but should be investigated by the scientists employing the model. This implies that the model application should be performed at an institute where such meteorological information is available.

There is still a lack of knowledge in the details of the removal processes. Even if one parameterizes these processes by the simplest approaches, there is not much information available on deposition velocities and scavenging coefficients for the contaminants under consideration. It is recommended by the Working Group that detailed studies on these problems be undertaken.

The model output data - concentration and deposition fields over the Mediterranean Sea - have to be compared with measured data. It is therefore essential to have one or more stations in remote areas of the Mediterranean Sea where the above quantities should be observed.

4.9 Coordination of the Program

For coordinating the research and monitoring and reviewing the results of these studies, the establishment of an Ad Hoc group of experts from the participating countries is recommended. The preliminary results of the pilot stage of the program and proposals for future monitoring and research activities could be considered at a workshop organized by the Ad Hoc group in 1987.

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4. RECOMMENDATIONS FOR FUTURE WORK

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4.1 Introduction

The Working Group discussed how to approach the assessment of the contribution of atmospheric transport to the total contamination load of the Mediterranean Sea. The input of contaminants originating from land-based runoff has been documented for a number of substances. At least in principle, this contaminant load is under the direct control of the riparian states. This is not the case for the airborne input of contaminants. Measurements in the Mediterranean region have already shown some evidence for long-range atmospheric transport of metals from diverse sources. Any strategy for abating contamination in the Mediterranean region must take into account this contribution.

4.2 Choice of Pilot Contaminant

The Working Group concurred with the choice of cadmium as a pilot contaminant for the study of the atmospheric transfer of harmful substances into the Mediterranean Sea (Reports of the 4th and 5th sessions of the Working Group, Monaco, 1982 and Athens, 1983). The Working Group considered recent research data and the desirability of including other metals (Cd, Pb, Hg) and select organic contaminants in future studies. The criteria for the selection of a pilot contaminant are outlined below:

(a) It should have land-based sources which ultimately should be identifiable and quantifiable.

(b) Its distribution ratio between the gaseous (vapor) and particulate form should be known. It would be preferable if the chosen contaminant did not have a significant gas (vapor) phase.

(c) Its known or anticipated concentration in the atmosphere and in the surface waters should be within the sensitivity of analytical techniques.

(d) Ideally, the substance chosen should be from ANNEX I of the Protocol for the Protection of the Mediterranean Sea Against Pollution from Land Based Sources.

(e) The concentration of the contaminant chosen for measurement should be referenced to the concentration of a conservative element of crustal origin and one of marine origin. (The Working Group recommends Al as the most suitable element for assessing crustal sources and Na for assessing the contribution of sea-source aerosols to Cd recycling.)

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ANNEX

List of participants

Members of the Working Group and invited experts	Participation in the meetings Monte Carlo 1982	Athens 1983	Athens 1985
P.E. Buat-Ménard		+	+
R.P. Chesselet	+		
F.S. Civili		+	+
G.C. Clerici	+	+	
A. Cruzado	+		+
R.A. Duce			+
A. Eliassen	+		
N.S. Fisher		+	-
R. Fukai	+		
W.D. Garrett (Chairman)	+		*)
Z. Janjic		+	
W. Klug	+	+	+
V. Koropalov	+		
D. Martin			+
J. Miller	+		+
V. Pravdic	+	+	
S. Menad Siahmed	+	+	
V. Smagin (Technical Secretary)	+	+	
A. Soudine (Technical Secretary)			+
A. Tsyban	+		
M. Waldichuk			+

*) Unable to attend but submitted a paper and edited the report.

PUBLICATIONS IN THE UNEP REGIONAL SEAS REPORTS AND STUDIES SERIES

No. 1 UNEP: Achievements and planned development of UNEP's Regional Seas Programme and comparable programmes sponsored by other bodies. (1982)

No. 2 UNIDO/UNEP: Survey of marine pollutants from industrial sources in the West and Central African region. (1982)

No. 3 UNESCO/UNEP: River inputs to the West and Central African marine environment. (1982)

No. 4 IMCO/UNEP: The status of oil pollution and oil pollution control in the West and Central African region. (1982)

No. 5 IAEA/UNEP: Survey of tar, oil, chlorinated hydrocarbons and trace metal pollution in coastal waters of the Sultanate of Oman. (1982)

No. 6 UN/UNESCO/UNEP: Marine and coastal area development in the East African region. (1982)

No. 7 UNIDO/UNEP: Industrial sources of marine and coastal pollution in the East African region. (1982)

No. 8 FAO/UNEP: Marine pollution in the East African region. (1982)

No. 9 WHO/UNEP: Public health problems in the coastal zone of the East African region. (1982)

No. 10 IMO/UNEP: Oil pollution control in the East African region. (1982)

No. 11 IUCN/UNEP:Conservation of coastal and marine ecosystems and living resources of the East African region. (1982)

No. 12 UNEP: Environmental problems of the East African region. (1982)

No. 13 UNEP: Pollution and the marine environment in the Indian Ocean. (1982)

No. 14 UNEP/CEPAL: Development and environment in the Wider Caribbean region: A Synthesis. (1982)

No. 15 UNEP: Guidelines and principles for the preparation and implementation of comprehensive action plans for the protection and development of marine and coastal areas of regional seas. (1982)

No. 16 GESAMP: The health of the oceans. (1982)

No. 17 UNEP: Regional Seas Programme: Legislative authority. (1985)

No. 18 UNEP: Regional Seas Programme: Workplan. (1982)

No. 19 Rev. 2. UNEP: UNEP Oceans Programme: Compendium of projects. (1985)

No. 20 CPPS/UNEP: Action Plan for the protection of the marine environment and coastal areas of the South-East Pacific. (1983)

No. 21 CPPS/UNEP:Sources, levels and effects of marine pollution in the South-East Pacific. (1983) (In Spanish only)

No. 22 Rev. 2. UNEP: Regional Seas Programme in Latin America and Wider Caribbean. (1985)

No. 23 FAO/UNESCO/IOC/WHO/WMO/IAEA/UNEP: Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MED POL) - Phase I: Programme Description. (1983)

No. 24 UNEP: Action Plan for the protection and development of the marine and coastal areas of the East Asian region. (1983)

No. 25 UNEP: Marine pollution. (1983)

No. 26 UNEP: Action Plan for the Caribbean environment programme. (1983)

No. 27 UNEP: Action Plan for the protection and development of the marine environment and coastal areas of the West and Central African region. (1983)

No. 28 Rev. 1. UNEP: Long-term programme for pollution monitoring and research in the Mediterranean (MED POL) - Phase II. (1983)

No. 29 SPC/SPEC/ESCAP/UNEP: Action Plan for managing the natural resources and environment of the South Pacific region. (1983)

No. 30 UNDIESA/UNEP: Ocean energy potential of the West and Central African region. (1983)

No. 31 A. L. OAHL and I. L. BAUMGART: The state of the environment in the South Pacific. (1983)

No. 32 UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA: Pollutants from land-based sources in the Mediterranean. (1984)

No. 33 UNDIESA/UNEP: Onshore impact of offshore oil and natural gas development in the West and Central African region. (1984)

No. 34 UNEP: Action Plan for the protection of the Mediterranean. (1984)

No. 35 UNEP: Action Plan for the protection of the marine environment and the coastal areas of Bahrain, Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia and the United Arab Emirates. (1983)

No. 36 UNEP/ECLAC: The state of marine pollution in the Wider Caribbean region. (1984)

No. 37 UNDIESA/UNEP: Environmental management problems in resource utilization and survey of resources in the West and Central African region. (1984)

No. 38 FAO/UNEP: Legal aspects of protecting and managing the marine and coastal environment of the East African region. (1983)

No. 39 IUCN/UNEP: Marine and coastal conservation in the East African region. (1984)

No. 40 SPC/SPEC/ESCAP/UNEP: Radioactivity in the South Pacific. (1984)

No. 41 UNEP: Socio-economic activities that may have an impact on the marine and coastal environment of the East African region. (1984)

No. 42 GESAMP: Principles for developing coastal water quality criteria. (1984)

No. 43 CPPS/UNEP: Contingency plan to combat oil pollution in the South-East Pacific in cases of emergency. (1984)

No. 44 IMO/ROPME/UNEP: Combating oil pollution in the Kuwait Action Plan region. (1984)

No. 45 GESAMP: Thermal discharges in the marine environment. (1984)

No. 46 UNEP: The marine and coastal environment of the West and Central African region and its state of pollution. (1984)

No. 47 UNEP: Prospects for global ocean pollution monitoring. (1984)

No. 48 SPC/SPEC/ESCAP/UNEP: Hazardous waste storage and disposal in the South Pacific. (1984)

No. 48/ Appendices SPC/SPEC/ESCAP/UNEP: Hazardous waste storage and disposal in the South Pacific. (1984)

No. 49 FAO/UNEP: Legal aspects of protecting and managing the marine and coastal environment of the East African region: National Reports. (1984)

No. 50 IUCN/UNEP: Marine and coastal conservation in the East African region: National Reports. (1984)

No. 51 UNEP: Socio-economic activities that may have an impact on the marine and coastal environment of the East African region: National Reports. (1984)

No. 52 UNEP: Arab co-operation for the protection and development of the marine environment and coastal areas resources of the Mediterranean. (1984)

No. 53 UNEP: UNEP Regional Seas Programme: the Eastern African Experience. (1984)

No. 54 UNIDO/UNEP: Contingency planning for emergencies associated with industrial installations in the West and Central African region. (1985)

No. 55 FAO/UNEP: Marine mammals: global plan of action. (1985)

No. 55/ Annex FAO/IUCN/IHC/UNEP: Marine mammals: global plan of action. (1985)

No. 56 GESAMP: Cadmium, lead and tin in the marine environment. (1985)

No. 57 IMO/UNEP: Oil spills and shoreline clean-up on the coasts of the Eastern African region. (1985)

No. 58 UNEP: Co-operative programmes sponsored by UNEP for the protection of the marine and coastal environment in the wider Indian Ocean region. (1985)

No. 59 UNEP: Environmental problems of the marine and coastal area of India: National Report. (1985)

No. 60 IUCN/UNEP: Management and conservation of renewable marine resources in the Indian Ocean region: Overview. (1985)

No. 61 UNEP: Action Plan for the protection, management and development of the marine and coastal environment of the Eastern African region. (1985)

No. 62 IUCN/UNEP: Management and conservation of renewable marine resources in the South Asian Seas region. (1985)

No. 63 IUCN/UNEP: Management and conservation of renewable marine resources in the Kuwait Action Plan region. (1985)

No. 64 IUCN/UNEP: Management and conservation of renewable marine resources in the Red Sea and Gulf of Aden region. (1985)

No. 65 IUCN/UNEP: Management and conservation of renewable marine resources in the East Asian Seas region. (1985)

No. 66 IUCN/UNEP: Management and conservation of renewable marine resources in the Eastern African region. (1985)

No. 67 UN/UNEP: Coastal erosion in West and Central Africa. (1985)

No. 68 GESAMP: Atmospheric transport of contaminants into the Mediterranean region. (1985)

No. 69 UNEP: Environment and resources in the Pacific. (1985)

No. 70 UNESCO/ROPME/UPM/UNEP: Proceedings of the Symposium/Workshop on oceanographic modelling of the Kuwait Action Plan (KAP) region. (1985)

No. 71 IUCN/ROPME/UNEP: An ecological study of the rocky shores on the southern coast of Oman. (1985)

No. 72 IUCN/ROPME/UNEP: An ecological study of sites on the coast of Bahrain. (1985)

No. 73 SPC/SPEC/ESCAP/UNEP: Ecological interactions between tropical coastal ecosystems. (1985)

No. 74 UNEP: Environmental problems of the marine and coastal area of Sri Lanka: National Report (1986)

No. 75 UNEP: Environmental problems of the marine and coastal area of Bangladesh: National Report (1986)

No. 76 UNEP: Environmental problems of the marine and coastal area of Maldives: National Report (1986)

No. 77 UNEP: Environmental problems of the marine and coastal area of Pakistan: National Report (1986)

No. 78 GESAMP: Organosilicons in the marine environment. (1986)

No. 79 H.I. SHUVAL: Thalassogenic diseases. (1986)

No. 80 GESAMP: Environmental capacity: an approach to marine pollution prevention. (1986)

No. 81 UNEP: Action Plan for the conservation of the marine environment and coastal areas of the Red Sea and Gulf of Aden. (1986)

No. 82 UNEP: Environmental problems of the South Asian Seas region: An overview. (1986)

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