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JOINT GROUP OF EXPERTS ON THE SCIENTIFIC ASPECTS
OF MARINE POLLUTION
- GESAMP -

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No. 26

Atmospheric Transport of Contaminants
into the Mediterranean Region



World Meteorological Organization

IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on
the Scientific Aspects of Marine Pollution (GESAMP)

ATMOSPHERIC TRANSPORT OF CONTAMINANTS
INTO THE MEDITERRANEAN REGION

World Meteorological Organization, 1985

NOTES

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Definition of Marine Pollution by GESAMP

"POLLUTION MEANS THE 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."

* * *

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EXPLANATORY NOTE

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.

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

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 present report, which is available in English only, has also been discussed and approved by the fifteenth session of GESAMP.

Financial support for the work of the GESAMP Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans was provided by the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP).

GESAMP REPORTS AND STUDIES PUBLICATIONS

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Rep. & Stud. No.	Title	Date	Language
1.	Report of the Seventh Session	1975	E,F,R,S
2.	Review of Harmful Substances	1976	E
3.	Scientific Criteria for the Selection of Sites for Dumping of Wastes into the Sea	1975	E,F,R,S
4.	Report of the Eighth Session	1976	E,F,R
5.	Principles for Developing Coastal Water Quality Criteria	1976	E
6.	Impact of Oil on the Marine Environment	1977	E
7.	Scientific Aspects of Pollution Arising from the Exploration and Exploitation of the Sea-bed	1977	E
8.	Report of the Ninth Session	1977	E,F,R
9.	Report of the Tenth Session	1978	E,F,R,S
10.	Report of the Eleventh Session	1980	E,F,S
11.	Marine Pollution Implications of Coastal Area Development	1980	E
12.	Monitoring Biological Variables related to Marine Pollution	1980	E,R
13.	Interchange of Pollutants between the Atmosphere and the Oceans (First report)	1980	E
14.	Report of the Twelfth Session	1981	E,F,R
15.	The Review of the Health of the Oceans	1982	E
16.	Scientific Criteria for the Selection of Waste Disposal Sites at Sea	1982	E
17.	The Evaluation of Hazards of Harmful Substances Carried by Ships	1982	E
18.	Report of the Thirteenth Session	1983	E,F,S,R
19.	An Oceanographic Model for the Dispersion of Wastes Disposed of in the Deep Sea	1983	E
20.	Marine Pollution Implications of Ocean Energy Development	1984	E
21.	Report of the Fourteenth Session	1984	E,R,S
22.	Review of Potentially Harmful Substances	1985	E
23.	Interchange of Pollutants Between the Atmosphere and Oceans (Second report)	1985	E
24.	Thermal Discharges in the Marine Environment	1984	E
25.	Report of the Fifteenth Session	1985	E
26.	Atmospheric Transport of Contaminants into the Mediterranean Region	1985	E

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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 Mediterranean 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 techniques 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 metalloids 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 reasonably 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

throughout 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

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

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

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

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 μm 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:

$$F = k c \dots\dots\dots (3)$$

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 nm to 1000 μm . 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 $4 \text{ m}\cdot\text{s}^{-1}$ 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
<u>Metals</u>				
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 <u>et al</u> , 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 <u>et al.</u> , 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
<u>Organics</u>				
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	0.3 - 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
<u>Hydrocarbons</u>				
n-Alkanes	0.2 - 13.3 ugl ⁻¹	(-1)- 266	Mediterranean	Saliot & Marty, in press
non-aro- matic	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^{2-} ; 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 meteorological variables