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

REPORTS AND STUDIES

No. 36

Pollutant modification of atmospheric and
oceanic processes and climate: some
aspects of the problem



WORLD METEOROLOGICAL ORGANIZATION

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

POLLUTANT MODIFICATION OF ATMOSPHERIC AND OCEANIC
PROCESSES AND CLIMATE: SOME ASPECTS OF THE PROBLEM

World Meteorological Organization, 1989

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."

For bibliographic purposes, this document may be cited as:

GESAMP - IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution. Pollutant modification of atmospheric and oceanic processes and climate: some aspects of the problem, 1989. Rep. Stud., GESAMP (36).

EXPLANATORY NOTE

The first draft of the present report was prepared at the sixth session of the WMO-led GESAMP Working Group No. 14 on the Interchange of Pollutants between the Atmosphere and the Oceans held in Paris from 6 to 9 January 1986. The list of participants is given as Annex I.

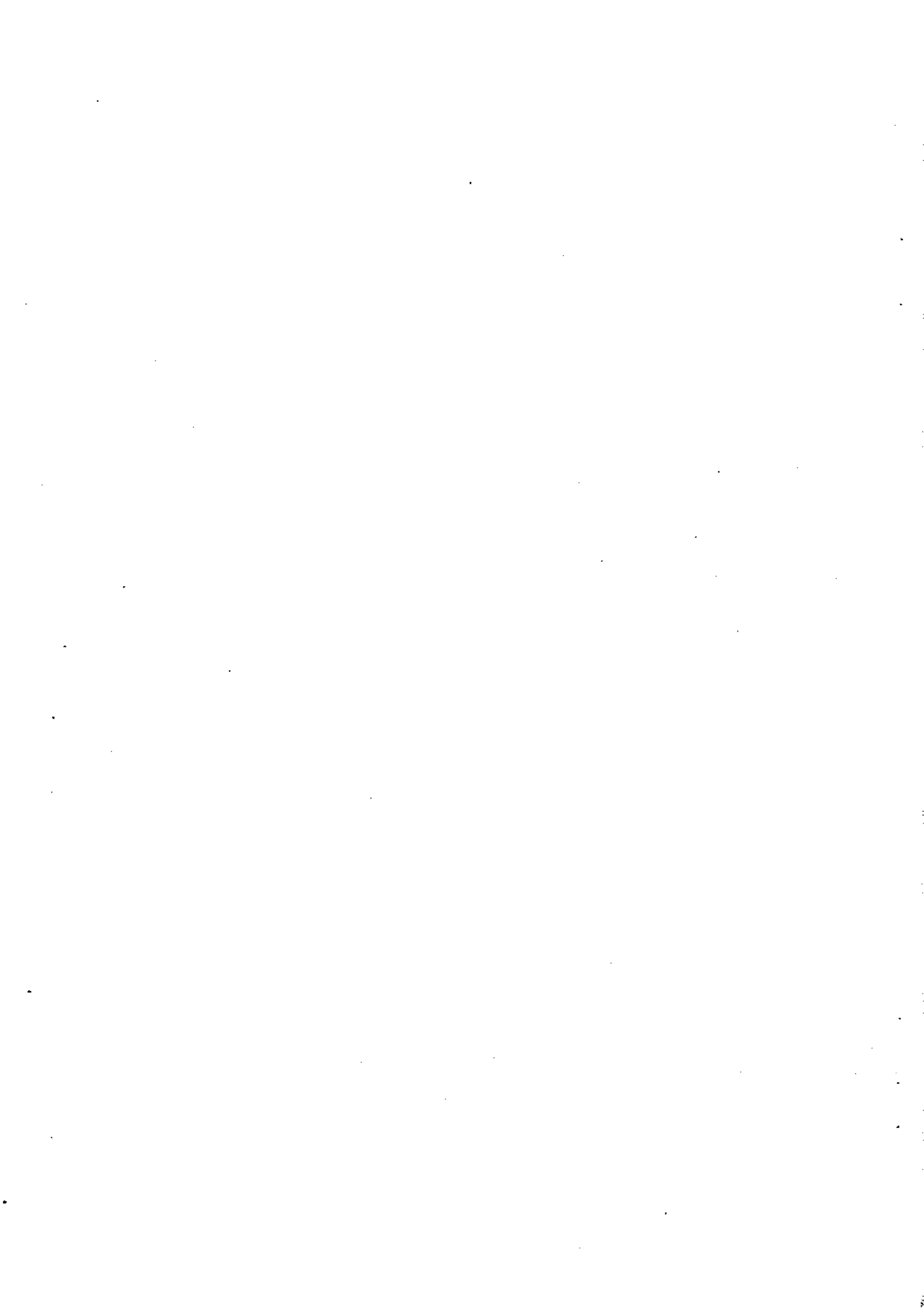
The GESAMP at its sixteenth session (London, 17-21 March 1986) endorsed the report in principle and recommended that the working group should continue its work during the intersessional period. The work done by correspondence was completed in March 1988.

The report, which is available in English only, was subsequently revised and updated to incorporate comments made by GESAMP at its eighteenth session (Paris, 11-15 April 1988) which adopted the report and recommended that it be published in the GESAMP Reports and Studies Series.

Financial support for the work of Working Group No. 14 was provided by the World Meteorological Organization (WMO), the United Nations Environment Programme (UNEP) and the Intergovernmental Oceanographic Commission (IOC).

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1. EXECUTIVE SUMMARY

The Sixth Session of the GESAMP Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans stressed the impact of contaminants on climate. This included the effects of such "greenhouse" gases as CO₂ increasing temperature and aerosols decreasing temperature, as well as contaminants and processes at the air-sea interface that affect the interchange of energy and material which could affect climate regionally and even globally. The effect of oil films in retarding transfer of gases between the atmosphere and the sea and in damping capillary and larger gravity waves, and hence reducing wind mixing in the upper layer of the sea, is one example of such contaminants and affected processes.

Carbon dioxide is clearly increasing in the atmosphere at the rate of about 1 ppmv (parts per million by volume) per year, starting at 315 ppmv in 1958 when good records commenced. It is estimated that the near-surface global temperature will increase by 1.5° to 4.5°K with a doubling of the atmospheric CO₂.

The global cycle of carbon dioxide indicates that the terrestrial biosphere and the oceans each cycle about 10² Gt (1 gigaton = 10¹⁵ g) carbon per year between themselves and the atmosphere, in a two-way flux if the system is in a steady state. This equilibrium has been perturbed naturally in the last 10⁴-10⁵ years at least, as shown by the analysis of air trapped in bubbles of glacial ice cores. Since the start of the agricultural/industrial revolution, man has added another perturbation by burning fossil fuels and mobilizing CO₂ from the fixed carbon in the land biosphere. For the period around 1980, the release of CO₂ from fossil fuel combustion is about 5 GtC yr⁻¹ and estimates of the release from biomass destruction, e.g., deforestation, ranges from 0 to 2 GtC yr⁻¹, depending on the technique of estimation. The major sink for man-mobilized CO₂ is the ocean which is estimated to accept about 2-3 GtC annually. The atmosphere retains about 2.5 GtC yr⁻¹; it is this residual CO₂ that contributes to the annual increase in atmospheric CO₂ concentration. The discrepancy between sources and sinks of man-made CO₂ is in the range of 0.5 to 1.5 GtC yr⁻¹, depending on the net biospheric input. Arguments are presented to show that the current input of CO₂ from the biosphere is no more than 1 GtC yr⁻¹, but uncertainty regarding the biomass contribution of CO₂ continues.

Some of the factors affecting the oceanic uptake of CO₂ from the atmosphere are presented. The gas transfer velocity is controlled mainly by the wind speed. The other variable that controls the CO₂ exchange flux is the partial pressure difference between the air and the sea. It is noted that there is a latitudinal variation in CO₂ flux, based on the observed CO₂ partial pressure distribution in the surface ocean. A net CO₂ flux of the order of 2 GtC yr⁻¹ emanates from the sea in the equatorial region between 16°S and 16°N. To balance this contribution, there would have to be a net flux of about 4 GtC yr⁻¹ from the atmosphere to the ocean north and south of this region.

Various models of the oceanic carbon cycle exist to estimate uptake of atmospheric CO₂ by the oceans. Diagnostic models have been developed in which the ocean is subdivided into a few well-mixed reservoirs connected by

first-order exchange fluxes. Stationary tracers (e.g., natural ^{14}C) and transient tracers (e.g., bomb-produced ^{14}C and ^3H , ^{85}Kr , and halocarbons) have been used to calibrate the models by circulating the advective and diffusive fluxes between the various boxes. Effects of the marine biosphere and its associated cycle of nutrients have begun to be included.

Recently, new types of circulation models of the oceanic carbon cycle, based on a realistic three-dimensional flowfield and mixing parameters of a general circulation model of the global ocean, have been introduced. These models make it possible to assess the effects of changes in the oceanic circulation, arising from climatic changes, on tracer distributions and the oceanic uptake capacity for CO_2 . They are preliminary, however, and lack certain features of the real ocean, particularly a realistic representation of the surface layer, including the marine biosphere.

With increasing temperatures due to rising atmospheric CO_2 concentration, inhomogeneities in sea-surface warming are expected owing to faster surface warming in areas with a shallow mixed layer and a strong thermocline as compared with areas of deep winter mixing or upwelling. Cold sea-surface temperature anomalies (SSTAs), relative to the temperature pattern expected at equilibrium with the CO_2 increase, are also likely to develop. SSTAs influence global weather patterns, as has been demonstrated by numerical experiments with weather forecast models. Good agreement has been found between the numerical experiments and available observations for both middle-latitude and tropical SSTAs. Rainfall increased near to warm anomalies and decreased in adjacent tropical regions. Major associated changes in atmospheric circulation arose. The response to equatorial SSTAs in middle latitudes is two to three times greater than for mid-latitude SSTAs of similar magnitude.

A second way that the ocean may modify the climatic response to a CO_2 increase is through the effect on ocean circulation and the distribution of temperature and salinity of changes in the atmospheric forcing at the surface due directly to the increase in CO_2 . Increased high-latitude precipitation would cause greater annual mean run-off, thus decreasing coastal salinities. Changes in the tropical rainfall distribution would effect changes in the density structure of the tropical oceans.

It was recognized that other man-made substances besides CO_2 , e.g., chlorofluorocarbons, nitrous oxide, methane and ozone, can influence the earth's radiative energy balance. Many authors claim that these radiatively active trace gases will cause a warming of the surface-tropospheric system of the same magnitude as that projected for increases in CO_2 . Such trace gases pose radiative/chemical/dynamical problems that are distinctly different and more complex than those of CO_2 . They could influence global climate through the greenhouse effect, but unlike CO_2 , they exhibit no important exchange processes with the oceans.

Both natural and man-made aerosols may influence climate by direct reduction of solar insolation transfer to the earth's surface and by change in the earth's albedo through aerosol interaction with cloud processes. Natural aerosols, e.g., volcanic emission, may play a more important role in climate changes than anthropogenic aerosols. During periods of extended air stagnation, accumulation of aerosols could be enough to change the solar energy input to coastal areas and regional seas. But, it is not expected that

anthropogenic aerosols would have much influence on global ocean climate through direct intervention with solar energy. The interaction of aerosols and clouds, on the other hand, may have a more significant impact on climate. Recently, investigators have postulated that natural sources of sulphur over the oceans may play an important role in regulating the cloud-condensation nuclei and hence the albedo. Others conclude that the effects of aerosols will probably not overshadow the impact of greenhouse gases as the most important cause of climate change over the next century.

Knowledge of the properties of the surface microlayer is important for better understanding of the exchange processes between the atmosphere and the ocean. Surface films, both of natural and man-made origin, are always present, but vary in physical and chemical properties and concentration. Several areas of particular interest to air-sea exchange of substances were identified: modification by surface films of sea-surface reflectivity, emissivity and absorption both for the visible and microwave spectral regions; influence of surface films on the properties of breaking waves and the air-bubble size distribution and life-times; effect of natural films in biologically highly productive zones and of anthropogenic films in oil spill and municipal sewage disposal areas on the rate of exchange of CO₂ and other non-reactive gases between the atmosphere and the ocean; effect of electrification of surface films due to mechanical (wind, waves) perturbation on salt enrichment and changes of ionic ratios in aerosols; and the effect of surface films of lipid and petroleum origin, combined with bubble formation, in concentrating particulate contaminants at the sea surface and in sea-to-land aerial transport of such contaminants as chlorinated hydrocarbons, bacteria and viruses.

Space-based satellite imagery to detect petroleum slicks on the sea surface and to determine the extent of coverage by such slicks was considered. Oil slicks have been observed from space by thermal imagers, optical photography, and imaging synthetic aperture microwave radar. Such systems might be used to determine the frequency and distribution of pollutant slicks on a global/regional basis. False images for microwave radar and photography may arise, however, from natural slicks, wind and current attenuation of capillary wave scatterers, dense cloud shadows and unrippled water under calm conditions. Natural slicks, ship wakes and effluents, upwelling, or thermal variability of the sea surface may also confuse thermal infrared imagery. Therefore, space-based sensing of sea-surface oil slicks would be difficult, unless supported by extensive sea-truth investigations. It was considered important, nevertheless, to continue testing methodologies to improve the capability for monitoring sea-surface oil slicks with space-based remote sensing systems.

It was noted that recent in situ research, coupled with coastal-zone colour imagery from space, has demonstrated that space-based detection of the effect of phytoplankton on ocean colour is possible. Space-based sensing of changes of phytoplankton biomass may become important for monitoring effects of climatic change on oceanic primary productivity.

2. INTRODUCTION

It is now well recognized that contamination of the oceans, and especially closed and semi-closed areas, is determined to a significant extent, by the entry of contaminants into the marine environment through the atmosphere. The interchange of contaminants between the atmosphere and the oceans is an important component of the biogeochemical cycles of many natural and man-made substances in the environment.

Within GESAMP, the Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans, established in 1977, assessed fluxes of selected contaminants between the atmosphere and the oceans. In addition, it described the main mechanisms governing contaminant interchange and examined the effects of contaminants on chemical, physical and biological air-sea interfacial processes. The air-sea exchange of contaminants or groups of contaminants, including carbon dioxide, sulphur gases, aerosols and trace elements, hydrocarbons and man-made radionuclides was reviewed (GESAMP, 1980, 1985a, b). The following processes and mechanisms were considered by the Working Group as important for air-sea interchange of contaminants: atmospheric transport of materials to and from the oceans, formation and distribution of cloud condensation nuclei, inversion in the sea-salt mass concentration in the marine atmosphere, production of bubbles and aerosols by breaking waves, petroleum films forming at the sea surface and residence of pollutants in the sea-surface microlayer (GESAMP, 1985a).

At the same time, it has become obvious that contaminants present at the atmosphere-ocean boundary, in the marine troposphere and within the sea itself could modify a number of physical, chemical and biological processes which ultimately could cause changes in the material and heat transfer between the atmosphere and the oceans and influence climate regionally or even on a global scale.

In the first report on interchange of pollutants between the atmosphere and the oceans prepared by the Working Group (GESAMP, 1980), it was shown that the air-sea interfacial exchange processes may be altered by detergents, petroleum and its derivatives, and the complex mix of surface-active components from municipal wastes and sewage sludge. Petroleum is the most widespread open-ocean pollutant which may affect the properties of the sea surface. Laboratory and field studies have demonstrated that organic surface films and oil spills attenuate capillary waves, alter surface temperature, modify the reflection and transmission of electromagnetic waves, change the stability of sea foam and bubble-bursting characteristics, reduce the exchange of gases (e.g., H_2O , O_2 , but usually only with artificially-added surface-active material), inhibit microscale turbulence and convective processes near the interface, and affect the activities of neustonic organisms in the sea-surface microlayer.

It was also understood that pollutants in the marine atmosphere, such as anthropogenic soot and dust, when present in sufficiently large quantities, could alter the solar radiation input to the seas, and consequently, the thermal characteristics of the sea and the troposphere. The introduction of cloud-condensation nuclei into the marine atmosphere modifies the physics of clouds by increasing the number of drops per unit volume. Through this process, clouds become more reflective, and hence change the earth's albedo.

On the basis of its conclusions on the above-mentioned matters, the Working Group in 1981 proposed that the GESAMP definition of marine pollution* be amended by the following wording: "... and altering ocean-related physical processes especially pertinent to climate".

This proposal was discussed at length by GESAMP XII and it was agreed that the Working Group should prepare an explanatory statement on process modification by pollutants for consideration at the next session. At the fifteenth session, GESAMP re-affirmed its request to the Working Group and approved the following, inter alia, terms of reference: (i) to provide a continuing review of air-sea material interchange with emphasis on the pollutant modification of atmosphere and ocean-related processes, especially those pertinent to climate, and the energy balance of the oceans; (ii) to study certain properties of the ocean mixed layer and the surface microlayer, which are modified by pollutants, to clarify mechanisms of mass and energy transfer between the atmosphere and the oceans, and to assess the potential for the remote detection of pollutants as a result of these surface and near-surface effects.

It was decided later by the Working Group that, at the first stage of studying these problems, attention should be paid mainly to the role of the global ocean in the magnitude and variations of tropospheric carbon dioxide concentrations, the knowledge of which is indispensable for modelling and predicting any resulting climatic changes and anomalies.

The orientation of the activities of the Working Group toward pollutant modification of the atmosphere, ocean-related processes and climate requires that these activities should be connected with, and take into account the results of, other international programmes and projects, such as the World Climate Research Programme (WCRP) (WMO/ICSU, 1985), and its World Ocean Circulation Experiment (WOCE) and Tropical Ocean and Global Atmospheric Programme (TOGA), and others. Summaries of the activities within some of these programmes are given in Annex II.

3. MAIN PROCESSES AND SIGNIFICANCE OF THEIR CHANGES

The Working Group discussed the effect of contaminants in modification of processes in the atmosphere, at the air-sea interface and in the sea (see Annex III), in the context of weather and climate modification. It is clear that certain processes are modified by contaminants, but the significance of

* "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."

these modifications in terms of climate modification cannot be assessed at present. It is likely that some of the effects are confined to local areas, e.g., regions with oil films, and the global impact is inconsequential. Some of the effects on processes are summarized in the matrix shown in Table 1.

4. SPECIFIC POLLUTANT PROBLEMS

4.1 Carbon Dioxide

4.1.1 Introduction

There is considerable evidence from climate models that the observed increase in the atmospheric concentration of carbon dioxide (CO₂) will lead to a significant warming of the atmosphere-ocean system [e.g., see the Villach, October 1985, Conference Report (WMO, 1986)].

In the models, this warming is due to the direct radiative effect of CO₂ enhanced by positive feedbacks due to water vapour, snow and ice and cloud extent. The equilibrium global near-surface warming for a doubling of CO₂ is estimated to be 1.5° to 4.5°K, with most recent results with model-dependent cloud cover nearer to the larger figure. This warming is larger in middle and high than in low latitudes.

The ocean is expected to modify this climate response directly in two ways. Firstly, the ocean's large thermal inertia will cause the ocean (and atmosphere) warming to lag behind that which would be in equilibrium with the CO₂ increase. Secondly, the atmospheric forcing of the ocean through momentum, heat and water transfer will be changed, thus modifying the ocean circulation and temperature and salinity structure. These aspects are discussed in Section 4.1.7.

The ocean's role in the global carbon cycle is crucial to predictions of future atmosphere CO₂ levels. Increases in other trace gases including methane, chlorofluorocarbons and nitrous oxide are together expected to lead to a warming of comparable magnitude to that caused by CO₂ (see Section 4.2.). The following discussion of CO₂ can also be applied to these gases except that the ocean plays a lesser part in their geochemical cycles.

4.1.2 The global carbon cycle

A summary of the principal carbon reservoirs on the earth and the major fluxes between them is given in Figure 1. Examination of the reservoir sizes immediately highlights the smallness of the atmosphere as a reservoir for carbon relative to the land biosphere, sedimentary deposits, the oceans and fossil fuel reserves. This means that even small transfers of carbon as CO₂ from the other reservoirs to the atmosphere can have a disproportionately large effect on the latter.

TABLE I. MODIFICATION OF PROCESSES BY CONTAMINANTS

PROCESS	TROPOSPHERE	AIR-SEA INTERFACE	SEA
PHYSICAL	<p>Soot and dust could alter the solar input and change the thermal characteristics of the troposphere. Cloud-condensation nuclei in the marine atmosphere modify the physics of clouds which may result in the modification of cloud formation patterns and the earth's albedo.</p>	<p>Organic films from petroleum hydrocarbons and/or detergents modify interfacial properties and exchange processes. Altered air-sea interfacial processes may influence the ocean-atmosphere exchange of gases (CO₂ and acid rain precursors) that are sources of acidity in coastal areas and seas, especially those affected by oil production and transportation.</p>	<p>Agricultural, forestry and construction silt runoff influences light penetration and possibly alters thermal structure in the euphotic zone. Estuarine areas and sites of municipal and industrial waste disposal would be of greatest concern.</p>
CHEMICAL	<p>Ozone is the source of the highly reactive radicals that control the chemistry of the troposphere. Changes in ozone can alter the concentrations of these radicals. Various atmospheric pollutants, e.g., nitrogen oxides and hydrocarbons, contribute to ozone through photo-oxidation processes.</p>	<p>Enrichment of organic films with petroleum hydrocarbons, organochlorines and metals occurs. This prevents ready transfer to the water column and enhances transfer to the atmosphere by bubble bursting. Exposure of substances in the surface film to the atmosphere and solar radiation promotes oxidation and photochemical processes.</p>	<p>Increased input of substances from man-made sources can change the minor element composition of seawater. Metal concentrations can be increased. Input of CO₂ can change the pH of seawater with certain consequences to chemical equilibria of ionic composition.</p>
BIOLOGICAL	<p>Transfer of bacteria, viruses and fungus spores from the sea to the atmosphere and potential transport to land by winds. This is a possible route for pathogens from sewage-polluted coastal areas to land animals and humans.</p>	<p>Pathological microorganisms could be concentrated in the surface film. Neustonic organisms can be affected by pollutants concentrated in the surface film. Erosion of the ozone layer by freons could lead to more UV light impinging on the sea surface and could affect the neuston adversely.</p>	<p>Dissolved constituents from municipal and industrial wastes, as well as from runoff, could be toxic to marine organisms or be bioaccumulated by them, posing a threat to consumers including man. Turbidity from suspended matter can reduce light penetration and primary productivity. Silt and other suspended materials can have adverse effects on sensitive marine organisms and habitats, e.g., coral reefs and mangroves.</p>

ATMOSPHERE

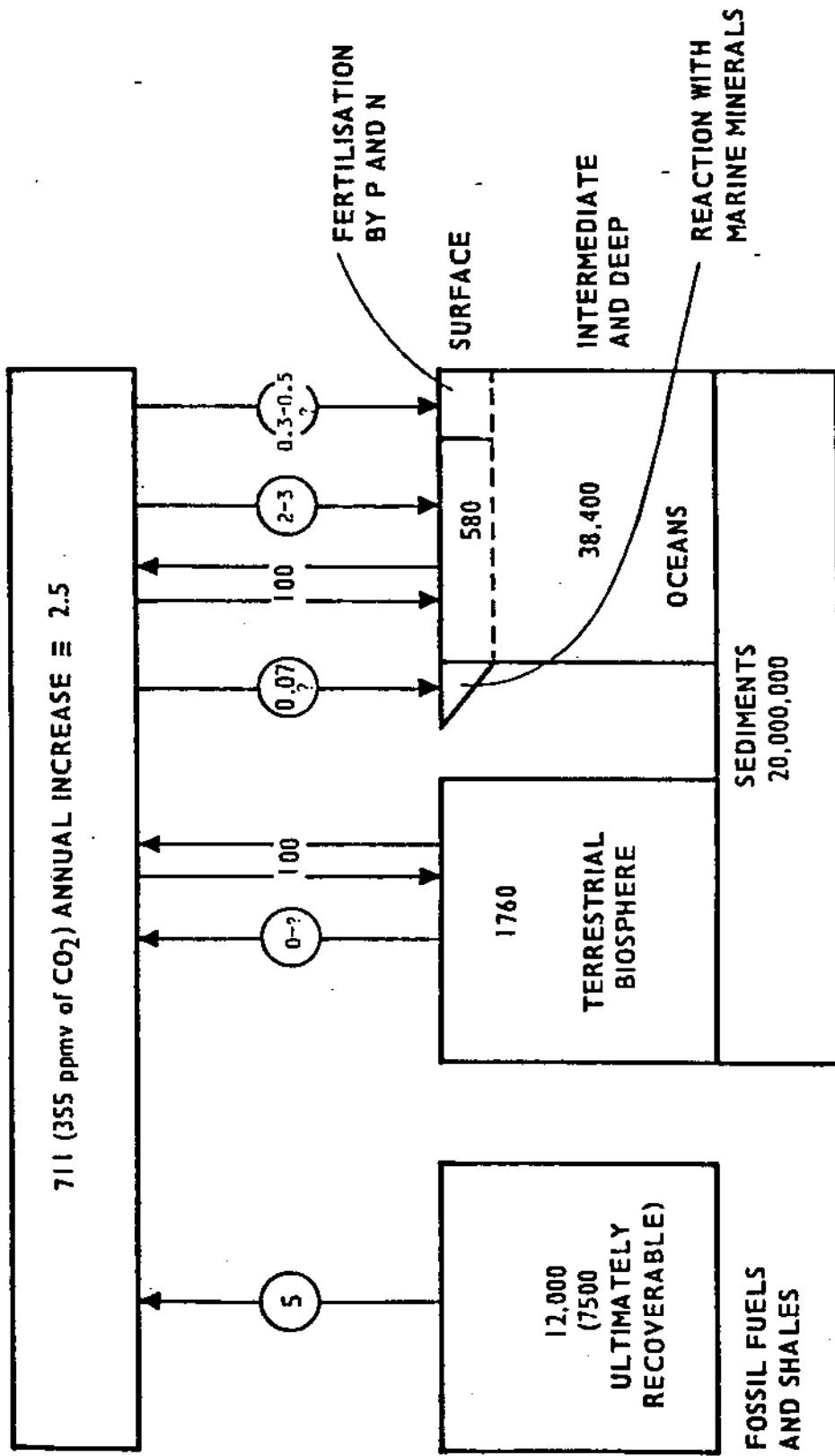


Figure 1. Global carbon reservoirs and present natural and anthropogenic fluxes between reservoirs. Reservoir sizes in GtC. Fluxes between reservoirs in GtC year⁻¹. Anthropogenic fluxes are circled. Question marks indicate fluxes for which considerable uncertainty exists. Updated from Liss and Crane (1983).

Both the land biosphere and the oceans each cycle approximately $10^2 \text{ Gt}^* \text{C yr}^{-1}$ between themselves and the atmosphere; this is a balanced two-way flux if the system is stationary. Perturbation of the steady-state situation can come about when the two-way fluxes are out of balance, which is what must have happened in the past to explain the atmospheric CO_2 variations over at least the last 10^4 - 10^5 years, shown by analysis of air trapped in ice cores (Neftel et al., 1982).

Since the industrial/agricultural revolution, man has applied another perturbation by burning fossil fuel and by net conversion of land biosphere (fixed carbon) to CO_2 . The sizes of these anthropogenic mobilizations are currently 5 GtC yr^{-1} from fossil fuel burning and anywhere from 0 to 2 GtC yr^{-1} from deforestation and changes in land use (see Section 4.1.6). The CO_2 enters the atmosphere and about 2.5 GtC yr^{-1} appears to remain there and leads to the well documented increase observed in atmospheric CO_2 partial pressure.

The major sink for man-mobilized CO_2 is the ocean which, according to current estimates, could have taken up 2-3 GtC of CO_2 per year during the last 25 years.

4.1.3 Ocean carbonate chemistry

In pure water CO_2 gas, although reasonably soluble, can be accommodated to only a very limited extent. Seawater, on the other hand, due to dissolved carbonates, contains about 150 times more carbon in the form of dissolved ionic species, mainly HCO_3^- , than does an equal volume of air at normal CO_2 partial pressure in equilibrium with it.

This fact makes the ocean the most important reservoir taking up CO_2 released by man to the atmosphere (Liss and Crane, 1983). As we shall see, however, the accommodating capacity of the ocean is much smaller than it might appear at first sight. This is so for two reasons: (1) the time needed to spread the CO_2 taken up over the whole ocean depth is considerable (see below); and (2) the uptake capacity of seawater is about a factor of 10 (the so-called buffer or Revelle factor) smaller than anticipated from the static equilibrium partition factor of 150 quoted before. As a consequence of both (1) and (2), it turns out that the oceans take up the equivalent of half of the CO_2 released by fossil fuel combustion.

* 1 Gt (gigaton) = 10^{15} g

4.1.4 Transfer of CO₂ between the air and the sea

The net flux (j) of CO₂ across the air-sea boundary can be expressed as the product of essentially two factors, the gas transfer velocity w and the difference ($\Delta p_{\text{CO}_2} = p_a - p_s$) between the partial pressures of CO₂ in the atmosphere p_a and the surface layer p_s of the ocean:

$$j = w \alpha \Delta p_{\text{CO}_2}$$

Hence both quantities may be assessed separately. The third factor, the gas solubility α (i.e., the amount of CO₂ dissolved in a unit volume of water per unit CO₂ partial pressure) is a quantity comparatively easy to estimate and therefore of minor interest here.

The gas transfer velocity is controlled primarily by wind speed driving the near-surface turbulence in the water and thus enhancing gas transfer. In the absence of surface waves, the gas transfer velocity w is a linear function of wind speed or rather of the friction velocity and nicely follows the hydrodynamical prediction by Deacon (1977). Laboratory experiments (Jähne et al., 1986) show, however, that with the onset of wind-induced surface waves the transfer velocity starts to exceed Deacon's prediction by up to a factor of 10. This excess factor can reasonably well be correlated with the mean square slope of the surface waves. This indicates that a highly irregular wind-induced wave field enhances surface renewal by the generation of additional turbulence. Since surface films damp or even suppress waves, they also reduce gas transfer to the predictions of the smooth surface model. Whether, and if so to what extent, over the open ocean surface films do reduce gas exchange, at a given wind speed, is essentially unknown. The definite degree of gas transfer enhancement by air bubbles at very high wind speed is also still an open question. It is clear that the greatest area of uncertainty over the magnitude of the gas transfer velocity is at high wind speeds. The reasons for this lack of knowledge are the difficulties of experimentally measuring transfer velocities in wind/wave tunnels and particularly in the field when the system is very turbulent. Likewise theoretical approaches are at their least reliable under such conditions. As far as we are aware, no experiments, whether field or laboratory, have ever been attempted on the effects of cyclones/hurricanes on transfer.

Nevertheless, it seems (Broecker et al., 1986) that laboratory experiments, field experiments by the radon deficiency method, and the geochemical ¹⁴C techniques yield consistent global average values for w . However, uncertainty still exists concerning the dependence of w on wind speed, which is knowledge required to estimate the latitudinal dependence of w needed for ocean CO₂ uptake modelling and for local estimates of air-sea CO₂ fluxes.

The other quantity which determines the CO₂ exchange flux is the partial pressure difference Δp_{CO_2} between air and sea. Considerable efforts have been undertaken to document this quantity on a global scale (Keeling, 1968; Takahashi et al., 1983).

The seasonal variation of the atmospheric CO₂ mixing ratio varies from a few ppm in the southern hemisphere to not more than 20 ppm in high northern latitudes (Pearman et al., 1983; Conway et al., 1985). Furthermore, annually averaged mean mixing ratios vary less than 4 ppm as a function of geographic location (Pearman et al., 1983; Pearman and Hyson, 1986). On the other hand, the partial pressure of CO₂ in the surface ocean varies spatially and temporally by up to ± 100 ppm and occasionally more. Hence its influence on the distribution of Δp_{CO_2} is much more pronounced.

The partial pressure of CO₂ at a given location in the surface ocean is determined by the complex interaction of several processes:

- gas exchange with the atmosphere;
- chemical equilibrium with the different components of dissolved inorganic carbon;
- depth of the mixed surface ocean layer;
- upwelling of and mixing with subsurface water;
- horizontal advection of waters with different history; and
- activity of the marine biosphere.

In particular, the effects of the marine biosphere are still poorly understood.

The general pattern of the mean annual distribution of $\Delta p\text{CO}_2$ consists of an equatorial belt of supersaturated waters with excess $\Delta p\text{CO}_2$ of up to 100 ppm, which is flanked by regions of undersaturated waters to the north and south. The distribution of $\Delta p\text{CO}_2$ in higher latitudes, however, is less well known owing to a seasonal bias in the available measurements.

The present distribution does not represent a steady state situation, since the anthropogenic input of CO₂ into the atmosphere has created a perturbation flux into the oceans on the order of 2-3 GtC yr⁻¹ (Figure 1), that is included in the pattern of the net flux as inferred from the measured $\Delta p\text{CO}_2$ distribution.

Based on a global average value of α_w derived from the pre-bomb ¹⁴C distribution, a net CO₂ flux on the order of 2 GtC yr⁻¹ emanates from the sea in the equatorial region between 16°S and 16°N. Correspondingly, a net flux of about 4 GtC yr⁻¹ would have to enter the ocean north and south of this region. The relative partitioning of this flux between the hemispheres may be inferred from the observed meridional atmospheric gradients of CO₂ concentration and its isotopic ¹³C/¹²C ratio (Keeling et al., 1985).

The evolution of the $\Delta p\text{CO}_2$ distribution with time as a consequence of increasing atmospheric CO₂ levels has not been observed accurately enough to estimate directly any changes in the air-sea fluxes of CO₂.

In order to clarify the role of the $p\text{CO}_2$ in the surface ocean in driving the air-sea flux, measurements of that property at a number of key locations for several years would be very valuable.

4.1.5 Models of the oceanic carbon cycle

The uptake of atmospheric CO₂ by the oceans can be estimated by means of a model of the oceanic carbon cycle. In the past, several models have been constructed that divide the ocean into a few well-mixed reservoirs (boxes), which are connected by first-order exchange fluxes. The exchange rates are then calibrated by tuning the predicted distributions of various stationary (e.g., natural ¹⁴C) and transient tracers (e.g., the bomb-produced ¹⁴C and ³H, ⁸⁵K, halocarbons) to the observations (Keeling, 1973b; Oeschger et al., 1978; Siegenthaler, 1983; Broecker and Peng, 1982).

This type of diagnostic ocean model has been optimized by increasing the subdivision of the oceans, inclusion of effects of the marine biosphere and its associated cycle of nutrients, and the use of inverse methods to obtain the unknown advective and diffusive fluxes between the various boxes (Bolin et al., 1983). Since all of these models are calibrated with essentially the same transient-tracer data, it is not surprising that their predicted uptake capacity of excess CO₂ is rather similar (Peng and Broecker, 1985), amounting to about 2 GtC yr⁻¹ around 1980.

Recently, new types of circulation models of the oceanic carbon cycle have been introduced. These models are based on the realistic three-dimensional flowfield and mixing parameters of a general circulation model (GCM) of the global ocean. This approach is promising in several ways:

° There is no need to tune any transport parameters, since they are derived directly from the primitive hydrodynamic equations and the boundary conditions imposed at the surface in the oceanic GCM. Therefore, the wealth of available tracer data may be used to validate the model.

° The fairly high horizontal resolution of the model (on the order of 500 km) allows model predictions of tracer distributions and fluxes on a regional scale.

° The model is prognostic; therefore, it is possible to assess the effects of changes in the oceanic circulation on tracer distributions and the oceanic uptake capacity for CO₂. This is important if the influence of climatic changes on the global carbon cycle is to be investigated.

The presently existing models of this type (Sarmiento, 1985; Maier-Reimer et al., 1985; Bacastow and Maier-Reimer, 1985) are, however, still preliminary, in that they lack certain features of the real ocean, most notably a realistic representation of the surface layer including the marine biosphere.

4.1.6 The effect of the biosphere on CO₂

Estimates based on ¹³C/¹²C recorded in tree-rings (Broecker and Peng, 1982) and on the atmospheric CO₂ history of the last 200 years determined from air bubbles trapped in Antarctic ice-cores (Siegenthaler and Oeschger, 1987), indicate, besides the known input from fossil fuel, an additional source of CO₂ attributed to the terrestrial biosphere. This source shows a peak around 1900 and a decline since then. During the time period 1959-1983 the net biospheric source contribution is estimated to lie between 0.0-1.0 GtC year⁻¹. These estimates are based on an assumed oceanic uptake capacity for CO₂ as given by state-of-the-art ocean carbon cycle models; which, however, have been validated by independent data (see section 4.1.5).

Woodwell et al., (1983), based on population and land use statistics, estimated that during 1980 between 1.8 GtC and 4.7 GtC year⁻¹ was released by the biosphere due to deforestation (80%) and changes in land use, primarily in the tropics. A subsequent study by the same group of investigators resulted in somewhat lower figures, giving as best estimate an annual release of 1.8 GtC for the year 1980 (Houghton et al., 1987). Bolin (1986) reviewed these estimates and concluded that this source has contributed 0.8-2.4 GtC year⁻¹ during the last decade.

Elliot et al. (1985) analyzed indepth the CO₂ concentrations measured at the Mauna Loa Observatory. They came to the conclusion that the CO₂ record at Mauna Loa is not consistent with net annual additions or subtractions of CO₂ other than from fossil fuels unless such additions have closely followed the trend of the fossil fuel input. Given the uncertainties, a net biotic addition between +0.7 and -0.2 GtC year⁻¹ is allowed by the analysis.

There is some evidence that increased plant production could have lead to a net uptake of CO₂ in the biosphere. Such a carbon flux has not been considered in the analysis by Woodwell et al., (1983) and by Houghton et al., (1987). Stimulation of land plants could have been effected either directly as a consequence of increasing atmospheric CO₂ levels (Kohlmaier et al., 1987) or from increased use of fertilizing agents in agriculture. Peterson and Mellillo, (1987), however, estimated the latter effect to contribute not more than 0.2 GtC year⁻¹, based on the assumption of a constant element ratio of carbon to phosphorus and nitrogen in terrestrial organic material. On the other hand, changes during the last 200 years in physiological parameters of plants growing in remote areas have been observed, such as a reduction of pore density per unit leaf area (Woodward, 1987) and increased in the size of tree-rings (LaMarche et al., 1984). Kohlmaier et al., (1987), find by means of a biota model that the increased storage of carbon in the biosphere due to the CO₂ fertilization effect could amount of 0.7-2.1 GtC year⁻¹.

If the CO₂ fertilization effect is real the net biospheric release of carbon to the atmosphere presently (deforestation minus fertilization) would lie in the range from 0 to 1 GtC year⁻¹, thus almost balancing the global carbon budget. Otherwise, an imbalance of 1 to 2 GtC year⁻¹ results, which has to be explained either by an oceanic sink being greater than currently acceptable, or by one or several, hitherto unidentified sinks.

The foregoing discussion deals only with the terrestrial biosphere. It is uncertain how the marine biosphere has responded to changing CO₂ concentrations in the atmosphere or what contribution it has made to atmospheric CO₂. Generally, it has been assumed that on an annual basis, the uptake of CO₂ by photosynthesis by marine plant life has been balanced by release of CO₂ from respiration and decay of marine plant and animal organisms. This may not be true. Increased input of nutrients from land as a result of agricultural practices, e.g., soil fertilization, could result in greater marine plant production. If the plants are harvested by marine fauna or man, or if they die and sink to enter the sediments, then CO₂ is removed from the surface layer of the sea, and ultimately from the atmosphere. The marine biosphere would become an enhanced sink for CO₂.

In the foregoing connection, recent studies of the mid-Atlantic Bight of the U.S.A., the south-eastern Bering Sea, and the Peruvian coast (Walsh et al., 1985) estimate that the present carbon loading to the continental slopes of the world, as a result of export of organic carbon from continental shelves, ranges from about 0.3 to 0.48 Gt C yr⁻¹. In earlier reports, it was proposed that the increased carbon to slope sediments of the mid-Atlantic coast may have occurred in response to eutrophication (Walsh et al., 1981), and off Peru in response to overfishing the anchovy, the major herbivore (Walsh, 1981), creating transient gradients in the vertical profiles of

sediment carbon. Walsh et al. (1985) used a combination of sedimentation and mixing rates of carbon, the C:N ratio (approx. 8) of the upper 50 cm of sediments, and the amount of nitrogen thought to be released from the coastal zone to make an independent estimate of anthropogenic carbon loading to world slopes of about 0.3 to 0.5 GtC yr⁻¹. Although the authors note that additional measurements are required to test their conclusions, they feel that their data set is consistent with the hypothesis that continental slopes are now areas for deposition and thus storage of anthropogenic releases of CO₂.

Another possible biogenic route for CO₂ uptake in the ocean is by dissolution of calcium carbonate mineral phases. The general situation is that near-surface waters are supersaturated with respect to calcitic solid phases, so that dissolution by excess CO₂ taken up from the atmosphere is not expected; only further down the water column (several km depth) does the system become undersaturated with respect to calcite. However, recent work in the N. Pacific (Betzer et al., 1984) has indicated that aragonite pteropods are subject to dissolution in quite shallow water (<2200m), and this may be an important mechanism for uptake of additional anthropogenic CO₂ by the near-surface oceans.

Other effects of CO₂ on the marine environment include changes in pH and temperature in the surface seawater layer. Projected increases in atmospheric CO₂ have been shown (Liss and Crane, 1983) to reduce pH by 0.3 for a doubling in atmospheric pCO₂. Increased atmospheric temperature by 1.5°-4.5°K, with a doubling of atmospheric CO₂ concentration, would also increase the temperature of the surface seawater. What impact these physical and chemical changes in the seawater would have on the marine biota can only be speculated on at present. The effect of pH change within the normal range for seawater, i.e., 7.5 to 8.5, would probably be insignificant, in that marine organisms should be able to adapt to such changes. However, a decrease in pH below the normal lower limit experienced by marine organisms could have adverse effects. Similarly, a temperature increase above the upper normal limit could cause population changes. Moreover, if temperature is an important variable triggering phytoplankton blooms, increased temperature due to higher CO₂ concentrations could temporally advance such blooms and change the marine ecosystem.

4.1.7 Oceanic modification of climatic effects of increasing CO₂

The ocean would be expected to warm as a result of increasing atmospheric CO₂ content. Because of the dependence of the ocean's thermal inertia on the depth of mixing, faster surface warming would be expected in areas with a shallow mixed layer and strong thermocline than in areas where deep mixing occurs in winter or upwelling of water from a few hundred metres is prevalent. These inhomogeneities in surface warming would lead to the development of cold sea-surface temperature anomalies (SSTAs), relative to the temperature pattern which would pertain at equilibrium with the CO₂ increase, and so also relative to the thermal forcing of the land.

A first estimate of these cold SSTAs is obtainable from results published by Bryan et al. (1982) on the response to a sudden quadrupling of CO₂. However, it should be remembered that the thermal lag obtained in such an experiment will be larger than that with a gradual CO₂ increase. Firstly, one may note in Bryan et al.'s results a faster warming near the ocean surface than at depth. After 10 years the surface warming is 1.5° to 3°K, compared with less than 0.5°K, at most depth below 600 m. The thermocline would thus be more stable with probable impacts on vertical mixing. The zonal mean surface changes show that the approach of SST to equilibrium was faster at 20°-45° latitude over the first 15 years. However, by 25 years, from the CO₂ increase, the response was much more uniform with the surface warming near 70% of the equilibrium figure at most latitudes. With an equilibrium warming of about 3°K in the tropics and 5° to 6°K at 45°-60° latitude, similar to more recent results for a doubling of CO₂, the implied zonally-averaged cold anomalies, are about 1° and 2°K in tropics and middle latitudes, respectively. Regional anomalies could be substantially larger.

Such SSTAs would be near the maximum currently observed on large horizontal scales. Thus the results of observational and modelling studies on the atmospheric effects of such anomalies may be relevant to CO₂ climate impact studies. The effects of SSTAs in models have been reviewed by Rowntree (1986, and personal communication). Generally, both for middle latitude and tropical SSTAs, good agreement has been found between numerical experiments and between experiments and available observational studies. Tropical SSTAs had major effects on tropical climate; rainfall was increased near warm anomalies and decreased in adjacent tropical regions. There were major associated changes in circulation. For example, with warm anomalies over the equatorial Pacific, upper troposphere anticyclonic cells develop near 15°N and S in the longitude of the SSTA, with increased easterly flow on the equatorial side (above decreased surface easterlies) and an enhanced subtropical poleward jet. Further north and south, a mid-latitude trough is introduced throughout the troposphere. Both in models and the real atmosphere, a downstream wavetrain can usually be identified, with an anticyclonic response near 60°-70° latitude and a cyclonic response further downwind. These features appear to depend on the location of the SSTA relative to climatological flow (see also Simmons, 1982).

The response to mid-latitude SSTAs was found to be generally consistent with earlier theoretical work, with a surface low near the warm SSTA and a middle tropospheric ridge at some 20° longitude downstream. In middle latitudes, the response to equatorial SSTAs is two to three times greater than that for mid-latitude SSTAs of similar magnitude. Thus, for the cold anomalies relative to the equilibrium state for increased CO₂, the mid-latitude responses to tropical and extra-tropical features could be of similar magnitude. However, non-uniformity of the heating of the tropical oceans could dominate the response both in the tropics and at middle latitudes. Such non-uniformity could be caused by the distribution of mixed-layer depth or upwelling or by anomalous atmospheric circulation in the tropics, in the same way that the onset and maintenance of equatorial Pacific anomalies can be attributed to particular wind patterns.

The second way in which the ocean may modify the climate response to a CO₂ increase is through the effect, on ocean circulation and the distribution of temperature and salinity, of changes in the atmospheric forcing at the surface due directly to the increase in CO₂. There is little agreement as yet concerning such changes. One feature noted in the Villach 1985 Conference statement (WMO, 1986) is that increased high-latitude precipitation may lead to greater annual mean run-off, so decreasing coastal salinities. Increased precipitation over high-latitude oceans may have a similar effect away from coasts. A reduction in sea ice would also modify the salinity distribution in the mixed layer, and it is possible that the impact of these changes on the density structure would have significant effects on temperature, the ocean circulation and marine life, additional to those resulting directly from the general warming. The density structure of the tropical oceans would also be affected by changes in the tropical rainfall distribution and a probable general increase in ocean evaporation. More modelling studies are needed to quantify these and other possible impacts, including those associated with the lag in ocean temperature response discussed above.

4.2 Other Radiatively Active Trace Gases

Besides the influence of CO₂ on climate as detailed in the last section, other trace gases may also act as "greenhouse" gases. In the last fifty years, the number of man-influenced gases released to the atmosphere has risen substantially. A decade ago, researchers first suggested that other gases, e.g. chlorofluorocarbons, nitrous oxide, methane, tropospheric ozone and others, could influence the radiative energy balance just as well as carbon dioxide (Ramanathan, 1975; Wang et al., 1976). Recently, this suggestion has been definitively reviewed by Ramanathan et al. (1985).

Table 2 lists trace gases that are currently considered to be the most important for the future state of the global atmospheric environment and gives average rates of their increase in the atmosphere. The best known example is the well-documented increase of CO₂ as measured over nearly three decades. More recently, the concentration increases of several other trace gases were also documented, the foremost being methane, nitrous oxide and carbon monoxide. These trace gases have probably existed in the Earth's atmosphere for aeons, but their concentrations are now being increased by anthropogenic activities. In addition, there are several fluorocarbon compounds in the atmosphere which are entirely man-made and radiatively active. The most important of them are trichlorofluoromethane (CCl₃F or F-11) and dichlorodifluoromethane (CCl₂F₂ or F-12). Other man-made chlorocarbons and fluorocarbons could also contribute to the possible depletion of the ozone layer in the stratosphere and to climate changes. These trace gases include methylchloroform (CH₃CCl₃), F-113, F-22, F-114 and CCl₄ (Rasmussen and Khalil, 1986).

The present sources of these trace gases appear to be as follows. For methane, wetlands and marshes are thought to be the largest natural sources, while the oceans, tundra, lakes, insects and other sources together contribute about as much as the wetlands. Rice paddy fields and domestic cattle appear to be the largest sources affected and controlled by human activities, while biomass burning and direct emissions also contribute significant amounts. The total yearly emissions are estimated to be 550Tg (1 Tg = 1 teragram = 10¹²g), about half of which comes from anthropogenic activities. For nitrous oxide the major natural sources are the soils and oceans, whereas combustion processes and agriculture constitute the anthropogenic sources.

Table 2
Concentration increases and effects of trace gases

Gas	Rate of increase % per yr	Effects	Sources	Lifetime (years)
Carbon dioxide	0.4 (0.2-0.7)	Added greenhouse effect	Natural; combustion	10-15
Methane	1.3 (1-2)	Added greenhouse effect; OH cycle; ozone (tropospheric and stratospheric)	Natural; food production	7-10
Nitrous oxide	0.3	Added greenhouse effect; ozone depletion (stratosphere)	Natural; combustion; agriculture	100
Carbon monoxide	5	Indirect effects, OH depletion (troposphere)	Natural; combustion; automobiles	0.2
F-11 and F-12	5	Added greenhouse effect; ozone depletion (stratosphere)	Anthropogenic	50-100
Others				
F-113	10	Ozone depletion (stratosphere)	Anthropogenic	Long
F-22	11			15
Methylchloroform	5	Added greenhouse effect		6
Carbontetra-chloride	3			50

The total emissions are $\sim 30 \text{ Tg year}^{-1}$, of which about 25% is anthropogenic. The sources of CO are many and varied. It was estimated that, in total, about 2,400 Tg of CO are emitted into the atmosphere every year, of which perhaps half is due to various human activities. No natural sources of the fluorocarbons have been found; the present anthropogenic emissions of F-11 and F-12 are about 0.4 Tg year^{-1} for each.

The increasing levels of the trace gases are likely to be caused by increasing emissions. For methane and CO, some of the increase may also stem from the fact that their cycles are related to that of OH radicals. As CO increases the concentrations of OH radicals may diminish. This would in turn remove less methane (and other trace gases) than under natural, undisturbed conditions of the atmosphere. Therefore, a possible depletion of OH may be the main effect of increasing CO and this could then disturb many chemical cycles and indirectly contribute to global warming and climatic changes. Based on measurement of old air in polar ice cores, there is some evidence that OH radical concentrations may already have been reduced by perhaps 20% over the past century. Moreover, the same studies have shown that the atmospheric levels of methane several hundred years ago were less than half of the present concentration.

The problem concerning the greenhouse effects of human activities has broadened its scope from the CO₂-climate problem to the trace gas-climate problem. Non-CO₂ greenhouse gases in the atmosphere are now adding to the greenhouse effect by an amount comparable to the effect of CO₂ (see Figure 2). This is a fundamental change from the situation during the period of 1850-1960 (WMO, 1985).

If the growth rates of trace gas concentrations (or their emission rates) that were observed during the 1970s continue unabated for the next several decades, non-CO₂ trace gases could have as much impact as CO₂ on future trends of surface and atmospheric temperatures. In addition to the direct radiative effect, many of the trace gases have indirect effects on climate. For example, addition of gases such as CH₄, CO and NO_x can alter tropospheric O₃, which is itself a radiatively active gas. Within the troposphere, the indirect climate effects can be as large as the direct effects. On the other hand, within the stratosphere, temperature changes are largely determined by indirect effects of CFCs. Stratospheric H₂O will increase owing to the oxidation of the increasing concentrations of CH₄, and can be influenced by the trace gases through their effect on tropical tropopause temperatures. Furthermore, increases in tropospheric H₂O, through the temperature - H₂O feedback, can perturb tropospheric chemistry and alter the concentration of CH₄ and O₃.

Contamination of the atmosphere influences the marine environment in two ways: (1) directly through the input of pollutants into the sea, changing the physical, chemical and biological processes in the upper mixed layer and sea-surface microlayer; and (2) indirectly through modification of atmosphere and ocean-related processes, especially those pertinent to climate, and the energy balance of the oceans. As a source or sink, the ocean plays an important role in the global cycles of radiatively active gases, i.e. CO₂, N₂O, O₃ and halocarbons, which can affect biogeochemical processes in the marine ecosystems through long-term climatic changes and vice versa.

For this report, which deals with process modifications over the oceans, the influence of these gases is only indirect in that they will influence climate globally.

4.3 Atmospheric Aerosol Particles

Through man's activities, considerable amounts of particulate matter and aerosol-forming gases are released to the atmosphere. Though much of this material is deposited close to its source, some pollutants can be transported thousands of kilometres and affect the chemistry of the atmosphere far from their origin. Scientists have been concerned that besides changing the natural chemical cycles of the atmosphere, these pollutants would also have an influence on the global climate (Wilson and Matthews, 1971). Although these concerns were first expressed over a decade ago, there are still many unknowns in understanding pollutant transport and interactions in the atmosphere. The form in which the materials are released, the chemical reactions that take place both inside and outside of clouds and the final deposition of the given pollutant substances are still poorly known.

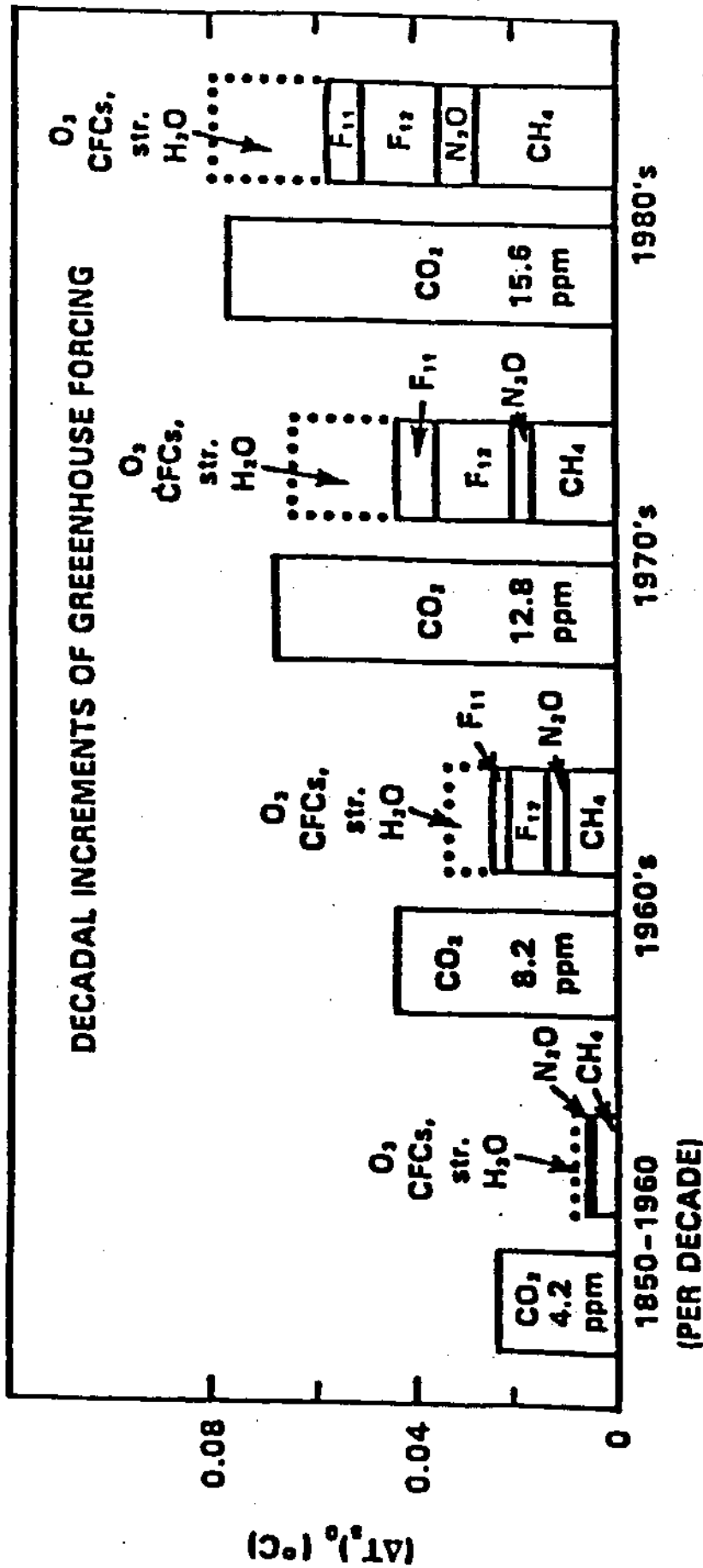


Figure 2. Decadal additions to global mean greenhouse forcing of the climate system. $(\Delta T_s)_0$ is the computed temperature change at equilibrium ($t \rightarrow \infty$) for the estimated decadal increases in trace gas abundances, with no climate feedbacks included. (WMO, 1985).

Whatever the uncertainties, some evaluation can be made of the role of man-made atmospheric pollutants on the climate. However, before this can be done, a distinction must be made between natural and anthropogenic materials put in the air. The eruption of the volcano El Chichon caused scientists to review more closely the importance of such a natural phenomenon on climate (Deluisi et al., 1983). Other more seasonal aerosol transport, such as that of Gobi and Sahara desert dust, may also be important in climate variations (Parrington et al., 1983; Heintzenberg, 1985). In both examples above, the natural aerosol would reduce the solar radiation reaching the earth's surface. It is thus important at the outset to realize that natural aerosols may play a more significant role than anthropogenic aerosols on climatic change (Deepak and Gerber, 1983).

Aerosols both natural and man-made may influence the climate of the oceans in two ways:

- (1) The direct reduction of insolation transfer to the earth's surface; and
- (2) Aerosol interaction with cloud processes that in turn change the earth's albedo.

For man-made aerosols, the first effect is probably only important for very limited regional areas, such as the northern coast of North America, parts of the Mediterranean and other industrial areas that border on the oceans. In general, these anthropogenic aerosols would not be expected to have much influence on the global ocean climate through direct intervention with solar energy. Only during periods of extended air stagnation would the accumulation of aerosols be enough to change the solar energy input to regional seas and coastal areas.

The second effect, i.e., the interaction of aerosols and clouds, may have a more important impact on climate. Pollution increases the number of dark light-absorbing particles in the atmosphere and, on the other hand, may also increase the atmospheric concentration of cloud-nucleating particles. Elemental carbon is believed to dominate the absorption, whereas sulphates are the major nuclei which influence droplet number. Though emission may vary for these two substances, under present industrial conditions, both should increase globally. This means either a decrease in global mean cloud albedo (because of increased absorption by carbon particles) or an increase in it (because of increasing cloud-drop concentrations). Twomey et al. (1984) suggest that the latter effect (brightening) is the dominant one for the global climate. They state that a 2% increase in the earth albedo caused by the increased cloud-drop concentration would be equal (in the opposite sense) to the doubling of CO₂. This hypothesis by Twomey et al. (1984) requires extensive measurements in order to quantify how such a mechanism would affect the world climate. It probably does not overshadow the effects of the greenhouse gases as the most important cause of climate change over the next century (WMO, 1986).

More recently, Charlson et al. (1987) have proposed a feedback mechanism by which sulphate particles, formed by atmospheric oxidation of marine-derived dimethylsulphide (DMS), may influence the climate by altering cloud albedo over the oceans. The scheme is illustrated in Figure 3. Certainly DMS produced by marine phytoplankton appears to be the dominant source of cloud condensation nuclei (CCN) over the remote oceans. Since the albedo of clouds increases with CCN number density, the proposed mechanism suggests that an increase in CCN would lead to a decrease in the amount of solar radiation absorbed by the earth and consequently to a cooling of the globe. The process could be rather sensitive to variations in the global rate of DMS production, with temperature changes of the order of 2°C possibly resulting from a two-fold change in the DMS flux from the oceans. It should be stressed that there are many uncertainties in this proposed climate control mechanism. Within the atmosphere many processes other than those involving sulphate aerosols can affect the radiation balance. Furthermore, it is not yet established that marine algae do indeed produce more DMS in response to elevated temperatures, as is implied by the postulated mechanism. The proposals of Charlson and co-workers are an important example of the ways in which the biota may potentially influence the chemistry and physics of the earth; the caveats mentioned merely serve to highlight areas for future research.

4.4 Chemistry of the Atmosphere-Ocean Boundary

The Working Group noted again that any understanding of the exchange processes between the atmosphere and the ocean involves knowledge of the properties of the surface microlayer. In this sense, molecular-level phenomena require special attention and further research.

Surface molecular films, both of natural origin, such as those from decaying biota, mostly zooplankton, or of man-made sources, such as petroleum hydrocarbons and surfactants, are always present, but vary in physical properties, concentration and chemical nature. Their spatial and temporal distribution is only now being understood on the basis of remote sensing (optical and microwave) data.

Microbiological and chemical processes are closely interrelated in the sea surface microlayer, with potential effects both on the uptake of contaminants by marine organisms as well as on the degradation of such chemicals by neustonic organisms. On the one hand, since the sea surface microlayer is enriched in substances such as PAHs and PCBs, enhanced uptake of such substances can occur by neuston. On the other hand, the elevated numbers of certain microorganisms associated with surface films and bubbles found in the microlayer implies that this is a region where degradation of such compounds by organisms will occur preferentially. This biological breakdown of organic compounds will, of course, occur simultaneously with their photochemical degradation brought about by the ready availability of solar radiation close to the sea surface.

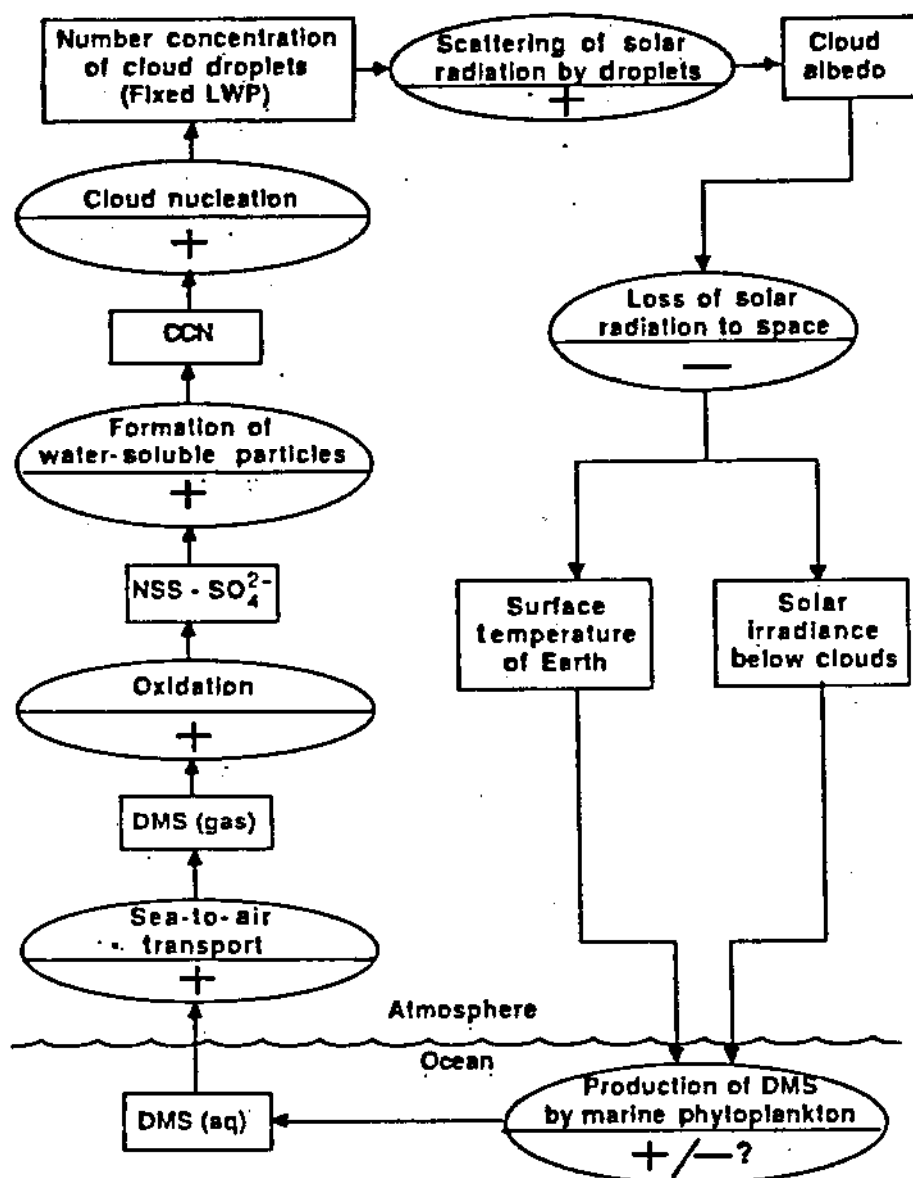


Figure 3. Conceptual diagram of a possible climatic feedback loop. The rectangles are measurable quantities, and the ovals are processes linking the rectangles. The sign (+ or -) in the oval indicates the effect of a positive change of the quantity in the preceding rectangle on that in the succeeding rectangle. The most uncertain link in the loop is the effect of cloud albedo on DMS emission; its sign would have to be positive in order to regulate the climate. (From Charlson et al., 1987.)

Several areas of interest were identified, most of which require additional research:

(i) modification of sea-surface reflectivity and absorbance, both for the visible and microwave spectral region, by surface films. This is particularly important for reliable remote-sensing techniques.

(ii) the influence of sea-surface films on the properties of breaking waves and the air-bubble size distribution and life-times. There is indication that sea-surface films influence the energetics of the boundary layer in both polar (electrical) and non-polar (chemical) components. It has been noted in particular that the time of relaxation (reformation) of the surface film is short (10 ms to 1 s) in comparison with the average life-time of an air bubble (100 s). Consequently, phenomena of transport of matter across the interface always involve film-covered surfaces.

(iii) it has been noted that there is no evidence available that natural surface films influence the rate of exchange of CO₂, or other non-reactive gases in most oceanic areas. However, in highly biologically-productive regions (whether coastal or open areas) or in areas under considerable pollution stress (petroleum spills, urban sewage disposal), the rate of exchange could be influenced. No reliable data exist. Field measurements are needed and research on this topic is recommended.

(iv) owing to the phenomenon of electrification of surface films in breaking waves and bubble formation, speciation and enrichment of ions, molecules and heavy metal complexes can be expected. There is indication, although no proof is available, that the electrification of surface films due to mechanical (winds, waves) perturbation, may cause salt enrichment in aerosols, including changes in Cl/I ratio, and possibly in the Na/K ratio. In addition, the sea-salt mass inversion phenomenon, discussed in previous reports (e.g., GESAMP, 1985a), may be traced back to stability phenomena in aerosols electrified during bubble ejection through surface films.

(v) the surface films of lipid and petroleum origin, combined with bubble formation, produce flotation phenomena increasing the residence time, and consequently the concentration of particulate contaminants at the sea surface. This phenomenon could be of particular importance for sea-to-land transport of such contaminants as chlorinated hydrocarbons, bacteria and possibly also viruses.

(vi) since the water close to the sea surface can contain elevated concentrations of various organic compounds, it is potentially a site for chemical reaction between substances crossing the interface and the microlayer material. For example, an atmospheric gas which can react with sea surface organic material may cross the interfacial region, and hence be taken up by the oceans, more rapidly than one for which no such reaction can occur. In the opposite sense, photochemical or biological reactions involving microlayer organics may produce gases which can then transfer into the atmosphere.

The Working Group also noted that most models and rate of exchange data for trace gases are based on the observed distribution of mixing ratios, C/C_{at} or P/P_{at} , where C and C_{at} are concentrations in the sea and atmosphere, and P and P_{at} are partial pressures of a substance in the seawater and atmosphere, respectively. Most models use simple first-order kinetic equations in which the net flux is a product of a transfer velocity factor, w , and the pressure or concentration difference as the driving force.

The resulting flux data are the best net values available, but they are subject to considerable calculation errors. It has been emphasized that the understanding of mechanisms influencing the transfer velocity factor is inadequate, and barely beyond phenomenological, particularly in the seasonal and regional variation, or temperature dependence, of this factor.

The Working Group recommended that research in all these fields would significantly improve the understanding of the capacity of the marine ecosystem to accommodate or assimilate such contaminants as CO_2 .

5. REMOTE SENSING OF MARINE POLLUTANTS/CONTAMINANTS

An early study of the effect of processes modified by organic surface films (petroleum or natural slicks) on remotely sensed signals was reported by this Working Group previously (GESAMP, 1980). Considerable scientific literature was cited which indicated that organic films on the sea attenuated capillary and short gravity waves, inhibited convective overturn of the surface water, modified bubble foam stability as well as the bubble bursting process, and reduced sea-surface roughness. These modified air/sea interfacial processes in turn reduced the backscattered power of microwave radar, modified light reflectance, caused cool or warm signatures in thermal IR imagery and altered the brightness temperature indicated by microwave radiometers. Details of the mechanisms by which the film-induced surface modification affected the remotely-sensed signals were described.

5.1 Petroleum Slicks

With these effects in mind, consideration was given to the possible use of space-based satellite imagery to detect petroleum slicks on the sea and to estimate the extent of sea-surface coverage by such oily layers. Both existing and proposed sensor systems were considered, as well as the size of the sensor resolution cell relative to that of oil slicks at sea. It was noted that oil slicks have been observed from space by thermal imagers, optical photography, and imaging synthetic aperture microwave radar. It was noted also that such systems might be used to determine the frequency and distribution of pollutant slicks on a global/regional basis, if there were sufficient data down-link capability and, most importantly, if sufficient sensor time could be dedicated to such a survey.

An additional impediment to the accurate remote monitoring of petroleum slicks is that there are a number of false image possibilities which could not be readily distinguished from petroleum. For microwave radar and photography, false images may arise from natural slicks, wind and current attenuation of capillary wave scatterers, dense cloud shadows and unrippled water under calm conditions. Thermal infrared imagery in some cases may be confused by natural slicks, ship wakes and effluents, upwelling or thermal variability of the sea surface. For these reasons, it was concluded that adequate space-based sensing of oil on the sea on a global basis would be difficult, unless supported by extensive sea-truth investigations. However, because of the importance of monitoring the distribution and extent of petroleum films on the sea, continuing consideration should be given to methodologies to accurately monitor this sea-surface pollutant through the use of space-based remote sensing systems.

5.2 Biomass

Recognizing that man-mobilized substances in the atmosphere may cause climate change with corresponding change in ocean temperature, the possibility of changes in primary productivity exists. It would be useful to monitor primary biological activity on a global basis to determine possible responses to natural and man-induced changes in the ocean. Recent in situ research, coupled with coastal zone colour-scanner imagery, has demonstrated that the phytoplankton effect on ocean colour can be detected from space. It is anticipated that further research will be required to improve the algorithms used to infer plankton biomass from remotely-sensed colour imagery. Use of a space-based sensor is important to the determination of global trends in biomass distribution, since shipboard sampling is slow, and since it is difficult to acquire sufficient samples for the determination of seasonal and spatial variability.

According to the First Implementation Plan for the World Climate Research Programme (WMO/ICSU, 1985), "The implementation of an ocean colour imager mission, together with support to research on the interpretation of ocean colour data, would provide important supporting information to the WCRP and essential data for understanding changes in the biosphere and global carbon cycle. The coincidence of the operation of an ocean colour imaging instrument with the field observation period of TOGA and WOCE would be desirable to take advantage of the enhanced availability of physical environmental data for interpretation of the biological phenomena under observation". The Working Group concurred with this statement.

6. SCIENTIFIC RECOMMENDATIONS

(1) There is a need for more modelling studies with coupled ocean-atmosphere models on a sufficiently fine resolution to give realistic simulations of the atmosphere and ocean circulations, and with gradual increases in CO₂ to allow proper assessment of transient effects.

(2) Assessment is needed of the impact on ocean mixing and marine processes of a more stable thermocline caused by more rapid warming of the surface than deeper layers.

(3) There is a need for research on the impact of increasing atmospheric CO₂ on the marine biosphere, as well as on the net effects of increased marine productivity arising from increased nutrient input on atmospheric CO₂ loading.

(4) Research is required to narrow the present uncertainty over the dependence of the transfer velocity for CO₂ (and other gases) on easily measurable meteorological parameters such as wind speed.

(5) Measurements of the partial pressure of CO₂ (pCO₂) in the surface ocean at a number of key locations for several years would be valuable in clarifying the role of pCO₂ in driving the air-sea flux of CO₂.

(6) Research is needed to evaluate the effect of increasing cloud-drop concentrations on global mean cloud albedo, and hence on climate, to test the hypothesis of Twomey et al. (1984).

(7) As well as the above work on CO₂, further studies are needed on other radiatively important gases, e.g., chlorofluorocarbons, nitrous oxide, methane and ozone, to determine their impact on climate from the point of view of the greenhouse effect.

(8) Research is needed on the modification of sea-surface reflectivity, emissivity and absorbance, both for the visible and microwave spectral region, by surface films.

(9) There is a need for further research on the influence of surface films on the properties of breaking waves, the size and number distributions of entrained air bubbles, and the lifetimes of bubbles and foams at the sea surface.

(10) Field measurements and research are needed in biologically highly-productive areas and in areas subjected to petroleum hydrocarbon spills and municipal sewage disposal to determine the influence of surface films on the rate of air-sea exchange of CO₂ and other gases.

(11) The capability for monitoring sea-surface oil slicks with space-based, remote-sensing systems should be enhanced through the development of high-resolution sensors.

In the period since this report was prepared the global ocean research programmes within the World Climate Research Programme, such as the World Ocean Circulation Experiment (WOCE), have been developed for implementation in the 1990s, as well as global ocean flux studies. These will go a long way towards covering the above identified research needs and provide the further scientific basis needed to evaluate further the questions and issues raised in this report. These global programmes of research on ocean-atmosphere interaction are detailed in Annex 2 of the present report.

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RELEVANT INTERNATIONAL PROGRAMMES

1. WORLD CLIMATE RESEARCH PROGRAMME

Objectives and Structure of the Programme

The WCRP activities are organized according to six sub-programmes which address, in different ways, the scientific objectives of the Programme. These objectives are:

- (i) establishing the physical basis of long-range weather prediction;
- (ii) understanding the predictable aspects of global climate variations over periods of several months to several years;
- (iii) assessing the response of climate to natural or man-made influences over periods of several decades.

It is understood that the first and second objectives are necessary stepping stones toward achieving the third, to acquire the scientific knowledge of the basic atmospheric, oceanic and ice processes which determine the mean state of climate and its response to a changing global environment. The six sub-programmes are the following:

The Atmospheric Climate Prediction Research Sub-programme aims to improve the atmospheric general circulation models which are already being used for numerical weather forecasting and, especially the formulation of heat sources and sinks in the atmosphere and at the earth's surface, which are important for long-range weather prediction and climate simulation. With respect of objective (i) above, the expected outcome is an improved capability to predict weather developments on time scales up to several weeks. To meet objectives (ii) and (iii), it will be necessary to develop atmospheric models which can be coupled effectively with interactive ocean models.

The Coupled Atmosphere-Ocean Boundary Layer Research (still in the conceptual definition phase) is designed to achieve, by a combination of large-scale analysis of the atmospheric flow, observation of basic atmospheric and oceanic variables, regional process studies and boundary layer modelling, a reliable determination of the air-sea fluxes of momentum, energy and water.

The Tropical Ocean and Global Atmosphere (TOGA) project aims to explore the predictability of the coupled system constituted by the tropical oceans and the overlying atmosphere, and the impact on the global atmospheric climate on time scales of months to years. TOGA calls for a ten-year programme of atmospheric and oceanic observations (1985-1995) and will undertake, for the first time, to determine the time-dependent heat storage and circulation of the tropical oceans using a combination of repeated oceanic measurements at relatively short time intervals of one to two months, real-time analysis of atmospheric fields and modelling of the tropical ocean response to atmospheric forcing. In addition, TOGA will provide real-time assessments of incipient climatic events such as El Niño phenomena in the Pacific region.

The World Ocean Circulation Experiment (WOCE) is a major oceanographic programme, exploiting new technological advances in space observing systems, geochemical analysis, hydrographic measurements and automatic data processing, to address the problem of describing and modelling the global ocean circulation and heat transport. WOCE aims to provide a spatially homogeneous global description of the world ocean, based on composite observations, for the purpose of testing global ocean circulation models and includes also a Southern Ocean Experiment to determine the linkages between the three major ocean basins and the Antarctic circumpolar current, and a Gyre Dynamics Experiment to elucidate the effects of oceanic eddies.

The Cryosphere Research Sub-programme is focused at present on the study of seasonal and interannual variations of sea ice and on the determination of the oceanic and atmospheric forcings which control them, with a view to incorporate the recent scientific advances in the knowledge of sea ice processes into fully interactive atmosphere-ocean-ice models, as required for the assessment of long-term climate variations and impacts.

Finally, the Climatic Sensitivity Assessment Sub-programme is meant to gain a quantitative knowledge of the various environmental and astronomical factors which may influence climate as well as investigate the specific physical mechanisms through which the effects of these factors may be felt.

2. PROGRAMMES ON OCEANIC CARBON DIOXIDE

In addition to the basic sub-programmes above, the SCOR/IOC Committee on Climatic Changes and Ocean (CCCCO) is considering a programme of study on the physical and biological phenomena which determine the fluxes of CO₂ between the global ocean and global atmosphere. The specific objectives of this programme would be to determine the temporal and spatial distributions of net CO₂ fluxes across the air-sea interface and what is the ocean-borne fraction of the secular changes in CO₂. Both of these would be evaluated as to how they change owing to secular changes in atmospheric CO₂ with changing climatic conditions. CCCC will investigate the biological processes and changes that affect these, determine what measurements can be accommodated within the TOGA and WOCE observational programmes, determine the measurements required, such as Ocean Colour Imagery, and finally determine modelling needed to: a) guide the observational programme; and b) describe the interaction between physical and biological systems.

The overall problem of the oceanic carbon cycle and its role in climate change is the subject of the Joint Global Ocean Flux Study (JGOFS) whose main goal is "to determine and understand on a global scale the processes controlling the time-varying fluxes of carbon and associated biogenic elements in the ocean, and to evaluate the related exchanges with the atmosphere, sea floor and continental boundaries". The scientific programme for JGOFS consists of four basic elements: global studies, process studies, coastal ocean studies and modelling. It is giving special importance to studies of carbon dioxide and the need for global satellite observations, especially of ocean colour. Regarding CO₂, as noted above, JGOFS will co-operate with WOCE in measuring oceanic CO₂ as well as with ICSU's International Geosphere-Biosphere Programme (IGBP). The support of such oceanic CO₂ measurements will be within the context of an overall JGOFS programme.

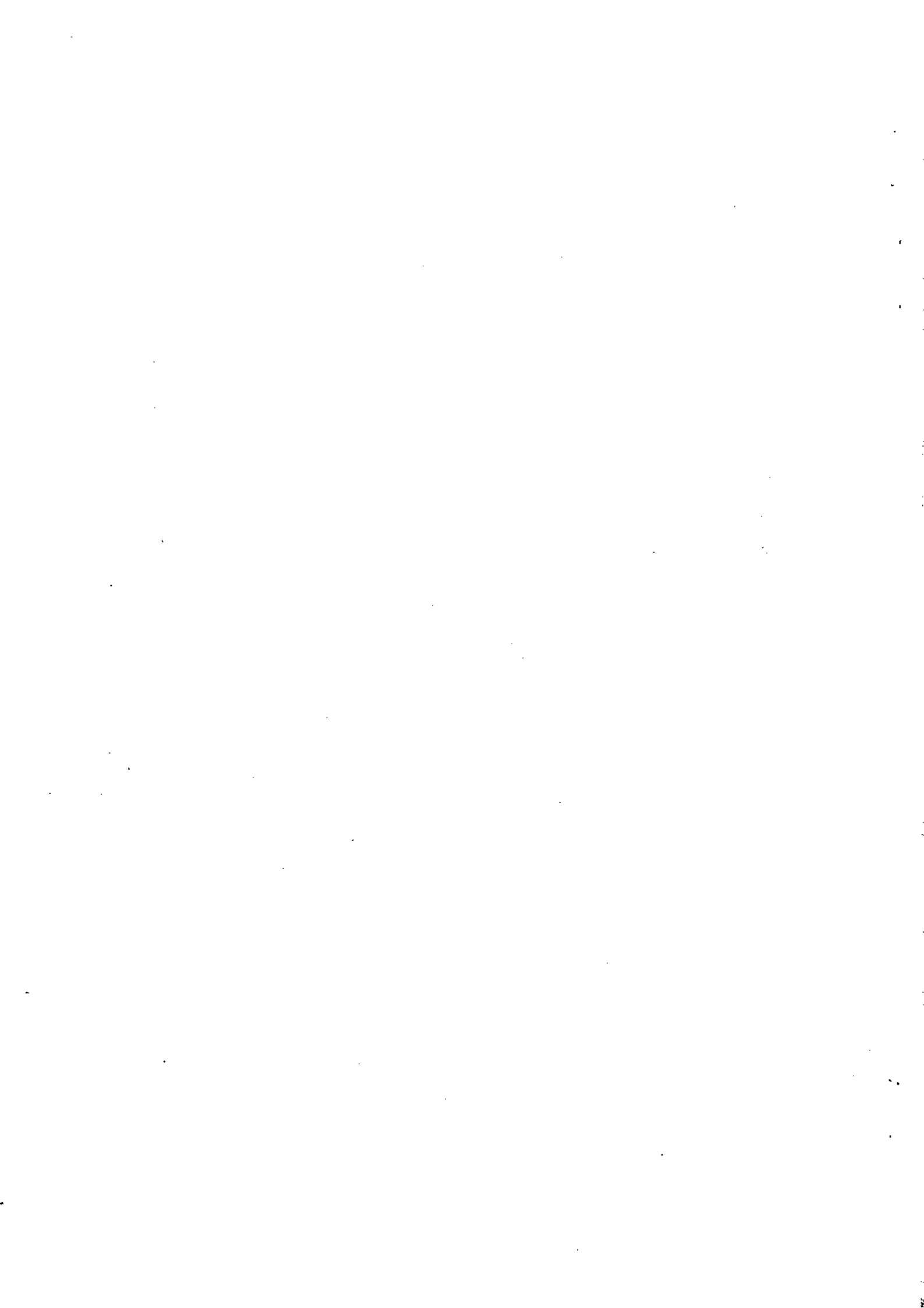
STATEMENT ON PROCESS MODIFICATION
BY POLLUTANTS

The GESAMP Working Group (No. 14) on the Interchange of Pollutants between the Atmosphere and the Oceans will consider those pollutants and man-mobilized substances which may modify ocean-related processes, including weather and climate. It has been documented (GESAMP Reports and Studies 13 and 23) that physical processes are altered by pollutants in the marine atmosphere, at the atmosphere-ocean boundary, and within the sea itself. Certain of these process modifications might influence weather and climate either regionally or on a global scale.

Examples of pollutant effects on important processes in the marine environment follow:

1. Increased nutrient inputs and ocean heating due to CO₂-induced climatic changes may alter type, number and distribution of organisms in the marine biosphere.
2. In the marine atmosphere anthropogenic carbonaceous material, i.e., soot and dust, in sufficiently large quantities could alter the direct solar input to the seas, and consequently alter the thermal characteristics of the sea and the troposphere. The introduction of cloud-condensation nuclei, mainly sulphur compounds, into the marine atmosphere modifies the physics of clouds by increasing the number of drops per unit volume. Through this process the clouds become more reflective and hence change the earth's albedo.
3. At the air-sea interface, pollutant organic films from petroleum and/or detergents are known to modify a number of interfacial properties and exchange processes. However, the Working Group has determined that, at the present time, petroleum films probably do not modify the interfacial exchange of matter or energy on a global scale, but that in certain coastal areas and seas, especially those affected by oil production and transportation, oil films could influence interfacial exchange processes on a smaller scale. Altered air-sea interfacial processes may influence the ocean-atmosphere exchange of CO₂ and Freons, and of natural substances as sources of atmospheric acidity, but further research is required to establish whether this influence really exists, and if so, to what extent.
4. Turbidity increases at sea from man-mobilized solids, e.g. from farming and construction in riverine inputs, will influence light penetration and possibly alter ocean thermal structure in the photic zone. Such effects would be of greatest concern in marine areas in the vicinity of river discharges and near disposal sites for municipal wastes.

It should be noted that processes modified by one pollutant may influence in important ways the sources, sinks and pathways of others. While regional influences of pollutants on significant processes are the more likely, the possibility of global effects caused by certain pollutants exists. In any study, it is essential to differentiate between natural and man-made sources of the process-altering substances and to demonstrate unambiguously the magnitude of the pollutant-induced changes from the temporal fluctuations of the normal background.



GESAMP REPORTS AND STUDIES PUBLICATIONS

These Reports may be obtained from any of the
Sponsoring Agencies in the Language(s) indicated:
English, French, Russian, Spanish

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 (Published also as UNEP Regional Seas Reports and Studies No. 42)	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,S
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 (Published also as UNEP Regional Seas Reports and Studies No. 16)	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,R,S
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,F,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

Rep. & Stud. No.	Title	Date	Language
25.	Report of the Fifteenth Session	1985	E,F,R,S
26.	Atmospheric Transport of Contaminants into the Mediterranean Region	1985	E
27.	Report of the Sixteenth Session	1986	E,F,R,S
28.	Review of Potentially Harmful Substances. Arsenic, Mercury and Selenium (Published also as UNEP Regional Seas Reports and Studies No. 92)	1986	E
29.	Review of Potentially Harmful Substances. Organosilicon Compounds (Silanes and Siloxanes) (Printed in limited number by IMO and published also as UNEP Regional Seas Reports and Studies No. 78)	1986	E
30.	Environmental Capacity. An approach to Marine Pollution Prevention (Published also as UNEP Regional Seas Reports and Studies No. 80)	1986	E
31.	Report of the Seventeenth Session	1987	E,F,R,S
32.	Land-sea Boundary Flux of Contaminants: Contributions from Rivers	1987	E
33.	Report of the Eighteenth Session	1988	E,F,R,S
34.	Review of Potentially Harmful Substances. Nutrients (in press)		
35.	The Evaluation of the Hazards of Harmful Substances Carried by Ships: Revision of GESAMP Reports and Studies No. 17	1989	E
36.	Pollutant Modification of Atmospheric and Oceanic Processes and Climate: Some Aspects of the Problem (Printed in limited number by WMO and will also be published in UNEP Regional Seas Reports and Studies)	1989	E
37.	Report of the Nineteenth Session	1989	E
38.	Atmospheric Input of Trace Species to the World Ocean	1989	E

