



# REGIONAL SEAS

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**GESAMP:**

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

***UNEP Regional Seas Reports and Studies No. 117***

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## PREFACE

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

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

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

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

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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 CO<sub>2</sub> 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 CO<sub>2</sub>.

The global cycle of carbon dioxide indicates that the terrestrial biosphere and the oceans each cycle about 10<sup>2</sup> Gt (1 gigaton = 10<sup>15</sup> 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 10<sup>4</sup>-10<sup>5</sup> 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 CO<sub>2</sub> from the fixed carbon in the land biosphere. For the period around 1980, the release of CO<sub>2</sub> from fossil fuel combustion is about 5 GtC yr<sup>-1</sup> and estimates of the release from biomass destruction, e.g., deforestation, ranges from 0 to 2 GtC yr<sup>-1</sup>, depending on the technique of estimation. The major sink for man-mobilized CO<sub>2</sub> is the ocean which is estimated to accept about 2-3 GtC annually. The atmosphere retains about 2.5 GtC yr<sup>-1</sup>; it is this residual CO<sub>2</sub> that contributes to the annual increase in atmospheric CO<sub>2</sub> concentration. The discrepancy between sources and sinks of man-made CO<sub>2</sub> is in the range of 0.5 to 1.5 GtC yr<sup>-1</sup>, depending on the net biospheric input. Arguments are presented to show that the current input of CO<sub>2</sub> from the biosphere is no more than 1 GtC yr<sup>-1</sup>, but uncertainty regarding the biomass contribution of CO<sub>2</sub> continues.

Some of the factors affecting the oceanic uptake of CO<sub>2</sub> from the atmosphere are presented. The gas transfer velocity is controlled mainly by the wind speed. The other variable that controls the CO<sub>2</sub> exchange flux is the partial pressure difference between the air and the sea. It is noted that there is a latitudinal variation in CO<sub>2</sub> flux, based on the observed CO<sub>2</sub> partial pressure distribution in the surface ocean. A net CO<sub>2</sub> flux of the order of 2 GtC yr<sup>-1</sup> 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<sup>-1</sup> 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 CO<sub>2</sub> by the oceans. Diagnostic models have been developed in which the ocean is subdivided into a few well-mixed reservoirs connected by

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 CO<sub>2</sub> 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.

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/ICSD, 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

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\* "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."

TABLE I. MODIFICATION OF PROCESSES BY CONTAMINANTS

PROCESS	TROPOSPHERE	AIR-SEA INTERFACE	SEA
PHYSICAL	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.	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 (CO <sub>2</sub> and acid rain precursors) that are sources of acidity in coastal areas and seas, especially those affected by oil production and transportation.	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.
CHEMICAL	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.	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.	Increased input of substances from man-made sources can change the minor element composition of seawater. Metal concentrations can be increased. Input of CO <sub>2</sub> can change the pH of seawater with certain consequences to chemical equilibria of ionic composition.
BIOLOGICAL	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.	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.	Dissolved constituents from municipal and industrial wastes, as well as from runoff, could be toxic to marine organisms or be bio-accumulated 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.



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  $\text{CO}_2$  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  $\text{CO}_2$ . The sizes of these anthropogenic mobilizations are currently  $5 \text{ GtC yr}^{-1}$  from fossil fuel burning and anywhere from 0 to  $2 \text{ GtC yr}^{-1}$  from deforestation and changes in land use (see Section 4.1.6). The  $\text{CO}_2$  enters the atmosphere and about  $2.5 \text{ GtC yr}^{-1}$  appears to remain there and leads to the well documented increase observed in atmospheric  $\text{CO}_2$  partial pressure.

The major sink for man-mobilized  $\text{CO}_2$  is the ocean which, according to current estimates, could have taken up 2-3 GtC of  $\text{CO}_2$  per year during the last 25 years.

#### 4.1.3 Ocean carbonate chemistry

In pure water  $\text{CO}_2$  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  $\text{HCO}_3^-$ , than does an equal volume of air at normal  $\text{CO}_2$  partial pressure in equilibrium with it.

This fact makes the ocean the most important reservoir taking up  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  released by fossil fuel combustion.

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

The partial pressure of CO<sub>2</sub> 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 CO<sub>2</sub> into the atmosphere has created a perturbation flux into the oceans on the order of 2-3 GtC yr<sup>-1</sup> (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  $\alpha_w$  derived from the pre-bomb <sup>14</sup>C distribution, a net CO<sub>2</sub> flux on the order of 2 GtC yr<sup>-1</sup> emanates from the sea in the equatorial region between 16°S and 16°N. Correspondingly, a net flux of about 4 GtC yr<sup>-1</sup> 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 CO<sub>2</sub> concentration and its isotopic <sup>13</sup>C/<sup>12</sup>C ratio (Keeling et al., 1985).

The evolution of the  $\Delta p\text{CO}_2$  distribution with time as a consequence of increasing atmospheric CO<sub>2</sub> levels has not been observed accurately enough to estimate directly any changes in the air-sea fluxes of CO<sub>2</sub>.

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 CO<sub>2</sub> 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 <sup>14</sup>C) and transient tracers (e.g., the bomb-produced <sup>14</sup>C and <sup>3</sup>H, <sup>85</sup>K, halocarbons) to the observations (Keeling, 1973b; Oeschger et al., 1978; Siegenthaler, 1983; Broecker and Peng, 1982).

Elliot et al. (1985) analyzed indepth the CO<sub>2</sub> concentrations measured at the Mauna Loa Observatory. They came to the conclusion that the CO<sub>2</sub> record at Mauna Loa is not consistent with net annual additions or subtractions of CO<sub>2</sub> 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<sup>-1</sup> is allowed by the analysis.

There is some evidence that increased plant production could have lead to a net uptake of CO<sub>2</sub> 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 CO<sub>2</sub> 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<sup>-1</sup>, 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 CO<sub>2</sub> fertilization effect could amount of 0.7-2.1 GtC year<sup>-1</sup>.

If the CO<sub>2</sub> 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<sup>-1</sup>, thus almost balancing the global carbon budget. Otherwise, an imbalance of 1 to 2 GtC year<sup>-1</sup> 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 CO<sub>2</sub> concentrations in the atmosphere or what contribution it has made to atmospheric CO<sub>2</sub>. Generally, it has been assumed that on an annual basis, the uptake of CO<sub>2</sub> by photosynthesis by marine plant life has been balanced by release of CO<sub>2</sub> 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 CO<sub>2</sub> is removed from the surface layer of the sea, and ultimately from the atmosphere. The marine biosphere would become an enhanced sink for CO<sub>2</sub>.

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<sup>-1</sup>. 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

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 CO<sub>2</sub>. However, it should be remembered that the thermal lag obtained in such an experiment will be larger than that with a gradual CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>, 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 CO<sub>2</sub> 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 CO<sub>2</sub>, 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.

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	Added greenhouse effect		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  $\text{CO}$  are many and varied. It was estimated that, in total, about 2,400 Tg of  $\text{CO}$  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  $0.4 \text{ Tg year}^{-1}$  for each.

The increasing levels of the trace gases are likely to be caused by increasing emissions. For methane and  $\text{CO}$ , some of the increase may also stem from the fact that their cycles are related to that of OH radicals. As  $\text{CO}$  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  $\text{CO}$  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.

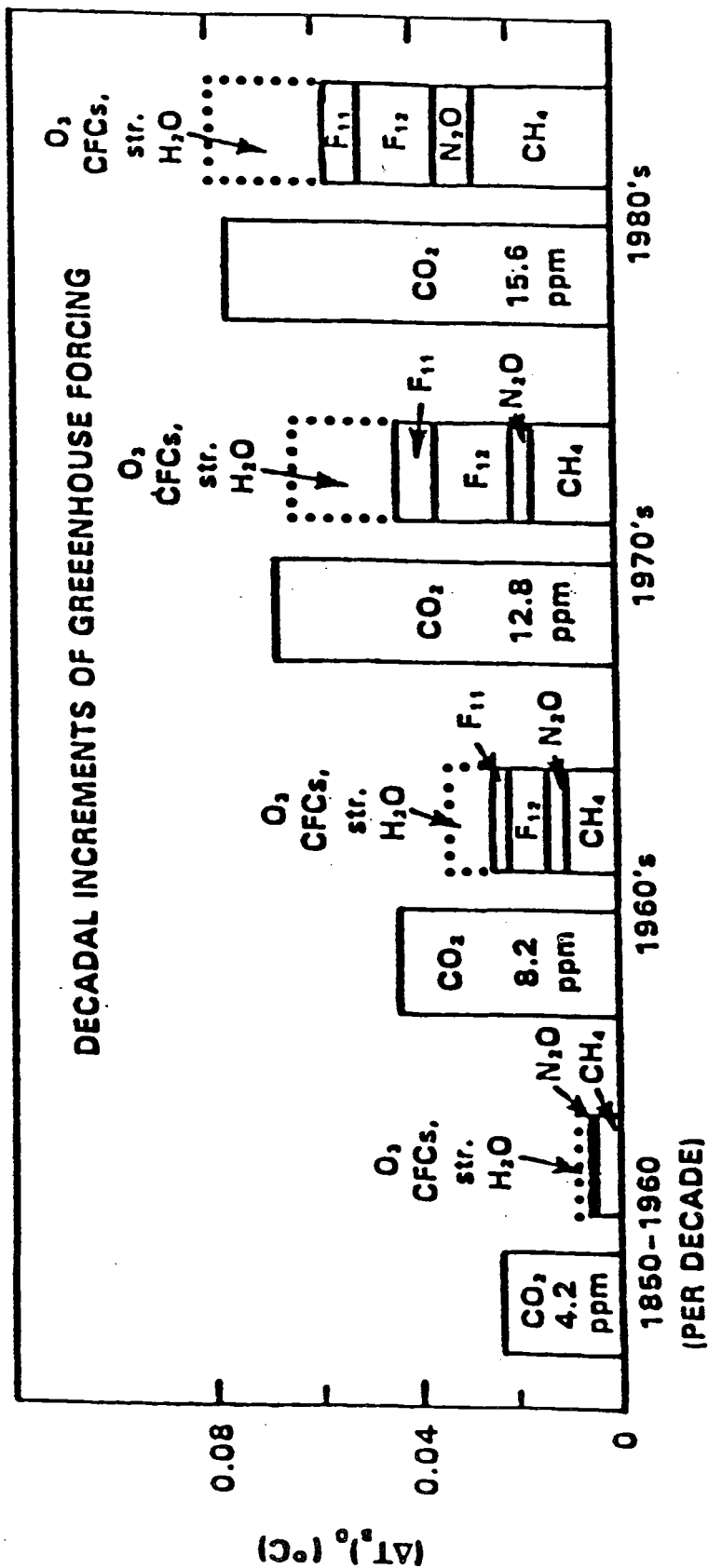


Figure 2. Decadal additions to global mean greenhouse forcing of the climate system.  $(\Delta T_s)_0$  is the computed temperature change at equilibrium ( $t \rightarrow \infty$ ) for the estimated decadal increases in trace gas abundances, with no climate feedbacks included. (MNO, 1985).

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.

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 CO<sub>2</sub>, 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.



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 CO<sub>2</sub> 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.

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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.

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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 CO<sub>2</sub>-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 CO<sub>2</sub> 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.

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