NILU: OR 39/2001

NILU: OR 39/2001
REFERANCE: O-100137
DATE: JUNE 2001
ISBN: 82-425-1284-1

Literature Review:
Trace Gases in the Coastal Zone

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Preface

The coastal zone is a unique environment in that it is the only place on the globe were terrestrial, oceanic, atmospheric, and human inputs of energy and matter all converge. It also supports the greatest concentration of living resources and people on the planet. The coastal zone is defined in the IGBP Land Ocean Interactions in the Coastal Zone (LOICZ) as the area from 200 m above to 200 m below sea level. This area includes estuaries and the continental shelf and slope. The coastal ocean, a part of the coastal zone from 1 to 200 m below the sea level represents about 7% of the ocean surface and less than 0.5% of its volume. Deep ocean waters, nutrient rich and with high concentration of trace elements, are transferred across the shelf edge and help to sustain the high productivity of biota in the coastal zone and shelf seas. It has been estimated that the coastal ocean accounts for about 14% of the global ocean primary productivity, 80% of the global organic matter burial, 90% of the mineralization in marine sediments, 80% of the global sink of suspended river load and associated elements and pollutants, more than 50% of the present day global carbonate deposition. Thus, the efficiency and the impacts of air sea exchange processes for trace gases in the coastal zone can be different form those in the open ocean. Very recent studies in Europe, where 200 million of 580 million Europeans live within 50 km of the coast, concluded that estuaries in Europe contribute with significant emissions of CH_4, N_2O, selenium and other gases.

The significance and the cycles and fluxes of trace gases in the coastal zone have been studied to lesser extent than for the open ocean. LOICZ has approached a literature review of the information available on the air sea exchange of trace gases in the coastal zone. In general, LOICZ is working *inter alia* to develop a global evaluation of the importance of coastal seas and river catchments as sinks and sources of carbon, nitrogen, and phosphorus, in the natural and athropogenically disturbed state and the relative importance of these materials and their biogeochemical cycles in climate and wider changes. Current efforts in LOICZ are making advances in addressing the dissolved and particulate pathways and relative fluxes of C, N and P in the global coastal zone, including the effects of humans in changing metabolic balance of coastal ecosystems and the ramifications of these changes on the relevant biogeochemical cycles.

Contents

Summary

Exchange of trace gases between the oceans and the atmosphere affects the atmospheric content and cycling of a range of chemical species which are related to climate change, ozone layer depletion, acid deposition, eutrophication, atmospheric particle formation, photo-oxidants, trace metals and persistent organic pollutants (POPs). The effects and impacts of air sea exchange of these gases can be local, regional, and global. Until now, most of the research has concentrated on the sea-air exchange of trace gases in the open ocean.

The literature review initiated by LOICZ and presented in this work is aiming at:

1. establishment of the relevance of the coastal zone for atmospheric sources and sinks of trace gases,
2. identification of those systems that contribute the most to these fluxes, and
3. brief description of biological and biochemical processes occurring in the ecosystems which determine the magnitude of these fluxes.

Major emphasis is on sea-air exchange of CH_4, N_2O, DMS, COS, and Hg, while CO_2 is not discussed here.

The flux rates of the studied trace gases from the coastal waters to the air are much higher than the rates for the open ocean and the contribution of the coastal areas t the total oceanic emissions of these trace gases can be significant on a global scale. This contribution can be as high as 50% and more for nitrous oxide and COS. Concerning the contribution of the trace gas production in the coastal areas to the total global production of these gases, it can be concluded that this contribution seems to be below 2% except for nitrous oxide. However, it should be pointed out that on the local and even regional scale the emissions in the coastal areas can be very important contributing substantially to the total emission of these gases in a studied area. Thus, there is a need to carry out studies in the future with the aim to provide more accurate understanding of the production and sea-air exchange processes for these gases around the world.

Literature Review:
Trace Gases in the Coastal Zone

1 Introduction

Exchange of trace gases between the oceans and the atmosphere affects the atmospheric content and cycling of a range of chemical species which are related to climate change, ozone layer depletion, acid deposition, eutrophication, atmospheric particle formation, photo-oxidants, trace metals and persistent organic pollutants (POPs). The effects and impacts of air sea exchange of these gases can be local, regional, and global. Examples of the gases of interest are as follows (Pacyna et al., 1998):

- carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4) - (greenhouse gases, radiation balance of the atmosphere, control of the HO concentrations in the atmosphere, impact on stratospheric ozone),
- sulfur and nitrogen species, particularly dimethyl sulfide (DMS) and its atmospheric oxidation products: sulfate and methanesulfonate, carbonyl sulfide (COS), ammonia (NH3), methylamines (MAs), and odd and even oxides of nitrogen (NO_x/y) - (acid deposition, eutrophication, formation of sub-micron particles with direct and indirect (albedo) effects on the atmosphere radiation budget),
- organo-halogens, e.g. CH_3X and CHX_3 where X can be Cl, Br, or I, carbon monoxide (CO) - (tropospheric oxidants, stratospheric ozone depletion, CO role in controlling the HO concentrations in the atmosphere),
- low molecular weight hydrocarbons, e.g. alkanes and alkenes - (affect redox chemistry)
- selected volatile trace metals, e.g. mercury (Hg), selenium (Se), and antimony (Sb) - (recycling of contaminants to and from the aquatic ecosystem),
- selected POPs - (toxicity to marine and terrestrial organisms).

The oceans are a net atmospheric source for the majority of the above gases on a global scale, except for CO_2 (a literature review by Frost and Upstill-Goddard, 1999). The oceans are a net atmospheric sink for CO_2 on a global scale but the situation is somewhat more complex. The importance and impacts of air sea exchange processes on a local and even regional scale can be different than that on global scale. This particularly applies to the coastal zone.

The coastal zone is a unique environment in that it is the only place on the globe where terrestrial, oceanic, atmospheric, and human inputs of energy and matter all converge. It also supports the greatest concentration of living resources and people on the planet. The coastal zone is defined in the IGBP Land Ocean Interactions in the Coastal Zone (LOICZ) as the area from 200 m above to 200 m below sea level. This area includes estuaries and the continental shelf and slope. The coastal ocean, a part of the coastal zone from 0 to 200 m below the sea level represents about 7 % of the ocean surface and less than 0.5 % of its volume

(LOICZ, 1994). Deep ocean waters, nutrient rich and with high concentration of trace elements, are transferred across the shelf edge and help to sustain the high productivity of biota in the coastal zone and shelf seas. It has been estimated that the coastal ocean accounts for about 14 % of the global ocean primary productivity, 80 % of the global organic matter burial, 90 % of the mineralization in marine sediments, 80 % of the global sink of suspended river load and associated elements and pollutants, more than 50 % of the present day global carbonate deposition (ELOISE, 1995). Thus, the efficiency and the impacts of air sea exchange processes for trace gases in the coastal zone can be different from those in the open ocean. Very recent studies in Europe, where 200 million of 580 million Europeans live within 50 km of the coast, concluded that estuaries in Europe contribute with significant emissions of CH_4, N_2O, selenium and other gases (Barnes et al., 1998; Upstill-Goddard et al., 2000; Frankignoulle, 2000).

The significance and the cycles and fluxes of trace gases in the coastal zone have been studied to the lesser extent than for the open ocean. LOICZ has approached a literature review of the information available on the air sea exchange of trace gases in the coastal zone. In general, LOICZ is working *inter alia* to develop a global evaluation of the importance of coastal seas and river catchments as sinks and sources of carbon, nitrogen, and phosphorus, in the natural and athropogenically disturbed state and the relative importance of these materials and their biogeochemical cycles in climate and wider changes. Current efforts in LOICZ are making advances in addressing the dissolved and particulate pathways and relative fluxes of C, N and P in the global coastal zone, including the effects of humans in changing metabolic balance of coastal ecosystems and the ramifications of these changes on the relevant biogeochemical cycles. To date, LOICZ has not attempted to study the significance of the cycles and fluxes of trace gases mentioned above.

The literature review initiated by LOICZ and presented in this work is aiming at:

- establishment of the relevance of the coastal zone for atmospheric sources and sinks of trace gases,
- identification of those systems that contribute the most to these fluxes, and
- brief description of biological and biochemical processes occurring in the ecosystems which determine the magnitude of these fluxes.

For the purpose of study we limited our discussion to the air-sea exchange for trace gases in the coastal zone to the areas which do not extend beyond the shelf.

Trace gases mentioned above are considered in this work except for CO_2. The latter gas is included in several LOICZ studies on carbon fluxes and will be discussed in another assessment in the context of the carbon flux change in the coast.

Persistent Organic Pollutants (POPs) are also beyond the scope of this report. POPs are semi-volatile and regarded as contaminants deposited from the atmosphere to the aquatic and terrestrial ecosystems as gases, on particles and with precipitation. Evidence is now quite clear that the gas exchange is a major contributor to atmospheric loading in large lakes, estuaries and the oceans

(Bidleman, 2000). Their gaseous transport from the sea to the air is considered as untested and possibly insignificant compared to the air to sea transport (Pacyna et al., 1998).

2 Major processes involved in the air-sea exchange of trace gases

During a last few decades a number of research efforts have been made aiming at the improvements of our understanding of processes governing gas transfer between the air and the sea and at more accurate quantitative assessment of fluxes of gases during this transfer. The above mentioned efforts were made mostly for trace gas transfer in the open ocean with the assessment of global fluxes. A review of our knowledge of environmental controls on gas transfer between the air and the open sea has been prepared by Frost and Upstill-Goddard (1999). They reviewed basic concepts, mechanistic models, and techniques to measure gas exchange in the field. In the most basic conceptual model of air-water gas exchange occurs through molecular diffusion and turbulent mixing. The former process takes over as the dominant transport mechanism with the increasing proximity to the interface between air and water. As a consequence, a stagnant boundary layer is formed on each side of the interface and a gas concentration gradient develops across each of the two stagnant boundaries for moderately reactive trace gases with measurable aquatic sources or sinks. The degree of near-surface turbulence is fundamentally related to the surface wind speed, although under certain circumstances factors such as precipitation intensity (e.g. Ho et al., 1997) and in the case of shallow water bodies, interactions with bottom topography (Roberts, 1984), may become important. However, Frost and Upstill-Goddard (1999) indicate that it is important to draw a distinction between the stagnant boundary layer, which is defined by purely physical constrains, and the sea-surface microlayer, defined from a microbiological perspective as the interface between the uppermost 1000 μm of the sea surface and the lower 50 to 500 μm of the atmosphere (GESAMP, 1995). The microlayer can be regarded as a selective micro-reactor because of its chemical and biological reactivity, which results in an accumulation of reactive trace species with the potential to form a reaction barrier to trace gas transport (GESAMP, 1995).

Frost and Upstill-Goddard (1999), following the work by Liss and Slater (1974) and Liss (1983), have also discussed the results of studies on the air- and water-phase resistances to gas transfer. It was concluded that for the chemically unreactive gases, such as the most of trace gases mentioned above, all of the resistance to gas transfer is in the water phase. Concerning the microlayer, its bacterial cells typically have enrichment factors of up to 10000 relative to the underlying bulk water, possibly as a consequence of hydrophobic interactions leading to bacterial adsorption at the air-seas interface (Powelson and Mills, 1996). This would result in the formation of the above mentioned reaction barrier to trace gas transport. In fact, surfactants and bacteria are likely to have very different effects. Bacterial uptake of atmospheric gases may explain the previously documented mismatch between evasive and invasive flux.

The air - sea exchange of trace gases has also been modeled in a number of approaches employing various types of mechanistic models. These models include:

- film models to estimate transfer velocities operative in the gas phase and in water,
- surface renewal models to estimate the renewal rate, which describes the effects of turbulence upon the interface and is the rate-limiting step to gas exchange, and
- the rubber cloth models, originally designed to model the heat transfer, allowing for a periodic thickening and thinning of the water-side boundary layer, with the generation of short wavelength, high amplitude waves leading to enhanced gas transfer.

Transfer velocity for various trace gases were also estimated on the basis of direct field studies using the gaseous tracers (e.g. Watson et al., 1991; Clark et al. 1995). Frost and Upstill-Goddard (1999) have summarized the results of these studies as well as the estimates of the transfer velocities in wind tunnels and wave-tanks, including the study of the relationship of an idealized gas exchange and wind speed, derived by Liss and Merlivat (1986).

Various field studies and laboratory data were used to study the impact of various physical, chemical, and biological parameters and processes on the trace gas exchange between the air and sea. Frost and Upstill-Goddard (1999) have reviewed some of them focusing on: 1) the wind speed and the non-linear dependence of gas exchange, 2) fetch dependence of the transfer velocities, 3) breaking waves and bubbles involvement in trace gas exchange, 4) the suppression of gas exchange by surfactants, 5) chemical enhancements of gas exchange, and 6) the formation of a cool skin on the ocean surface as a consequence of a net ocean to atmosphere heat flux. The impact of temperature and humidity on air - water gas exchange was also reviewed. The conclusion was drawn by Frost and Upstill-Goddard (1999) that a great number of parameters and processes have an impact on the sea - air exchange of trace gases. Although several studies have been carried out on this subject, large uncertainties still remain in the assessment of gas transfer velocities and fluxes.

3 Importance of the ocean as a source and/or sink for studied trace gases

The ocean may act as source and a sink for various compounds. For the trace gases considered in this review the ocean is mainly their source rather than sink. The discussion on the importance of oceanic fluxes for these gases presented here is based on the outcome of recent research in the field and other reviews, specially those by Rapsomanikis (1994) and Liss et al. (1997a).

3.1 Methane

Oceanic sources and sinks of methane are considered of minor importance (Pacyna et al., 1998). Continental shelf waters and upwelling areas may be supersaturated with methane which is mainly produced in anoxic environments as a final step in the anaerobic degradation of organic matter. It may also be produced in the water column by yet unknown biological or chemical processes, Conrad and Seiler (1988). A very small number of worldwide measurements exist for the flux of methane across the ocean atmosphere interface and for the upwelling areas of the world's oceans, measurements are scarce (Owens et al., 1991). It appears that oceanic emissions of 5 to 20 ktonnes of CH_4/yr may represent only 2% of the global CH_4 budget (IPCC, 1996). This emission range corresponds well with the estimates of 11 to 18 ktonnes of CH_4/yr by Bange et al. (1994). Model calculations indicate that even with increasing tropospheric methane concentrations, the ocean will remain a source of atmospheric methane (Bange et al., 1994). More data from the world's ocean are needed in order to account for spatial and temporal variations of CH_4 emissions and importance of different parameters and processes on these variations. One study during the 1994 SW monsoon in the Arabian Sea/ northwestern Indian Ocean (NWIO) indicates that seasonal changes in wind speed rather than seasonal changes in air - sea partial pressure differences due to monsoon-driven mixing and upwelling are the dominant control on air-sea exchange of methane in the NWIO (Upstill-Goddard et al., 1999).

It shall also be added, that methanhydrates on the ocean floor may burst and give large methane fluxes.

3.2 Nitrous oxide

There is an important contribution from the oceans to the global budget of N_2O. Its annual atmospheric concentration is currently increasing by 0.2-0.3%, indicating an imbalance of 30% in its global budget (see Table 1). If this is due to underestimating emission sources and not due to overestimating the stratospheric sinks of N_2O (reaction with singlet oxygen), then shelf and upwelling areas may be the missing source. Contemporary estimates of the oceanic contribution to the atmospheric N_2O, estimated to be between 20 and 30 % (Khalil and Rasmussen, 1992), is dominated by disproportionately large contributions from biologically productive waters, such as in coastal and upwelling regions. It can be concluded that climatically induced modifications to these regions experiencing strong wind-driven upwelling may have profound effects on future biogas emissions from the oceans.

More recent studies by Bange et al. (1996) and Barnes and Owens (1998) indicated that previous estimates of the N_2O flux from coastal regions, including those in Table 1, are seriously underestimated. Bange et al. (1996) estimated, using two different parameterizations of the air-sea process, an annual global sea-to-air flux of 11 to 17 Mtonnes N_2O, thus about 4 times more than presented in Table 1. This would mean that about 50 % of the total flux of N_2O to the atmosphere would arrive from the oceans. Bange et al. (1996) also concluded that 60 % of this flux would originate in the coastal areas (estuaries and coastal upwelling included), mainly due to high emissions from estuaries.

Nitrous oxide production in oceanic waters has been associated with oxygen minimum and nitrification processes but also with oxygen denitrification processes. There is a need to improve the spatial and temporal data on N_2O fluxes. The imbalance in the global N_2O budget remains an unanswered question.

Table 1. Estimated sources and sink N_2O (on the basis of data in IPCC, 1996).

	Range of annual change (Mtonnes N as N_2O)
Source	
Oceans	1.4-2.6
Soils (tropical forests)	2.2-3.7
Soils (temperate forests)	0.7-1.5
Combustion	0.1-0.3
Biomass burning	0.02-0.2
Fertiliser	0.01-2.2
Sink	
Removal by soils	?
Photoanalysis in the stratosphere	7-13
Atmospheric increase	4-4.5

3.3 Volatile sulfur compounds (VSC)

The direct emission of $(CH_3)_2S$ (dimethyl sulfide; DMS) by certain phytoplankton species and its emission via the enzymatic cleavage of its precursor compound dimethyl sulfonium propionate (DMSP), result in dissolved DMS within the photic zone. DMS is ubiquitous and the predominant volatile sulfur compound in marine surface waters. The hypothesis that climate and phytoplankton activity are connected, rests on the fact that cloud condensation nuclei (CCN) in marine remote areas are formed by the atmospheric oxidation products of DMS. The cloud droplet size and hence the cloud albedo depends on the number concentration of CCN.

Table 2: Global oceanic DMS concentration and annual fluxes (Andreae, 1990).

Biogeographic region	**Mean concentration (nM)**	**Total flux (Teramole S)**
Oligothropic	2.4	0.2-0.6
Temperate	2.1	0.1-0.3
Upwelling	4.9	0.2-0.7
Coastal/Shelf	2.8	0.1-0.2
	Mean: 3.0	Total 0.6-1.7

The DMS fluxes from the different biogeographical regions of the oceans to the atmosphere are summarized in Table 2 (Andreae, 1990).

The production or consumption of DMS and its emission to the atmosphere in upwelling areas is not well documented. It appears that climatic General Circulation Models (GCM’s) show an atmospheric cooling above upwelling areas. However, a direct function relation between DMS ocean water concentrations and atmospheric temperatures or cloud coverage, remains to be established. An establishment of a large data base of over 15,000 global DMS measurements can help defining this function (Kettle et al, 1999). Some interesting trends have already been apparent from this data base. There is a distinct annual cycle in DMS sea surface concentration at high and mid latitudes in both the northern and southern hemispheres. In the Northern Hemisphere DMS concentration increases during the spring-summer months (e.g. Uher et al., 2000). The authors attributed the high DMS levels in summer to seasonal changes in cycling rates rather than to the phytoplankton biomass. The annual cycle of DMS concentrations in Southern hemisphere is similar but shifted by six months. The global DMS concentration maps were produced providing a boundary condition for the flux of DMS to the atmosphere. These maps can be considered as tools to predict the flux of DMS to the atmosphere and the subsequent production of sulfate aerosols.

The DMS flux calculations have been made at the Biogeochemistry Group of the University of East Anglia (e.g., Turner et al., 1996). Surface sea water concentrations of DMS are sufficient that its emission accounts for ca 50 % of the global biogenic source of sulfur to the atmosphere (Bates et al., 1992; Liss et al., 1997b). It was pointed out that although temperature has some effect, it is essentially the differences in wind which cause the large discrepancies in the DMS fluxes, which overall differ by a factor of about 2. Pronounced differences along the western European margin were found between fluxes in September and July, with DMS concentrations and fluxes being the highest in July (Uher at el., 2000).

The global ocean flux of DMS seems to contribute significantly to the global annual emissions of gaseous sulfur compounds (see Table 3). However, this contribution can be less significant on a local and regional scale. Turner et al. (1996) concluded that the annual DMS flux is a small contribution to the total atmospheric sulfur burden of the North Sea region.

Carbonyl sulfide (COS) is another significant volatile sulfur compound of high atmospheric concentration (~500 pptv). Its oxidation in the stratosphere may be responsible for the stratospheric sulfate layer (Chin and Davis, 1995). COS is present in the surface sea waters and it has been shown that there exists a relationship between photochemical activity and COS diel production cycle. This cycle could be described within the experimental uncertainty using a simple kinetic model, which includes terms for COS photo-production, hydrolysis removal, and air-sea exchange. Model estimates by Uher and Andreae (1997) concluded that COS photo-production and hydrolysis are the main processes controlling the sea surface COS concentration. Air -sea exchange rates were at least one order of magnitude lower than the rates of COS production and hydrolytic decay, making both surface concentrations and COS emissions extremely sensitive to variations in COS productivity and hydrolysis removal.

One of the most important findings in recent years is that of the COS "winter sink" in the mid to high latitude regions (Ulshofer et al., 1995) and the discovery of net ocean uptake in the subtropical gyres (Weiss et al., 1995). The important consequence of these findings is that the marine COS source is most likely dominated by the contribution from coastal and shelf areas.

The geographical distribution of sea surface COS is tied with the global distribution pattern of chromophoric dissolved organic matter (CDOM), as discussed in Uher and Andreae, 1997). The CDOM levels are the highest in coastal waters due to freshwater runoff indicating that the COS fluxes are the highest in the coastal regions. This conclusion supports earlier discussion on the importance of the coastal seas in emission of COS to the atmosphere.

Estimates of the global gaseous sulfur compounds emissions from various sources are listed in Table 3 (IPCC, 1996).

Table 3: Estimates of global, annual, gaseous sulfur compounds emissions (on the basis of information in IPCC, 1996)

	Flux (Mtonnes S)
Anthropogenic (mainly SO_2) from fossil fuel combustion	80
Biomass burning (SO_2)	7
Oceans (DMS)	40
Soils and plants (H_2S, DMS)	10
Volcanoes (H_2S, SO_2)	10
Total	147

3.4 Organo-halogens

Moore and Tokarczyk (1993) reported on the measurement of volatile biogenic halocarbons in the Northwest Atlantic, and the following is extracted from their paper.

The ocean is the main reservoir for the halogens, chlorine, bromine, and iodine where the elements exist in solution chiefly as halide ions. Being relatively unreactive and yet highly soluble, these elements have long residence times in the ocean. A very small proportion of each exists as organic compounds, the more volatile of which are carriers of gaseous halogens into the atmosphere. Although the flux of chlorine and bromine from ocean to atmosphere is dominated by the particulate halides in sea salt, this material is readily rained out, and it is smaller fluxes of gaseous compounds which frequently mix more extensively into the atmosphere. The less reactive compounds such as methyl chloride can penetrate even to the stratosphere (Wofsy et al., 1975). Organic compounds of iodine tend to be the most readily photolyzed (e.g., CH_3I) with a lifetime of circa 5 days (Zafiriou, 1974), and so mix only into the lower troposphere. Bromomethanes, having atmospheric residence times ranging from several weeks for bromoform (Cicerone et al., 1988) to circa 1,5 years for methyl bromide (Prather and Watson, 1990), vary in the extent of their vertical penetration into the atmosphere.

Methyl iodide has been suggested (Lovelock et al., 1973) to be the main carrier of iodine from the ocean to the atmosphere (e.g., Dean, 1963; Duce et al., 1963). Organo-bromine compounds have received attention as sources of bromine atoms to the atmosphere where it is speculated they might account for the destruction of ozone that has been observed in several studies of the Arctic boundary-layer in springtime (Barrie et al., 1988; Oltmans and Komhyr, 1986, Solberg et al. 1996), although a mechanism involving the reaction of particulate sea-salt bromide has also been proposed to account for the same phenomenon (Finlayson-Pitts et al., 1990).

In some cases the atmospheric distributions have pointed to the existence of a marine source of specific compounds for example, dibromomethane (CH_2Br_2), bromoform ($CHBr_3$), dibromochlormethane ($CHBr_2Cl$), and bromodichlormethane ($CHBrCl_2$) (e.g., Class and Ballschmiter, 1988). Though we refer to these compounds as biogenic halocarbons, we are aware that they have some anthropogenic sources such as treatment of water by chlorination (e.g., Rook, 1974; Bellar et al., 1974).

The $CHBr_3$ ubiquitous presence and distribution is characterized by higher concentrations in shelf waters which have been attributed to macroalgal production (Moore and Tokarczyk, 1993), and generally low, more uniform levels in pelagic stations. A suite of naturally produced volatile halomethanes which are potential sources of gaseous halogens to the atmosphere have been measured in the water column of the NW Atlantic Ocean. Bromoform, chlorodibromomethane, dichlorobromomethane, dibromomethane, and methyl iodide all showed higher concentrations in coastal waters than in the pelagic zone. Such a distribution is consistent with known sources of these compounds in macro-algae. Carpenter et al. (2000) and Lewis et al. (2001) indicated that there is a definite evidence of the origin of the above mentioned compounds from macroalgae. Chloroiodomethane alone showed elevated concentrations in surface open ocean waters, and its distribution is interpreted as indicating production by phytoplankton, either directly or through an intermediate such as di-iodomethane. The latter explanation is supported by post-cruise estimates of the di-iodomethane distribution. Whereas most of the compounds measured by Moore and Tokarczyk (1993) have higher concentrations in the upper water column, both dibromochloromethane and bromodichloromethane showed increases with depth which would be consistent with a slow reaction of surface-derived bromoform with chloride.

Recently Carpenter and Liss (2000) have discussed the sources and fluxes of bromoform and the reactive organic bromine gases concluding an increase in the current estimate of global macroalgal bromoform production by an order of magnitude to 135 ktonnes/yr. The total global emission rate would be about 220 ktonnes/yr. The authors conclude further that regions of remote open ocean may well simply be in equilibrium with the atmosphere. Carpenter and Liss (2000) suggested that in regions where the ocean is supersaturated, an aquatic bromoform lifetime of the order of months could explain some proportion of open ocean levels purely by transport of coastal waters enriched in bromoform by macroalgae.

In WMO (1995) the following scientific summary is provided for methyl bromide:

Four potentially major sources for atmospheric methyl bromide (CH_3Br) have been identified: the ocean, which is a natural source, and three others that are almost entirely anthropogenic (agricultural usage, biomass burning, and the exhaust of automobiles using leaded gasoline). The estimated uncertainty range for these sources is large, with oceans ranging from 60 to 160 ktonnes/yr, agriculture from 20 to 60 ktonnes/yr, biomass burning from 10 to 50 ktonnes/yr, and automobile exhaust from 0.5 to 22 ktonnes/yr. There are also two minor anthropogenic sources, structural fumigation (4 ktonnes/ yr) and industrial emissions (2 ktonnes/yr).

Measurements of CH_3Br yield a global average ground-level atmospheric mixing ratio of approximately 11 pptv. The concentration in the Northern Hemisphere is higher by about 30% than the concentration in the Southern Hemisphere.

There is no clear long-term change in the concentration of CH_3Br during the time period of the systematic continued measurements (1978-1992). One possible explanation is that CH_3Br from automobiles may have declined while, at the same time, emissions from agricultural use may have increased, leading to relatively constant anthropogenic emissions over the last decade.

The magnitude of the atmospheric sink of CH_3Br due to gas phase chemistry is well known and leads to a lifetime of 2 ± 0.5 yr. The recently postulated oceanic sink leads to a calculated atmospheric lifetime due to oceanic hydrolysis of 3.7 yr, but there are large uncertainties (1.3 to 14 yr). Thus the overall atmospheric lifetime due to both of these processes is 1.3 yr with a range of 0.8 to 1.7 yr. Recently there has been some controversy about this lifetime. There are suggestions in the 1998 WMO assessment that methyl bromide has a considerably shorter lifetime (WMO, 1999). However, there are still many experts who actually disagree with this shorter lifetime.

Recognizing the quoted uncertainties in the size of the individual sources of CH_3Br, the most likely estimate is that about 40% of the source is anthropogenic. The major uncertainty in this number is the size of the ocean source. Based on the present atmospheric mixing ration and the current source estimate, a lifetime of less than 0.6 yr would require identification of new major sources and sinks.

Novel biogenic iodine-containing trihalomethanes and other short lived halocarbons were recently measured in the coastal East Atlantic (Carpenter et. al, 1999; Carpenter et al., 2000). Halocarbon production rates were measured for 10 species of brown, green, and red macroalgae. It was concluded that macroalgae were found to account for only 12, 64, and 54 % of the CH_3Br, CH_3I, and CH_2ICl concentrations, respectively, in coastal waters. Globally, Manley and Dastoor (1987) have estimated that macroalgal production of CH_3Br and CH_3I comprise only below 0.1 % of the global oceanic sources. The findings for CH_2ICl support previous suggestions of an open ocean source (Moore et al., 1995).

Similar conclusions were derived by Baker et al. (2001). They indicate, that the global productivity of macrophytes for the monohalomethanes, organo-chlorines and organo-iodines amounts to, at most, a fraction of 1 % of the calculated net global flux required to account for observed levels. However, the contribution to atmospheric levels of other halocarbons, notably the polyhalogenated bromo-alkanes, may be much larger, and release of all halocarbons may affect atmospheric levels and chemistry on a localized near-shore scale.

3.5 Non-methane hydrocarbons

Non-methane hydrocarbons are important reactive gases in the atmosphere, which provide a sink for hydroxyl radicals and play key roles in the production and destruction of ozone in the troposphere. Little is known about the production mechanisms of these compounds in sea water, although it has been suggested that alkenes are produced by a photochemical mechanism acting on dissolved organic matter (e.g., Ratte et al., 1993;1995).

A database of dissolved C_2-C_4 hydrocarbons in the surface water of the oceans was compiled by Plass-Dülmer et al (1995) based on more than 1000 measurements. Hydrocarbon emission rates were calculated using a diffusive microlayer approach and climatological wind data. This database was used to calculate averages and ranges of variation, and an attempt has been made to identify the environmental factors which have an impact on the hydrocarbons dissolved in seawater. Mean concentrations were 134 pmol/L for ethene, 59 pmol/L for propene, and 37 pmol/L for 1-butene. Alkane concentrations are lower with an average value of 22 pmol/L for ethane and less than 14 pmol/L for the other alkanes and acetylene. Ninety percent of the concentrations of an individual compound generally ranges within an order of magnitude. Ethene concentrations are significantly anticorrelated with the transfer velocities of the sea-air exchange. Ethene concentrations are not correlated with the solar radiation, chlorophyll, and the water temperature. Averaged emissions of C_2-C_4 hydrocarbons extrapolated to the global ocean of 2100 ktonnes/yr are calculated, with ethene alone contributing about 40% to the total. The oceanic source plays a minor role in global budgets compared to continental sources.

Table 4: Global NMHC emissions from the ocean.

Compound	In situ	σ^a	All data	90% Upper limit^b
Ethene	0.89	0.47	1.40	2.17
Propene	0.52	0.30	0.82	1.27
Sum of butenes	0.40	0.21	0.63	0.97
Σ C_2-C_4 alkenes	1.80		2.85	4.41
Ethane	0.16	0.26	0.32	0.54
Propane	0.10	0.11	0.20	0.35
Sum of butanes	0.06	0.09	0.11	0.19
Σ C_2-C_4 alkanes	0.32		0.63	1.07
Σ C_2-C_4 hydrocarbons	2.13			

Values in 1000 ktonnes/yr: ^{a} Standard deviations of in-situ data. ^{b} Upper limit of 90% of all data

C_2-C_4 alkanes and several alkenes were measured in the Southern Ocean (Lewis et al., 2001). The alkane isomer distributions and abundances were found in broad agreement with literature sea - air exchange rates. It was concluded that in dynamically stable maritime air, midday maximum in ethene, propene, and isoprene concentrations indicate photochemically driven sources near to the sea surface.

Broadgate et al. (1997) have studied the relationship between phytoplankton and isoprene in surface waters. They suggested that chlorophyll data can be used to estimate isoprene concentrations and fluxes from the ocean to the atmosphere. These fluxes are very small but it is possible that the rapid reactions of isoprene with hydroxyl radicals in the atmosphere could influence the production of formaldehyde locally over the ocean (see also Ayers et al., 1997), which in turn may increase the concentration of peroxy radicals.

3.6 Ammonia and methylamines and other nitrogen (N) species

About 40% of the N fixed by human activities is injected into the ocean. In some areas, anthropogenic N deposited from the atmosphere can change the natural N cycle of the upper ocean, particularly near the surface (Michaels et al., 1993, Owens et al., 1992; Paerl, 1985; Paerl and Fogel, 1994). Most anthropogenic reactive N added to the open ocean is quickly incorporated into organic matter and transported and held below the surface thus maintaining the near-surface depletion.

The increases in N mobilization relative to that of C and mobilization and distribution of N relative to P imply that large regions of the world where N has historically been the limiting factor are shifting to regions where N is in excess and some other nutrient (e.g., P) is becoming the limiting factor.

Anthropogenic N fixation is driven by two processes, energy and food production, each of which is controlled by two factors: human population and the standard of living. Both factors will probably increase with time. Future anthropogenic N-fixation rates can be estimated using past trends in energy, fertilizer use, and legume cultivation. For N fixation during fossil-fuel production, Galloway (1989) estimated that N emissions in 2020 will range from 30 to 60 Mtonnes N/yr; in 1980 the value was only about 20 Mtonnes N/yr. More recently, Galloway et al. (1994) estimated that the 2020 value will be on the order of 46 Mtonnes N/yr more than double the 1980 value, with the less-developed regions having the highest increase. This estimate agrees well with the 2025 estimate of Legget et al. (1992) of 43 Mtonnes N/yr.

Future N-fixation rates by fertilizer production are estimated by analyzing historical rates. In 1989, about 78 Mtonnes N/yr is fixed by fertilizer production and about 50 Mtonnes N/yr is consumed in less-developed regions and the rest is consumed in more-developed regions. Asia has the greatest increase in consumption of fertilizer N.

Ammonia and its methylated derivatives, the methylamines, are dynamic constituents of the cycle of reduced nitrogen, widely distributed in the marine environmental intimately involved in marine nitrogen fertility (e.g., King, 1988). They are end products of the microbial turnover of labile organic matter and their concentrations in surface sea waters are likely to be principally mediated by the structure, activity, and seasonality of the microbiological cycle (Gibb et al., 1999a). Their exchange across the air-sea interface is likely to present only a small, yet important loss from the aqueous cycle contributing an important source of base to the remote atmosphere.

The atmosphere seems to play a crucial role in the redistribution of ammonia and methylamines particularly in remote and oligotropic regions (Gibb et al., 1999a;

Gibb et al., 1999b). Through their association with aerosols and rainwater non sea-salt sulfates, ammonia and methylamines are also implicated in the redistribution of sulfur. However, Gibb et al. (1999b) concluded that sea water and atmospheric fluxes, residence times, transformations and fates are poorly characterized for methylamines and ammonia. Therefore, characterization of their distributions and fluxes, as well as influence on atmospheric composition, pH, and cloud albedo should be made with caution.

3.7 Mercury

Mercury represents in this report contaminants. In Europe, air-sea exchange fluxes of mercury were measured within the EUROTRAC Air-Sea Exchange (ASE) program, mostly around the North Sea and the English Channel (e.g. Baeyens and Leermakers, 1996). Recently, the Mediterranean Atmospheric Mercury Cycle System (MAMCS) project was carried out to assess the behavior and fate of mercury in the Mediterranean Sea region (MAMCS, 2000). Measurements of Hg evasion from the surface water to the air were also carried out within MAMCS, indicating an evasion rate of 3 ng/m^2 hr and the total emission in the Mediterranean Sea of 70 tonnes/ yr. This can be compared with about 340 tonnes of Hg emitted to the atmosphere from all anthropogenic sources in Europe in 1995 (Pacyna et al., 2001)

There has been much work conducted in the equatorial Pacific Ocean on possible linkages between elemental mercury production in the ocean and paleoproductivity (e.g., Fitzgerald and Mason, 1996). The equatorial Pacific Ocean plays an important role in the planktonic production of new carbon in the oceans, and influences the modern carbon dioxide cycle. This region is also especially important to the overall biogeochemical cycling of mercury. On the basis of information from the glacial record, Fitzgerald and Mason (1996) suggest that the production an evasion of elemental mercury from the ocean is following the changes of paleoproductivity. They speculate that the glacial record of mercury deposition provides a tracer of the variation in the oceanic production of carbon with time.

A few studies on mercury evasion from sea water were reviewed during the NATO Workshop on Global and Regional Mercury Cycles, organized in Novosibirsk, Russia (Baeyens et al., 1996). It was concluded that there are areas of the ocean where atmospheric deposition exceeds gas evasion and regions where the opposite is true. The flux estimate of mercury evasion is reasonable and has been constrained by normalizing elemental mercury production and evasion to primary productivity. However, it was underlined that the validity of this normalization needs further investigation along with studies designed to assess the role of biological reduction, especially by microorganisms, in elemental mercury formation. How important is low productivity in limiting mercury reduction? Finally, it was concluded that the role of regional circulation patterns in the ocean and atmosphere in controlling mercury evasion needs to be determined (Mason et al., 1996).

Mercury evasion rates from sea surface to the atmosphere have been reviewed by Cossa et al. (1996). It was pointed out that the atmospheric deposition to the entire ocean is globally balanced by the elemental mercury evasion. However, since the atmospheric deposition in the Siberian Arctic exceeds clearly the evasion, whereas the evasion exceeds the deposition in the productive zone at lower latitudes, a net atmospheric transfer of mercury to high latitudes is probably occurring.

4 Why the coastal seas are different than the open ocean with respect to the air - sea exchange of trace gases?

Although the coastal and open oceans form a water continuum and various processes and mechanisms governing the exchange of gases and particulate matter at the sea - air interface are similar in the coast and the open ocean, there are differences in these two ecosystems resulting in differences in the air-sea exchange of trace gases. In general, there are different anthropogenic and natural drivers and pressures, as well as different ecosystem properties in the coastal and open ocean, which result in differences in air - sea exchange for trace gases in these two ecosystems.

4.1 Drivers of ecosystem change in the coastal zone

Major anthropogenic drivers of the environmental change in the coastal ocean, also defined as drivers of the coastal zone function changes, include:

- industrialization and urbanization in the coastal zone,
- deforestation, agriculture and land use changes in the coastal zone,
- aquaculture,
- exploitation of living resources, including coastal fishery,
- exploitation of mineral resources, including the crude oil and natural gas,
- tourism,
- atmospheric and riverine transport of contaminants from land-based sources outside the coastal zone,
- sea-going transport, and
- a lack of coastal zone management.

Also natural drivers, related mostly to the climate change would contribute to the changes of coastal zone functioning and structure.

The above mentioned drivers result in various pressures on the coast leading to the following consequences:

- increased pollution and deterioration of water quality due to enhanced fluxes and concentrations of nutrients, pesticides, other persistent organic pollutants, heavy metals, oil related contaminants, artificial radionuclides, algal toxins, and phytoplankton pigments,
- erosion in the coast,
- habitat loss and modification,
- coastal flooding,
- biodiversity reduction, and
- saltwater intrusion.

The above mentioned issues would results in changes of biophysical, chemical and hydrological properties and characteristics of the coastal ocean and affect the efficiency of various coastal functions, including biogeochemical cycling and ecological interactions at the compartment interfaces, and thus sea-air exchange also for trace gases.

Major anthropogenic drivers of environmental change in the open ocean can be defined as:

- exploitation of living resources, including fishing,
- exploitation of mineral resources,
- sea-going transport and other maritime operations,
- waste disposal,
- coastal water intrusion, and
- long-range transport of chemicals from land-based sources.

Climate change is also defined as the major natural driver of the environmental change in the open ocean. There are various ways in which global change may affect the production and emission of trace gases through:

- enhanced UV-B effects, both direct (photo-production: COS, CO, and photo-degradation: DMS), and indirect (effects on ecosystem structure) (e.g., Zepp et al., 1998),
- changes in wind patterns, storm frequency, precipitation patterns, and surface temperature that may affect the hydrology in the surface ocean (however, indifferent way for coastal and open sea regions,
- changes in precipitation and runoff which may affect CDOM levels in coastal waters but not in the open ocean,
- global nitrogen enrichment that affects the nitrogen cycle especially in the coastal zone, with important implications for global N_2O emissions (Barnes and Owens, 1998).

Global change - surface ocean interactions are currently being discussed by the IGBP community in connection with the establishment of a new SOLAS program.

Consequences of major drivers of the change in the open ocean are similar to the consequences of coastal ocean drivers except that they are less pronounced. Their impact on hydrography may, however, be different for the coastal ocean and the open ocean. The proximity of the coast to the major anthropogenic drivers causes this difference.

In summary, the coastal ocean is more efficiently and more often affected by the anthropogenic drivers of environmental change than the open ocean. As a result, the ecosystem functioning and structure in the coast is changing quicker and to major degree than the ecosystem functioning and structure in the open ocean. Biogeochemical cycling, including the interface processes, such as sea-air exchange is affected by these differences between the coast and the open ocean.

Although the above mentioned summary of the differences between the coastal and open ocean contains somewhat obvious conclusions, it should be underlined that the majority of research in sea-air exchange of various chemicals, including trace gases has been carried out in the open ocean. Only recently more attention in this research has been placed also on the coastal waters.

4.2 Issues specific for air - sea exchange for trace gases in the coastal ocean

A number of issues should be considered when describing the air-sea exchange for trace gases in the coastal ocean as compared to this exchange in the open ocean.

Proximity to the emission sources and regions has already been mentioned. The coastal zone, and particularly estuaries are obligate pathways for the transfer of dissolved and particulate matter from the continent to the marine system. European estuaries are subject to intense anthropogenic disturbance reflected in elevated loading of detrital organic matter which induces high respiration rates for trace gases (e.g., Frankignoulle et al., 1998). On the other side, the along-slope currents at different depths can advect trace gas concentration patterns originating from vertical exchanges occurring in entirely different source areas.

The tidal regime of some estuaries leads to an increased residence time of the fresh water in the estuarine mixing zone, and pronounced changes in the speciation of various chemicals may occur leading to enhanced exchange of trace gases at the air-sea interface.

The shelf break zone is the area where the sea-air exchange processes for many trace gases are the most effective resulting in enhanced production of trace gases. In general, the efficiency of sea-air exchange processes depends on the part of the coastal zone systems which include estuarine embayments (inner estuaries) and river plumes at sea (outer estuaries). The relative importance of these systems, in terms of respective areas, depends on hydrological conditions, such as freshwater flow, the tidal regime, and the topography of the estuary (e.g., Frankignoulle et al., 1998). In macrotidal estuaries, most of the mixing between fresh water and seawater occurs within the inner estuary, resulting in more efficient sea-air exchange of chemicals. These processes in the outer estuary are less efficient.

The factors determining air-water exchange in estuaries quite complicated and change likely along the estuary from primarily stream driven exchange inn the upper estuary to wind driven exchange inn the mouth (Middelburg et al., 2001). Most of the turbulence in tidal estuaries is due to the tidal currents and their interaction with wind and bottom topography and clearly depends on the tidal energy and depth and morphology of the estuary.

Recent studies within the EU research programs (e.g., Wollast et al., 1998) indicate clearly that continental margin has a significant role in the exchange of gases between the air and the sea through the activities of biological organisms, which are more available in the coastal areas then in the open ocean. Correlations have been established between the trace gas distributions and the temperature, pigments, and chlorophyl to provide a picture of the source-sink cycle for these gases. These correlations are quite clear in the coastal zone.

Natural wetlands are the ecosystems often found in the coastal zone. They are thought to be a significant source of some of the studied trace gases, such as methane (Cicerone and Oremland, 1988). Methane produced in the sediment can be transported to the air through three mechanisms: ebullition, molecular diffusion and via the vegetation present (Chanton and Dacey, 1991). Emergent wetland plants typically have large internal gas spaces which allow gas transport between the methane-rich sediment in which they are rooted and the atmosphere (van der Nat et al., 1998). Therefore, in tidal freshwater marshes plants and daily fluctuations in water level may affect methane emission by controlling its production, oxidation, and transport (van der Nat and Middelburg, 2000).

4.3 Methane

Studies carried out within the EU project on biogas transfer in estuaries: BIOGEST (Frankignoulle, 2000) concluded that the methane flux rates in estuaries can be up to 1000 larger than these rates in the open ocean. The European estuaries seem to contribute as much as 580 ktonnes of methane each year, which is about 2.5 % of the total methane emissions in Europe.

On a global scale, Middelburg et al. (2001) estimated on the basis of their studies of median air-water concentrations that a minimum methane emission from estuaries can be about 1100 ktonnes/ yr. These authors also used the global exchange coefficient approach by Bange et al. ((1994) to estimate that the estuaries may emit as much as 1800 to 3000 ktonnes methane per year. Therefore, the contribution of methane emissions from estuaries worldwide is probably at the level of 10 % of the contribution of the open ocean emissions of this trace gas and around 0.2 % of the total global methane emission. Other recent studies (e.g., by Upstill-Goddard et al., 1999; Upstill-Goddard et al., 2000) indicate that substantial methane emissions originate from low salinity regions. Therefore, contribution of methane from the coastal zone to the total emissions of this gas can be significantly higher, perhaps even a few times higher than the above estimate of 0.2 %. This subject needs further investigation.

The distribution of dissolved methane in the well-mixed estuaries reflects the importance of estuarine sinks and sources of methane (Middelburg et al., 2001). Dissolved methane concentrations initially decrease with increasing salinity, before decreasing again off-shore. The initial decrease of dissolved methane with increasing salinity in the European estuaries is related to a high river end-member concentration and subsequent consumption of methane by oxidation and/ or loss to the atmosphere. Middelburg et al. (2001) concluded that methane oxidation is an important sink of methane in estuaries, but it strongly depends on the temperature and salinity with very low oxidation rates at salinities above 6 (also De Angelis and Scranton, 1993).

The sources of methane at intermediate to high salinities likely include intertidal flats and marshes. Plants have had a stimulating effect on methane emissions from tidal marshes. In general, plants serve as direct conduits to the atmosphere. Van der Nat and Middelburg (2000) concluded that flooding reduces methane emission, probably by blocking the primary sites of methane release in the lower part of the plant stems.

4.4 Nitrogen compounds

The elevated nutrient loading enhances nitrous oxide production via denitrification of nitrate in the oxygen-depleted zones and nitrification of ammonia in more aerated waters in the coastal ocean (Wollast, 1983; Soetaert and Herman, 1995). However, nitrous oxide air-sea exchange in the coastal areas has not been studied to the extent as in the open ocean. Therefore it is difficult to quantify the fluxes of this gas escaping the coastal ocea. The results of the EU BIOGEST project conclude that flux rates of nitrous oxide from the European estuaries to the air can be up to 100 larger that these rates from the open ocean (Frankignoulle, 2000). Accoring to this project results, flux of nitrous oxide from the European estuaries is about 120 ktonnes /yr, contributing as much as 9.4 % to the total anthropogenic emissions of this gas in Europe.

The BIOGEST project results also indicate that the nitrous oxide emissions from the European estuaries contribute between 5 to 10 % to the global ocean emissions of this gas. Taking into account the fact that the global ocean contributes between 20 to 30 % to the total emissions of the gas, the contribution of the European estuaries to the global emissions of nitrous oxide is very low according to the BIOGEST project. However, two comments shall be added: 1) it is expected that the estuaries worldwide will substantially increase the contribution to the global emissions of nitrous oxide from the European estuaries, and 2) emissions from estuaries are important on a local scale. Bange et al. have computed the nitrous oxide emissions from the coastal waters using the approaches of Liss and Merlivat (1986) and Erickson (1993). They concluded that the annual global flux of nitrous oxides from the sea to the air is between 11 and 17 Mtonnes and attributed 60 % of this flux to coastal areas. Thus, the coastal ocean flux would contribute as much as 30 %.

High rates of nitrous oxide production were also measured over the western Indian shelf (Naqvi et al., 2000).

More studies have been carried out on the behavior of other nitrogen gases in the coastal zone. Some of these studies, such as the EU NICE project, have studied the nitrogen cycling in estuaries (Dalsgaard, 1998), while others, such as the EU ANICE project have concentrated on the assessment of the nitrogen inputs into the coastal ecosystems (de Leeuw, 1998). Inputs of nitrogen compounds to the coastal seas were also in otyher regions, such is in the Chesapeake Bay in the North America (U.S. EPA, 1994), northern Russian coast (e.g. LOIRA, 2000) and in Asia (Acid Rain 2000, 2000). Inputs of nitrogen compounds to the sea are often regulated by a number of international agreements within various marine conventions on the reduction of these inputs, such as the OSPARCom convention on the protection of the North Sea and the north-eastern Atlantic, the HELCOM convention on the Baltic Sea, and the MEDPOL convention on the protection of the Mediterranean Sea. The results of the above mentioned studies and monitoring programs conclude that the coastal sea is a sink of the nitrogen compounds and not a source of nitrogen gases, except for some areas where ammonia can be released due to high concentrations of ammonium cations in the sea water (Liss et al., 1997).

4.5 Volatile sulfur compounds (VSC)

Anoxic sediments in the region of the turbidity maximum in the coastal ocean enhance not only methane production but also the production of hydrogen sulfide, with subsequent emission to the atmosphere. Eutrophic conditions are also very favorable for the production of gases such as DMS and COS. Sea to air fluxes of these gases show strong seasonality as concluded by Wollast et al. (1998). They have studied the correlations between DMS distributions and temperature, pigments and chlorophyl. The results of these studies clearly indicated that continental margin has a significant role in the exchange of DMS between the air and the sea through the activities of biological organisms in this area. The coupling between the sulfur (and carbon) cycles in *Phaeocystis* dominated blooms was then examined in the EU ESCAPE project (Stefels et al., 1998) to assess the phytoplankton role in this cycling. However, the findings by Uher et al., (2000) indicate that although there is some evidence for a relation between DMS levels and chlorophyl, phytoplankton abundance may often be less important than other factors.

Concerning the DMS fluxes from the coastal seas, Uher et al. (2000) concluded that the DMS fluxes from the temperate open ocean slightly exceed the DMS fluxes from coastal/ shelf areas. The tendency towards higher emissions from temperate open ocean areas was due to the generally higher transfer coefficients in these areas that outweighed the effect of elevated DMS levels in coastal/ shelf regions. On the other hand, it is known that blooms of DMS-producing coccolithophores occur all along the continental shelf edge in May and June (Holligan et al., 1987). It is therefore likely that pulses of elevated DMS production regularly occur all along the shelf break in spring and summer (Baker et al., 2000).

There were a few approaches to estimate the COS flux for the coastal regions. Andreae and Ferek (1992) estimated the all season average flux of COS for coastal and shelf regions to be 438 nmol per m^2 daily. Mihalopoulos et al. (1992) calculated the summer average of the COS flux for subtropical/ temperate coastal seas to be 178 nmol per m^2 daily. This discrepancy is not unusual and can be related to differences in the saturation ratios, which are reported to vary from 2 to 22 in coastal seas (Mihalopoulos et al., 1992). The above mentioned fluxes were calculated assuming the saturation ratio of 9.

The COS fluxes for the coastal ocean can be compared with the COS fluxes for the open ocean (e.g., Weiss et al., 1995). It is very difficult to generalize on this comparison but the coastal ocean fluxes seem to be about one to two orders of magnitude higher than the fluxes from the open ocean (in Uher and Andreae, 1997).

4.6 Other gases

Very limited information is available from the literature on the sea-air exchange processes and fluxes of organo-halogens and non-methane hydrocarbons (NMHCs) in the coastal ocean. The available literature data describe these processes and quantify fluxes in the open ocean. A review of these data is presented earlier in this report. As the sea to air flux of organo-halogens can be related to the macroalgal production, and the flux of non-methane hydrocarbons to the phytoplankton abundance, it can be suggested that the flux rates for these two groups of trace gases are higher in the coastal ocean than the flux rates in the open ocean. Broadgate et al. (1999) have made the first measurements of NMHCs from macroalgae and found that, indeed, many NMHCs are produced by macroalgae. Rockpools containing macroalgae on the West Coast of Ireland show levels of many NMHCs elevated up to a factor of 60 above the open seawater levels at the same site. For many NMHCs , emissions from macroalgae are species dependent, temperature dependent and related to light availability. One of these NMHCs is isoprene. Broadgate et al. (1999) measured for the first time that macroalgae (seaweeds) emit isoprene.

Taking into account the differences in the macroalgal production and phytoplakton abundance in the coastal and open ocean, it can be suggested that the flux rates for organo-halogens and non-methane hydrocarbons in the coastal ocean are less than one order of magnitude higher than the flux rates in the open ocean. If this suggestion is acceptable, the contribution of coastal sea emissions of organo-halogens and non-methane hydrocarbons to the total ocean emissions are small and insignificant for the global emissions of these compounds. However, this does not mean that the fluxes are insignificant on local coastal scale. For example, emissions from rockpools may contribute significant levels of NMVOCs and therefore affect the oxidant balance in the coastal zone. Seasonal measurements of many NMVOCs in the North Sea show that concentrations can range over 2 orders of magnitude over the year (Broadgate et al., 1997).

Mercury flux from the coastal sea to the air can be important source of the atmospheric emissions of this contaminant at a regional (e.g., European) and global scale. The EU BIOGEST project has approached to determine the estuarine flux rate for mercury in Europe (Frankignoulle, 2000), estimating this rate to be up to one order of magnitude higher than the flux rate in the open ocean (MAMCS, 2000), depending on the water and air temperature and proximity to major land-based sources of the contaminant. This would mean that the total Hg emissions from the European estuaries can be as high as 12 tonnes each year, thus, about 17 % of the emissions of mercury from the surface waters of the whole Mediterranean Sea and about 3.5 % of the total anthropogenic emissions of this contaminant in Europe (Pacyna et al., 2001). Therefore, the coastal emissions of mercury shall be regarded as important contribution to the total budget of this toxic contaminant in Europe. It can only be suggested, that the coastal emissions of mercury can be even more important in Asia due to large inputs of this contaminant to the Asian coast with the major rivers and atmospheric deposition in the past. Combustion of coal in China and other Asian countries is the main source of mercury emissions to the global atmosphere (Pacyna and Pacyna, 2000). However, no studies have been carried out to confirm the hypothesis of large coastal flux of mercury to the atmosphere in Asia.

4.7 Concluding remarks

The coastal ocean is a source of selected trace gas emissions to the atmosphere. The most important trace gases emitted in appreciable amounts from the coastal ocean include methane, nitrous oxides, DMS and COS, and mercury. The production of these gases in the coastal ecosystems, particularly estuaries, and the sea to air flux have been studied in a few projects, mostly in Europe. Information on the production and sea to air flux of other trace gases in the coastal ecosystems is very limited and it is rather difficult to conclude on the significance of these fluxes.

Processes of trace gas production and transport from the ocean surface to the atmosphere are complicated and require multidisciplinary studies, including various aspects of biology, meteorology, hydrology, chemistry and physics. Vast majority of efforts to explain the production and water to air transport have been carried out with the use of models and measurements in the open ocean and far less in the coastal ocean.

Flux rates for transport of methane, nitrous oxide, DMS, COS, and mercury from the surface water to the air are higher for the coastal areas than the open sea, for some gases up to several orders of magnitude. A comparison of these flux rates for the coastal zone and the open ocean is presented in Table 5, using the data from the EU BIOGEST project (Frankignoulle, 2000) and other literature data. The contribution of emissions of these gases from the European estuaries to the total European emissions is rather low, except for the contribution of nitrous oxide. This information is also presented in Table 5. Limited information on flux rates for methane, nitrous oxide, DMS, COS, and mercury in other regions of the globe makes it difficult to assess the above mentioned contribution on a global scale. A typological approach, under development within LOICZ, can be useful to scale up the information on flux rates in the European estuaries to obtain a global picture. First approximation by the authors of this report indicates that on a global scale the estuaries will contribute with about a few percent to the total emissions of methane, DMS and COS, and a bit more to the total emissions of nitrous oxide. This suggestion, however, should be considered as a crude approximation and would need new studies for refinement.

Table 5. Fluxes of some biogases in estuaries and their contribution to the total budgets for these gases on the basis of the literature review in this work

Compound	**Estuary to open ocean flux rate ratio**	**Quantity of estuary emissions in Europe, ktonnes/yr**	**Estuary contribution to total European emissions %**	**Coastal sea contribution to the total sea to air flux**	**Coastal sea contribution to global emission %**
CH_4	~ 1000	580	2.5	up to 30%	0.2 - 2.0
N_2O	~ 100	120	9.4	up to 60%	2.0 - 15.0
DMS	1 - 3	60 (as S)	1.0 [*1]	up to 10%	2.0 [*1]
COS	10 - 100			up to 50%	
Hg	~ 10	12×10^{-3}	3.5	up to 20%	~ 0.5

[*1] Contribution to the total European or global emissions of sulfur

The flux rates of methane, nitrous oxide, DMS, COS, and mercury from the coastal waters to the air are much higher than the rates for the open ocean and the contribution of the coastal areas to the total oceanic emissions of these trace gases can be significant on a global scale. As presented in Table 5, this contribution can be as high as 50 % and more for nitrous oxide and COS. Concerning the contribution of the trace gas production in the coastal areas to the total global production of these gases, it can be concluded that this contribution seems to be below 2 % except for nitrous oxide (Table 5). However, it should be pointed out that on the local and even regional scale the emissions in the coastal areas can be very important contributing substantially to the total emissions of these gases in a studied area. Thus, there is a need to carry out studies in the future with the aim to provide more accurate understanding of the production and sea-air exchange processes for these gases around the world.

5 Future changes of fluxes of trace gases in the coastal zone and future research needs to study these changes

Future changes of sea-air fluxes of trace gases in the coastal areas are directly and indirectly dependent of the changes of socio-economic and natural drivers of the environmental change in the coastal ecosystems. Sea-air fluxes are one of the pressures on the coastal ecosystem. Direct relationship between the socio-economic drivers changing the coastal ecosystem and the fluxes of trace gases from the coastal ocean to the air can be illustrated through the enhanced input of precursors of nitrous oxide, methane, DMS and COS, and gaseous mercury to the sea. These precursors include organic matter, nitrates, ammonium, sulfates, mercury deposited to the sea on particles from the air or transported with rivers to the coast. Indirect relationship between drivers and the fluxes of trace gases can be analyzed taking into account the change of natural drivers of the environmental change in the coastal zone, such as climate change and its consequences such as, biodiversity reduction and habitat loss and modification.

It is somewhat easier to discuss the future changes of socio-economic drivers of the environmental change in the coastal areas than the change of natural drivers. In general, it is foreseen that the migration of people to settle down in the coastal areas will continue in the future. This would contribute to further urbanization and probably industrialization in the coast. As a consequence, there will be more demands for the production of food and energy in the coastal regions, resulting in the increased aquaculture and exploitation of living resources. It is also expected that the exploitation of mineral resources will continue in the future. In addition to increased number of people who are going to settle down in the coastal areas, tourism in the coastal areas is also expected to grow. It is outside the scope of this project to discuss in detail the degree of the above mentioned changes of socio-economic drivers of the environmental change in the coastal zone in a quantitative manner. However, it is important to point out that one should expect more pressure on the coast due to increased socio-economic activities within and outside the coastal areas.

Current development of climate change and its consequences on the coast indicates changes of various meteorological, hydrological, physical, chemical and biological parameters (variables) that ultimately influence the production and sea to air flux of trace gases. These parameters include air temperature and wind speed and frequency, salinity and temperature of surface waters, intrusion of saltwater, concentrations of oxygen, algal toxins and phytoplankton pigments, etc. On the basis of the past trends of global warming, frequent formation of algal blooms, increased transport of particulate matter, including organic matter with rivers and to some extend atmospheric deposition, and enhanced primary production in the ocean in various regions of the world, one could expect that the sea to air flux of trace gases in the coastal areas will increase in the future.

In order to quantify future changes of the sea-air exchange of trace gases in the coastal zone and the ecosystem consequences of this change much more research is needed on the processes and parameters affecting the production and atmospheric emission of these gases from the coastal waters. This research is going to be multidisciplinary in order to assess the multi-compartment cycling of carbon, nitrogen, sulfur and contaminants and the production of trace gases from their precursors.

A part of the future research efforts shall focus on the development of models to simulate the fluxes of trace gases and their precursors in the coastal ecosystems and to assess the importance of various meteorological, chemical, physical, hydrological and biological parameters for the formation of these fluxes. These models can be quite complicated as they need an interface between abiotic and biotic modeling. This environmental modeling shall be supported and validated by short term and long term measurements. Models would need a support from measurements during the model parameterization. Results from short term measurements and laboratory experiments are often very useful for the model parameterization. Long term monitoring is required for validation of the model estimates. A monitoring network on a global scale would need to be approached in the coastal zone with a set of common variables and a support from remote sensing. An example of such monitoring can be the one designed within the IOC Coastal Panel of the Global Ocean Observing System (GOOS, 2000).

Scaling approaches would need to be further developed in the future in order to help translating the results of measurements and modeling in one region on a more general, preferably even global scale. This task has been started within LOICZ (e.g., LOICZ, 1999). In this way the information on trace gas fluxes from estuaries in one region could be used to assess this flux in another region and even assess the global flux.

6 Acknowledgements

The authors are grateful to many scientists for providing the data needed for this review and preparing comments and additions for this report. The authors would like to thank specially to:

- Dr. Robert C. Upstill-Goddard and Dr. Guenther Uher of the department of Marine Sciences and Coastal Management, the University of Newcastle, Newcastle upon Tyne, the UK,
- Dr. Wiliam T. Sturges and Dr. Gill Malin of the School of Environmental Sciences, the University of East Anglia, Norwich, the UK,

- Dr. Nicola Carslaw of the School of Chemistry, the University of Leeds, Leeds, the UK,
- Dr. Wendy Broadgate of the IGBP Secretariat, Natural Sciences, Stockholm, Sweden,
- Dr. L.J. Carpenter of the Department of Chemistry, the University of York, Heslington, the UK,
- Dr. Stuart W. Gibb of the Environmental Research Institute, the North Highland College, Thurso, Scotland,
- Dr. Michel Frankignoulle of the University of Liege, Liege, Belgium,
- Dr. Jack J. Middelburg of the Netherlands Institute of Ecology, Yerseke, the Netherlands, and
- Dr. Hermann W. Bange of the Institute for Marine Research, Kiel, Germany.

This work has been prepared within the contracts from the LOICZ International Project Office and the Norwegian Research Council (NFR). The authors are grateful for the financial support from LOICZ and NFR.

7 References

Acid Rain 2000 (2000) Looking back to the past and thinking of the future. The 6th International Conference on Acidic Deposition, Tsukuba, Japan, 10-16 December, 2000, Dordrecht, Kluwer Academic Publishers.

Andreae, M.O. (1990) *Mar.Chem., 30,* 1-29.

Andreae, M.O. and Ferek, R.J. (1992) Photochemical production of carbonyl sulfide in seawater and its emission to the atmosphere. G*lobal Biogeochem.Cycles, 6,* 175-183.

Ayers, G.P., Gillett, R.W., Granek, H., de Serves, C. and Cox, R.A. (1997) Formaldehyde production in clean marine air. *Geophys.Res.Lett., 24,* 401-404.

Baeyens, W. and Leermakers, M. (1996) Particulate, dissolved and methylmercury budgets for the Scheldt estuary in Belgium and the Netherlands. In: *Global and regional mercury cycles: sources, fluxes and mass balance.* Ed. by: W. Baeyens, R. Ebinghaus and O. Vasiliev. Dordrecht, Kluwer Academic Publishers.

Baker, A.R., Turner, S.M., Broadgate, W.J., Thompson, A., McFiggans, G.B., Vesperini, O., Nightingale, P.D., Liss, P.S. and Jickells, T.D. (2000) Distribution and sea-air fluxes of biogenic trace gases in the eastern Atlantic Ocean. *Global Biogeochem. Cycles, 14,* 871-886

Baker, J.M., Sturges, W.T., Sugier, J., Sunnenberg, G., Lovett, A.A., Reeves, C.E., Nightingale, P.D. and Penkett, S.A. (2001) Emissions of CH3Br, organochlorines and organoiodines from temperate macroalgae. *Chemisphere,* in press.

Bange, H.E., Bartell, U.H., Rapsomanikis, S. and Andreae, M.O. (1994) Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane. *Global Biogeochem. Cycles,* 8, 465-480.

Bange, H.E., Rapsomanikis, S. and Andreae, M.O. (1996) Nitrous oxide in coastal waters. *Global Biogeochem. Cycles, 10,* 197-207.

Barnes, J. and Owens, N.J.P (1998) *Mar.Pollut.Bull.*, *37,* 247-260.

Barrie, L.A., Bottenheim, J.W. R.C., Schnell, Crutzen, P.J., and Rasmussen, R.A. (1988) Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere. *Nature, 334,* 138-141.

Bates, T.S., Lamb, B.K., Guenther, A., Dignon, J. and Stoiber, R.E. (1992) Sulfur emissions to the atmosphere from natural sources. *J.Atmos.Chem. 14,* 315-337.

Bellar, T.A., Lichtenberg, J.J. and Kroner, R.C. (1974) The occurrence of organohalides in chlorinated drinking waters. *J.Am. Water Works Assoc., 66,* 703-706.

Bidleman, T.F. (2000) Air-water gas exchange of POPs. In: *Assessment of the sources, atmospheric fluxes, environmental cycling, effects and sinks of persistent organic pollutants.* Ed. by: E. Brorstrøm-Lunden, F. Wania, J.M. Pacyna and T.F. Bidleman. Copenhagen, The Nordic Council of Ministers, Denmark. (TemaNord 2000:514).

Broadgate, W.J., Liss, P.S. and Penkett, S.A. (1997) Seasonal emissions of isoprene and other reactive hydrocarbon gases from the ocean. *J.Geophys.Res., 24,* 2675-2678.

Broadgate, W.J., Malin, G., Kuepper, F., Thompson, A., Liss, P.S. and Kloareg, BB. (1999) First measurements of isoprene and other non-methane hydrocarbons from seaweeds. Presented at the IGAC Conference, Bologna, Italy, September 1999.

Carpenter, L.J. and Liss, P.S. (2000) On temperate sources of bromoform and other reactive organic bromine gases. *J.Geophys.Res., 105,* 20539-48.

Carpenter, L.J., Malin, G., Liss, P.S. and Kupper, F.C. (2000) Novel biogenic iodine-containing trihalomethanes and other short-lived halocarbons in the Coastal East Atlantic. *Global Biogeochem. Cycles, 14,* 1191-1204.

Carpenter, L.J., Sturges, W.T., Penkett, S.A., Liss, P.S., Alicke, B., Hebestreit, K. and Platt, U. (1999) Short-lived alkyl iodides and bromides at Mace Head, Ireland: links to biogenic sources and halogen oxide production. *J.Geophys.Res., 104,* 1679-89.

Chanton, J.P. and Dacey, J.W.H. (1991) Effects of vegetation on methane flux, reservoirs, and carbon isotopic composition. In: *Trace gas emissions by plants.*

Ed. by: T. Sharkey, E. Holand and H. Mooney. San Diego, CA, Academic Press.

Chin, M. and Davies, D.D. (1995) A reanalysis of carbonyl sulfide as a source of stratospheric background sulfur aerosol. *J.Geophys.Res. 100,* 8993-9005.

Cicerone, R.J., Heidt, L.E. and Pollock, W.H. (1988) Measurement of atmospheric methyl bromide and bromoform, *J. Geophys. Res. 93,* 3745-3749.

Cicerone, R.J. and Oremland, R.S. (1988) Biogeochemical aspects of atmospheric methane. *Global Biogeochem. Cycles, 2,* 299-327.

Clark, J.F., Schlosser, P., Wanninkhof, R., Simpson, H.J., Schuster, W.S.F. and Ho, D.T. (1995) Gas transfer velocities for SF6 and 3H in a small pond at low wind speeds. *Geophys.Res.Letters, 22,* 93-6.

Class, Th. and Ballschmiter, K. (1988) Chemistry of organic traces in air, VIII, Sources and distribution of bromo- and bromochloromethanes in marine air and surface water of the Atlantic Ocean. *J. Atmos. Chem., 7,* 35-46.

Conrad, R. and Seiler, W. (1988) Methane and hydrogen in sea water (Atlantic Ocean) *Deep Sea Res., 35A,* 1903-1917.

Cossa, D., Coquery, M., Gobeil, C. and Martin, J.-M. (1996) Mercury fluxes at the ocean margins. In: *Global and regional mercury cycles: sources, fluxes and mass balance.* Ed. by: W.Baeyens, R. Ebinghaus and O. Vasiliev. Dordrecht, Kluwer Academic Publishers.

Dalsgaard, T. (1998) Nitrogen cycling in estuaries. In: *Third European marine science and technology conference proceedings, project Synopsis, Vol. II: Strategic marine research. Lisbon, Portugal, 23-27 May.*

De Angelis, M.A. and Scranton, M.I. (1993) Fate of methane in the Hudson River and estuary. *Global Biogeochem. Cycles, 7,* 509-523.

Dean, G.A. (1963) The iodine content of some New Zealand drinking waters with a note on the contribution from seaspray to the iodine in rain, New Zealand. *J. Sci., 6,* 208.

Duce, R.A., Wasson, J.T., Winchester, J.W., and Burns, F. (1963) Atmospheric iodine, bromine and chlorine, *J. Geophys. Res., 68,* 3943.

ELOISE (1995) Research at the land-ocean-atmosphere interface in the Environment Programme (1991-1994). Brussels, European Commission, Coastal Sciences (*Ecosystem Research Report No. 14)* Belgium

Erickson, III D.J. (1993) A stability dependent theory for air-sea gas exchange. *J. Geophys.Res. 98,* 8471-8488.

EU BIOGEST (2000) Biogas transfer in Estuaries. Third annual report. Liege.

Finlayson-Pitts, B.J., Livingston, F.E. and Berko, H.N. (1990) Ozone destruction and bromine chemistry at ground level in the Arctic spring. *Nature, 343,* 622-625.

Fitzgerald, W.F. and Mason, R.P. (1996) The global mercury cycle: oceanic and anthropogenic aspects. In: *Global and regional mercury cycles: sources, fluxes and mass balance.* Ed. by: W.Baeyens, R. Ebinghaus and O. Vasiliev. Dordrecht, Kluwer Academic Publishers, the Netherlands.

Frankignoulle, M. (2000) Biogas transfer in Estuaries. The (BIOGEST) project report to the EU. Liege.

Frankignoulle, M., Abril, G., Borges, A., Bourge, I., Canon, C., Delille, B., Libert, E. and Theate, J.-M. (1998) Carbon dioxide emission from European estuaries. *Science, 282,* 434-436.

Frost, T. and Upstill-Goddard, R.C. (1999) Air-sea gas exchange into the millenium: progress and uncertainties. In: *Oceanography and marine biology: an annual review.* Ed. by: A.D. Ansell, R.N. Gibson and M. Barnes. London, Taylor and Francis.

Galloway, J.N. (1989) Atmospheric acidification: projections for the future. *Ambio, 18,* 161-166.

Galloway, J.N., Levy II, H. and Kadsibhatla, P.S. (1994) Year 2020: Consequences of population growth and development on deposition of oxidized nitrogen. *Ambio, 23,* 120-123.

GESAMP (1995) The sea surface microlayer and its role in global climate change. (*GESAMP Reports and Studies No. 59).*

Gibb, S.W., Fauzi, R., Mantoura, C. and Liss, P.S. (1999a) Ocean-atmosphere exchange and atmospheric speciation of ammonia and methylamines in the region of the NW Arabian Sea. *Global Biogeochem. Cycles, 13,* 161-178.

Gibb, S.W., Fauzi, R. Mantoura, C., Liss, P.S. and Barlow, R.G. (1999b) Distributions and biogeochemistries of methylamines and ammonium in the Arabian Sea. *Deep-Sea Res. II, 46,* 593-615.

GOOS (2000) Strategic design plan for the coastal component of the global ocean observing system (GOOS). Paris, Intergovernmental Oceanographic Commission IOC/INF-1146 (GOOS Report No. 90).

Ho, D.T., Bliven, L.F. and Wanninkhof, R. (1997) The effect of rain on air-water gas exchange. *Tellus, 49B,* 149-58.

Holligan, P.M., Turner, S.M. and Liss, P.S. (1987) Measurements of DMS in frontal regions. *Cont.Shelf Res. 7,* 213-224.

IPCC (1996) Climate Change 1995. The science of climate change. Contribution of working group I to the second assessment report of the intergovernmental panel on climate change. Cambridge, Cambridge University Press.

Kettle, A.J., Andreae, M.O., Amouroux, D., Andreae, T.W., Bates, T.S., Berreheim, H., Bingemer, H., Boniforti, R., Curran, M.A.J., DiTullio, G.R., Helas, G., Jones, G.B., Keller, M.D., Kiene, R.P., Leck, C., Levasseur, M., Malin, G., Maspero, M., Matrai, P., McTaggart, A.R., Mihalopoulos, N., Nguyen, B.C., Novo, A., Putaud, J.P., Rapsomanikis, S., Roberts, G., Schebeske, G., Sharma, S., Simo, R., Staubes, R., Turner, S. and Uher, G. (1999) A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month. *Global Biogeochem. Cycles, 13,* 399-444.

Khalil, M.A.K. and Rasmussen, R.A. (1992) The global sources of nitrous oxide. *J.Geophys.Res., 97, 14,* 651-60.

King, G.M. (1988) Distribution and metabolism of quaternary amines in maroine sediments. In: *Nitrogen cycling in coastal marine environments.* Ed. by: T.H. Blackburn and J. Sørenson. Chichester, Wiley.

de Leeuw, G. (1998) Atmospheric nitrogen inputs into the coastal ecosystem. In: *Third European marine science and technology conference proceedings, project synopsis, Vol. II: Strategic marine research. Lisbon, Portugal, 23-27 May.*

Leggett, J., Pepper, W.J. and Swart, R. J. (1992) Emissions scenarios for the IPCC: an update. In: *Climate Change 1992.* Ed. by: J.T. Houghton, B. A. Callander, and S.K. Varney. New York Cambridge University Press.

Lewis, A.C., Carpenter, L.J. and Pilling, M.J. (2001) Non-methane hydrocarbons in Southern Ocean boundary layer air. *J.Geophys.Res., 106,* 4987-4994.

Liss, P.S. (1983) Air-sea Exchange of Gases and Particles. Ed. by: P.S. Liss and W.G.N. Slinn. Dordrecht, D. Reidel Publishing.

Liss, P.S. and Merlivat, L. (1986) Air-sea gas exchange rates: introduction and synthesis. In: *The role of the air-sea exchange in geochemical cycling.* Ed. by: P. Buat-Menard. Dordrecht, D.Reidel Publishing, the Netherlands.

Liss, P.S. and Slater, P.G. (1974) Flux of gases accros the air-water interface. *Nature, 274,* 181-4.

Liss, P.S., Grimalt, J.O., Hov, Ø., Johannessen, T., Larsen, S.E. Oost, W.A. and de Leeuw, G. (1997a) Report of the working group on gases. In: *Sea-air exchange: modeling and processes.* Ed. by: J.M. Pacyna, D.Broman and E. Lipiatou. Brussels, European Commission, Marine Science and Technology Programme, (EUR 17660 monograph).

Liss, P.S., Hatton, A.D., Malin, G., Nightingale, P.D. and Turner, S.M. (1997b) Marine sulphur emissions. *Phil.Trans.R.Soc.Lond B Biol.Sci 352,* 159-169.

LOICZ (1994) Land-ocean interactions in the coastal zone. Implementation plan. Stocholm, (*The IGBP Global Change Report No. 33),* Sweden.

LOICZ (1999) 4Th open science meeting of LOICZ on regimes of coastal change. Bahia Blanca, Argentina, 15-18 November, 1999. Conference proceedings.

LOIRA (2000) Proceedings of the third workshop on land-ocean interactions in the Russian Arctic (LOIRA), Moscow, Russia, 5-8 December.

Lovelock, J.E., Maggs, R.J., and Wade, R.J. (1973) Halogenated hydrocarbons in and over the Atlantic. *Nature, 241,* 194-196.

MAMCS (2000) Mediterranean atmospheric mercury cycle system (MAMCS). The EU ENV4-CT97-0593 project. Final report. Rende.

Manley, S.L. and Dastoor, M.N. (1987) Methyl halide production from the giant-kelp, Macrocystis, and estimates of global methyl halide production by kelp. *Limnol. Oceanogr., 32,* 709-715.

Mason, R.P., Ozerova, N.A., Akagi, H., Cossa, D., Fitzgerald, W.F. and Horvat, M. (1996) Working group report on oceanic mercury cycling. In: *Global and regional mercury cycles: sources, fluxes and mass balance.* Ed. by: W.Baeyens, R. Ebinghaus and O. Vasiliev. Dordrecht, Kluwer Academic Publishers.

Michaels, A.F., Siegel, D.A., Johnson, R.J., Knap, A.H., and Galloway, J.N. (1993) Episodic inputs of atmospheric nitrogen to the Sargasso Sea: Contributions to new production and phytoplankton blooms. *Global Biogeochem. Cycles, 7,* 339-351.

Middelburg, J.J., Nieuwenhuize, J., Iversen, N., Høgh, N., de Wolde, H., Helder, W., Seifert, R. and Christof, O. (2001) Methane distribution in European tidal estuaries. *Biogeochemistry,* in press.

Mihalopoulos, N., Nguyen, B.C., Putaud, J.P. and Belviso, S. (1992) The oceanic source of carbonyl sulfide (COS). *Atmos.Environ., 26A,* 1381-1394.

Moore, R.M. and Tokarczyk, R. (1993) Volatile biogenic halocarbons in the Northwest Atlantic. *Global Biogeochem. Cycles, 7,* 195-210.

Moore, R.M., Tokarczyk, R., Tait, V.K., Poulin, M. and Geen, C. (1995) Marine phytoplankton as a natural source of volatile organohalogens. In: *Naturally produced organohalogens.* Ed. by: A. Grimvall and E.W.B. de Leers. Dordrecht, Kluwer Academic, the Netherlands.

van der Nat, F.-J.W.A., Middelburg, J.J., van Meteren, D. and Wielemakers, A. (1998) Diel methane emission patterns from Scirpus lacustris and Phragmites australis. *Biogeochemistry, 41,* 1-22.

van der Nat, F.-J., and Middelburg, J.J. (2000) Methane emission from tidal freshwater marshes. *Biogeochemistry, 49,* 103-121.

Oltmans, S.J. and Komhyr, W.D. (1986) Surface ozone distributions and variations from 1973-1984. Measurements at the NOAA geophysical monitoring for climate change baseline observatories. *J. Geophys. Res., 91,* 5229-5236.

Owens, N.J.P., Law, C.S., Mantoura, R.F.C., Burkill, P.H. and Llewellyn, C.A. (1991) Methane flux to the atmosphere from the Arabian Sea. *Nature, 354,* 293-296.

Owens, N.J.P., Galloway, J.N. and Duce, R.A. (1992) Episodic atmospheric nitrogen deposition to oligotrophic oceans. *Nature, 357,* 397-399.

Paerl, H.W. (1985) Enhancement of marine primary production by nitrogen-enriched acid rain. *Nature, 315,* 747-749.

Paerl, H.W. and Fogel, M.L. (1994) Isotopic characterization of atmospheric nitrogen inputs as sources of enhanced primary production in coastal Atlantic Ocean. *Mar. Biol., 119,* 635-645.

Pacyna, E.G., Pacyna, J.M. and Pirrone, N. (2001) European emissions of atmospheric mercury from anthropogenic sources in 1995. *Atmos. Environ.,* in press.

Pacyna, J.M., Broman, D. and Lipiatou, E. (1998) Sea-air exchange: modeling and processes. Brussels, European Commission, Marine Science and Technology Programme, (EUR 17660 monograph).

Pacyna, J.M. and Pacyna, E.G (2000) Assessment of emissions/ discharges of mercury reaching the Arctic environment. Kjeller, Norwegian Institute for Air Research (NILU OR 7/2000).

Plass-Dulmer, C., Koppmann, R., Ratte, M. and Rudolph, J. (1995) Light nonmethane hydrocarbons in seawater. *Global Biogeochem. Cycles, 9,* 79-100.

Powelson, D.K. and Mills, A.L. (1996) Bacterial enrichment at the gas-water interface of a laboratory apparatus. *Appl. Environ. Microbiol., 62,* 2593-7.

Prather, M.J. and Watson, R.T. (1990) Stratospheric ozone depletion and future levels of atmospheric chlorine and bromine. *Nature, 344,* 729-734.

Rapsomanikis, S. (1994) Oceans as sources or sinks of biologically produced gases relevant to climatic change. EUROTRAC annual report 1993, part 3: ASE, ISS, Garmisch-Partenkirchen.

Ratte, M., Plass-Dulmer, C., Koppmann, R., Rudolph, J. and Denga, J. (1993) Production mechanisms of C2-C4 hydrocarbons in seawater: field measurements and experiments. *Global Biogeochemical Cycles, 7,* 369-378.

Ratte, M., Plass-Dulmer, C., Koppmann, R. and Rudolph, J. (1995) Horizontal and vertical profiles of light hydrocarbons in sea water related to biological, chemical and physical parameters. *Tellus, 47B,* 607-623.

Roberts, P.V. (1984) Dependence of oxygen transfer rate on energy dissipation during surface aeration and in stream flow. In: *Gas transfer at water surfaces.* Ed. by: W. Brutsaert and G.H. Jirka. Dordrecht, D. Reidel Publishing.

Rook, J.J. (1974) Formation of haloforms during chlorination of natural waters. *J. Water Treat. and Exam., 23,* 234-243.

Soetaert, K. and Herman, P.M.J. (1995) Carbon flows in the Westerschelde Estuary (the Netherlands) evaluated by means of an ecosystem model (MOSES). *Hydrobiologia, 311,* 247-66.

Solberg, S., Schmidbauer, N., Semb, A., Stordal, F. and Hov, Ø. (1996) Boundary-layer ozone depletion as seen in the Norwegian Arctic in spring, *J. Atmos. Chem., 23,* 301-332.

Stefels, J., Malin, G., and Wassmann, P. (1998) Carbon and sulphur dynamics during Phaeocystis blooms in North. Norwegian and Dutch coastal waters: an overview of the ESCAPE project. In: *Proceedings of the Second Annual Scientific Conference on European Land-Ocean Interaction Studies, Huelva, Spain, 30 Sept.-3 October.*

Turner, S.M., Malin, G., Nightingale, P.D. and Liss, P.S. (1996) Seasonal variation of dimethyl sulphide in the North Sea and an assessment of fluxes to the atmosphere. *Mar.Chem., 54,* 245-262.

Uher, G. and Andreae, M.O. (1997) Photochemical production of carbonyl sulfide in North Sea water: a process study. *Limnol.Oceanogr., 42,* 432-442.

Uher, G. Schebeske, G., Barlow, R.G., Cummings, D.G., Mantoura, R.F.C., Rapsomanikis, S.R. and Andreae, M.O. (2000) Distribution and air-sea gas exchange of dimethyl sulfide at the European western continental margin. *Mar. Chem., 69,* 277-300.

Ulshofer, V.S., Uher, G. and Andreae, M.O. (1995) Evidence for a winter sink of atmospheric carbonyl sulfide in the northeast Atlantic Ocean. *Geophys.Res.Lett. 22,* 2601-2604.

Upstill-Goddard, R.C., Barnes, J, and Owens, N.J.P. (1999) Nitrous oxide and methane during the 1994 SW monsoon in the Arabian Sea/ nortwestern Indian Ocean. *J.Geophys.Res. 104,* 30067-30084.

Upstill-Goddard, R.C., Barnes, J., Frost, T., Punshon and Owens, N.J.P. (2000) *Global Biochem. Cycles, 14,* 1205-1217.

U.S. EPA (1994) Deposition of air pollutants to the great waters. First report to congress. U.S. Research Triangle Park, NC, Environmental Protection Agency, (EPA-453/R-93-055),

Watson, A.J., Upstill-Goddard, R.C. and Liss, P..S. (1991) Air-sea exchange in rough and stormy seas measured by a dual-tracer technique. *Nature, 349,* 145-7.

Weiss, P.S., Johnson, J.E., Gammon, R.H. and Bates, T.S. (1995) A reevaluation of the open ocean source of carbonyl sulfide to the atmosphere. *J.Geophys.Res. 100,* 23083-23092.

WMO (1995) Scientific assessment of ozone depletion: 1994. WMO Global ozone research and monitoring project. Geneva, (Report No. 37).

WMO (1999) Scientific assessment of ozone depletion: 1998. WMO Global ozone research and monitoring project. Geneva.

Wofsy, S.C., McElroy, M. B. and Yung, Y.S. (1975) The chemistry of atmospheric bromine. *Geophys. Res. Lett. 2,* 215-218.

Wollast, R. (1983) Interactions of carbon and nitrogen cycles in the coastal zone. In: *Ocean margin processes in global change.* Ed. by: B.Bolin. Chichester, Wiley.

Wollast, R., Chou, L., Huthnance, J., Larsen, S., Fouzi Mantoura, Wassmann, P. and van Weering, T. (1998) Ocean Margin Exchange II - Phase I. In: *Third European Marine Science and Technology Conference Proceedings, project Synopsis, Vol. I: Marine Systems. Lisbon, Portugal, 23-27 May.*

Zafiriou, O. (1974) Photochemistry of halogens in the marine atmosphere, J. *Geophys. Res. 79,* 2730-2732.

Zepp, R.G., Callaghan, T.V. and Erickson, D.J. (1998) *J. Photochem.Photobiol. 46,* 69-82.

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P.O. Box 100, N-2027 Kjeller, Norway

REPORT SERIES Scientific Report	REPORT NO. OR 39/2001	ISBN 82-425-1284-1 ISSN 0807-7207	
DATE	SIGN.	NO. OF PAGES 38	PRICE NOK 60,-

TITLE Literature Review: Trace Gases in the Coastal Zone	PROJECT LEADER Jozef M. Pacyna
	NILU PROJECT NO. O-100137
AUTHOR(S) Jozef M. Pacyna and Øystein Hov	CLASSIFICATION * A
	CONTRACT REF. LOICZ

REPORT PREPARED FOR
LOICZ (Land Ocean Interactions in the Coastal Zone) program of IGBP, P.O. Box 59, NL-1790 AB Den Burg, Texel, The Netherlands

NFR, Postboks 2700 St. Hanshaugen, 0131 OSLO

ABSTRACT

NORWEGIAN TITLE

KEYWORDS		
Trace gases	Coastal Sea	Sea-air exchange

ABSTRACT (in Norwegian)

** Classification*	*A*	*Unclassified (can be ordered from NILU)*
	B	*Restricted distribution*
	C	*Classified (not to be distributed)*