

Paper on Coastal Ecosystem Greenhouse Gas Budget



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• Introduction

CarboEurope – GHG is one of the EU CarboEurope projects aiming at better understanding and quantifying the carbon balance of Europe, Siberia and the Amazon basin, in a view of the Kyoto Protocol. Another objective of the CarboEurope projects is to develop a prototype of a reliable, consistent monitoring and verification system, which will facilitate calculating the full carbon balance of Europe. The cluster comprises of 15 projects funded by the EU Research Directorate General under its program on “Energy, Environment and Sustainable Development”, Key Action on Global Change, Climate and Biodiversity.

CarboEurope - GHG is a Concerted Action on Synthesis of the European Greenhouse Gas Budget. Project objectives are two-fold. The first is to provide a synthesis based on current research results of the European greenhouse gas budget, including both human induced and biospheric sources and sinks. The second is to use this as a basis for making recommendations for methodological improvements that will allow multi-disciplinary integration of various sources of data and for improvement of “a priori” input to inverse atmospheric models. Achieving these objectives will provide the scientific foundation for a full carbon and, even broader, full greenhouse gas accounting by 2010.

One of the specific studies within the CarboEurope-GHG project is the “Coastal ecosystems greenhouse gas budget”. The major objectives of this study are: 1) to establish the importance of the coastal zone as a source or sink for atmospheric sources and sinks of greenhouse gases, 2) to identify those systems making a major contribution to sea-air trace gas exchange, and 3) to describe the underlying biogeochemical processes determining the magnitude of trace gas exchange in these ecosystems.

The exchange of trace gases between coastal ecosystems and the atmosphere directly impacts global warming and a diverse range of other climate change related phenomena, including, ozone depletion, acid deposition, eutrophication, atmospheric particle formation, and the cycling and reactivity of photo-oxidants. The effects can be local, regional, and global.

For the purpose of this specific study discussion is limited to those regions that do not extend beyond the shelf, mainly in Europe.

It should also be noted that there are other specific studies within the CarboEurope – GHG project that deal with:

- wetlands and peatlands greenhouse gas budget, and
- freshwater greenhouse gas budget,

as well as with:

- forest greenhouse gas budget,
- agricultural greenhouse gas budget,
- grasslands greenhouse gas budget, and
- lateral carbon transport through trade.

Trace gases considered in this work include CO₂, N₂O, CH₄, DMS, COS and CS₂.

• 2. Coastal zone definition

Coastal waters of the European continental margin may be defined both from management and biogeographic perspectives. From a management perspective, coastal waters are usually defined as the 'national shelf area' of continental shelves and margins, which extends 200 nautical miles or more from the shore, and defines the sovereign area of coastal states with regard to resource management under the UN Convention on the Law of the Sea. The combined 'national shelf area' of European States including Iceland and excluding the Russian Federation comprises 2.3×10^6 km², accounting for significant fractions of global national shelves (9.5%, Pruetz and Cimino, 2000) and physiographic shelves (8.5%, <200 m, Menard and Smith, 1966), respectively.

Biogeographic classifications may be considerably more complex, depending on the choice of biological, chemical, and physical descriptors used in the definition of their extent. Contemporary classification schemes are often based on the concept of the 'two-layered ocean', where the ocean is divided into mixed surface and deeper layers, separated from each other by a pycnocline barrier. Within this concept, vertical position and strength of the pycnocline are determined by physical forcing and fundamentally control biogeochemical cycling in the surface ocean (see e.g., Hooker *et al.*, 2000; Longhurst *et al.*, 1995; Longhurst, 1998). On continental shelves and margins, physical forcing is also modified by interaction with bottom topography and coastal geomorphology, in shallow waters often to the extent that the concept of the 'two-layered ocean' cannot be applied, therefore leading to many distinct features in coastal seas (e.g. tidally mixed areas of the southeastern North Sea and English Channel, Otto *et al.*, 1990). A review of regional coastal oceanography would go far beyond the scope of this study, and the reader is referred to previous publications (e.g. Walsh, 1988). It is, however, worth noting that the European coastal ocean shows considerable variability on a variety of scales (<1km to >100km, Huthnance, 1995) and displays features such as tidal and shelf fronts (McMahon *et al.*, 1995; Pingree *et al.*, 1975), shelf break upwelling (Pingree and Mardell, 1981; Pingree *et al.*, 1986), and coastal upwelling (Fiúza *et al.*, 1982; Haynes *et al.*, 1993), all linked to enhanced productivity and biogeochemical cycling. In addition, coastal seas are significantly affected by freshwater discharge and nutrient loads from riverine and atmospheric inputs, and the effects of these inputs are often enhanced in semi-enclosed, shallow water bodies with restricted exchange to the open sea.

Given the influence of bottom topography on the distinct hydrographic and biogeochemical regimes of coastal waters, it is plausible to operationally define the coastal zone as the waters of the physiographic shelf down to 200 m depth, and this approach is adopted here. It is worth noting though that the effects of processes such as coastal upwelling and shelf break fronts may reach beyond the 200 m depth contour. For example, upwelling filaments off the western Iberian Peninsula may extend up to 200 km beyond the shelf break at the peak of the upwelling season (Haynes *et al.*, 1993). However, the areal extent of such features can be considered small compared to that of the entire European shelf.

European shelf seas account for a significant fraction of world shelves (12.2%, Table 1). The wide continental shelves of the Barents and British Seas together account for 50% of European coastal waters, and the narrow shelves of Western Europe only for an additional 19%. The remaining 31% are from enclosed seas (Baltic, Mediterranean, and Black/Azov Seas) and the Caspian Sea, a brackish inland sea at the geographic boundary of south-eastern Europe. Each of the above regions show distinct hydrography and ecosystem characteristics, which have been described elsewhere (Hardisty, 1990; Ketchum, 1983; Mandych 1995; Otto *et al.*, 1990; Postma and Zijlstra, 1988).

The European coastline is home to a variety of estuarine and intertidal environments, which on the merits of their exceptionally high productivity (up to 8 times that of continental shelves, Whittaker and Likens, 1975) deserve separate treatment. Freshwater inputs, semi-enclosed nature, shallow bottom topography and restricted exchange with the coastal ocean are common characteristics of these environments, which include estuaries, deltas, the Wadden Sea, fjords, sea lochs, rías, bays and lagoons. Marine intertidal areas, vegetated (salt marshes) and unvegetated (mud flats) were also considered below, when data were available. In the following we adopt the term 'estuarine systems' for all the aforementioned coastal domains with restricted exchange with the coastal ocean.

The EU CORINE Land Cover project (http://reports.eea.eu.int/CORO_landcover/en/tab_abstract_RLR) gives the areal extent of European estuaries, lagoons, salt marshes and mud flats as $0.025 \times 10^6 \text{ km}^2$. However, this figure should be regarded as an underestimate, due to inadequate data cover and significant inconsistencies with regard to the classification of coastal, marine environments. For example, (1) intertidal areas of the Wadden Sea are only provided for German waters but not for the Netherlands, (2) estuarine areas are sometimes classed as inland 'water courses' or 'water bodies' (see e.g. Rhine, Gironde), and (3) many estuarine systems with restricted exchange with the coastal sea are wrongly classified as 'sea and ocean' (e.g. Wadden Sea, sea lochs, rías). Furthermore, data are still lacking for the Norwegian, Swedish and Russian coasts and for parts of the Black Sea and Mediterranean coasts. In conclusion, physiogeographic data suitable for the assessment of total European trace gas emissions from estuarine systems are still lacking, and further work is required to integrate existing GIS and remote sensing information. In order to obtain a rough first guess of the areal extent of European estuarine systems, we calculated European estuarine and marine intertidal areas from global cover (estuarine: $1.4 \times 10^6 \text{ km}^2$, salt marsh: $0.4 \times 10^6 \text{ km}^2$, Walsh, 1988) multiplied by the fractional contribution of Europe to the global shelf area (0.12). This suggested estuarine and intertidal surface areas of $0.17 \times 10^6 \text{ km}^2$ and $0.04 \times 10^6 \text{ km}^2$, respectively, i.e. roughly 4% of European shelf waters. For comparison, an inventory of 163 UK estuaries alone, excluding sea lochs, gives an estuarine surface area of 531 km^2 (Davidson and Buck, 1997), 8 western European estuaries studied in the EU BIOGEST project cover an area of 1416 km^2 (Middelburg *et al.*, 2002), the Netherlands and German Wadden Seas are approximately 7000 km^2 (estimated from maps), suggesting some $0.01 \times 10^6 \text{ km}^2$ of estuarine area along fractions of the UK, French and southern North Sea coasts alone. Given the presence of many other large estuarine environments, e.g. fjords of > 100 km length around Norway, the above figures for European estuarine and intertidal areas seem plausible despite considerable remaining uncertainty.

• 3. Drivers of ecosystem change in the coastal zone

Several studies on the impacts of anthropogenic and natural drivers of ecosystem change within the European coastal zone were undertaken during the EU ELOISE programme. This is a framework for more than 60 EU projects studying material fluxes and biogeochemical cycling in the European coastal zone, changes in the structure and functioning of coastal ecosystems due to changes in these fluxes, and various aspects of coastal zone management (Pacyna, 2004). Major drivers and their impacts are presented in Table 2 (Nunneri *et al.*, 2003) and can be summarised as follows:

- climate change: changes in temperature, rainfall, sea level, and weather conditions represent a threat to which coastal areas are particularly susceptible. It is especially noteworthy that these processes impact parameters affecting sea-to-air trace gas exchange, reviewed in section 4 below,
- agriculture and forestry: changes in farming practices and cropping regimes directly affect agricultural landscapes and simultaneously alter catchment river discharge, modifying sediment, nutrient and contaminants fluxes into soil and riparian waters, all of which eventually finds its way into estuaries and coastal waters. This driver is of particular importance for the flux of methane and nitrous oxides to and from coastal waters,
- urbanization and infrastructure: the expansion of the built environment is frequently at the expense of habitat and biodiversity and may stimulate disturbance to ecosystem processes, but it can also alter the hydrological properties of catchments and interrupt the natural dynamics of coastal processes,
- tourism: this driver is closely connected with further urbanization and thus with locally and seasonally varying inputs of nutrients and contaminants to the coastal zone,
- industry and trade: industrial discharges in the catchment reach the coastal areas via river runoff, while the impact of ports and harbours is more direct,
- fisheries and aquaculture: over fishing and the unrestricted use of certain fishing techniques can cause significant impacts, particularly the destruction of the bottom habitat. Aquaculture is strongly connected with water contamination and thus may affect the sea-air exchange process for selected trace gases, and
- energy: increased demands for energy can affect the coastal zone in various ways, including the alteration of riverine hydrography through damming and thus alteration of water and sediment input to the coastal zone, disturbance of wildlife and altered water temperature and contaminant discharges. Thus, this driver also affects parameters having an impact on sea-air exchange.

Present trends of major drivers, pressures and impacts have recently been assessed within the ELOISE projects (Nunneri *et al.*, 2003) for the Baltic Sea, Black Sea, Mediterranean Sea, North Sea and the Atlantic coast. The results of this assessment are presented in Table 3.

Four drivers were found to be especially important in the European coastal zone: urbanization and transport, tourism, expansion of industrial activities and trade, and expansion of fisheries and aquaculture. Examination of the impact grouping revealed that three categories were judged to be of particular significance (Nunneri *et al.*, 2003): coastal squeeze and habitat loss, changes in biodiversity in terms of species composition, and the loss of fisheries productivity. Other impacts were judged significant but they were not as extensively distributed as the three primary impact categories.

There are various ways in which anthropogenic and natural drivers and their pressures may affect the production and emission of trace gases in the coastal zone. Some examples of these impacts can be defined 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,
- changes in precipitation and runoff which may affect CDOM levels in coastal waters,
- nitrogen enrichment that affects the nitrogen cycle in the coastal zone, with important implications for global N₂O emissions (Naqvi *et al.*, 2000),
- sulphur and contaminant enrichment in coastal waters that affects the cycle of these chemicals in the coastal waters and has implications for emissions of trace sulphur gases and selected gaseous metals, such as mercury.

In summary, the effects of anthropogenic drivers of environmental change are much more intense in coastal seas than the open ocean. Consequently, the resulting responses in coastal ecosystem functioning and structure are also far greater. Biogeochemical cycling, including the interface processes, such as sea-air exchange is affected by these differences between the coast and the open ocean.

• 4. Sea air exchange mechanisms

The past several years have seen substantial advances in our understanding of air-sea gas exchange; however this is still insufficient to adequately parameterize the fundamental controlling processes. The physical and biogeochemical controls of gas exchange are many and the relative importance of each remains unclear. Consequently, various parameterizations and measurement techniques are available, giving rise to considerable uncertainty. For example Frankignoulle *et al.* (1998) estimated the estuarine contribution to CO₂ emissions from Western Europe at ~5-10% based on gas exchange measurements with a floating dome. However, subsequent work implies floating dome estimates to overestimate gas exchange by a factor ~ 2 relative to alternative methods (Raymond and Cole, 2001). If so the estuarine CO₂ contribution estimated by Frankignoulle *et al.* (1998) could reduce to ~ 2.5-5%, with implications for other parts of their CO₂ budget.

Gas exchange in coastal waters is effected both through turbulent and diffusive transfer at the air-water interface and through bubble ebullition; the latter principally applies to CH₄ but can also be significant for other trace gases. This review addresses the current state of research in these areas by reviewing basic concepts and recent progress towards understanding the important controlling variables.

4.1 Conceptual Framework

Excluding the process of bubble ebullition, air-water gas exchange is driven by molecular and turbulent diffusion. While the former operates on typically sub-millimetre vertical scales close to the air-water interface, the latter is defined by the scales of length and velocity of turbulent eddies. Away from the air-water boundary turbulent motions dominate gas transport but as the boundary is approached, these motions are progressively weakened due to the viscous properties of the water surface. This gives rise to the concept of “diffusive sub-layers” on either side of the interface, which provide resistance to gas transfer, and in which gas concentration gradients develop (Figure 1). For gases that are very soluble or react with water, the atmospheric sub-layer provides the greatest resistance to gas exchange, whereas for sparingly soluble gases transport through the aqueous sub-layer is the rate limiting step. Most gases of biogeochemical interest (e.g. CO₂, O₂, CH₄, N₂O, DMS, COS, CS₂, CO) fall into the latter category and so for these the airside boundary can be ignored for all practical purposes.

Various models of gas transfer have developed from the concept of diffusive sub-layers. In particular the large density contrast between water and air has facilitated models based on analogies with heat and mass exchange over solid porous walls, which is well studied (e.g. Deacon, 1977). Such analogies are apparently robust for an unbroken water surface with low interfacial turbulence, but not for more energetic regimes with wave breaking and bubble formation, where the aqueous sub-layer is disrupted and the exchange of sparingly soluble gases is enhanced (Jähne *et al.*, 1987; Asher and Wanninkhof, 1998).

The most widely used such modelling approach is that of surface renewal (Danckwerts, 1951), in which water in the aqueous sub-layer is continuously and randomly renewed by turbulent eddies from below. The idealized mechanism is one in which disruption of the aqueous sub-layer is both complete and instantaneous, and recovery is immediate. This leads to the concept of a characteristic renewal rate, τ , which is the mean time between successive renewals. In practice surface renewal is influenced by several variables, including free convection under calm conditions, wind induced mixing at low to high wind speeds, changes in air-water momentum transfer due to drag, thermal stratification due to insolation, wave damping, buoyan-

cy effects from precipitation, and surfactants to name but a few (e.g. Schluessel *et al.*, 1997; Soloviev *et al.*, 2002). Moreover, not all turbulent eddies will impinge fully on the water surface. Consequently, the aqueous sub-layer depth varies spatially and temporally. A more detailed treatment of surface renewal theory is beyond the scope of this contribution, and Liss (1983), Jähne and Haussecker (1998); Frost and Upstill-Goddard (1999) discuss surface renewal models in varying levels of detail.

Surface renewal theory is consistent with the concept of a gas transfer velocity, k_w , which incorporates details both of the turbulent transport (r), and diffusionally-mediated transport expressed via the molecular gas diffusivity, D :

$$k_w = \sqrt{Dr} \quad (1)$$

Physical forcing of gas exchange expressed through k_w relates to the rate of gas transfer, F , across the air-water interface as follows:

$$F = k_w \Delta C = k_w (C_w - \alpha C_a) \quad (2)$$

where α is the dimensionless Ostwald solubility coefficient, ΔC is the gas concentration difference between bulk water at the base of the aqueous sub-layer (C_w) and surface water in equilibrium with air (αC_a), and C_a is the gas concentration in air (Figure 1). From (2) it is clear that control of gas exchange can be exerted by modifying either k_w or the dissolved gas concentrations (i.e. ΔC), or both. Some controlling processes are specific to one or the other, while others influence both. Measuring ΔC is comparatively straightforward for some species, although several important issues arise. By contrast, k_w can only be estimated indirectly in the field through costly, dedicated experiments and the relative roles of the controlling variables are much more controversial. For this reason much effort has focused on the parameterisation of k_w .

The analogy between gas, heat and mass transfer (e.g. Deacon, 1977) allows the thermodynamic control of k_w to be expressed through the "Schmidt number", Sc , defined as the ratio of the transfer coefficients of momentum (i.e. kinematic viscosity of water, ν) and mass (i.e. gas diffusivity, D). Hence

$$Sc = \frac{\nu}{D} \quad (3)$$

and

$$k_w = Sc^n f(u, l) \quad (4)$$

where the Schmidt number exponent n varies between $-1/2$ and $-2/3$ depending on the surface boundary conditions. Classical surface renewal theory (Danckwerts, 1951) predicts k_w to be proportional to $Sc^{-1/2}$. The term $f(u, l)$ expresses the functional dependence of k_w on turbulence in terms of a turbulent velocity (u) and a turbulent length scale (l) (MacIntyre *et al.*, 1995). Turbulent length scales cover several ranges; the largest is governed by the size of the largest eddies, which are dictated by the thickness of the boundary layer. In coastal waters the largest eddies may scale with water depth or the depth of the thermocline. The intensity of turbulence is measured by the turbulent dissipation rate of kinetic energy, ϵ defined by

$$\epsilon = u^3 / l \quad (5)$$

(Taylor, 1935). Various attempts have been made to scale k_w in terms of u and l (i.e. ϵ) but because a spectrum of eddy sizes impinges on the aqueous boundary layer (Brumley and Jirka, 1988), such models have limited physical reality (MacIntyre *et al.* 1995).

4.2 Wind speed and wind related turbulence

Turbulence at the air-water interface results from the interaction of several geophysical forcings, which complicates quantifying k_w . Considerable efforts have therefore focused on deriving simple empirical relationships for k_w based on wind speed. Measuring wind speed is comparatively straightforward. Moreover, large spatial and temporal datasets are available from ships and coastal land stations, although the latter can sometimes be remote from the area of study. Nevertheless, obtaining reliable wind speed estimates can be problematic (DeFelice, 1998; Nightingale *et al.*, 2000; Frost and Upstill-Goddard, 2002). Ship-based measurements may require correcting for the vessel speed and heading, lateral rolling and for flow distortion by the superstructure, which can cause errors of up to 10% in measured wind speeds (Taylor *et al.*, 1995; Yelland *et al.*, 1998; Nightingale *et al.*, 2000). For these reasons wind data from fixed platforms or buoys have sometimes been preferred (Wanninkhof *et al.*, 1993; Nightingale *et al.*, 2000). For large well-equipped research ships adjusting wind speeds to take account of these problems is complex but achievable (Yelland *et al.*, 1998), but it is beyond the capabilities of smaller craft engaged in coastal work. Similarly, data from land stations may be susceptible to flow modification and/or wind shielding by the local topography or even by the wind mast and instrumentation (Frost and Upstill-Goddard 2002).

Numerous studies in wind tunnels and in the field have nevertheless shown strong correlations between k_w and wind speed (e.g. Liss, 1983; Merlivat and Memery, 1983; Jähne *et al.*, 1984; Liss and Merlivat, 1986; Wanninkhof and Bliven, 1991; Wanninkhof, 1992; Wanninkhof *et al.*, 1993, 1997; Wanninkhof and McGillis, 1999; Nightingale *et al.*, 2000; Frost and Upstill-Goddard, 2002). For all of these the functional relationship can be expressed generically as

$$k_w = a Sc^n U_{10}^b \quad (6)$$

where U_{10} is the wind speed at a standard height of ten metres above the water surface and a and b are empirically derived constants.

Figure 2 shows k_w vs wind speed parameterisations from several recent studies. All show strong non-linearity, and of particular note is the strong divergence between their predicted k_w 's at high wind speed. The strong non-linearity means that k_w for a given mean wind speed is a direct consequence of the wind speed distribution over the time interval of measurement. Therefore for the same mean wind speed k_w estimated over a long time interval with variable winds will be higher than if estimated over a short time interval with steady winds. For example the Liss and Merlivat (1986) relationship was based on short-term steady winds (Figure 2), hence it is expected to underestimate k_w for long-term mean winds. Wanninkhof (1992) developed this reasoning to derive alternative quadratic dependences of k_w on either short-term (steady) or long-term (variable) mean winds. Nightingale *et al.* (2000) combined their k_w vs wind speed data from the North Sea with measurements from Georges Bank (Wanninkhof *et al.*, 1993), as modified by Asher and Wanninkhof (1998), and the West Florida Shelf (Wanninkhof *et al.*, 1997). With these data sets corrected for atmospheric stability and interpreted in a consistent manner there was no significant difference between them and a best fit accounted for 80% of the total variance in the data set (Nightingale *et al.*, 2000). Although this represents progress towards reconciling data sets of diverse provenance, the large uncertainties that remain reveal strong control of k_w by additional factors not scaling with wind speed in a straightforward way. This is perhaps not unexpected because wind is only an external forcing of the aqueous boundary; although it influences surface waves and near-surface turbulence, it does not influence gas exchange directly (Bock *et al.*, 1999). It therefore seems inescapable that using wind speed alone to predict k_w is fundamentally flawed.

Improved parameterization of k_w should result by substituting for wind speed, parameters that better define the downward momentum flux from the air to the water surface, such as the shearing stress, τ . Conventionally τ is expressed in terms of the friction velocity in air, u_{*a} , which represents the magnitude of the velocity fluctuations in turbulent atmospheric boundary layer flow, such that

$$\tau = \rho_a u_{*a}^2 \quad (7)$$

where ρ_a is the air density. For a region of constant momentum flux, i.e. constant τ , u_{*a} is also constant (McIntosh and Thom, 1973).

On either side of the air-water interface the wind stress is equal, hence u_{*w} , the friction velocity in water, can be readily derived from u_{*a} . Jähne *et al.* (1984) derived a general expression of the dependence of k_w on u_{*w}

$$k_w = \beta^{-1} u_{*w} Sc^n \quad (8)$$

where β is a variable related to the surface turbulence.

Various studies have substituted u_{*w} for wind speed in order to better characterise k_w (e.g. Wanninkhof *et al.*, 1987; De Leeuw *et al.*, 2002), and satellite remote sensing now offers the prospect of robust large scale estimates of u_{*a} (Elfouhaily *et al.*, 1998).

The wind profile in turbulent boundary layer flow can be represented by

$$U_z = (u_{*a}/K) \ln(z) / z_o \quad (9)$$

where U_z is the wind speed at height z above the surface, K is von Kármán's constant, $= 0.4$, and z_o is the surface roughness length (McIntosh and Thom, 1973).

It follows from (9) that for a specified z higher z_o (i.e. a rougher sea) will require less wind to generate a given value of t specified by u_{*a} . Rewriting (9) as

$$\ln(z) = [(K/u_{*a}) U_z] + \ln(z_o) \quad (10)$$

and plotting U_z versus $\ln(z)$ gives a straight line of slope $= K/u_{*a}$, with z_o defined by the intercept on the ordinate. It is convenient to relate z_o to τ expressed through the dimensionless drag coefficient, C_D , which is a function of z and represents the effectiveness with which momentum is transferred downward to the water surface

$$\tau = \rho_a C_{D(z)} (u_{*a})^2 \quad (11)$$

Considering (7) and (11)

$$C_{D(z)} = (u_{*a} / U_z)^2 \quad (12)$$

From the above C_D is independent of U_z and constant C_D implies constant z_o , hence C_D is unique to a particular surface (McIntosh and Thom, 1973). Non-uniqueness of the relationship between C_D and wind speed is well established for coastal waters (e.g. Smith, 1988; Mahrt *et al.*, 1996; Janssen, 1997; Smith *et al.*, 1996; Vickers and Mahrt, 1997).

4.3 Wave geometry and sea surface roughness

Implied values of z_o in North Sea coastal waters (Smith *et al.*, 1992; Geernaert *et al.*, 1986) exceed those for the open ocean (e.g. Smith, 1980; Yelland *et al.*, 1998), and this has been interpreted in terms of the effect of water depth on sea state (Geernaert *et al.*, 1986). Nevertheless, the dependence of z_o on sea state remains rather poorly defined (Donelan *et al.*, 1997; Drennan *et al.*, 1999 a,b; Taylor and Yelland, 2001). Significant effort has therefore focused on defining z_o in terms of sea state related variables. One such variable is wave slope, S , defined by H_s/L_p , where H_s and L_p are respectively, the significant wave height and the wavelength of waves at the peak of the wave spectrum (e.g. Hsu 1974). Another is wave age defined by c_p / u^*a , or c_p / U_{10} , where c_p is the phase speed at the peak of the wave spectrum (e.g. Smith *et al.*, 1992; Johnson *et al.*, 1998).

Taylor and Yelland (2001) attempted to reconcile existing parameterizations of z_o for the North Sea based on wave age (Smith *et al.*, 1992; Vickers and Mahrt, 1997) using a relationship based on wave slope

$$\frac{z_o}{H_s} = A \left(\frac{H_s}{L_p} \right)^B \quad (13)$$

where $A (= 1200)$ and $B (= 4.5)$ are empirically derived coefficients.

In this way Taylor and Yelland (2001) predicted the effects on C_{D10} (the value of C_D at the standard height of ten metres) of wave duration and fetch, and water depth. In contrast to wave age based formulae that predict increased C_{D10} for “young”, short fetch waves (e.g. Smith *et al.*, 1992), using (13) predicts that for short duration and fetch z_o and hence C_{D10} is similar to or slightly less than for long fetch. This is because the effect of wave steepness is effectively cancelled out by the small wave height. For the same reason enhanced z_o is not predicted for short duration wind events (Taylor and Yelland, 2001). In contrast, and importantly for coastal waters, the effect of water depth on z_o is pronounced. Increasing bottom friction during shoaling leads to initial decreases in c_p , H_s , L_p and C_{D10} . However, as the water depth approaches $\sim 0.2 L_p$, H_s approaches a constant value and both wave steepness and C_{D10} increase rapidly. With further shallowing H_s again increases as the breaking wave regime is approached (Taylor and Yelland, 2001). Using (12) Taylor and Yelland (2001) thus derived a polynomial relationship between C_{D10} and U_{10} applicable to coastal waters for wind speeds in the range 5 - 30 m s⁻¹. This predicts significantly higher C_{D10} and a less rapid increase of C_{D10} with increasing U_{10} than in the open ocean.

The implications of the Taylor and Yelland (2001) analysis for coastal waters are that firstly, for a given wind speed, k_w should increase with distance inshore as surface roughness increases through shoaling, and secondly, k_w might be expected to vary significantly with the tidal height in shallow water.

Another important consideration is that for z_o variations over short length scales, the effective value of z_o approaches the largest z_o values encountered over the averaging length (Mason, 1988). Hence for the case of near-shore waters with offshore winds z_o will be dictated by the coastal topography, in contrast to the situation for onshore winds of the same intensity.

4.4 Wave breaking and bubble formation

Long fetch waves in the open ocean can begin to break at wind speeds as low as 2-3 m s⁻¹ (Monahan and O’Muircheartaigh, 1986), although in coastal waters wave breaking generally occurs at ~ 10 -12 m s⁻¹. This leads to increased surface turbulence and bubble formation, and both processes are implicated in the increase of k_w at high wind speed (e.g. Merlivat and Memery, 1983; Monahan and Spillane, 1984; Woolf and Thorpe, 1991; Asher *et al.*, 1996; Melville, 1996; Woolf, 1997; Asher and Wanninkhof, 1998; Asher *et al.*, 2002; Komori and Mitsumi, 2002). However, identifying the relative roles of wave breaking and bubble formation is hampered by the

long timescales over which k_w has traditionally been estimated in the field.

Bubble mediated gas transfer was identified as the most significant contributor to gas exchange during wave breaking in an experimental gas exchange facility (De Leeuw *et al.*, 2002). Bubble penetration depths $>16\text{m}$ have been observed during wave breaking (Farmer *et al.*, 1993) and the resulting change in bubble internal gas pressure drives gas transfer across the bubble-water interface even when the gas partial pressure in surface-water is at or near atmospheric equilibrium (Memery and Merlivat, 1985; Woolf and Thorpe, 1991; Woolf, 1993). A detailed treatment of bubble-mediated gas transport is given in Leifer and Patro (2002).

Woolf and Thorpe (1991) and Woolf (1993) identify an additional gas transfer velocity due to bubbles, k_b , and a bubble-generated supersaturation term W , in the classical gas exchange equation:

$$F = (k_w + k_b) [C_w - \alpha C_a (1 + \Omega)] \quad (14)$$

Unfortunately this and similar models (e.g. Merlivat and Memery, 1983; Keeling, 1993) lack sufficient supporting quantification of bubble properties such as size spectra, volume concentrations and depth distributions. Bubble size spectra are particularly important as it is only for bubble radii $< 500\text{ mm}$ in diameter that gases completely dissolve or come to equilibrium with the surrounding water (Merlivat and Memery, 1983; Keeling, 1993; Leifer and Patro, 2002). Moreover very small bubbles can persist for long periods and they may be advected over large distances, for example in strong tidal flow. Although bubble properties can now be estimated with reasonable accuracy (e.g. De Leeuw *et al.*, 2002; Komori and Mitsumi, 2002), a high degree of variability complicates the parameterisation of k_b in terms of related field variables such as wind speed or wind fetch; De Leeuw *et al.* (2002) found large spatial and temporal variations in bubble properties both for the North Sea and for the North Atlantic and the two data sets were indistinguishable.

In contrast to the dominant role for bubble-mediated transfer reported in some studies (e.g. Merlivat and Memery, 1983; De Leeuw *et al.*, 2002), others have found a much more modest bubble contribution during wave breaking (e.g. Asher *et al.*, 2002; Komori and Mitsumi, 2002). Asher and Wanninkhof (1998) empirically related k_w to the combined effects of bubble generation and turbulence during wave breaking

$$k_w = [(47 U_{10} + (1.5 \times 10^{-5} W_c - 47 U_{10})) Sc^{0.5} + W_c (-37/\alpha + 10440\alpha^{-0.41} Sc^{0.24})] \quad (15)$$

where W_c is the fractional area whitecap coverage.

The first term on the right hand side of (15) expresses the effects of wind and whitecap generated turbulence and the second expresses solubility dependent, bubble-mediated exchange. From hourly measurements of k_w by direct covariance, Asher *et al.* (2002) applied a relationship relating W_c to U_{10} , consistent with an earlier proposal for a cubic relationship between k_w with U_{10}^3 (Wanninkhof and McGillis, 1999)

$$W_c = 3.7 \times 10^{-6} (U_{10} - 1.2)^3 \quad (16)$$

Using (15) and (16) Asher *et al.* (2002) calculated a maximum 25% contribution from bubbles to k_w for CO_2 during GASEX-98 in the N. Atlantic. During laboratory experiments Komori and Mitsumi (2002) found only a 7% bubble contribution to k_w for CO_2 , even at wind speeds as high as 18 m s^{-1} . Based on these findings the primary influence of breaking waves on air-sea CO_2 exchange would appear to result from

increased turbulence, although the bubble contribution would increase for less soluble gases (Leifer and Patro, 2002).

In an alternative approach to the problem of wave breaking Toba and Koga (1986) describe a wave breaking parameter R_B , which is related to u_a and the spectral peak angular frequency of wind waves, ω_p

$$R_B = u_a^2 / \omega_p \nu \quad (17)$$

Zhao and Toba (2001) showed this to better correlate with W_c than either U_{10} or u_a

$$W_c = 3.88 \times 10^{-7} R_B^{1.09} \quad (18)$$

Substituting (18) into (17) (Zhao *et al.*, 2003) gives

$$k_w = 0.13 R_B^{0.63} \quad (19)$$

In this treatment the dependence of k_w on R_B and hence on ω_p links k_w explicitly to the development of the wind waves. Larger peak frequencies correspond to smaller values of k_w for the same value of U_{10} , hence (19) predicts strong control of k_w by wind fetch. Zhao *et al.*, (2003) interrogated the validity of (19) by reference to a composite data set compiled from numerous wind tunnel and field studies, and concluded it to more robustly parameterize k_w than either u_a or ω_p .

Nightingale *et al.* (2000) show an overall increase in k_w with significant wave height for the southern North Sea, and fetch dependence is implicated in the estimates of k_w for San Francisco Bay based on ^{222}Rn (Hartman and Hammond, 1984). Fetch dependence is also implied from a comparison of mean wind speed and k_w for several lakes of varying size (Wanninkhof, 1992), although such data may be complicated by short term fluctuations in other variables (Frost and Upstill-Goddard, 2002).

4.5 Role of temperature and salinity

Temperature and salinity influence the solubility, α , of a dissolved gas (e.g. Wiesenburg and Guinasso, 1979; Weiss and Price, 1980) and its Schmidt number, Sc , (Wanninkhof, 1992), impacting both ΔC (through α) and k_w (through Sc). Wanninkhof (1992) gives temperature and salinity dependent solubility functions for some relevant biogases, including CO_2 , O_2 , CH_4 and N_2O . For these, solubility typically decreases by about 50% over the temperature range 0-25°C at any specified salinity, and by about 20% over the salinity range 0-35 for any specified temperature (Wanninkhof, 1992). By contrast Sc changes by only a few percent over the salinity range 0-35, but it decreases approximately 3-fold between 0°C and 20°C (Wanninkhof, 1992). Hence temperature in particular is important in defining both ΔC and k_w , and knowledge of the thermohaline structure of a water body therefore has important implications for quantifying gas exchange.

Strong vertical and lateral gradients in salinity and temperature are characteristic features of coastal shelves and estuaries (e.g.; Atkinson *et al.*, 1987; Otto *et al.*, 1990; Hill *et al.*, 1994; Simpson, 1994; Gibbs *et al.*, 2000), and this complicates estimating ΔC in particular. A prime example is the use of coastal research vessels to collect "surface" water samples, typically through a hull-mounted inlet at ≥ 2 m depth, or by CTD with similar minimum depth constraints. In the case of strong vertical stratification the water column structure close to the air-water interface may not be adequately resolved by such sampling, leading to significant error in estimating gas fluxes. Similarly, lateral variability complicates integrating ΔC over large areas. Although surface microprofilers have been developed for the high resolution profiling of temperature and salin-

ity close to the air-water interface (e.g. Ward and Minnet, 2002), these instruments are not routinely available and they may prove impractical for use in large, laterally inhomogeneous systems due to time constraints.

Such improved instrumentation has nevertheless contributed to a better understanding of the fine thermohaline structure close to the air-water interface (Shay and Gregg, 1986; Brainerd and Gregg, 1993; Ward and Minnet, 2002). This region is not continuously mixing; solar heating coupled with evaporation/precipitation can result in strong diurnal signals in temperature and salinity, especially at low wind speeds, with the thermal effects being most important. The result can be a daytime near-surface layer actively mixing with a diurnal thermocline below, or thermal stratification to the surface (MacIntyre *et al.*, 2002a, b). The consequent confinement of surface generated turbulence may lead to large vertical gradients in dissolved gases, revealing an important link between thermohaline structure, wind speed and gas exchange. During GasEx-98 in the North Atlantic, under calm conditions (wind speed $< 2 \text{ m s}^{-1}$) and strong insolation a diurnal thermocline of up to several K was established across the upper 0.5 m of the water column, accompanied by increased surface salinity through evaporation (Soloviev *et al.*, 2002). Due to the stable stratification, dissolved O_2 losses through air-sea gas exchange were not replenished from below by turbulent mixing (Soloviev and Lukas, 1997) hence near-surface O_2 supersaturation fell by $\sim 50\%$ (Soloviev *et al.*, 2002). It is only when the near-surface temperature gradient begins to weaken through net heat export that turbulent eddies are able to bring deeper waters to the surface and reduce the vertical contrast in dissolved gases. In such situations obtaining ΔC from measurements either below the surface layer or within the surface layer during the early morning or late evening will overestimate the daily gas flux. Soloviev *et al.* (2002) showed that ignoring the diurnal mixed layer dynamics gave gas exchange flux errors $\sim 30\%$ at low wind speeds for open ocean sites, decreasing to a few percent at higher wind speeds. For supersaturated gases such as O_2 the temperature dependence of α increases the degree of saturation, enhancing the effect of the diurnal cycle on gas exchange, whereas for undersaturated gases such as CO_2 , the degree of saturation and the effect of the diurnal cycle on gas exchange are suppressed. Further modifications to surface layer gases may occur through temperature enhancement of chemical reactions and/or bacterial processes (Panin *et al.*, 2002).

Importantly, the diurnal cycle of surface heat gain and loss can be a stronger control of gas exchange than turbulence related variables. During seasonal stratification of an Amazonian floodplain lake the upper mixed layer deepened from $\sim 0.5 \text{ m}$ during daytime to $\sim 6 \text{ m}$ during the night, even though wind speeds were higher during the day (Engle and Mellack, 2000). At this location gas fluxes are about a factor of five higher at sunrise and sunset than at noon (Crill *et al.*, 1988). MacIntyre *et al.* (2002a) investigated the relative importance to gas exchange of wind speed and convective motions due to heat loss for a tropical lake. They examined diurnal variations in the shear and convective velocity scales, respectively u_* and w_* .

$$u_* = (\tau/\rho)^{1/2} \quad (20)$$

$$w_* = (Bh)^{1/2} \quad (21)$$

where B is the buoyancy flux and h is the depth of the actively mixing layer.

Wind speeds $> 8 \text{ m s}^{-1}$ ($u_* > 0.008 \text{ m s}^{-1}$) did not cause mixed layer deepening, and indeed on one occasion rapid shoaling was observed for a 7 m s^{-1} wind. Mixed layer deepening only occurred when the lake began losing heat, i.e. when w_* exceeded 0.003 m s^{-1} . This was in late afternoon, with wind speeds $\sim 4\text{--}6 \text{ m s}^{-1}$ ($u_* 0.004\text{--}0.007 \text{ m s}^{-1}$). During the night w_*/u_* was $\sim 2\text{--}3$, highlighting the importance of heat loss to gas exchange. Although gas exchange due to heat loss will be impor-

tant in all stratified waters, in sheltered fetch limited coastal areas such as embayments it may be especially relevant.

An additional consideration is the existence of a characteristic temperature gradient, Δ , across the aqueous sub-layer itself due to net heat transfer between the atmosphere and the water surface, resulting in a "cool skin", hence day length and cloud cover are important controlling variables (Schluessel and Soloviev, 2002). Although the basic physics of the cool skin is well established (Saunders, 1967; Fairall *et al.*, 1996) its direct measurement (by infrared radiometry) is complicated by sensor stability and calibration errors (Fairall *et al.*, 1996). Models have therefore been developed to relate skin temperature to that of bulk water (Fairall *et al.*, 1996; Castro *et al.*, 2003). Direct cool skin measurements by infrared radiometry in Californian coastal waters gave a typical thickness $\sim 200 \mu\text{m}$ for wind speeds $\sim 1\text{--}2 \text{ m s}^{-1}$, decreasing to $\sim 20\text{--}30 \mu\text{m}$ wind speeds $> 7 \text{ m s}^{-1}$ (Hanafin and Minnet, 2002).

In the open ocean Δt is usually $\sim 0.1\text{--}0.5 \text{ K}$ (e.g. Schluessel *et al.*, 1990; Wong *et al.*, 1995; Fairall *et al.*, 1996). For wind speeds $< 6 \text{ m s}^{-1}$, Δt shows significant variability but beyond this a mean "cool skin" $\Delta t \sim 0.14 \text{ K}$ is common, with no evidence of a wind speed dependence above 10 m s^{-1} (Donlon and Robinson, 1997; Donlon *et al.*, 1999). Presumably turbulent heat transport forced by surface winds governs heat transport at high wind speeds whereas below 6 m s^{-1} , molecular and convective heat transport both become dominant (Donlon *et al.*, 1999). Persistence of the thin skin at high wind speeds reflects heat transport by conduction even when the surface renewal frequency is high (Hanafin and Minnett, 2002). This is in contrast to earlier work that proposed its disappearance beyond a wind speed of 8 m s^{-1} (e.g. Katsaros, 1980).

Values of Δt approaching 1 K are not uncommon (Van Scoy *et al.*, 1995) and 1.5 K has been observed during high insolation (Donlon *et al.*, 1999). Although changes in α are small for such temperature differences, changes in Sc are greater (Wanninkhof, 1992). By correcting global ocean CO_2 uptake for the cool skin effect, Robertson and Watson (1992) revised the ocean sink for CO_2 upward by $\sim 0.7 \text{ Gt C yr}^{-1}$. This was later revised to $\sim 0.17\text{--}0.35 \text{ Gt C yr}^{-1}$ (Van Scoy *et al.*, 1995), equivalent to $\sim 8\text{--}16\%$ of the total ocean CO_2 sink (Gloor *et al.*, 2003).

It follows that the skin effect will always be superimposed upon the fine temperature structure below the aqueous boundary, further complicating the estimation of ΔC . During night time for example, the uppermost 0.5 m or so of the water column may be well mixed, but have a cool skin. In contrast during daytime the surface layer may be warmed through insolation but still maintain a cool skin if the absorption of short-wave radiation by the aqueous boundary is insufficient to overcome its heat loss by sensible and latent heat fluxes. In this case, the depth at which the bulk water temperature is recorded can have implications for both the apparent sign and the magnitude of Δt (Donlon *et al.*, 1999; Ward and Minnet, 2002).

Large horizontal and vertical salinity and temperature gradients arise through various other mechanisms in coastal waters. In shelf seas tidal exchange with adjacent water bodies typically induces strong frictional stresses that in combination with wind shear and the interaction of tidal currents with the seabed, gives rise to vigorous water column mixing. Where the water column is relatively shallow it may be permanently well mixed, but in deeper waters, especially where tidal and or wind shear is relatively weak, insolation can cause strong seasonal stratification, such as in the northern North Sea during summer (Otto *et al.*, 1990; Simpson, 1994). In estuaries large variations in salinity structure arise through the interaction of freshwater inputs with tidal currents and wind stress (Geyer, 1997). Where river discharge is dominant strong stratification can result, and this may be further complicated by lateral and temporal variability (e.g.

Atkinson *et al.*, 1987). Similarly in fjords, a combination of low rates of tidal exchange and buoyancy from runoff or precipitation commonly results in a temporally persistent, low salinity surface layer, typically ~ 1m deep (Kaartvedt and Svendsen, 1990; Gibbs *et al.*, 2000).

Where seasonal stratification is pronounced, depletion of the mixed layer inventory of supersaturated gases through air-water exchange can be much greater than for the case of diurnal stratification (Soloviev *et al.*, 2002). If mixed layer gas concentrations are driven rapidly towards atmospheric equilibrium, there are clear implications for estimating seasonal gas budgets and air-sea fluxes based on limited temporal sampling. Winds, convection due to surface heat loss, and upwelling all act to disrupt stratification and thereby modify dissolved gas distributions. In a study of the effect of wind driven upwelling on the seasonal cycle of thermal stratification and water column mixing along the Galician coast (Casas *et al.*, 1997), summer upwelling initiated the mixing of water masses with contrasting levels of preformed nutrients, stimulating primary productivity (Estrada, 1984; Casas *et al.*, 1997) and presumably resulting in enhanced gas concentrations in surface waters. Large-scale upwelling of dissolved biogases and its effect on seasonal gas exchange in coastal waters is well documented (e.g. Upstill-Goddard *et al.*, 1999; Bange *et al.*, 2001). On the other hand, winds blowing onshore push outer shelf waters toward the coast and if this occurs following a period of upwelling, a convergence front can result in mid-shelf (Castro *et al.*, 1994), leading to downward export of dissolved gases to deeper water.

Rates of gas exchange, J , between the mixed layer and deeper waters can be estimated from

$$J = K_z dC/dz \quad (22)$$

where dC/dz is the dissolved gas gradient and K_z is the vertical eddy diffusivity.

K_z can be derived by several methods, including microstructure profiling (e.g. Wüest *et al.*, 1996), measuring tracer distributions (e.g. Benitez-Nelson *et al.*, 2000; Law *et al.*, 2001), and modelling (e.g. Zervakis *et al.*, 2003).

4.6 Rainfall

It has been shown that the rate of air-water gas exchange can increase measurably during precipitation (Ho *et al.*, 1997, 2000; Bock *et al.*, 2002; Frost and Upstill-Goddard, 2002). In the laboratory k_w scales with the kinetic energy flux (KEF) to the water surface supplied by the raindrops, which leads both to increased turbulence and enhanced bubble entrainment (Ho *et al.*, 1997; 2000). Ho *et al.* (2000) examined the relative importance of these two processes in the laboratory and found gas exchange due to bubble entrainment to increase both with the rainfall rate and the raindrop size. Although in a real rainfall event the relationship between individual drop sizes and their frequencies is likely to be complex, in general larger raindrops penetrate more deeply. Hence they generate larger bubbles with longer residence times, which maximizes the potential contribution to gas exchange. Nevertheless, Ho *et al.* (2000) showed that turbulence effects dominate; the maximum enhancement to k_w through bubble entrainment was only ~ 20% of the total and was greatest for low solubility gases.

On first inspection enhanced gas exchange due to rainfall might be expected to be especially important in coastal regions that are generally sheltered from prevailing winds. However in reality the situation may be somewhat more complex than this because of precipitation induced changes to sea surface physical properties. These include stabilization effects arising from decreased near-surface salinity, enhanced

surface mixing, the additional heat flux due to rain versus surface temperature differences, changes in the air-to-sea momentum flux, and the damping of short gravity waves (Schluessel *et al.*, 1997).

For low rain rates at low wind speeds, free convective forcing of gas exchange (Soloviev and Schluessel, 1994) may be suppressed by rain induced density stratification. Only when the rain rate and/or the wind speed exceeded threshold values would the surface turbulence be sufficient to overcome the stratification (Green and Houk, 1979), but it remains unclear what are the appropriate threshold values (Ho *et al.*, 2000). Moreover the combined effect of wind and rain on k_w is not well known. Frost and Upstill-Goddard (2002) attempted to isolate rainfall control of k_w at a small lake by removing control of k_w due to wind speed, but they derived only a weak correlation between their corrected k_w 's and the rain rate. This was due in large part to practical sampling problems (Frost and Upstill-Goddard, 2002), but also to the implicit assumption of a straightforward relationship between the relative fractional contributions to k_w from rainfall and wind speed. Increased wind stress at the water surface due to momentum transfer through rain is well known (Caldwell and Elliott, 1972), and this can shift the breaking of small waves to those with shorter wave length, due to enhanced surface wind drift currents (Schluessel *et al.*, 1997). Hence the combined effect of rain and wind speed on gas exchange is unlikely to be a simple linear addition of their effects individually.

The effect of rainfall on the cool skin has been investigated through surface renewal modelling corroborated by field data (Schluessel *et al.*, 1997). Decreased periods of surface renewal due to rainfall were followed by additional, rain-induced surface cooling ~ 0.1 K. For rain rates < 5 cm hr⁻¹ the mean temperature difference across the cool skin was not completely destroyed, and a freshwater skin with a salinity difference > 4 was established under strong rainfall (Schluessel *et al.*, 1997).

4.7 Surfactants

Suppression of k_w by surfactants is well known (Goldman *et al.*, 1988; Frew, 1997; Bock *et al.*, 1999; Frew *et al.*, 1990; 2002) and is effected through the modification of surface hydrodynamics (Tsai, 1996, 1998; McKenna and McGillis, 2004). By introducing a finite interfacial stress in the plane of the air-water interface surfactants create a highly dissipative viscous boundary and consequent flow damping. The number of eddies impacting the interface decreases substantially, reducing surface divergence and vorticity, hence surface renewal weakens and the turbulent length scale increases (McKenna and McGillis, 2004). The result is an increased aqueous sub-layer depth and a decreased k_w , consistent with surface renewal theory. By contrast, turbulent motions below the interface are unaffected (McKenna and McGillis, 2004). In regions of high surfactant concentration, k_w parameterisations based on bulk turbulence measurements may therefore be erroneous.

Both soluble and insoluble surfactants occur in natural waters, and both are effective in suppressing k_w (Goldman *et al.*, 1988; Frew *et al.*, 1990; Bock *et al.*, 1999). A maximum 60% decrease in k_w was reported for a circular wind flume covered with soluble surfactant (Bock *et al.*, 1999) and Frew (1997) reported up to 90% k_w suppression in similar experiments. In contrast Goldman *et al.* (1988) found gas exchange reductions $\sim 10\%$ for oceanic waters and $\sim 50\%$ for coastal waters for a turbulent interface without wind shear, and Frew *et al.* (1990) found reductions ~ 5 -50% for various phytoplankton exudates.

In the oceans polysaccharides derived from phytoplankton are the major surfactant source (Zutic *et al.*, 1981; Gasparovic *et al.*, 1998), although lipids and proteins can also be important (Liss and Duce, 1997). Due to their biological source surfactant

concentrations broadly correlate with primary productivity and hence show large seasonal variation (Zvonaric and Zutic, 1979). Goldman *et al.* (1988) were first to demonstrate a general decrease in k_w between the open ocean and coastal waters as productivity increased inshore. Corresponding increases in surfactant concentrations are typically an order of magnitude although there is substantial small-scale spatial variability, an example being the occurrence of intense surface slicks along frontal boundaries (Frew *et al.*, 2002).

Data on surfactant distributions are rather sparse, and this has inhibited efforts to quantify the surfactant effect on k_w globally. Therefore using satellite-derived chlorophyll-*a* as a surrogate for surfactants has been proposed (Asher, 1997). Refining this approach by extension to related satellite measurements may have potential for mapping surfactant in the open ocean (Liu *et al.*, 2000; Lin *et al.*, 2002), but for coastal waters this approach will almost certainly be compromised by additional surfactant inputs from industrial and urban sources (Cincinelli *et al.*, 2001; Zoller and Hushan, 2001; Petrovic *et al.*, 2002). While the effects of some such sources are rather localised (Temara *et al.*, 2001) others can be traced further offshore (Bester *et al.*, 2001). Another complication is the possibility of transformations in surfactant composition resulting from strong physicochemical gradients, for example in estuaries. Ahel and Terzic (2003) observed strong biological removal of an anthropogenic aromatic surfactant during estuarine mixing, with maximum reactivity in the region of the freshwater-saltwater interface. In general estuarine surfactant removal should reflect the balance of inputs and removal kinetics and residence time considerations. For a constant surfactant source, resultant fluxes to the coastal ocean would therefore likely be highest in winter.

During experiments in a wind-wave facility (Broecker *et al.*, 1978) continuous, insoluble surfactant films began to be disrupted beyond a threshold wind speed of 13 m s^{-1} , presumably due to wave breaking. In practice the actual threshold value will likely differ in the environment and be related to surfactant concentration (Frew, 1997; Bock *et al.*, 1999). On the other hand it has been proposed that insoluble surfactants might be reabsorbed to the sea surface following film disruption (Tsai and Liu, 2003). If so, under some circumstances k_w might be suppressed by surfactants even at high wind speeds with breaking waves, thereby offsetting to some extent the expected abrupt increase in k_w due to wave breaking (Asher *et al.*, 1996; Tsai and Liu, 2003).

In direct contrast to the behaviour of surfactants during wave breaking, a study of the surfactant response to rain drop impacts showed that in the absence of surfactant losses by droplet ejection due to splashing, insoluble surfactant films reformed immediately following drop impact, whereas soluble surfactant films showed permanent disruption and surfactant loss (Saylor, 2003).

Unsurprisingly therefore, there is no unique relationship between k_w and surfactant concentration, or between k_w and either wind speed or capillary wave slope for surfactant covered waters. Frew *et al.* (2002) derived a power law dependence of k_w on surface active organic matter for the California Bight. Although these authors also noted relationships between surface active organic matter, wind speed and capillary wave slope that implied complex interactions between them, in laboratory experiments Saylor and Handler (1999) could find no apparent relationship between surfactant concentration and capillary waves; when k_w was plotted as a function of the mean square capillary wave slope, the presence of surfactants was found to only negligibly affect gas exchange. Based on available experimental data, Asher (1997) proposed a linear relationship between k_w and U_{10} in the presence of surfactant, for $U_{10} < 12.5 \text{ m s}^{-1}$, whereas Tsai and Liu (2003) used a power curve describing the rate of decrease of k_w with wind speed to adjust the "rough surface" and "smooth-surface"

regimes of Liss and Merlivat (1986) for surfactant effects. Figure 3 compares the k_w vs U_{10} curves for these two studies with the parameterizations of Liss and Merlivat (1986) and Wanninkhof (1992). The differences between the curves of Asher (1997) and Tsai and Liu (2003) highlight the uncertainties inherent in surfactant based scaling of k_w .

Notwithstanding these uncertainties, Tsai and Liu (2003) evaluated the role of surfactants in modifying the global air-sea CO_2 flux using $\Delta p\text{CO}_2$ climatologies (Takahashi *et al.*, 1997), satellite derived U_{10} and sea surface temperatures, and chlorophyll-*a*. Using an upper limit for chlorophyll-*a* that approximated the lower limit of primary productivity in coastal waters, their calculated suppression of CO_2 draw down exceeded their calculated suppression of CO_2 efflux. This result was not a physical effect of the gas exchange process but instead reflected the relationship between $p\text{CO}_2$ draw down and primary productivity, and by implication surfactant concentration. In a qualitative sense this finding may be especially relevant to coastal waters that experience both $p\text{CO}_2$ draw down and CO_2 efflux, depending on season (e.g. Frankignoulle *et al.*, 1998). Modifying CO_2 exchange fluxes to take account of the asymmetry in seasonal surfactant concentrations might therefore have important implications for the annual biogas budgets of coastal waters.

4.8 Microscale wave breaking

Microscale wave breaking, the breaking of small-scale waves without air entrainment (Banner and Phillips, 1974), is a widespread phenomenon that is initiated at wind speeds well below those associated with whitecaps (Melville, 1996). Microbreaking waves evolve from gravity-capillary waves and are typically $\sim 0.1 - 1\text{m}$ in length, with amplitudes $\sim 0.01-0.1\text{m}$ (Zappa *et al.*, 2001; Siddiqui *et al.*, 2002). In addition to their small scale, microbreaking waves tend to have a random spatio-temporal distribution (Siddiqui *et al.*, 2002), making them difficult to detect and quantify.

Jähne *et al.* (1987) first proposed the control of k_w at low to moderate wind speeds by enhanced surface renewal in the turbulent wakes of microbreaking waves. Csanady (1990) subsequently defined k_w in terms of the fractional surface area ϕ covered by surface divergence due to microbreaking

$$k_w = \phi u_* \gamma Sc^{-1/2} \quad (23)$$

where γ is a dimensionless constant.

Developments in the use of passive infrared (IR) imagery (Jessup *et al.*, 1997) have enabled the quantification of microbreaking induced surface renewal in the laboratory (Zappa *et al.*, 2001; Siddiqui *et al.*, 2002). Because the IR signal is a direct result of the renewal process that affects the gas flux it offers advantages over methods based on the use of wave statistics such as slope. Zappa *et al.* (2001) defined k_w in terms of the fraction of the surface area A_B in which the aqueous sublayer is renewed in the wakes of microbreaking waves

$$k_w = A_B k_B + (1 - A_B) k_{NB} \quad (24)$$

where k_B and k_{NB} are respectively, the gas transfer velocities inside and outside A_B .

In laboratory experiments A_B increased from ~ 0.25 to ~ 0.4 for windspeeds increasing from 4.2 to 8.3 m s^{-1} , but was suppressed by added surfactant (Zappa *et al.*, 2001). Fulfilling the condition $k_B \gg k_{NB}$, k_w and A_B were linearly correlated, with the line of best fit passing through the origin irrespective of the presence of added surfactant (Zappa *et al.*, 2001). In subsequent experiments Zappa *et al.* (2002) showed k_B to

increase from $\sim 0.25 k_w$ for $A_B \ll 0.05$ to $\sim 0.75 k_w$ for $A_B \sim 0.4$. These studies together confirm the proposal of Csanady (1990) and give strong support to the notion that microscale breaking is a fundamental control of k_w for low to moderate winds.

Microscale wave breaking has long been implicated in observed increases of local wave slope during laboratory experiments (Banner, 1990). The degree of correlation between mean square wave slope ($\langle S^2 \rangle$) and k_w is a measure of wave stability and hence turbulence (Jähne *et al.*, 1987), and it has been suggested that the effects of surfactants are incorporated within $\langle S^2 \rangle$ (Frew, 1997). Zappa *et al.* (2002) found a mean contribution to $\langle S^2 \rangle$ by microscale wave breaking $\sim 30\%$. Provided that z_o associated with microscale wave breaking always contributes significantly to $\langle S^2 \rangle$, this mechanism could explain why $\langle S^2 \rangle$ is observed to correlate to k_w for a range of surfactant concentrations (Frew, 1997; Bock *et al.*, 1999; Zappa *et al.*, 2001, 2002).

Winds interacting with surface currents travelling in the opposite direction can lead to enhancements of microscale wave slope, thereby increasing the frequency of microscale wave breaking (Long and Klinke, 2002). Given the importance of microscale wave breaking to gas exchange (Zappa *et al.*, 2001, 2002) this is likely to be especially important in coastal waters with strong tidal currents. Hence for any specified wind speed and direction, gas exchange rates might differ significantly between ebb and flood tides.

4.9 Bottom driven turbulence

An important role for bottom driven turbulence in shallow streams, rivers and channels has long been recognised (O'Connor and Dobbins, 1958; Langbein and Durum, 1967; Jackson, 1976; Kawanisi and Yokosi, 1994; Longuet-Higgins, 1996), but its contribution to surface renewal and hence gas exchange in estuaries and on coastal shelves is by contrast, not well studied. In shallow streams and rivers surface turbulence occurs through bottom stress and gas exchange is a function of water depth and flow velocity (O'Connor and Dobbins, 1958; Langbein and Durum, 1967). Given an optimal combination of tidal current velocity, water depth and wind speed, predictive models show that turbulence due to bottom stress might also contribute to surface renewal and gas exchange in tidally active coastal waters (Cercio, 1989).

A synthesis of predictive equations based on U_{10} and bottom turbulence in estuaries concludes that wind stress dominates turbulence for all systems > 10 m deep or with $U_{10} > 8 \text{ m s}^{-1}$ but that for all other situations either wind or bottom stress may dominate turbulence (Raymond and Cole, 2001). These authors also showed estuaries to have a higher mean k_w than either lakes or the oceans, consistent with the available tracer estimates of k_w in estuaries (Clark *et al.*, 1994; Carini *et al.*, 1996). Although this may to some extent reflect the contribution to gas exchange from bottom driven turbulence, the analysis also incorporated measurements derived with floating domes, which tend to return higher mean values of k_w than do other methods (Raymond and Cole, 2001).

Zappa *et al.* (2003) provide the most conclusive evidence to date for an important contribution from bottom driven turbulence to gas exchange in estuaries. Using passive IR imagery of skin temperatures they examined the evolution of surface turbulence over a tidal cycle in the Parker River/ Plum Island Sound estuary. During low tidal flow the skin layer was relatively smooth, surface features due to upwelling were ~ 1 cm across with renewal timescales ~ 10 – 100 s. In contrast, Zappa *et al.* (2003) observed active and energetic disruption of the surface layer during peak tidal flow; thin cool veins of convergence separated larger warmer areas of strong upwelling with spatial scales ~ 0.1 – 1 m and rapid renewal times ~ 0.1 s. When tidal velocity increased from 0.2 m s^{-1} to 0.8 m s^{-1} the rate of surface renewal increased five fold (Zappa *et al.*,

2003). At low wind speed ($1.9 \pm 0.5 \text{ m s}^{-1}$), k_w increased three fold between low and high tide, co-varying with tidal speed and the rates of surface renewal and turbulent dissipation. Maximum rates of surface renewal during peak tidal flow ($\sim 1.6 \text{ s}^{-1}$) were comparable to those observed in laboratory experiments or in the oceans at low wind speeds (Haussecker *et al.*, 1995; Zappa *et al.*, 2001), whereas maximum rates during low tidal flow ($\sim 0.3 \text{ s}^{-1}$) were much lower than strongly wind forced laboratory values (Zappa *et al.*, 2001).

Bottom generated turbulence has also been observed in tidally active waters on coastal shelves. Turbulent bursts away from the seabed, so-called “boils”, have been estimated to reach 25% of the forcing current speed (Heathershaw, 1974). Impingement of these features on the water surface has been demonstrated numerically (Tsai, 1998), in the laboratory (Kumar *et al.*, 1998) and in the field (Nimmo-Smith *et al.*, 1999). Nimmo-Smith *et al.* (1999) carried out surface sonar and video imaging in a flat-bottomed, 45 m deep, tidally active region of the southern North Sea 54 km offshore. Under strong tidal flow they identified surface eddies of upwelled water of mean diameter $0.93 \pm 0.22H$, where H is the water depth, covering $\sim 20\%$ of the sea surface. Characteristic discoloration was consistent with the resuspension of bottom sediment. In contrast during low tidal flows with wind speeds $> 4 \text{ m s}^{-1}$ these features were undetectable (Nimmo-Smith *et al.*, 1999). Similar features in fast flowing shallow rivers and narrow channels are observable at low winds due to their steepening effect on short surface gravity waves (Jackson, 1976; Longuet-Higgins, 1996). If common in tidal shelf seas, as seems likely (Nimmo-Smith *et al.*, 1999), surface boils could be significant contributors to surface renewal and hence gas exchange.

Based on the estuarine data of Zappa *et al.* (2003), the use of empirical relations for k_w that do not take adequate account of the role of bottom driven turbulence (e.g. Raymond and Cole, 2001) may lead to underestimates of air-sea gas exchange in coastal waters at low wind speeds. Further complications are likely where changes in wind direction impact near-surface shear modulated by tidal currents, or where land morphology leads to the formation of additional eddies that contribute to surface renewal. Furthermore, in regions that are seasonally or even permanently stratified bottom driven turbulence may be periodically or permanently prevented from reaching the surface.

4.10 The biology of the sea-surface microlayer

Recent interest has focused on a possible biogeochemical role for the sea surface microlayer in air-sea gas exchange; this is a region a few tens of μm deep at the air-water interface that is chemically and microbiologically distinct from the bulk water below (Hardy and Apts, 1984; GESAMP, 1995; Liss and Duce, 1997). Substantial bacterial enrichment of the microlayer (the so-called “bacterioneuston”) is well documented (e.g. Kjelleberg *et al.*, 1979; Hardy, 1982; Hardy and Apts, 1984) and evidence suggests it to comprise a distinct taxa (Norkrans, 1980; Franklin, 2001). Microlayer enrichments of DMS are reported (Yang, 1999; Yang *et al.*, 2001) and the bacterioneuston has been implicated in the microlayer consumption of atmospheric CO (Conrad and Seiler, 1982; Conrad *et al.*, 1982) and in the production of CO₂ (Hardy, 1973; Hardy and Apts, 1989; Garabetian, 1990). Nevertheless, there have only been three direct studies of bacterioneuston related gas exchange to date. Conrad and Seiler (1988) directly estimated invasive and evasive k_w for CH₄, CO, N₂O and H₂ using a free-floating flux box in the tropical Atlantic Ocean. They found significant invasion-evasion mismatches in k_w for similar conditions of turbulence. With a similar approach, Frost (1999) found a corresponding mismatch of up to 8% for CH₄ in the coastal North Sea off the north-eastern UK coast. Both sets of results were interpreted to reflect microbial gas consumption by the bacterioneuston, the only plausible gas sink in the experiments (Conrad and Seiler, 1988; Frost, 1999). Upstill-Goddard *et al.*

(2003) measured “apparent k_w ’s” for CH_4 , N_2O , and SF_6 (all normalised to $Sc = 600$) during invasive and evasive gas exchange in a laboratory gas exchange tank variously augmented with methanotrophs, or with bacterial cultures devoid of methane mono-oxygenase activity. Experiments with added methanotrophs showed enhancements of k_w for $\text{CH}_4 \sim 12 \pm 10\%$ relative to N_2O or SF_6 , consistent with active metabolic control of CH_4 exchange by the bacterioneuston (Upstill-Goddard *et al.*, 2003). Importantly, coastal regions are characterized by high productivity and hence high bacterial numbers, hence the associated bacterioneuston may be especially well developed. Combined with high ambient levels of dissolved trace gases, this could make the coastal zone an especially important region for trace gas processing by the bacterioneuston. Nevertheless coastal data are currently restricted to a few CH_4 measurements by Frost (1999) in the North Sea.

4.11 Bubble ebullition

Direct gas efflux to the atmosphere via bubble ebullition from sediments can be an important mechanism for air-sea CH_4 exchange, especially in coastal regions. Although methanogenesis is inhibited by sulphate reducers, in coastal sediments the flux of metabolizable organic carbon is commonly high enough that some survives burial through the zone of sulphate reduction, fuelling methanogenesis. (e.g. Wever *et al.*, 1998). When the resulting CH_4 concentrations exceed CH_4 solubility, bubbles form and may be periodically released to rise to the water surface. Air-sea gas exchange via this process is necessarily excluded from routine flux estimates based on (2), even though for CH_4 it could exceed the efflux due to diffusion/turbulent exchange (Ostrovsky, 2003). Besides CH_4 , bubble ebullition may also be significant for CO_2 , H_2S , COS and CS_2 and CH_3SH , via “scavenging”, i.e. by diffusional exchange across the bubble surface (Roden and Tuttle, 1992; Chanton and Whiting, 1995; Leifer and Patro, 2002). Martinova (1998) found that the relative gas compositions of bubbles may be related to the total bubble gas flux; as this increased the relative proportions of CH_4 and CO_2 increased while N_2 and O_2 both declined.

Unfortunately, few studies have directly assessed gas ebullition from sediments (e.g. Whiting and Chanton, 2001; Leifer and Patro, 2002; Ostrovsky, 2003), hence the detailed processes affecting gas ebullition and consequent air-sea exchange remain poorly quantified.

Even so, sediment perturbation, for example through increased sediment shear stress due to bottom currents (Keller and Stallard, 1994; Joyce and Jewell, 2003), and changes in atmospheric pressure (Mattson and Likens, 1990; Dove *et al.*, 1999) or hydrostatic pressure are clearly important. In tidally influenced regions, discrete pulses of ebullition have been observed at low tide associated with hydrostatic pressure changes $\sim 5\text{--}7\%$ (Martens and Klump, 1980; Martens and Chanton, 1989). In addition to such temporal asymmetry in ebullition rates, significant lateral asymmetry can also arise from the relatively larger excursions in hydrostatic pressure in comparatively shallow locations (Ostrovsky, 2003). A positive relationship between ebullition rates and wind speed has also been observed for shallow lakes (Keller and Stallard, 1994). Temperature is also implicated in the control of ebullition rates (e.g. Zimov *et al.*, 1997), through its control of gas solubility and rates of methanogenesis, as is seasonality of organic matter supply (Martens *et al.*, 1998). Bubble hydrodynamics and the physical properties of the water column impact subsequent gas transport to the air-water interface (Leifer and Patro, 2002). Contamination by surfactants is a major control of bubble hydrodynamics that directly impacts bubble rise velocity. The roles of specific surfactant properties, including absorption/desorption, diffusion coefficients and solubility are treated quantitatively by Leifer and Patro (2002). Water depth is also important. In coastal waters ~ 3 m deep, minimal bubble dissolution has been observed during migration to the surface (Martens and Klump, 1980), with corre-

4.12 Summary comments

spondingly small changes in bubble gas compositions (Martens and Chanton, 1989). In contrast for waters deeper than 5 m Joyce and Jewell (2003) found that only a minor fraction of the CH_4 released by bubble ebullition from lake sediments reached the air-water interface.

Significant progress towards understanding of the important controls on air-water gas transfer has been made during the past several years, and these advances are continuing. One thing that has become very clear is that the environmental controls on k_w are strongly interdependent, and hence variable in their impact. Consequently, developing a full and unique parameterization of k_w currently remains elusive, and whether or not this will prove to be achievable in the longer term is uncertain. This argument applies equally to coastal waters and the wider marine system.

Notwithstanding these limitations it is nevertheless encouraging that the synthesis of Nightingale *et al.* (2000) for example, which is based on parameterizing k_w solely in terms of U_{10} , is able to largely reconcile tracer measurements of k_w vs U_{10} from the North Sea, Georges Bank, and the West Florida Shelf, accounting for 80% of the total variance in the combined data set. Further refinements beyond this will demand substantial additional effort, and it remains to be seen whether this parameterization applies equally well in other areas.

For estuaries there have been recent advances towards understanding the roles of bottom driven turbulence and tidal state in gas transfer (Clark *et al.*, 1994; Raymond and Cole, 2001; Zappa *et al.*, 2003).

Regarding ΔC the problem is comparatively straightforward because this parameter can be directly measured "instantaneously", in contrast to k_w . Obtaining accurate concentration fields for dissolved gases is a question of suitable spatial and temporal coverage, although in practice this can represent a significant challenge.

In conclusion, the effort required to refine existing biogas flux estimates from coastal waters is potentially large. Although some of the more important aspects have been identified above, cost or logistical difficulties may in practice compromise such effort to varying degrees. Perhaps the most important step forward in the immediate future would be a better appreciation of the uncertainties associated with trace gas flux estimates. Such uncertainties are rather poorly constrained at present. However, through advances in some aspects of gas exchange described above there now exists an opportunity for this situation to improve.

•5. Trace gases in the coastal zone

One of the most important contrasts between the open ocean and the coastal zone is the dominance of terrestrially derived material in the latter. On a global scale, approximately 40% of the freshwater and particulate matter entering the coastal zone is transported by the ten largest rivers (Chen, 2002).

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 are quite complicated and change from primarily stream driven exchange in the upper estuary to wind driven exchange in the mouth (Middelburg *et al.*, 2002). 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 are significant for the exchange of gases between the air and the sea through the activities of biological organisms, which are more available in coastal areas than in the open ocean. Correlations have been established between the trace gas distributions and the temperature, pigments, and chlorophyll to provide a picture of the source-sink cycle for these gases. These correlations are quite clear in the coastal zone.

5.1 Carbon oxides

Among the trace gases, carbon dioxide (CO₂) is of major importance because it contributes about 55% of anthropogenic greenhouse warming (Mackenzie, 1998). Human activities presently release about 7.7 Gigatons of carbon per year (1 GtC = 1 PgC, 1 Pg = 10¹⁵g) to the atmosphere (Mackenzie, 1998), by fossil fuel burning and change in land use (e.g. deforestation). It is well established that 3.3 GtC year⁻¹ remain in the atmosphere. The ocean behaves as a sink, estimated at 2.2 GtC year⁻¹ and the terrestrial biosphere is often assumed to trap the remaining 2.2 GtC

year⁻¹ (Sarmiento and Sundquist, 1992; Sundquist, 1993; Broecker and Peng, 1998; Mackenzie, 1998). However, this budget does not consider explicitly the CO₂ fluxes in the coastal ocean primarily because it is difficult to include this region in global circulation models and because of a lack of field data on the spatial distribution and temporal variability of the partial pressure of CO₂ (pCO₂), which ultimately determines the direction of its air-sea exchange. Very few data are available in the literature on air-sea CO₂ exchanges in coastal ecosystems, as clearly shown by Figure 4. The aim here is to discuss CO₂ dynamics and related atmospheric budgets in two major European coastal ecosystems: estuaries and continental shelves.

5.1.1 European estuaries

Estuaries are major pathways for the transfer of dissolved and particulate material from the continent to the marine system through rivers. They are extremely dynamic systems usually characterized by strong physico-chemical gradients, enhanced biological activity (both heterotrophic and autotrophic) and intense sedimentation and resuspension. Rivers deliver important quantities of carbon in the form of dissolved inorganic carbon (bicarbonate), particulate and dissolved organic carbon, as well as living organisms to estuaries, but only a modified fraction of each is transferred further to the adjacent shelf and open ocean. Similarly, incoming tides transport marine materials into the estuary, where part of them may be degraded, consumed, transformed or stored. Estuaries consequently act as a modifying filter, their efficiency depending on the component involved and the physical, chemical and biological characteristics of the estuarine system (Wollast, 1983).

Profound changes are observed in the speciation of organic and inorganic compounds in response to these factors, particularly in the European estuaries of the North Atlantic system, which are additionally subject to macro-tidal variations. The tidal regime of these estuaries leads to an increased residence time of fresh water in the estuarine mixing zone and the generation of a turbidity maximum, often with an associated oxygen-depleted zone within which various anaerobic processes may be stimulated (Wollast, 1988). In addition, as a result of supporting the major population centres within their catchments, European estuaries are subject to intense anthropogenic disturbance reflected in elevated loadings of detrital organic matter, nutrients and toxic trace elements. All these features increase the potential for biogenic gas production within estuaries.

Intense respiration of detrital organic matter produces large quantities of dissolved CO₂, inducing partial pressures exceeding 1000 ppm in estuarine waters and generating very high CO₂ fluxes to the atmosphere (Kempe, 1982). The elevated nutrient loading enhances N₂O production within the estuary, via denitrification in the oxygen depleted zones and nitrification. The photoproduction of CO in surface water is stimulated by terrestrially-derived dissolved organic matter transported by the estuaries. Anoxic sediments in the region of the turbidity maximum enhance H₂S and CH₄ production and methylation of various metals, with subsequent diffusion to the water column and volatilization. On the other hand, high primary production may occur either by photosynthesis when turbidity allows sufficient light penetration and chemo-autotrophic processes, for example by nitrifying bacteria. The eutrophic conditions are also highly favourable for the production of DMS and COS.

The European Commission funded a research project BIOGEST (BIOGas transfer in ESTuaries, 1996-1999, <http://www.ulg.ac.be/oceanbio/biogest/>) and the three main objectives were:

- 1- to determine the distribution of biogases affecting climate and atmospheric chemistry in the surface waters of European estuaries.
- 2- to evaluate the fluxes of atmospheric biogases from European estuaries and their

impact on the global budget.

- 3- to understand the major biological processes which are responsible for biogases distributions.

Ten estuaries were investigated (Elbe, Ems, Rhine, Thames, Scheldt, Loire, Gironde, Sado and Douro) in terms of CO₂ distribution and atmospheric fluxes. The seasonal variability (four cruises) was investigated in 3 of these estuaries (Rhine, Scheldt and Gironde).

The main result is that European estuaries act as a significant source of CO₂ to the atmosphere (Frankignoulle *et al.*, 1998) and the flux amounts to between 30 and 60 Tg C per year (1 Tg = 10¹²g), which corresponds to 5 to 10% of the present anthropogenic emission from Western Europe. The proposed values depends however on the surface ratio between the inner estuary and the outer estuary on the shelf.

5.1.2 European continental shelf

The role of continental shelves in the global carbon cycle has been the subject of a few major national and international research programmes (e.g. KEEP, KUSTOS, OMEX, SEEP, SES, TROPICS) but it is not yet clear if these regions act as a sink or as a source of atmospheric CO₂ (Garrels and Mackenzie, 1971; Smith and Mackenzie, 1987; Walsh, 1988; 1989; 1991; Smith and Hollibaugh, 1993; Ver *et al.*, 1994; 1999a; 1999b; Kempe, 1995; Mackenzie *et al.*, 1998; Wollast, 1998). The continental shelf is the site of intense physical and biological processes from which important air-sea gradients of CO₂ can be expected (Mackenzie, 1991), but the air-sea CO₂ exchanges are still poorly known. The causes of these uncertainties are multiple. Firstly, these regions show high variability in time and space that is usually not adequately monitored by sparse or incomplete data sets. Secondly, the budgets proposed in the literature are based on indirect calculations and use different approaches and a variety of experimentally determined processes that yield different conclusions from one author to another, even within the same research programme (SEEP I and II projects). The role of the shelves in the inorganic carbon cycle is uncertain because it results from the integration of production/degradation/export of organic carbon, burial/dissolution of carbonates in the shallow sediment and input of inorganic carbon from rivers and coastal upwellings. The best way to identify these areas as a global source or sink for atmospheric carbon dioxide is to integrate CO₂ fluxes over a complete year, an approach frequently used in open ocean studies (Takahashi *et al.*, 1997).

The European continental shelf is of particular interest because it offers a wide diversity of coastal systems: narrow and very productive areas with major freshwater input (e.g. the North Sea), wide open shelf with important energy and matter exchange with the open ocean (Biscay, Celtic Sea) and finally an upwelling system along the Iberian coast. Hereafter, we summarize the main conclusions from intensive and seasonal CO₂ surveys in areas covering the North Sea, its Southern Bight, the English Channel, the Armorican Sea, the Celtic Sea, the Gulf of Biscay and the Galician Sea (Frankignoulle and Borges, 2001; Borges and Frankignoulle, 1999; 2001; 2002a; 2002b; 2002c; 2003).

The open waters of the Southern Bight of the North Sea behave annually as a sink for atmospheric CO₂ (Frankignoulle and Borges, 2001; Borges and Frankignoulle, 2002a). The estuarine plume (outer estuary) of the Scheldt is the site of two antagonistic effects in terms of CO₂ distribution: on the one hand, the Scheldt provides highly CO₂ over-saturated water and organic carbon, but, on the other hand, nutrient input is likely to induce high primary production which tends to decrease CO₂. The Scheldt estuarine plume is strongly supersaturated in CO₂, except during the spring phytoplanktonic bloom, and, the annual integration of the computed CO₂ fluxes shows that this area

behaves as a net source of CO₂ which accounts for about 20% of the efflux observed in the inner Scheldt (Borges and Frankignoulle, 2002a).

On the open European continental shelf, including the Celtic Sea, the Armorican Sea and the Gulf of Biscay, Frankignoulle and Borges carried out 18 cruises covering most of the area and the four seasons. Their results show that the shelf is a significant sink for atmospheric CO₂ which accounts for about 45% of the North Atlantic Ocean one (Frankignoulle and Borges, 2001). This confirms the "continental shelf pump" hypothesis (Tsunogai et al, 1999), which suggests that continental shelves worldwide could be a net sink of 0.5 to 1.0 GtC.year⁻¹.

However, the work carried out in the English Channel suggests that the continental shelf pump hypothesis is not a universal rule, even for temperate shelf ecosystems. Borges and Frankignoulle (2003) show that the Channel on an annual time scale is neutral from the point of view of atmospheric CO₂ fluxes. This is mainly related to a relatively low export and/or burial of organic carbon (based on literature estimates of new primary production) and intense benthic calcification (that releases CO₂) from extensive brittle star *Ophiothrix fragilis* populations.

Dissolved inorganic carbon dynamics have been extensively studied in the Galician upwelling system (Borges and Frankignoulle, 2001; 2002b; 2002c) and on an annual scale this system is a net sink of CO₂ that is stronger than the adjacent open North Atlantic waters. The only other comprehensive study of air-sea CO₂ fluxes of a coastal upwelling system is off the Omani coast by Goyet et al. (1998). These authors show that this particular coastal upwelling system is a net source of CO₂ to the atmosphere. If the air-sea fluxes computed off the Galician coast are considered representative of the whole of coastal upwelling areas, this would then imply a reduction of only 4% of the "continental shelf pump" as assessed by (Tsunogai et al., 1999). If we assume that the air-sea CO₂ fluxes off the Omani coast by (Goyet et al., 1998) are representative of the whole of coastal upwelling areas, this would imply a 17% reduction of the "continental shelf pump". Although, neither our computations nor those of Goyet et al. (1998) can be regarded as representative of the CO₂ air-sea fluxes for the entirety of coastal upwelling areas, considering the wide range of reported pCO₂ values, they highlight the potential importance of coastal upwelling systems in verifying and evaluating the "continental shelf pump".

5.2 Nitrous oxide and methane

Nitrous oxide (N₂O) and methane (CH₄) are atmospheric trace gases, which, directly and indirectly, influence the present-day climate of the Earth (IPCC, 2001; WMO, 2003). Thus, an assessment of the natural and anthropogenic sources and sinks as well as the formation pathways of N₂O and CH₄ is essential both to understand past Earth's climate variability and to estimate the future development of Earth's climate. The world's oceans including their coastal zones, as natural sources of N₂O and CH₄, play a major role in the global budget of atmospheric N₂O, but only a minor role in the global budget of atmospheric CH₄ (IPCC, 2001). However, measurements of oceanic N₂O and CH₄ are still sparse and the derived emission estimates are associated with large uncertainties (Bange et al., 1994; Bange et al., 1996b; Bates et al., 1996; Nevison et al., 1995; Seitzinger et al., 2000; Suntharalingam and Sarmiento, 2000). The objective here is to give an overview of the distributions of N₂O and CH₄ in European coastal areas and to reassess their emissions to the atmosphere.

N₂O in oceanic environments is mainly formed as a byproduct during nitrification (NH₄⁺ → NO₂⁻ → NO₃⁻) and as an intermediate during denitrification (NO₃⁻ →

$\text{NO}_2^- \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$). In both processes, the yield of N_2O strongly depends on the concentration of dissolved oxygen (O_2). Both processes are microbial and occur in the water column, in the sediments and in the interior of suspended particles. CH_4 is formed during the decomposition of organic material during methanogenesis. Since CH_4 formation requires strictly anaerobic conditions, its formation occurs in the sediments, in the interior of suspended particles or in zooplankton guts during grazing. Additionally, CH_4 is oxidized under aerobic as well as anaerobic conditions in the water column and in the sediments. At the continental shelf CH_4 can be released directly to the water column through mud volcanoes, via groundwater input or seeping at pockmark structures.

The European coastal areas consist of the complete Baltic and the North Seas as well as parts of the Mediterranean Sea (i.e. the Adriatic and Aegean Seas) and the Black Sea, parts of the Northeast (NE) Atlantic Ocean (i.e. the English Channel, the Celtic (Irish) Sea and the Bay of Biscay) and parts of the Arctic Ocean (i.e. the Norwegian and Barents Seas) (Figure 5). Also included in the studies are estuaries, fjords and other systems at the interface between the continental shelf and the terrestrial environment (Figure 6). An overview of the locations of the studies discussed in the text is given in Figure 7 and Figure 8. For details of the environmental settings (i.e. hydrography, biogeochemical conditions etc.) of the marginal seas, estuaries etc. mentioned in the text the reader is referred to appropriate publications and textbooks.

In the literature dissolved N_2O and CH_4 are generally either expressed as a concentration (in nmol L^{-1} or mL L^{-1} as for CH_4 in some cases) or saturation (in %), which is the ratio of the measured gas concentration to the expected equilibrium concentration. The equilibrium concentration in turn depends on the water temperature, salinity, ambient air pressure and the atmospheric N_2O or CH_4 concentration (Weiss and Price, 1980; Wiesenburg and Guinasso Jr., 1979). Thus, a saturation of 100% indicates that the water phase is in equilibrium with the overlying atmosphere. Saturation values <100% indicate undersaturation (i.e. uptake of N_2O or CH_4 into the water phase) whereas saturation values >100% stand for supersaturation (i.e. N_2O or CH_4 release from the water phase to the atmosphere).

5.2.1 Overview: Nitrous oxide

Arctic Ocean

There seem to be no N_2O data available from the coastal areas of the Arctic Ocean.

Baltic Sea

First measurements (during July–September 1977 and May–June 1980) of N_2O in the surface layer (0–0.5m) of the central and northern Baltic Sea were in the range from 79% to 148% (with an average of 123% for the Baltic Proper) indicating that the Baltic Sea was a source of N_2O to the atmosphere (Rönner, 1983). In the well-oxygenated water column below the mixed layer, increasing N_2O concentrations were generally associated with an increase of nitrate (NO_3^-) and a decrease of oxygen (O_2) (Rönner, 1983). However, N_2O concentrations sharply drop down within the oxic/anoxic interface in the deep basins of the central Baltic Sea and remain constant at levels close to zero in anoxic deep waters (Brettar and Rheinheimer, 1991; Rönner, 1983). Based on the observed negative correlation between N_2O and O_2 and the positive correlation between N_2O and NO_3^- , (Rönner, 1983) concluded that in oxygen-rich waters N_2O is produced during nitrification. In contrast, the depletion of N_2O in the anoxic waters of the deep basins of the Baltic Sea is caused by N_2O consumption during denitrification (Brettar and Rheinheimer, 1991; Rönner, 1983).

A seasonal study (five campaigns between 1994 and 1997) in the shallow lagoons of the southern Baltic Sea/western Oder River estuary area (the so-called Bodden waters

with water depths ranging from 0.5 to 8.5 m) revealed saturations in the range from 91% to 312%, with a pronounced maximum at the sampling station near the mouth of the Peene River in March (Bange *et al.*, 1998a). Thus, Bange *et al.* (1998a) concluded that enhanced N_2O concentrations in the Bodden waters were linked to the seasonal peak of the Peene River run off. However, the prevailing cause for the N_2O concentrations in the Bodden waters remained unclear since the enhanced N_2O concentrations could either have been caused directly through input of high riverine N_2O concentrations or indirectly through a high input of NO_3^- which in turn might have fuelled sedimentary denitrification (Dahlke *et al.*, 2000). Incubation of sediment cores from the Bodden waters showed both consumption and release of N_2O ; however, no correlation was found between nitrification and denitrification activities in the cores and N_2O formation (Dahlke *et al.*, 2000).

Two seasonal studies in the shallow estuarine waters of the Limfjorden and Norsminde Fjords at the east coast of Jutland, Denmark, revealed that considerably enhanced dissolved N_2O concentrations (up to 490 nmol L^{-1}) occurred during spring which were partly associated with high riverine NO_3^- input (Jensen *et al.*, 1984; Jørgensen and Sørensen, 1985). In the two Danish fjords N_2O flux to the atmosphere was mainly balanced by N_2O released from sedimentary denitrification (Jensen *et al.*, 1984; Jørgensen and Sørensen, 1985).

The North Sea

The first survey of dissolved N_2O in the North Sea was performed by Law and Owens (1990) in June 1986 and July 1987. They found a mean N_2O surface (0-1m) saturation of 102% in the northern and central North Sea and a mean surface saturation of 130% in the southeastern part of the North Sea (i.e. the German Bight) indicating that the North Sea acted a source of N_2O to the atmosphere. Nitrification was suggested as the source of N_2O in the water column, whereas the contribution of N_2O produced by sedimentary denitrification was shown to be negligible (Law and Owens, 1990). Bange *et al.* (1996b) measured mean surface saturations of 104% and 100% for the central North Sea (September 1991) and the German Bight (September 1991 and 1992), respectively.

Estuaries located along the western North Sea are generally a source of N_2O to the atmosphere. However, considerable seasonal and spatial variability along the estuarine salinity gradient of the N_2O saturations have been observed. In the Colne River estuary, for example, N_2O saturations ranged from about 80% up to 5190% (Dong *et al.*, 2002; Robinson *et al.*, 1998). In the Humber estuary N_2O saturations during a study from March to December 1996 ranged from 100% to 4250% (avg. 425%) (Barnes and Owens, 1998). N_2O saturations in the Tweed estuary from September 1997 to March 1997 were in the range from 96%-110% (avg. 100%) (Barnes and Owens, 1998). Comparable to the estuaries located along the English coast, N_2O saturations in the Scheldt estuary at the Dutch North Sea coast were in the range from 100% to 3100% (seasonal study from October 1993 to July 1996 by de Wilde and de Bie (2000)). Additionally, De Bie *et al.* (2002) calculated a median N_2O saturation of 710% for the Scheldt estuary during 13 monthly surveys along the salinity gradient from April 1997 to April 1998.

Two different dominating pathways for N_2O formation in estuaries along the North Sea coast have been identified: (i) water column nitrification in the turbidity maximum zone (TMZ) in the low salinity regions of the Scheldt and Humber Estuaries (Barnes and Owens, 1998; De Bie *et al.*, 2002; De Wilde and De Bie, 2000) and (ii) sedimentary denitrification in the Colne Estuary (Dong *et al.*, 2002; Robinson *et al.*, 1998). It seems that the evolved estuarine N_2O formation pathway strongly depends on local settings such as the water column distributions of O_2 and nutrients (NH_4^+ and NO_2^-)

as well as the microbial community (De Bie *et al.*, 2002; Dong *et al.*, 2002).

Investigation of the N₂O emission rates from intertidal sediments along the Scheldt Estuary from September 1990 to December 1991 and in the western Wadden Sea from April 1989 to March 1990 revealed a high degree of spatial and seasonal variability (Kieskamp *et al.*, 1991; Middelburg *et al.*, 1995). Interestingly, intertidal sediments can even act as a temporary sink for atmospheric N₂O (Kieskamp *et al.*, 1991; Middelburg *et al.*, 1995). No clear relationship of N₂O emission rates either with nitrification nor denitrification rates were detected (Middelburg *et al.*, 1995). However, Middelburg *et al.* (1995) were able to establish a linear relation between the annual integrated N₂O emission rates from the intertidal sediments and the nitrogen loading.

English Channel, Bay of Biscay

A comprehensive study of N₂O cycling was carried out in the Tamar Estuary (south-west England) during August 1988 and June 1990 (Law *et al.*, 1992). N₂O saturations were in the range from about 100% to 330% and were attributed to sedimentary denitrification and to a minor degree to water column nitrification in the TMZ, terrestrial runoff and sewage input (Law *et al.*, 1991; Law *et al.*, 1992). Additionally, denitrifying bacteria in epiphytic communities on the surface of the macroalgae *Enteromorpha* sp. from the Tamar estuary showed a high potential for N₂O production during spring-summer (Law *et al.*, 1993).

N₂O saturations in the Gironde Estuary (southwest France) measured during a campaign in November 1991 ranged from 106% to 165% (average 132%) (Bange *et al.*, 1996b). A further study of the N₂O distribution in the Gironde estuary in June 1997 indicated that the highest N₂O surface concentrations are found in the TMZ. Abril *et al.* (2000) found a good correlation between suspended particulate matter and dissolved N₂O and concluded that N₂O is produced in the MTZ; however, the processes responsible for N₂O formation (water column nitrification or sedimentary denitrification) have not been deciphered (Abril *et al.*, 2000).

Mediterranean Sea, Adriatic Sea, Aegean Sea

N₂O saturations along five transects in the Gulf of Lions (northwestern Mediterranean Sea) and the adjacent Rhone River Plume in June 1998 and March-November 1997 ranged from 0% to appr. 200% (i.e. 15 nmol L⁻¹) and up to 41 nmol L⁻¹, respectively (Marty *et al.*, 2001). N₂O saturations in the inner Gulf of Thermaikos (northwestern Aegean Sea) during April 1998 were found to be in the range from 84% to 309% (Marty *et al.*, 2001). Associated measurements of the bacterial production showed nitrifying and denitrifying activities in suspended particulate matter, however, a direct relationship between the measured N₂O concentrations and N₂O formation rates was not found (Marty *et al.*, 2001).

Measurements during a study from May 1996 to January 1998 in the shallow Sacca di Goro, a coastal lagoon in the Po River delta in the northern Adriatic Sea, revealed N₂O saturations in the range from 0% – 6635% with highest N₂O fluxes to the atmosphere in autumn and winter (Leip, 1999). N₂O saturations at one station in the open Adriatic Sea in August 1996 were found to be slightly undersaturated (85% – 100%) in the surface (0-20m) and supersaturated (up to 140%) down to the bottom at 70m (Leip, 1999). Leip (1999) attributed the high N₂O saturation in the lagoon to input of N₂O by the Po River. Additionally, the spatial N₂O distribution in the lagoon seemed to be influenced by the incoming Adriatic Sea water and sedimentary N₂O production (Leip, 1999).

A survey of N₂O surface concentrations during a cruise in the coastal waters of the

eastern Ionian Sea and the northern Aegean Sea in July 1993 showed a mean N_2O saturation of about 107% (Bange *et al.*, 1996a). During the same cruise a mean N_2O saturation of 103% was found in the Amvrakikos Bay (at the west coast of Greece). Interestingly, N_2O concentrations along the salinity gradient in the Amvrakikos Bay showed a positive correlation with the salinity indicating that N_2O was not produced in the Amvrakikos Bay (Bange *et al.*, 1996a).

Black Sea

In July 1995 the mean N_2O saturations on the Black Sea's northwestern shelf/Danube River plume and in the open Black Sea were 112% (Amouroux *et al.*, 2002). No correlation between N_2O concentrations and salinity was found and the formation pathways remained unidentified (Amouroux *et al.*, 2002).

Arctic Ocean: Norwegian Sea, Barents Sea

In the Barents Seas considerably enhanced CH_4 concentrations (up to $56,7 \text{ nmol L}^{-1}$) were found over a pockmark field east of Bear Island (Lammers *et al.*, 1995). However, surface CH_4 concentrations were found to be near equilibrium or slightly supersaturated (up to 3.8 nmol L^{-1} , i.e. 125%) because the high CH_4 plume concentrations are rapidly oxidized or diluted by mixing with ambient waters with lower CH_4 concentrations (Lammers *et al.*, 1995).

Baltic Sea

Surface CH_4 saturations in the Baltic Sea generally show a great spatial and seasonal variability (Bange *et al.*, 1994; Abril and Iversen, 2002; Bange *et al.*, 1998a; Bussmann and Suess, 1998; Heyer and Berger, 2000; Schmaljohann, 1996). Mean area-weighted CH_4 surface saturations in the southern and central basins of the Baltic Sea were 113% and 395% in February and July/August 1992, respectively (Bange *et al.*, 1994). CH_4 saturations in the shallow, well ventilated coastal fjords of the southwestern Baltic Sea such as the Randers Fjord, Eckernförde Bay and the shallow lagoons of Bodden waters in the southern Baltic Sea/western Oder River estuary area range from slightly below equilibrium (62%) to values up to appr. 25,700,000% ($642,000 \text{ nmol L}^{-1}$) (Abril and Iversen, 2002; Bange *et al.*, 1998a; Bussmann and Suess, 1998; Heyer and Berger, 2000).

Measurements of CH_4 concentrations in the anoxic deep waters of the central basin of the Baltic Sea (Gotland Basin) during January/February 1990 revealed values of up to 400 nmol L^{-1} , whereas in the oxygenated water column CH_4 concentrations were considerably lower ($4.5 - 120 \text{ nmol L}^{-1}$) (Dzyuban *et al.*, 1999). Fenchel *et al.* (1995) reported CH_4 concentrations exceeding $30,000 \text{ nmol L}^{-1}$ in the bottom water of the anoxic basin of the Marianger Fjord (east coast of Denmark) in August 1994. Accumulation of CH_4 (up to 2700 nmol L^{-1}) in Kiel Harbour has been observed during stagnation periods when the water column became anoxic during the end of the summers of 1992 and 1993 (Schmaljohann, 1996).

In the Baltic Sea, the interplay of the various CH_4 formation and consumption processes seems to be complex. There are several factors which have been identified to cause the observed high seasonal and spatial variability of dissolved CH_4 . Rivers entering the estuarine systems of the Baltic Sea seem to be enriched in CH_4 thus riverine CH_4 can be responsible for enhanced CH_4 concentrations in the upper estuaries/fjords or near coastal areas (Abril and Iversen, 2002; Bange *et al.*, 1994; Bange *et al.*, 1998a). The main CH_4 formation process is methanogenesis in the sediments. However, sedimentary aerobic CH_4 oxidation provides an effective barrier for sedimentary CH_4 to reach the water column (Abril and Iversen, 2002; Dahlke *et al.*, 2000; Schmaljohann, 1996). Nevertheless, CH_4 release (e.g., via diffusion) from the sediments still provides the sig-

5.2.2 Overview: Methane

nificant source for dissolved CH_4 in the water column (Fenchel *et al.*, 1995; Schmaljohann, 1996). In the water column itself, considerable rates of aerobic as well as anaerobic CH_4 oxidation have been observed in a few studies (Abril and Iversen, 2002; Fenchel *et al.*, 1995). Shifts from oxic to anoxic conditions significantly enhance CH_4 formation in the sediments (Schmaljohann, 1996) and water column (Dzyuban *et al.*, 1999). Moreover, seasonal variations of water temperature, wind speeds and availability of organic matter have been identified to regulate, directly or indirectly, estuarine CH_4 emissions to the atmosphere (Abril and Iversen, 2002; Bange *et al.*, 1998a; Heyer and Berger, 2000).

Apart from methanogenesis, natural seepage of CH_4 , as observed in the CH_4 -rich pockmark structures of the Eckernförde Bay (Bussmann *et al.*, 1999), in the Kattegat (Dando *et al.*, 1994; Laier *et al.*, 1992) and in the Stockholm Archipelago (Söderberg and Flodén, 1992) are significant sources of dissolved CH_4 in the water column, but poorly quantified in terms of their significance for CH_4 emissions to the atmosphere.

North Sea, English Channel, Bay of Biscay, coastal NE Atlantic

CH_4 surface measurements during a transect from the southern North Sea to the NE Atlantic in November 1980 (Conrad and Seiler, 1988) showed a clear trend of mean saturations from about 140% in the southern North Sea to 100% in the Bay of Biscay. Comparable CH_4 saturations (95% – 130%) were observed in the open southern North Sea by Bange *et al.* (1994) and Scranton and McShane (1991). A strong CH_4 concentration gradient towards the Dutch coast (up to 12,000%) associated with the Rhine River plume was observed by Scranton and McShane (1991) and De Wilde and Duyzer (1995) during two measurement campaigns in March 1989 and October 1993, respectively. During a cruise from east to west along 58°N in the central North Sea which was followed by a transect to the German Bight in May 1994, Rehder *et al.* (1998) observed a remarkably high spatial variability of CH_4 surface saturations in the range from 103% to 50,000% (i.e., 1453 nmol L⁻¹) (Rehder *et al.*, 1998). The extraordinary high values were resulting from CH_4 released from an abandoned borehole (Rehder *et al.*, 1998). During the same cruise, enhanced CH_4 saturations (from 130% up to >1000%) were observed in the Skagerrak (eastern North Sea), the Dogger Bank (central North Sea) and the German Bight/Elbe River estuary (Rehder *et al.*, 1998). During a series of measurements along the English east coast and southern North Sea (Dutch coast; Upstill-Goddard *et al.*, 2000) found CH_4 saturations from 74% to 2245%.

A series of CH_4 measurements have been performed in several estuaries along the North Sea (Elbe, Ems, Rhine, Scheldt, Thames, Humber, Tyne), the Bay of Biscay (Loire and Gironde) and the NE Atlantic (Douro and Sado) yielding CH_4 saturations from significantly undersaturated (70% in the Gironde) up to highly supersaturated (49,700% in the Rhine River) (De Wilde and Duyzer, 1995; Middelburg *et al.*, 2002; Upstill-Goddard *et al.*, 2000). The distribution of CH_4 saturations along the estuarine salinity gradients showed great seasonal and spatial variabilities. Generally, CH_4 saturations at the interface to the coastal waters were comparable to those measured in the open North Sea and the open Bay of Biscay. Maximum estuarine CH_4 saturations were observed in the upper parts of the estuaries at low salinities. In the Framvaren Fjord (south coast of Norway) CH_4 concentrations from about 1000 nmol L⁻¹ (surface) up to 26,000 nmol L⁻¹ (anoxic bottom water) were measured (Lidstrom, 1983).

In contrast to the various studies in the Baltic Sea (see above), it seems that less attention has been paid to identify the responsible CH_4 formation/consumption processes in the North Sea area. Scranton and McShane (1991) measured CH_4 oxidation rates in the water column and concluded that loss by oxidation is a minor sink in view of the high sea-to-air emissions. Anaerobic CH_4 oxidation in the anoxic water column of

Framvaren Fjord was observed by Lidstrom (1983). Riverine input, sedimentary release and formation within the turbidity maximum zone have been suggested as possible sources for estuarine CH_4 , however, the processes themselves have not been identified (Middelburg *et al.*, 2002; Rehder *et al.*, 1998; Scranton and McShane, 1991; Upstill-Goddard *et al.*, 2000).

There is increasing evidence that the release of so-called geological CH_4 from natural seepages and abandoned boreholes contribute significantly to the atmospheric CH_4 emissions especially from the North Sea (Judd *et al.*, 1997; Rehder *et al.*, 1998). In the Sagerrak, for example, large areas of CH_4 -charged sediments and associated plumes of CH_4 gas bubbles in the water column have been identified (Hempel *et al.*, 1994; Hovland, 1992; Zimmermann *et al.*, 1997). Further areas where CH_4 -rich sediments have been verified are the UK shelf (Judd *et al.*, 1997; Judd *et al.*, 2002), the Belgian coast (Missiaen *et al.*, 2002), the Spanish Atlantic coast (Garcia-Gil *et al.*, 2002) and the western Irish Sea (Yuan *et al.*, 1992). However, it is difficult to assess the atmospheric emissions solely based on seabed seepage rates and/or plumes of gas bubbles (Judd *et al.*, 1997; Leifer and Kumar Patro, 2002).

Mediterranean Sea, Adriatic Sea, Aegean Sea

CH_4 concentrations along five transects in the Gulf of Lions (northwestern Mediterranean Sea) and the adjacent Rhone River Plume in June 1998 and March–November 1997 ranged from 0 nmol L^{-1} to 1263 nmol L^{-1} and up to 1363 nmol L^{-1} , respectively (Marty *et al.*, 2001). There was a clear trend from maximum CH_4 concentrations at the Rhone River mouth to the open Mediterranean Sea. CH_4 concentrations in the inner Gulf of Thermaikos (northwestern Aegean Sea) during April 1998 were found to be in the range from 0 to 1378 nmol L^{-1} (Marty *et al.*, 2001).

Associated measurements showed bacterial production of CH_4 in suspended particulate matter, however, a direct relationship between the measured CH_4 concentrations and CH_4 formation rates was not found (Marty *et al.*, 2001). CH_4 at one station in the open Adriatic Sea in August 1996 was found to be supersaturated (appr. 400% – 450%) in the surface layer (0 – 10m) and supersaturated as high as 2750% below the surface layer down to 70m (Leip, 1999).

A survey of CH_4 surface concentrations during a cruise in the coastal waters of the eastern Ionian Sea and the northern Aegean Sea in July 1993 showed a mean CH_4 saturation from 148% (3.2 nmol L^{-1}) to 231% (4.8 nmol L^{-1}) (Bange *et al.*, 1996a). During the same cruise a mean CH_4 saturation of 522% (11.1 nmol L^{-1}) was found in the Amvrakikos Bay (at the west coast of Greece).

CH_4 gas release from geological sources has been reported from the northern Adriatic Sea (Conti *et al.*, 2002). In the central Aegean Sea, hydrothermal systems also release a considerable amount of gas to the water column, however, in the sampled gas bubbles plumes, the fraction of CH_4 was generally less than 10% (Dando *et al.*, 1995).

Black Sea

In July 1995 the mean CH_4 surface saturations on the Black Sea's northwestern shelf and in the Danube River plume were 567% (13 nmol L^{-1}) and 5340% (131 nmol L^{-1}), respectively (Aouroux *et al.*, 2002). A comparable range of CH_4 concentrations (22 – 380 nmol L^{-1}) were observed by Ivanov *et al.* (2002) at 11 stations during a cruise on the northwestern shelf of the Black Sea in August 1995. CH_4 was formed by methanogenesis in the shallow shelf sediments with higher formation rates in summer than in spring (Ivanov *et al.*, 2002). Despite the fact that considerable CH_4 oxidation rates occur in the sediments and in the water column, CH_4 release from the sediments seem to maintain the high CH_4 concentrations in the water column (Ivanov *et al.*, 2002).

5.2.3 Emission estimates

Occurrence of shallow gas-charged sediments and CH_4 bubble plumes has been reported from many areas along the Black Sea coast (see e.g. Dimitrov, 2002; Tkeshelashvili *et al.*, 1997; Ergun *et al.*, 2002; Kutas *et al.*, 2002). However, the contribution of gas seepages to the overall high CH_4 concentrations in the water column and the atmospheric emissions are largely unknown. CH_4 seeps along the shelf slope, which are already located within the zone of the permanent anoxic deep waters, were found to be associated with thick microbial mats with potentially high anaerobic CH_4 oxidation rates (Michaelis *et al.*, 2002).

N_2O

The majority of the N_2O surface saturation data presented above indicate that European coastal waters are generally supersaturated with N_2O (especially in estuarine systems), despite the fact that in some cases undersaturations (<100%) have been observed. Since saturations greater than 100% result in a N_2O flux from the ocean surface to the atmosphere, European coastal waters are a net source of N_2O to the atmosphere. N_2O saturations for various European shelf areas and estuaries are listed in Table 4 and Table 5. Studies, which either do not report N_2O saturations explicitly or do not allow reconstructing N_2O saturations, were not included. If there were multiple studies for the same location, only the study with the better seasonal coverage was listed. From the data listed in Table 4 and Table 5 we calculated mean N_2O saturations of 113% and 465% for the European shelf and estuaries, respectively. Based on the mean N_2O saturations we calculated mean N_2O emissions of $0.12 \text{ Tg N yr}^{-1}$ and $0.19 \text{ Tg N yr}^{-1}$ for the European shelf and estuaries, respectively (for details see Table 6). The resulting overall N_2O emissions range from 0.15 to 0.4 Tg N yr^{-1} (with a mean of $0.31 \text{ Tg N yr}^{-1}$). Our estimate is in good agreement with the result ($0.29 \text{ Tg N yr}^{-1}$) from a recent model study of Seitzinger and Kroeze (1998) in which the N_2O formation was quantified via denitrification and nitrification in European coastal waters (i.e. NE Atlantic between 45° and 66°N , Baltic Sea, Mediterranean Sea and Black Sea). In their study, N_2O formation was linked to riverine nitrate inputs, which in turn were estimated as a function of the atmospheric deposition of nitrogen oxides (NO_y), fertilizer use and sewage inputs (Seitzinger and Kroeze, 1998). Their model calculations yielded annual N_2O productions of 0.06 Tg N ($=10^{12}\text{g}$) and 0.23 Tg N for the European estuaries/continental shelf and rivers, respectively. Global estimates of the N_2O emissions from coastal areas are in the range from 1.9 Tg N yr^{-1} (Seitzinger and Kroeze, 1998) to 6.7 Tg N yr^{-1} (Bange *et al.*, 1996b). Thus, European coastal waters may contribute up to 16% of present global coastal N_2O emissions. Using current trends of the increase of the human population, fertilizer use and NO_y deposition, (Kroeze and Seitzinger, 1998) predicted the N_2O production in European coastal waters for the year 2050. The resulting N_2O estimates were $0.10 \text{ Tg N yr}^{-1}$ and $0.33 \text{ Tg N yr}^{-1}$ for the European estuaries/continental shelf and rivers, respectively, suggesting that future coastal N_2O production might increase by 67% and 43% respectively. However, the overall global coastal N_2O production in 2050 might increase to 4.9 Tg N yr^{-1} indicating that the future contribution by European coastal waters (9%) to the global production will be lower than today (Kroeze and Seitzinger, 1998).

CH_4

CH_4 in the surface layer is generally supersaturated, except for a few cases (see text above). Therefore, European coastal waters are a net source for atmospheric CH_4 . CH_4 surface concentrations range from slightly undersaturated ($= 1 - 4 \text{ nmol L}^{-1}$) to extremely supersaturated ($= 642,000 \text{ nmol L}^{-1}$) indicating a high seasonal and spatial variability. CH_4 saturations for various European shelf areas and estuaries are listed in

Table 7 and Table 8. Studies, which either do not report CH_4 saturations explicitly or do not allow reconstructing CH_4 saturations, were not included. If there were multiple studies for the same location, only the study with the better seasonal coverage was listed. From the data listed in Table 7 and Table 8 we calculated mean CH_4 saturations of 224% and 3643% for the European shelf and estuaries, respectively. Based on the mean CH_4 saturations we calculated mean CH_4 emissions of $0.13 \text{ Tg C yr}^{-1}$ and $0.24 \text{ Tg C yr}^{-1}$ for the European shelf and estuaries, respectively (for details see Table 9). The resulting overall CH_4 emissions range from 0.25 to $0.48 \text{ Tg C yr}^{-1}$ (with a mean of $0.37 \text{ Tg C yr}^{-1}$). Our emission estimate for the European shelf (excl. estuaries) is in good agreement with a previous estimate by Bange *et al.* (1994). They estimated a total flux of $0.11 \text{ Tg C yr}^{-1}$ for the European coastal shelf waters (North Sea, Baltic Sea, Mediterranean Sea, Black Sea; excl. estuaries) which represents about 1.5% of the overall global CH_4 emissions from the shelf (excl. estuaries) (Bange *et al.*, 1994). We conclude that emissions from the European shelf and estuarine areas contribute significantly to the overall global CH_4 oceanic emissions (0.3 Tg C yr^{-1} for the open ocean, Bates *et al.* (1996)). However, our overall estimate still seems to be a severe underestimation since estuarine CH_4 fluxes and CH_4 fluxes from geological sources were not adequately represented: For example, Upstill-Goddard *et al.* (2000) estimated an annual CH_4 emission of 0.09 Tg C from estuaries in the southern North Sea alone. Judd *et al.* (1997) estimated the CH_4 flux to the atmosphere by natural seepages on the UK shelf to be in the range from 0.09 to 2.6 Tg C yr^{-1} . Moreover, Dimitrov (2002) computed that annually between 0.02 Tg C and 0.11 Tg C are emitted from the Bulgarian shelf (Black Sea) to the atmosphere by natural CH_4 seepages. Adding the mean fluxes via natural CH_4 seepages from the North Sea and the Bulgarian shelf (Judd *et al.*, 1997; Dimitrov, 2002) and the estimate by Upstill-Goddard *et al.* (2000) yields an atmospheric CH_4 flux of about 1.5 Tg C yr^{-1} . This value is certainly a severe underestimation since natural seepages from CH_4 -bearing sediments, which occur all over at the European shelf (for an overview see Fleischer *et al.* (2001)), as well as the major part of estuarine CH_4 emissions is not adequately represented. In view of the fact that open ocean emissions for CH_4 have been estimated to be as low as 0.3 Tg C yr^{-1} (Bates *et al.*, 1996) it is obvious that the significance of coastal CH_4 emissions on a regional (European) and on a global scale is much higher than previously thought.

5.2.4 Uncertainties

The emission estimates discussed above are associated with large uncertainties: Data coverage. Despite an increasing number of studies dealing with the distribution of N_2O and CH_4 in coastal waters, their distributions in large parts of the coastal areas (in Europe as well as globally) are still unknown. Seasonality. Since the formation of N_2O and CH_4 is mainly driven by biological processes, the observed variability is influenced by the pronounced seasonality of various parameters such as temperature, riverine nutrient inputs etc. Unfortunately, most studies are biased towards the summer months. Air-sea exchange models. There are still considerable uncertainties associated with the applied air-sea exchange models, thus the choice of the model introduces an additional bias. Furthermore the choice of the used wind speeds (i.e. in-situ wind speeds vs. climatological data) is resulting in an additional variability. These and other uncertainties have been discussed in section 4 of this report.

5.2.5 Summary comments

N_2O

Based on the data presented, three main conclusions can be drawn:

Highest N_2O saturations were observed in estuaries and fjords, whereas in open

coastal waters (i.e. shelf waters not influenced by freshwater) N_2O saturations are close to the expected equilibrium saturation. This indicates that N_2O is exclusively formed in estuarine systems.

European coastal waters are a net source of N_2O to the atmosphere; however, the major contribution comes from the estuarine/river systems and not from the open shelf areas. European shelf areas contribute significantly (up to 16%) to the global oceanic N_2O emissions.

It is obvious that sedimentary denitrification and water column nitrification seem to be the major N_2O formation processes. However, the yield of N_2O from both processes strongly depends on the local O_2 concentrations, thus O_2 is the key factor regulating N_2O production (and its subsequent emissions to the atmosphere). Additionally, N_2O distributions in estuaries show a pronounced seasonal variability. In anoxic waters, such as the deep basin of the central Baltic Sea or parts of the shallow Po River delta, N_2O is consumed by water column denitrification.

There might be two further, however, largely unknown N_2O sources in European coastal areas: First, coastal upwelling brings N_2O from subsurface layers to the surface, thus it can be an additional, physically driven, source of N_2O to the atmosphere (Nevison *et al.*, 2004). Despite small local upwelling areas along the European coasts, a large coastal upwelling site is found at the Atlantic coast of Portugal. However, studies on N_2O during the upwelling events along the coast of Portugal are not known yet. Second, organic matter release from fish farming activities could increase the dissimilatory nitrate reduction to ammonium (DNRA) in the sediments underlying the fish cages, whereas denitrification was found to be unaffected (Christensen *et al.*, 2000). DNRA, however, might be an additional source of N_2O (Welsh *et al.*, 2001).

Future N_2O emissions from coastal areas strongly depend on nitrogen inputs to coastal waters and will most probably increase in the future (Kroeze and Seitzinger, 1998). Eutrophication and/or increasing deposition of nitrogen-containing aerosols already increased the number of coastal areas with severe O_2 depletion on a global scale (UNEP, 2004). This, in turn, might result in conditions favourable for enhanced N_2O production as observed along the West Indian shelf where N_2O surface saturations up to 8250% (436 nmol L⁻¹) have been measured due to a dramatic depletion of O_2 concentrations (Naqvi *et al.*, 2000).

CH_4

Based on the data presented, three main conclusions can be drawn:

CH_4 concentrations show a high temporal and spatial variability in European coastal waters. Maximum concentrations were observed in estuarine/fjord systems indicating that CH_4 is mainly formed in shallow coastal regions.

European coastal areas are a net source of atmospheric CH_4 . Natural CH_4 seepages and associated CH_4 bubble plumes as observed in the shallow North and Baltic Seas and in the Black Sea, are an additional source which has not been quantified adequately for the European coastal waters. Thus, it seems that European coastal CH_4 emissions are considerably underestimated.

The main CH_4 formation process is methanogenesis in the sediments and its subsequent release to the water column. Shifts from oxic to anoxic conditions significantly enhance CH_4 formation in the sediments and water column. Sedimentary aerobic and anaerobic CH_4 oxidation processes reduce CH_4 concentrations, however, it seems that

these processes cannot prevent CH₄ from accumulation.

CH₄ emissions from coastal upwelling areas are of regional importance as observed in the well-studied coastal upwelling centres in the Arabian Sea and the coast off Oregon (Bange *et al.*, 1998b; Rehder *et al.*, 2002). Thus, an additional CH₄ source can be CH₄ emissions from the upwelling region along the coast of Portugal, however, studies on CH₄ in this region are not known yet. Indeed enormous amounts of methane are stored as methane hydrates and free gas in the pores of sediments (Zhang, 2003 and references therein). Methane in this form may reach the atmosphere through different pathways: Methane hydrate dissolves or dissociates as it rises through the water column. Zhang argues that methane-driven oceanic eruptions occur and provide a pathway for methane to rapidly enter the atmosphere. However in this context CH₄ releases from mud volcanoes and gas hydrates seem to be of minor importance because they are usually located in the deeper parts of the continental shelf slope and the CH₄ plume concentrations are rapidly oxidized or diluted by mixing with ambient waters with lower CH₄ concentrations before reaching the atmosphere (Damm and Budéus, 2003).

Future CH₄ emissions from coastal areas strongly depend on inputs of nutrients and organic matter to coastal waters and will most probably increase in the future. Eutrophication already increased the number of coastal areas with severe O₂ depletion on a global scale (UNEP, 2004). This, in turn, might result in conditions favourable for enhanced CH₄ production.

5.3 Volatile sulphur compounds (VSC)

Marine emissions of reduced sulphur gases are an essential element of the global sulphur cycle and the main source of biogenic sulphate aerosols, which play important roles in atmospheric chemistry and climate change. Early work by Lovelock *et al.* (1972) provided the first direct evidence of dimethyl sulphide (DMS) in seawater and suggested that oceanic DMS emissions are responsible for the transfer of biogenic sulphur from sea to land required to balance the terrestrial inputs of oxidised sulphur into the oceans. Since then, subsequent work confirmed that DMS is the dominant volatile sulphur compound in surface seawater, responsible for more than 95% and 20% of marine and global sulphur emissions, respectively (see Andreae, 1990 for details; Andreae and Jaeschke 1992; IPCC, 2001). Once emitted, DMS oxidation by free radicals in the troposphere yields predominately sulphur dioxide, which then undergoes gas-to-particle conversion to form sulphate aerosol. This biogenic sulphate aerosol has been linked to radiative forcing of climate change caused by aerosol optical depth and indirect effects of biogenic sulphate on cloud formation and albedo (Andreae and Crutzen, 1997; Charlson *et al.*, 1987; Schwartz, 1988; Shaw, 1983). Importantly, scenarios of DMS-induced climate change involve biosphere – climate feedback mechanisms, in which the production of biogenic aerosol itself is influenced by the climate effects it causes. However, the overall direction of this feedback still remains uncertain (Andreae and Crutzen, 1997), highlighting requirements for future research on the major controls of DMS release and its possible consequences for future climates.

In addition to DMS, carbonyl sulphide (COS) has also been implicated in radiative forcing of climate change. With regard to total sulphur emissions the contribution of COS is almost negligible (ca. 0.2%, Andreae and Jaeschke, 1992). Even so, COS is by far the most abundant sulphur species in the troposphere, because its slow gas phase oxidation gives rise to long tropospheric residence times (2 – 6 years, Khalil and Rasmussen, 1984; Ulshöfer and Andreae, 1998) and a tropospheric loading roughly three times that of even aerosol sulphate (5 Tg S, Andreae and Crutzen, 1997). Consequently, COS is transported into the stratosphere, where its photo-oxidation is believed to be a significant if not the dominant source of sulphuric acid aerosol in the

absence of major volcanic eruptions (Chin and Davis, 1995; Crutzen, 1976; Engel and Schmidt, 1994; Sze and Ko, 1979).

Much of the recent interest in the COS budget has been stimulated by the effects of stratospheric aerosol on Earth's radiation balance (Turco *et al.*, 1980) and heterogeneous chemistry of stratospheric ozone depletion (Fahey *et al.*, 1993). Marine COS emissions alone are thought to contribute approximately 20% (Andreae and Crutzen, 1997; Watts, 2000) to its global sources. However, considering additional COS inputs from the tropospheric oxidation of marine-derived DMS (25%, Barnes *et al.*, 1994) and carbon disulphide, CS₂ (10%, Chin and Davis, 1993) gives a total marine contribution of approximately 55%. In addition, recent work indicated that the contribution of marine-derived CS₂ to the atmospheric COS budget may be even higher than the marine COS flux itself (Kettle *et al.*, 2001), further illustrating the importance of the oceans as an atmospheric sulphur source.

In addition to DMS, COS and CS₂, previous work also considered the possible contributions of hydrogen sulphide (H₂S) and methanethiol to marine sulphur emissions. Early work predating the discovery of seawater DMS by Lovelock *et al.* (1972) speculated that the oceans may be a significant source of H₂S. Subsequent measurements, however, at best indicate a minor contribution of marine-derived H₂S (less than 0.3% of total S emissions, Andreae and Jaeschke, 1992; Andreae *et al.*, 1991; Shooter, 1999). Similarly, sulphur gas measurements up to the mid 1990s provided no evidence for a significant contribution of methanethiol to marine sulphur emissions. In contrast, recent measurements with improved analytical techniques indicated that sea surface concentrations of methanethiol (CH₃SH) may be approximately one order of magnitude higher than those of COS and CS₂ (Kiene, 1996; Ulshöfer *et al.*, 1996; Xu *et al.*, 2001). Global flux estimates for this gas are still lacking. However, available emission rate estimates indicate that the sea-to-air flux of methanethiol may account for as much as 20% of that of DMS (Kettle *et al.*, 2001), suggesting a significant contribution to the global sulphur budget. In view of the potential importance of methanethiol emissions, future work is required to clarify its importance for the atmospheric sulphur cycle.

This study focuses on DMS, COS and CS₂, which - on the basis of present understanding - are considered the main source of biogenic aerosol sulphate in troposphere and stratosphere. H₂S was excluded here, because there is general agreement that its contribution is insignificant on a global scale. Similarly, methanethiol was excluded here, because the paucity of available data presently precludes further analysis of its possible contribution to regional and global budgets.

As part of the CarboEurope - GHG project, specific study *Coastal Ecosystems Greenhouse Gas Budget*, this study addresses the regional contribution of the European coastal zone to atmospheric sulphur. Nature and areal extent of the European coastal zone is briefly summarised in Chapter 2. In the following, we discuss distribution and air-sea exchange of reduced sulphur gases within the context of our present understanding of reduced sulphur gas cycling. To support this discussion, important production and removal pathways are briefly mentioned in the relevant sections, although it is not intended here to provide an exhaustive review of the mechanisms of reduced sulphur cycling.

5.3.1 Dimethylsulphide

DMS cycling.

DMS is formed from algal-derived dimethylsulphoniopropionate (DMSP) by enzymatic cleavage via algal or bacterial DMSP lyase (Ledyard and Dacey, 1994; Stefels and Boekel, 1993), along with acrylic acid. Algal synthesis of DMSP is highly species

dependent and often highest in prymnesiophytes (e.g. *Phaeocystis*, coccolithophores) and dinoflagellates, although certain chrysophyceae and bacillariophyceae (diatoms) may also contain high levels of intracellular DMSP (Iverson *et al.*, 1989; Keller *et al.*, 1989; Liss *et al.*, 1994; Turner *et al.*, 1988). The ecological role of DMSP is still uncertain and may involve osmoregulation (Dickson and Kirst, 1987; Vairavamurthy *et al.*, 1985), cryoprotection (Kirst *et al.*, 1991), chemical defence via acrylic acid formation (Wolfe *et al.*, 1997) and antioxidant function (Sunda *et al.*, 2002).

DMS release is affected by a variety of factors related to plankton population dynamics and trophic interactions. These include enhanced DMS release during cell lysis (Nguyen *et al.*, 1988), zooplankton grazing (Dacey and Wakeham, 1986) and viral infection (Malin *et al.*, 1998), but also involve competing DMSP degradation pathways that lead to the formation of methanethiol and other, as yet unidentified organosulphurs (Kiene 1992; 1996). Mass balance calculations suggest that algal-derived DMSP and DMS are rapidly recycled in the upper ocean and that only approximately 1% of DMSP is lost to the atmosphere as DMS (Andreae, 1990; Archer *et al.*, 2002). Initially, microbial consumption was believed to be the dominant DMS removal process (Kiene and Bates, 1990), while photochemical losses were thought to be small and in the order of gas exchange loss (Brimblecombe and Shooter, 1986). Recent work, however, indicated that DMS photodegradation is important and may exceed microbial consumption under favourable conditions (Brugger *et al.*, 1998; Hatton, 2002; Kieber *et al.*, 1996; Simó and Pedrós-Alió, 1999; Toole *et al.*, 2003). Environmental controls of precursor formation (DMSP), trophic interactions, air-sea exchange, and photo-oxidation all contribute to a complex web of biogeochemical and geophysical interactions, which remains difficult to resolve (see e.g. Simó, 2001).

The above findings illustrate the complexity of food web dynamics and geophysical interactions involved in DMS cycling. Given this complexity, it is not surprising that attempts to explain geographical DMS distribution patterns on the basis of algal abundance, taxonomy or productivity alone have seen little success (Simó, 2001). Furthermore, DMS displays pronounced seasonal variability, characterised by summer maxima coinciding with low algal and DMSP abundance (DMS summer paradox). Available evidence suggests that seasonal and geographical patterns are related to DMS cycling rates (Dacey *et al.*, 1998; Uher *et al.*, 2000) driven by biogeochemical and geophysical forcings that have been parameterised by combinations of mixed layer depth, phytoplankton abundance, irradiance and nutrient limitation terms at coarse spatial resolution (1 x 1 degree) (Anderson *et al.*, 2001; Simó and Dachs, 2002). Such parameterisations, however, may not resolve the pronounced small-scale variability in coastal waters, which occurs at scales ranging from approximately < 10 km to 100 km (Uher *et al.*, 2000). In the following, we review available data on DMS distribution and flux around Europe, and discuss these data within the context of present knowledge about their geographical and seasonal variation.

DMS distribution.

An overview of available DMS measurements on European shelves and adjacent open ocean waters is presented in Table 11. Results in Table 11 are grouped by study area, starting with north-western European shelf (Northeast to Southwest), followed by enclosed seas (Baltic, Mediterranean, and Black Seas) and estuarine systems. It is worth noting that most publications don't report data separately for shelf and open ocean water. Therefore, the results in Table 11 refer to overall averages and ranges of DMS concentration and air-sea flux, unless otherwise stated. The geographical data coverage is further illustrated in Figure 9, which shows DMS sampling locations around Europe extracted from the latest data compilation in Kettle *et al.*, (1999), available from the U. S. National Oceanic and Atmospheric Administration

(<http://saga.pmel.noaa.gov/dms/>). The sampling locations shown ($n = 3300$) fall within an area of 30°W to 60°E and 34°N to 77°N , selected to cover all European shelves including those of the Black and Caspian Seas, and comprise 1929 shelf (≤ 200 m water depth) and 1371 open ocean samples (> 200 m water depth). Data from Table 11 not included in Figure 9 are predominantly from north-western European shelf areas in the North Sea (Archer *et al.*, 2002; Burkill *et al.*, 2002; Nedwell *et al.*, 1994), off western Ireland (Baker *et al.*, 2000; Locarnini *et al.*, 1998), and in the English Channel and Celtic Sea (Kettle *et al.*, 2001). Further data postdating Kettle *et al.*, (1999) are from the eastern Mediterranean and Black Seas (Besiktepe *et al.*, 2004) and from a variety of estuarine systems (Bodenbender *et al.*, 1999; Cerqueira and Pio, 1999; Despiu *et al.*, 2002; Harrison *et al.*, 1992; Moret *et al.*, 2000; Sciare *et al.*, 2002; van Duyl *et al.*, 1998). Thus, improvements in overall spatial coverage since Kettle *et al.*, (1999) were comparatively few, except for estuarine systems and the fairly well studied areas around the British Isles. In the following we discuss our data compilation (Figure 9, Table 11) with regard to geographical and seasonal coverage around Europe.

Barents, Greenland and Norwegian shelves.

No data are as yet available for the large shelf areas of the Barents, Greenland and Norwegian Seas, except very few measurements around Iceland (Belviso *et al.*, 2000; Holligan *et al.*, 1993). DMS concentrations in adjacent open ocean waters are variable. Low concentrations were observed in autumn (< 0.3 nM, Belviso *et al.*, 2000). A spring bloom in the central Barents Sea, dominated by diatoms and *Phaeocystis pouchetii*, showed moderate to high DMS concentrations (2.8 – 25.3 nM), which were attributed to physiological factors, frontal systems, and reduced air-sea exchange and photochemical losses due to partial ice cover (Matrai and Vernet, 1997). The highest concentrations were reported for summer coccolithophore blooms south of Iceland (up to 45 nM, Holligan *et al.*, 1993). Coccolithophore blooms are also common in the Barents and Norwegian Seas (Brown and Yoder, 1994), and recent evidence suggests that rising sea surface temperatures and freshwater inputs may increase the frequency of coccolithophore blooms in the Barents Sea region (Smyth *et al.*, 2004). In the light of the above results and the large area coverage of the Barents, Greenland and Norwegian shelves (32% of European shelves, Table 11), their contribution to coastal European DMS emissions is likely to be important and requires further study.

North and Irish Seas, including English Channel.

The shelf areas around Britain and Ireland show the best data coverage around Europe (Fig. 9, Table 11), particularly in the southern North Sea and the English Channel. DMS concentrations were highly variable, ranging from below 0.1 nM to 'hot spots' reaching 312 nM (see <http://saga.pmel.noaa.gov/dms/> and Kettle, 1999). Concentrations below 0.1 nM were observed mostly in the winter months January and February, and only occasionally during late autumn and early spring (October to December and March to April). DMS 'hot spots' with concentrations above 30 nM occurred mostly from May to July and were most abundant in the shallow waters of the southern North Sea along the Belgian, Dutch and German coasts (Liss *et al.*, 1993; Turner *et al.*, 1996), where coastal waters are characterised by high nutrient loads and pronounced tidal mixing (Otto *et al.*, 1990). Other DMS 'hot spots' were associated with frontal systems along western Ireland and the Celtic Sea shelf break (Baker *et al.*, 2000; Locarnini *et al.*, 1998; Turner *et al.*, 1988; Uher *et al.*, 2000), tidal fronts in the western English Channel and along the eastern UK coast (Holligan *et al.*, 1987; Turner *et al.*, 1988; Uher *et al.*, 2000) and algal blooms in the north-eastern North Sea (Turner *et al.*, 1989).

Pronounced patchiness of sea surface DMS was reported previously for other coastal areas such as the Peruvian upwelling, characterised by 'hot spots' of 50 to 200 km in diameter superimposed on background levels around 3 nM (Andreae, 1985). On the European western continental margin, 'hot spots' occurred on distinctly smaller scales (<20 to 100 km diameter; average 40 km) and were estimated to enhance overall DMS concentrations by some 40% in July. These results indicate that 'hot spots' associated with distinct hydrographic features on the western European shelf significantly enhance summer DMS concentrations.

There is evidence that hydrographic features such as tidal and shelf break fronts often support blooms of prominent DMSP producers. For example, high levels of DMS were observed in *Phaeocystis* blooms in the southern North Sea (Liss *et al.*, 1994) and western English Channel (Holligan *et al.*, 1987), in blooms of the dinoflagellate *Gyrodinium aureolum* in frontal systems in the western English Channel (Turner *et al.*, 1988) and off western Ireland (Baker *et al.*, 2000), and in coccolithophore blooms associated with frontal systems off northeast Scotland (Turner *et al.*, 1988) and in the western English Channel (Holligan *et al.*, 1987). These findings suggest that the interplay between local hydrography, ecosystem structure and speciation is important with regard to DMS distribution patterns in coastal seas.

Seasonal effects are arguably the most important control of DMS variability around the British Isles. Turner *et al.*, (1988) reported an approximately 70-fold difference between average DMS concentrations from January and July/August, similar to seasonal amplitudes reported for the southern North Sea (Liss *et al.*, 1993; Nedwell *et al.*, 1994; Turner and Liss, 1985; Turner *et al.*, 1989). The most comprehensive information on seasonal variations comes from a compilation of data collected in 1989 in the southern North Sea (Turner *et al.*, 1996). This compilation presented spatially averaged monthly means with highest concentrations in May (25 nM) and lowest levels in February (0.13 nM). The monthly mean for May 1989 was approximately three times higher than that of previous cruises into the same area, indicating strong interannual variability. Turner *et al.*, (1996) speculated that the high DMS levels in May 1989 were caused by unusually low air-sea gas exchange losses due to low wind speeds. However, modelling studies suggest that anthropogenic nutrient inputs into the southern North Sea favour high DMS levels associated with spring blooms of *Phaeocystis* around May (van den Berg *et al.*, 1996). It is therefore plausible that the southern North Sea indeed exhibits a seasonal maximum around May, even though the 1989 data may be unusually high. It is also worth noting in this regard that anthropogenic eutrophication may have caused a 2.5-fold increase in DMS in the southern North Sea (van den Berg *et al.*, 1996). It is therefore possible that the seasonal pattern in Turner *et al.* (1996) may be different from that of other parts of the North and Irish Seas, even though it may well be typical for the southern North Sea. Other work from temperate regions has reported seasonal maxima around July (Dacey *et al.*, 1998; Leck *et al.*, 1990; Uher *et al.*, 2000), i.e. significantly later than in the North Sea. This time lag may reflect distinct hydrography and ecosystem characteristics. Further regional time series studies are required to improve our understanding of contrasting seasonal patterns.

Bay of Biscay and Western Iberian shelves.

Measurements in the Bay of Biscay and along the Iberian Peninsula are comparatively few and are mostly from open ocean waters (> 200 m water depth, Staubes-Diederich, 1992; Uher *et al.*, 2000). These data indicate background concentrations of 2 to 4 nM off the shelf, and local maxima from 7 to 19 nM in areas of wind-driven upwelling off western Iberia (Uher *et al.*, 2000). Uher *et al.* (2000) observed enhanced DMS concentrations in upwelling filaments some 30 km off the western Iberian shelf

break. These measurements were carried out in the early upwelling season, when cold-water filaments are only weakly developed. The areal extent of DMS 'hot spots' is likely to be greater at the height of the upwelling season around September, when upwelling filaments reach maximum lengths of 200 to 250 km (Haynes *et al.*, 1993). Additional measurements are required to assess the combined effects of upwelling and other seasonal factors on the DMS distribution off western Iberia.

Baltic Sea, including Kattegat and Skagerrak.

Data coverage in the Baltic Sea is limited to western parts of the Bothnian and Gotland basins, and to the Kattegat and Skagerrak, which connect the Baltic and North Seas (Leck *et al.*, 1990; Leck and Rodhe, 1991). Data from the Kattegat and Skagerrak collected in July 1988 indicate surface concentrations from 3.4 nM to 7.5 nM with an average of 4.7 nM. In the western Bothnian and Gotland basins, DMS concentrations were only around 2.5 nM with the lowest concentrations in the northwestern Bothnian (Leck and Rodhe, 1991). DMS concentrations collected along a transect extending from a Swedish fjord (Himmerfjärden) into the Gotland basin (September, 1987, Leck *et al.*, 1990) varied from 0.5 nM to 2 nM and showed highest DMS concentration near a sewage outlet within the fjord. The seasonal variation of DMS was studied at a coastal station in the western Gotland basin. Results from this time series indicate DMS concentrations below 0.3 nM before and after ice cover in December and March, enhanced concentrations following spring blooms in April/May, and a seasonal maximum of 15 nM around July/August. This seasonal maximum was attributed to zooplankton grazing pressure inferred from zooplankton abundance (Leck *et al.*, 1990). It is worth noting here that no data are available so far for the Belt, Arkona, Bornholm and eastern Gotland basins, the Bothnian Bay to the north, and the Gulfs of Riga and Finland. Given the restricted circulation between individual basins and the pronounced regional differences in the seasonal cycles of phytoplankton in the Baltic Sea (Ketchum, 1983), the seasonal pattern in the western Gotland basin may not be representative of the entire Baltic Sea.

Mediterranean Sea.

Previous work on the Mediterranean Sea reports mainly from the north-western Mediterranean (Belviso *et al.*, 1993; Simó *et al.*, 1997; Simó *et al.*, 1995) and from the waters around Greece (Rapsomanikis, unpublished data as in Kettle *et al.*, 1999) and Turkey (Besiktepe *et al.*, 2004), and falls into the months April to July and October. No data are available for the Tyrrhenian, Ionian and Adriatic Seas around Italy and for the Levantine Basin in the east.

In the northwestern Mediterranean, DMS showed mean concentrations of 0.7 nM in April and 3.7 nM in June, and values up to 19 nM off the Ebro and Rhone deltas and off Barcelona (Simó *et al.*, 1997; Simó *et al.*, 1995). Samples collected in May in the central Ligurian Sea off Villefranche sur Mer showed concentrations around 4.6 nM. DMS concentrations in the southern Mediterranean Sea in September (< 0.5 nM to 23 nM) were broadly similar to those in the northwestern Mediterranean, but are excluded from Table 11, because they only report open ocean data outside Europe (Belviso *et al.*, 2003).

Around Greece, DMS concentrations varied from 0.2 nM to 18.1 nM (average: 3.7 nM), with highest values off Corfu (18.1 nM) and Amvrakikos Bay (5 to 8 nM), western Greece (Rapsomanikis, unpublished data as in Kettle *et al.*, 1999). In October, DMS concentrations in the Aegean and north-eastern Mediterranean were lower (average: 2.4 nM), while sewage-affected areas in the Marmara Sea showed up to 7

nM DMS (Besiktepe *et al.*, 2004). Overall, the results presented above appear to indicate seasonal variation with higher values towards late spring/summer, and also increased DMS concentrations in near-coastal areas affected by terrestrial and anthropogenic inputs.

Black Sea and Sea of Azov.

DMS concentrations are available for north-western and south-eastern areas in the months July and October, respectively (Amouroux *et al.*, 2002; Besiktepe *et al.*, 2004). The mean DMS concentration on the north-western shelf was 7.5 nM, slightly below the average of 8.2 nM for the open Black Sea. The highest DMS levels (up to 12 nM) were encountered within the Danube plume. However, chlorophyll-normalised DMS concentrations increased with increasing salinity. These findings suggest that the plankton communities in the open Black Sea were more prolific DMS producers than those on the shelf, in broad agreement with results from U.S. east coast estuaries (Iverson *et al.*, 1989). Hence, the DMS distribution was attributed to the combined effects of riverine inputs and algal speciation on DMS production (Amouroux *et al.*, 2002). Limited data from the south-eastern Black Sea in October indicate little spatial variation around a mean DMS concentration of 1.4 nM (Besiktepe *et al.*, 2004). These results are indicative of seasonal changes similar to those observed in the southern North Sea (Turner *et al.*, 1996). Further work is required to improve our knowledge of spatial and temporal variability in the Black Sea. Future studies should also include the shallow Azov Sea, which has been neglected in previous work.

Caspian Sea.

To our best knowledge, no data are available for the Caspian Sea. Further studies of the Caspian Sea are highly desirable, given that its surface area is roughly equivalent to that of the Baltic Sea (Mandych, 1995).

Estuarine systems.

The last section in Table 2 summarises DMS measurements from a variety of estuarine systems, including data from 6 western European estuaries, Norsminde Fjord (Denmark), the western Wadden Sea, Ría de Aveiro (Portugal), Toulon Bay (French Mediterranean), Venice Lagoon (Northern Adriatic), and from intertidal areas of south-east England and the German Wadden Sea.

The average DMS concentration in six western European estuaries, calculated from average concentrations in the salinity range 0 to 30 with equal weighting for each individual estuary, was 1.3 nM (Sciare *et al.*, 2002), significantly lower than adjacent shelf waters (see Table 11). Data from the Scheldt estuary in May and July were only 25 to 50% higher than in December, suggesting that the seasonal amplitude of estuarine DMS is small and significantly below that in the adjacent southern North Sea (Turner *et al.*, 1996). Variability between estuaries was also low. For example, average DMS concentrations in the Elbe, Ems, Scheldt, and Gironde estuaries all fell in the range 0.2 nM to 0.7 nM, and only the Loire (1.3 nM) and Rhine (4.2 nM) estuaries showed higher DMS levels. In contrast to low seasonal and inter-estuarine variability, DMS varied strongly with salinity. Local maxima at salinities below 10 were observed in the Scheldt (1.2 to 2.4 nM) and Loire (3.8 nM) estuaries. Local maxima (1.4 to 2.5 nM) were also observed near the mouths of the Elbe, Ems and Gironde estuaries. With the exception of one December transect in the Scheldt estuary, all estuaries also showed an overall trend towards increasing DMS with increasing salinity. This trend was strongest in the outer Rhine estuary, where DMS levels reached 10 nM at salinity 30. The axial DMS distribution was attributed to patterns of phytoplankton abun-

dance and increasing levels of DMS-producing plankton with increasing salinity (Sciare *et al.*, 2002), as previously reported from U.S. east coast estuaries (Iverson *et al.*, 1989). Comparison of the above findings and estuarine typology (Lemaire *et al.*, 2002) suggests lowest DMS in estuaries with high suspended matter loads (Ems, Gironde) and highest DMS in the outer parts of estuaries characterised by high inorganic nutrients loads, short residence times and moderate suspended loads (Elbe, Rhine). Thus, estuarine typology might help to identify estuaries likely to show enhanced DMS levels.

Along the southern North Sea, DMS was also studied in other estuarine systems, characterised by reduced freshwater inputs and pronounced tidal mixing. In the Oosterscheldt, a former estuarine channel of the River Scheldt (Dutch southwest coast), average DMS levels in May 1985 were 7.0 nM and reached a maximum of 22.7 nM (Turner, unpublished data from Kettle *et al.* (1999)). Time series studies in the Marsdiep, a tidal inlet in the south-western Wadden Sea, showed pronounced seasonality characterised by low winter values (0.07 nM to 0.81 nM), a sudden increase to an annual maximum of 17 to 40 nM in April (monthly mean ca. 11 nM) followed by elevated levels around 7 nM in late spring/early summer (Kwint and Kramer, 1996; van Duyl *et al.*, 1998). The annual DMS maximum was associated with spring blooms dominated by *Phaeocystis globosa* and the DMS decrease in late April/May was attributed to a shift from DMSP cleavage (forming DMS) to demethylation during the late stages of the bloom (van Duyl *et al.*, 1998). It is worth noting that the annual DMS maximum in the Wadden Sea appears to occur approximately one month earlier than that of the adjacent North Sea (Turner *et al.*, 1996) and 2-3 months earlier than that in the Baltic Sea (Leck *et al.*, 1990). DMS concentrations in the Norsminde Fjord at the eastern coast of Jutland, Denmark, were 2.2 nM (Jørgensen & Okholm-Hansen 1985), much lower than in the Wadden Sea.

Further seasonal information is available from estuarine systems of south-western Europe on the Portuguese Atlantic coast, the French Mediterranean coast and in the Adriatic. In the Canal de Mira, an elongated shallow arm extending south from the inlet of Ria de Aveiro (Portugal), average DMS levels were 2.9 nM and 5.3 nM in winter and summer, respectively, and reached levels up to 20 nM during summer (Cerqueira and Pio, 1999). DMS concentrations in Toulon Bay in the north-western Mediterranean Sea varied from 3.6 to 21 nM (average: 9.8 nM) (Despiau *et al.*, 2002). Interestingly, no clear, seasonal pattern was evident in Toulon Bay. Instead, DMS concentrations remained high throughout the year and showed peak concentrations of up to 15 nM in January. The elevated DMS levels in Toulon Bay were attributed to effects of anthropogenic inputs, which were particularly strong in the eutrophic, inner bay. The shallow lagoon of Venice in the northern Adriatic also displayed enhanced DMS levels around an annual average of 4.6 nM (Moret *et al.*, 2000). DMS levels were lowest from September to January (ca. 1 to 2 nM) and highest during phytoplankton blooms from later winter to early spring. This pattern appears to be similar to that found in the south-western Wadden Sea (Kwint and Kramer, 1996). However, winter levels were significantly higher and elevated spring and summer levels were sustained over a longer period.

The emission of DMS from intertidal areas has been studied in the northern German Wadden Sea (Bodenbender *et al.*, 1999), and on the south-eastern UK (Harrison *et al.*, 1992) and Portuguese coasts (Cerqueira and Pio, 1999). Unvegetated mud flats in the Canal de Mira, Ria de Aveiro (Portugal), showed a seasonal pattern with maximum emissions around July, and dominated the DMS flux from the study area during low tide, when the exposure of intertidal areas is highest. Interestingly, mud flat emissions exceeded sea-to-air emissions during winter and still accounted for 37% of total emissions in summer, when dissolved DMS levels were highest. These data indicate that

DMS emissions from mud flats may be regionally important dependent on their areal extent (Cerqueira and Pio, 1999). Data from unvegetated mud flats in the Colne Estuary, UK, and the northern German Wadden Sea indicate only moderate to low DMS emissions despite high DMS porewater concentrations, (3.7 – 7.8 μM , Harrison *et al.*, 1992). These low DMS emissions are in agreement with similar DMS emissions from unvegetated intertidals reported in Dacey *et al.* (1987). In contrast, vegetated areas such as *Spartina alterniflora* salt marshes may be significant even on global scales (Dacey *et al.*, 1987). However, no reports are available for vegetated intertidal areas within Europe.

In summary, estuarine systems (with the exception of estuaries with high suspended matter load) appear to be able to sustain elevated DMS levels similar to those found in productive shelf areas such as frontal systems and the southern North Sea. The seasonal patterns, however, are different from those on the shelf, particularly with regard to elevated winter concentrations and a shift of the seasonal maximum towards late winter/early spring. These features may result from the combined effects of geomorphology, terrestrial and anthropogenic inputs on local hydrography and ecosystem characteristics. Similarly, riverine inputs and anthropogenic nutrient loads were found to have caused enhanced DMS levels in other restricted exchange environments (Himmerfjärden (Baltic Sea), Amvrakikos Bay (Mediterranean Sea)) and near-coastal waters affected by river plumes (e.g. Ebro, Rhone, and Danube plumes, see text above). Therefore, terrestrial and anthropogenic inputs seem to have locally significant effects on DMS distribution and flux. However, given that the surface area of estuarine systems is comparatively small (i.e. in the order of 4% or less of the surface area of EU shelves, see text above) and that DMS concentrations appear only similar to other DMS ‘hot spots’ on the shelf, the contribution of estuarine systems to EU shelf emissions are probably modest despite their potential to be locally significant.

DMS emission estimates – major uncertainties and constraints.

Local DMS flux estimates in Table 11 span two orders of magnitude with an average near 9 $\mu\text{mol m}^{-2} \text{d}^{-1}$. Some of this variability is undoubtedly due to spatio-temporal variability in surface wind speeds used in the calculation of DMS sea-to-air flux. In addition, the choice of air-sea gas-exchange models used to calculate the DMS fluxes also contributes to the considerable variability in Table 11. These and other uncertainties associated with air-sea gas exchange models are discussed elsewhere in this report. Here, it is worth noting that the uncertainty in the spatio-temporal distribution of sea surface DMS is most probably more important than variability from air-sea exchange models and wind speed data, which together account for an estimated uncertainty of around 50% (Kettle and Andreae 2000). Therefore, the following discussion will focus on the much larger uncertainties related to regional and seasonal data coverage.

Our discussion of available DMS data has already highlighted three important issues regarding the current data coverage. Firstly, no data are as yet available for the Barents, Greenland, and Norwegian shelves, the Caspian and Azov Seas, the Adriatic (Northern Mediterranean Sea) and large parts of the Baltic Sea (See Figure 9, Table 11). These areas alone account for some 50% of the total European shelf area (Table 1). Hence, DMS emissions from European shelves seem poorly constrained with regard to spatial data coverage alone. Secondly, DMS data are strongly biased towards the summer months, with some 80% of shelf data collected from April to September and ca. 47% of shelf data alone collected in the months June and July near the annual maximum of sea surface DMS (see Kettle *et al.*, 1999). In addition, full seasonal coverage appears to be limited to parts of the Baltic and North Seas, the English Channel and some estuarine systems, whereas winter data are unavailable for the Irish and Celtic Seas, the Bay of Biscay and western Iberian shelves, and the Mediterranean and

Black Seas. Furthermore, significant differences between the seasonal patterns of distinct study areas such as the southern North Sea, the Baltic Sea and some estuarine systems preclude straightforward extrapolations of seasonal patterns to shelf regions with inadequate data coverage. Thirdly, the DMS distribution on the European shelf is characterised by pronounced mesoscale variability with 'hot spots' of elevated DMS concentrations often related to regional hydrographical features. These 'hot spots' appear to be more widespread in summer, when they can significantly enhance summer DMS concentrations (Uher *et al.*, 2000). Thus, mesoscale variability seems tied to seasonal variability, probably via combinations of geophysical and ecological controls operating on regional scales.

Given the strong regional and seasonal variability of sea surface DMS, improved emission estimates should ideally be based on climatological fields of DMS concentrations and geophysical variables integrated via regional biogeography. Such an approach would still be constrained by the inadequacies of available data and would also require detailed analysis, which is beyond the scope of this review. However, based on the assembled DMS concentrations and geophysical data in Kettle *et al.* (1999), it is possible to derive a preliminary emission estimate that might serve as a guide to future work.

A first guess for the mean, annual DMS concentration on European shelves and adjacent open ocean waters was obtained by interrogating the DMS database from Kettle *et al.* (1999). First, the data subset shown in Figure 1 was divided into winter and summer subsets for shelf (water depth ≤ 200 m) and open ocean areas (water depth > 200 m), and the arithmetic mean was calculated for each. To minimise seasonal bias, the mean, annual DMS concentrations were then calculated as the arithmetic means of winter and summer concentrations. For European shelves, winter and summer averages were 0.76 nM and 8.43 nM, respectively. For comparison, adjacent open waters showed 1.86 nM in winter and 6.20 nM in summer. The comparatively high winter concentrations in the open ocean are most likely too high, because they are based solely on few data from the month October ($n = 84$), and much higher than lowest winter concentrations on the western European shelf (< 0.1 nM, see text above). The summer concentrations on the shelf seem only 36% higher than those in the open ocean. However, the comparatively high summer average for the adjacent open ocean is also likely due to bias towards mid-summer, as illustrated by the low number of measurements outside June/July ($n = 411$, i.e. ca. 32% of all open ocean summer measurements). Furthermore, excluding all June/July data, we obtained averages of 10 nM and 2.9 nM for shelves and open oceans, respectively. These preliminary results suggest that summer concentrations on European shelves are significantly higher than those in the adjacent open ocean. However, further work is necessary to assess the effects of spatial and seasonal bias.

On the basis of winter and summer means in Table 12, we estimated the annual means for European shelves and open oceans at 4.6 nM and 4.0 nM, respectively. The annual mean for the open ocean areas is skewed towards mid-summer and therefore excluded from further discussion. Our annual mean for European shelves (4.6 nM) is significantly higher than annual means for coastal areas from Andreae (1990, 2.8 nM) and Bates *et al.* (Bates *et al.*, 1987, 1.2 nM). Some of these differences may be explained by differences in the classification and extent of 'coastal' areas. For example, coastal areas from Andreae (1990) are classified via primary production, roughly twice that of global physiographic shelves (Menard and Smith 1966), and coastal areas from Bates *et al.* (1987) denote areas with water depth exceeding 400 meters. In addition, the low value from Bates *et al.* (1987) is entirely based on measurements from the US west coast (20 to 50° N) and therefore probably reflects regional differences between eastern Pacific and European shelves. In order to assess the importance of restricted exchange environments, we also calculated the annual, mean DMS concentration of European estuarine systems from averages in Table 11. The mean for estuarine systems was 4.4 nM (Table 12), very similar to the mean for European

shelves. These preliminary results indicate that European estuarine and shelf concentrations are broadly similar to each other and significantly higher than global means for the coastal ocean from previous work.

In order to assess the importance of coastal, marine emissions from Europe, we estimated the DMS flux from European shelves and estuarine systems from their respective areas and annual mean DMS concentrations (Table 13). We used two air-sea exchange models to account for uncertainty in flux estimates (Liss and Merlivat 1986; Wanninkhof 1992). The DMS emissions listed in Table 13 represent averages of our flux calculations. Our preliminary estimate for the European shelf, including estuarine systems, indicates emissions of 21 Gmol a^{-1} ($1 \text{ Gmol} = 1 \cdot 10^9 \text{ mol} = 32 \text{ Gg S}$). For comparison, European estuarine systems alone only account for 0.16 to 1.1 Gmol a^{-1} , i.e. approximately 1 to 5% of European coastal emissions. These findings indicate that estuarine systems make only a minor contribution to European coastal DMS emissions, chiefly due to their limited surface area. Similarly, DMS emissions from intertidal areas are also likely to be small. For example, assuming mean annual DMS fluxes of $1 \text{ to } 2 \mu\text{mol m}^{-2} \text{ d}^{-1}$ from intertidal areas (see Table 11) and an upper limit for European intertidal surface area of $0.04 \times 10^6 \text{ km}^2$ (see text above) yields annual emissions in the order of 0.015 to 0.03 Gmol a^{-1} , i.e. approximately 0.1% of European shelf emissions. While this rather crude estimate remains poorly constrained with regard to spatial coverage, intertidal areas seem unlikely to contribute significantly to the European DMS budget, mainly as a consequence of modest emission rates and limited surface area.

The significance of European coastal DMS emissions may be illustrated by comparison to recent estimates of global emissions. For example, our European coastal emissions from Table 13 account for 2.9% of global emissions from Kettle and Andreae (2000, $0.7 \text{ Tmol DMS a}^{-1}$). Given that European shelves contribute only 0.9% to the global ocean surface area, our preliminary estimate indicates a disproportionately large contribution to global emissions, i.e. roughly three times higher than the global average per area unit. In summary, we find that European coastal shelves make a small but significant contribution to global emissions, primarily due to elevated DMS concentrations in the coastal waters around Europe.

5.3.2 Carbonyl sulphide

COS cycling.

COS in surface seawater is mainly produced photochemically (Ferek and Andreae 1984), possibly via photosensitised oxidation of low molecular weight sulphur compounds (Zepp and Andreae 1994) or by photodegradation of dissolved organic matter (DOM) itself (Uher and Andreae 1997b). COS formation rates are highest in the UV-B range and decrease with increasing wavelengths (Weiss *et al.*, 1995a; Zepp and Andreae 1994), consistent with the involvement of humic-like coloured dissolved organic matter (CDOM) either as photosensitiser or as substrate. COS production rates generally increase with increasing dissolved organic matter abundance and are closely linked with optical CDOM characteristics (Uher and Andreae 1997b). On this basis, the distribution pattern of COS, with highest concentrations in near-coastal waters, was attributed to variations in CDOM abundance (Uher and Andreae 1997a; Ulshöfer *et al.*, 1996; Weiss *et al.*, 1995a; Zepp and Andreae 1994). COS may also be formed via dark, non-photochemical pathways, as has been inferred from differences between the calculated hydrolysis rate (Elliott *et al.*, 1989) and the observed dark decay in surface seawater (Flöck and Andreae 1996; Ulshöfer *et al.*, 1996; von Hobe *et al.*, 2002) or laboratory incubations (Uher and Andreae 1997b; Weiss *et al.*, 1995a). This dark production has been parameterised as a function of temperature and mid-UV CDOM absorbance (von Hobe *et al.*, 2002) and may be explained by reactions of polysul-

phides with carbon monoxide (Kamyshny *et al.*, 2003) or microbial pathways such as thiocyanate hydrolysis (Katayama *et al.*, 1993). Stimulation of COS release after addition of thiocyanate to soils (Lehmann and Conrad 1996) suggests that thiocyanate degraders may also contribute to microbial COS production observed in estuarine sediments (Cutter and Radford-Knoery 1993) and intertidal areas (Aneja *et al.*, 1979). The dominant sink of dissolved COS is its hydrolysis to CO₂ and H₂S. COS turnover due to hydrolysis shows time constants ranging from hours to days, dependent on seawater temperature and pH (Elliott *et al.*, 1989), and accounts for up to 98% of COS removal (Uher and Andreae 1997a). Since photoproduction and hydrolysis rates are of similar magnitude, dissolved COS shows a pronounced diel cycle with maximum concentrations in the afternoon and lowest concentrations before sunrise (Andreae and Ferek 1992; Mihalopoulos *et al.*, 1992; Uher and Andreae 1997a; Ulshöfer *et al.*, 1996). This diel cycle is also affected by vertical mixing and by daily patterns of mixed layer stratification with reduced downward mixing towards the afternoon (Doney *et al.*, 1995; Najjar *et al.*, 1995). Emission estimates need to consider the significant diel variations in sea surface COS (Mihalopoulos *et al.*, 1992).

The photochemical nature of COS production leads to strong seasonal variations in mid to high latitude regions (Mihalopoulos *et al.*, 1992). This seasonal variation may even lead to persistent undersaturation with respect to atmospheric concentrations and consequently to oceanic uptake of atmospheric COS (Ulshöfer *et al.*, 1995). Recent work also reported persistent undersaturation in oligotrophic areas of the subtropical Pacific Ocean (Weiss *et al.*, 1995b) and night-time undersaturation in large parts of the Atlantic Ocean (Xu *et al.*, 2001). These results led to downward revisions of open ocean COS emissions (Weiss *et al.*, 1995b; Xu *et al.*, 2001) and further illustrate the need for representative seasonal and regional data coverage.

COS distribution.

Table 14 summarises available COS measurements on European shelves and adjacent open ocean waters. Results in Table 14 are grouped by study area, starting with north-western European shelf (Northeast to Southwest), followed by enclosed seas (Mediterranean Sea) and estuarine systems. Unlike for DMS, no global database of COS measurements is available so far. Therefore, our discussion of geographical and seasonal coverage around Europe has to rely on original publications. It is worth noting here, that some publications do not allow separation of results into shelf and open ocean data.

North and Irish Seas, including English Channel.

COS measurements around Britain are limited to the southern North Sea and English Channel regions (Table 14). In the southeastern North Sea, average COS concentrations varied from 49 pM to 118 pM (Staubes-Diederich 1992; Uher and Andreae 1997a; Ulshöfer and Andreae 1998), and highest diel maxima up to 365 pM were observed in the Elbe plume towards end of April. COS concentrations in near-coastal waters off southern England and northern France were slightly higher than those in the southeastern North Sea (Mihalopoulos *et al.*, 1992; Turner and Liss 1985; Watts 1991). Summer data from the English Channel and Celtic Sea region were also similar and showed peak concentrations during June (160 pM, Xu *et al.*, 2001) and August (350 pM, Staubes-Diederich 1992). Overall, these results suggest that near-coastal waters affected by terrestrial inputs show the highest COS concentrations.

The data in Table 14 also provide evidence for pronounced seasonal changes in sea surface COS. The only mid-winter data available are from the western English Channel and Celtic Sea shelf in early January. These data show persistent undersaturation (SR = ca. 0.65) and low concentrations (ca. 7-8 pM) broadly similar to those in the adja-

cent open ocean (Ulshöfer *et al.*, 1995). These results suggest that winter uptake of atmospheric COS may also occur in parts of the coastal ocean. However, overall supersaturation in the months October and November (Kettle *et al.*, 2001; Staubes-Diederich 1992; Xu *et al.*, 2001) suggests that this winter sink, should it exist, is probably limited to a period around the winter solstice when light levels are lowest. COS concentrations in summer were ca. 50 pM to 150 pM, and thus more than ten times higher than corresponding winter concentrations (ca. 5 pM).

Bay of Biscay and Western Iberian shelves.

Measurements in the Bay of Biscay and off western Iberia are mostly from open ocean waters and suggest slightly elevated COS levels off Northwest Iberia in June (ca. 25 pM, Xu *et al.*, 2001) and August (ca. 60 pM, Staubes-Diederich 1992). Previous work also noted similar, elevated COS levels in the West African (Xu *et al.*, 2001) and Peruvian upwellings (Ferek and Andreae 1983). It is therefore plausible to assume that regional upwelling may have caused the enhanced COS levels off Northwest Iberia, possibly via changes in DOM nature and abundance. Further studies are required to assess the importance of upwellings for COS distribution and flux.

Mediterranean Sea.

Summer concentrations in coastal waters of the north-western Mediterranean and around Greece suggest COS concentrations around 50 pM and significant supersaturation (SR: 5.2 to 7; Table 14), approximately two to three times higher than in adjacent open ocean waters (Mihalopoulos *et al.*, 1992; Ulshöfer *et al.*, 1996). These data indicate that the coastal Mediterranean Sea is a significant source of atmospheric COS in summer. No data on seasonal changes are available so far. However, seasonal studies from coastal waters of similar latitude suggest persistent supersaturation throughout the year (Mihalopoulos *et al.*, 1992).

Other Coastal Shelf Areas.

No data are as yet available for the large shelf areas of the Barents, Greenland and Norwegian Seas. For open ocean waters of comparable latitude, available data suggest slight undersaturation (arctic; 65° - 80° latitude: saturation ratio (SR) = 0.85), and for subarctic waters (50° - 65° latitude) compiled saturation ratios (SR) for winter and summer are 0.95 and 1.78, respectively (Ulshöfer and Andreae 1998). These data indicate moderate annual emissions from areas with latitudes $\geq 50^\circ$, probably due to moderate, annual irradiance levels combined with low hydrolysis losses in these comparatively cold waters (annual sea surface temperature $< 0^\circ\text{C}$ – 13°C). It is plausible to assume higher COS levels in shelf waters, because photoproduction rates are expected to be higher in coastal waters and downward mixing of surface-produced COS is likely to be limited by bottom topography. Given the large shelf areas of the Barents, Greenland and Norwegian shelves (32% of European shelves, Table 1), further studies are required to assess their contribution to European COS emissions.

Other important shelf areas currently without data coverage include the Baltic Sea, and the Black, Azov, and Caspian Seas. Thus geographical coverage remains comparatively poor and restricted to less than one quarter of European shelf areas.

Estuarine systems.

European estuarine waters showed average COS concentrations of approximately 200 to 800 pM, roughly one order of magnitude higher than in adjacent coastal waters (Harrison *et al.* 1992; Jørgensen & Okholm-Hansen 1985; Sciare *et al.* 2002; Watts 1991). Highest COS levels were reported for the Rhine estuary (up to 1010 pM) in

July, and attributed to moderate turbidity levels and high solar elevations near the summer solstice (Sciare *et al.*, 2002). In contrast, lowest COS were observed in the turbidity maximum zones of Ems, Scheldt, and Gironde, and the lowest average COS concentration was observed in the turbid Gironde estuary in September (170 pM). Thus, estuarine COS levels were attributed to the combined effects of estuarine turbidity and solar elevation on COS photoproduction (Sciare *et al.*, 2002). Large DOM gradients and diel variations in photoproduction are also likely to contribute to the pronounced variability of estuarine COS (Ulshöfer and Andreae 1998). Data from European estuaries in Sciare *et al.* (2002) cover the months May to September but do not show a clear seasonal trend. Likewise, previous work in U.S. east coast estuaries found highly variable COS levels (60 pM - 1470 pM) but no definitive seasonal trend (Zhang *et al.*, 1998). The only data set with annual coverage is from the Colne estuary, southeast England (Harrison *et al.*, 1992), and suggest winter and summer concentrations of 234 pM and 742 pM, respectively. These observations indicate a summer/winter ratio of approximately 3, in broad agreement with results from the Northeast Atlantic (Ulshöfer *et al.*, 1995). However, spatial and diel variability within estuaries is high and therefore could have masked seasonal variations in other work. The seasonal cycle of COS emissions from intertidal areas has been studied in detail at two coastal sites in the southern North Sea (Table 14). Annually averaged flux rates were 800 to 900 nmol m⁻² d⁻¹ (Bodenbender *et al.*, 1999; Harrison *et al.*, 1992), i.e. similar to sea-to-air flux rates from estuaries (Zhang *et al.*, 1998) and approximately ten times higher than corresponding flux rates from adjacent self areas (Table 14). Importantly, emissions from intertidal areas remained high in winter (Bodenbender *et al.*, 1999; Harrison *et al.*, 1992). These results, together with the persistently high COS levels in estuarine surface waters suggest that estuarine systems are locally significant COS sources throughout the entire year.

COS emission estimates – major uncertainties and constraints.

As for DMS, limited geographical and seasonal data coverage is arguably the largest uncertainty in current COS emission estimates. Spatial coverage is much weaker than that for DMS and heavily biased towards shelf waters along the western European coast (southern North Sea, English Channel), while approximately three quarters of European shelves remain unstudied to date (see Table 1 and Table 14). In contrast to DMS, limited geographical coverage is also aggravated by pronounced concentration differences between shelf waters (5 – 140 pM) and estuarine systems (170 pM - 775 pM). Given the persistently high COS levels in estuarine and near-coastal waters, defining the spatial extent of these waters seems particularly important. Furthermore, seasonal variations in photoproduction and downward mixing cause pronounced seasonal changes in sea surface COS concentrations (see, Ulshöfer *et al.*, 1995). Importantly, low winter levels may lead to undersaturation and ocean uptake of atmospheric COS. However, winter data are scant and restricted to parts of the Celtic Sea and English Channel (Ulshöfer *et al.*, 1995; Xu *et al.*, 2001). Consequently, the spatial and temporal extent of coastal ocean COS uptake remains poorly constrained and urgently requires further study.

The limitations of current data coverage around Europe still preclude detailed COS emission estimates on regional scales. Nevertheless, currently available data are sufficient to distinguish between shelf waters and estuarine systems and to consider winter/summer scenarios. A first guess for the mean, annual COS concentration in European shelf waters and estuarine systems was calculated from the publications listed in Table 14. We grouped the data into winter (October to March) and summer data (April to September) and calculated the arithmetic means for each. Estuarine data from Watts (1991) did not allow extraction of separate winter and summer means and were counted towards the summer subset. When only saturation ratios were available, COS concentrations were calculated from the given saturation ratios and an average atmos-

pheric COS mixing ratio for European shelf areas, following the procedures of Ulshöfer *et al.* (1995). The average atmospheric mixing ratio (606 ppt COS) was obtained from atmospheric measurements in European coastal areas reported in Staubes-Diederich (1992), Uher and Andreae (1997a), Ulshöfer and Andreae (1998) and Ulshöfer *et al.* (1996) (Table 14). Salinity and temperature values were the same as those used for DMS (Table 13).

On the basis of winter and summer means, we estimated the annual mean COS concentrations (saturation ratios) in European shelf waters and estuarine systems at 54 pM (3.0) and 355 pM (20), respectively (Table 15). Thus, estuarine COS concentrations seem approximately seven times higher than those on the shelf. It is worth noting here that the winter means of shelves and estuarine systems differ even by a factor of 15. These results clearly indicate that persistently high winter levels (234 pM) contribute significantly to the high annual mean of estuarine systems. Our annual average for the European shelf is approximately two times lower than previous estimates for subtropical/temperate (Mihalopoulos *et al.*, 1992; Ulshöfer and Andreae 1998) and global coastal/shelf areas (Andreae and Ferek 1992). However, our summer mean (93 pM) is in broad agreement with previous seasonal estimates in Mihalopoulos *et al.* (1992) and Ulshöfer and Andreae (1998). Our comparatively low annual mean for European waters may be explained by spatial and seasonal variability, because the estimates in Mihalopoulos *et al.* (1992) and Ulshöfer and Andreae (1998) are for lower latitudes (20° to 50° latitude) and include higher winter data (SR = 4.5) from the subtropical Indian Ocean (Mihalopoulos *et al.*, 1992). In contrast, our COS winter data are based on much lower concentrations from recent work in the Celtic Sea and English Channel areas (SR = 0.9) (Ulshöfer *et al.*, 1995; Xu *et al.*, 2001). Furthermore, we have for the first time distinguished between shelf waters and estuarine systems, and therefore our shelf average was expected to be below those reported in previous work.

In order to assess the importance of COS emissions from shelf waters and estuarine systems, we calculated emission estimates from their surfaces areas and annual mean COS flux rates, respectively. As for DMS, we used two air-sea exchange models to derive fluxes from wind speed and COS concentration difference across the air-sea interface (Liss and Merlivat 1986; Wanninkhof 1992). Our flux calculations used a mean atmospheric mixing ratio of 606 ppt COS (see above), salinity and temperature values from Table 13. The resulting emission estimates are summarised in Table 16. For the European shelf, excluding estuarine systems, we estimated COS emissions of 0.19 Gmol a⁻¹. For comparison, European estuarine systems alone account for 0.014 to 0.10 Gmol a⁻¹, depending on the choice of the area cover used in the calculations. Thus, estuarine emissions account for some 7 to 50% of European coastal COS emissions. These preliminary data clearly indicate that estuarine systems contribute significantly to COS emissions, mainly due to persistently high COS concentrations throughout the entire annual cycle. For comparison, we also estimated annual COS emissions from intertidal areas based on flux rates from Table 14 and an upper limit for European intertidal surface area of 0.04 x 10⁶ km² (see text above). Our initial estimate indicates modest emissions of 0.013 Gmol a⁻¹, i.e. slightly less than the lower end of COS emissions from estuarine waters. These results suggest that intertidal areas may be locally important COS sources, but are less likely to make a significant contribution to the European coastal COS source.

The importance of European coastal COS emissions can be further illustrated by comparison with previous estimates of the global marine COS source by Ulshöfer and Andreae (1998). The combined European estuarine and shelf sources account for 0.20 to 0.29 Gmol a⁻¹. Thus, the European coastal source accounts for 21 to 31% of global coastal emissions and 8 to 12% of global marine emissions, respectively (Ulshöfer and Andreae 1998). This disproportionately large contribution may be explained by two issues related to our approach towards the geographical classification of European coastal waters. Firstly, we considered European shelf areas above 50°N, which had

been excluded from previous estimates (Mihalopoulos *et al.*, 1992; Ulshöfer and Andreae 1998). Therefore, our European shelf area from Table 1 accounts for more than a quarter of the global coastal area used in previous estimates (Mihalopoulos *et al.*, 1992; Ulshöfer and Andreae 1998). Secondly, we considered separate contributions from estuarine systems, which may account for up to one third of our coastal European source. In summary, our results indicate that European coastal waters, and estuarine systems in particular, contribute significantly to global ocean COS emissions.

5.4 Carbon disulphide

The production pathways of CS₂ are less well studied than that of COS. Earlier work by Lovelock (1974) showed that CS₂ concentrations in porewaters of surficial sediments of a stagnant bay were approximately five times higher than those in the overlying water. These results together with the finding that CS₂ concentrations generally increase towards the coast (Kim & Andreae 1992; Lovelock 1974) have lead to the speculation that sedimentary inputs may be an important source in shallow coastal waters. However, to our best knowledge the sedimentary source strength has never been quantified, and sediment profiles are only available for exposed intertidal areas (Bodenbender *et al.* 1999). Therefore, the overall contribution of sedimentary production to dissolved CS₂ remains unclear. Recent work has identified additional, photochemical and phytoplankton-related production pathways that help to explain CS₂ supersaturation in deeper waters, where sedimentary inputs are unlikely to occur (Xie *et al.* 1998; Xie *et al.* 1999). As for COS, CS₂ photoproduction is closely related to CDOM absorbance in the mid-UV range and increases upon addition of low molecular weight organosulphurs such as cysteine, consistent with the idea of photosensitised oxidation of reduced sulphur compounds. Further evidence for a photochemical CS₂ source comes from recent observations that sea surface concentrations of CS₂ display diel cycles similar to those of COS albeit with a smaller diel amplitude (Kettle *et al.* 2001; Staubes *et al.* 1990). The smaller diel variation may be attributed either to slow CS₂ removal (Kettle *et al.* 2001) or to the presence of additional non-photochemical source terms. Algal CS₂ production was observed in axenic monocultures of marine phytoplankton species, and was shown to vary strongly between species and with physiological state (Xie *et al.* 1999). Given the absence of in-situ production rates and the strong variability observed in laboratory incubations, conclusions regarding the role of algal CS₂ production remain speculative. Nevertheless, scaling of laboratory rates to the global ocean suggested that algal CS₂ production may potentially be important if CS₂ producers were indeed widespread (Xie *et al.* 1999). However, field observations showed little correlations between CS₂ concentration and indicators of phytoplankton abundance (Kim & Andreae 1992; Xie & Moore 1999). Therefore, the above findings suggest that photoproduction is most likely the dominant CS₂ source, even though sedimentary and algal sources may at times also be important.

Apart from air-sea gas exchange loss, no other removal processes of sea surface CS₂ have been identified so far. Air-sea gas exchange loss rates are considered small compared to photochemical production and significantly slower than efficient removal processes for other sulphur gases, for example COS hydrolysis. Therefore, the absence of other significant sinks may be consistent with the only moderate diel amplitude of sea surface CS₂. Other possible CS₂ removal processes include microbial oxidation by denitrifiers (Jordan *et al.* 1997), hydrolytic CS₂ degradation by thiocyanate degrading *thiobacillus* strains (Sorokin *et al.* 2001), and CS₂ consumption by methanogens (Kelly & Smith 1990). However, the role of microbial processes in CS₂ cycling is as yet largely unknown and requires further study.

CS₂ distribution.

As for COS, no electronic database currently exists for CS₂. Therefore, our analysis is

based on comparatively few original publications, which report mainly from the North and Irish Seas. Overall, data coverage around Europe is similar to that of COS. The main results, summarised in Table 8, are discussed in detail below.

North and Irish Seas, including English Channel.

CS₂ concentrations in the North and Irish Seas varied from 11 pM to 52 pM. CS₂ concentrations towards the lower end of this range were found in the north-eastern North Sea off Norway (11 pM, Leck & Rodhe 1991), areas of the southern North Sea (16 pM, Staubes-Diederich 1992; Turner & Liss 1985), off western Ireland (14 pM, Xie & Moore 1999), and the English Channel (11 pM, Kettle *et al.* 2001). In contrast, highest CS₂ concentrations were reported from near-coastal waters (36 pM to 49 pM, Lovelock 1974; Watts 1991) and biomass-rich waters of the English Channel and Celtic Sea shelf (52 pM, Staubes *et al.* 1990). These observations are consistent with earlier findings that CS₂ concentrations generally increase along the gradient from open ocean to near-coastal waters (Kim & Andreae 1992), possibly due to increased photoproduction in combination with additional sedimentary and algal sources in shallow, productive waters.

Baltic Sea, including Kattegat and Skagerrak.

CS₂ summer concentrations in the Baltic Sea and the Kattegat and Skagerrak regions were similar to those found in the adjacent north-eastern North Sea (11 pM, Leck & Rodhe 1991), and thus fell towards the low end of CS₂ concentrations off north-western Europe.

Other Coastal Shelf Areas.

No data are as yet available for large shelf areas around Europe, including the Barents, Greenland and Norwegian Seas, the western Iberian Shelf, the Mediterranean Sea, and the Black, Azov, and Caspian Seas. It is worth noting here that only few coastal data outside Europe are available to date, chiefly from the Labrador Sea and the eastern US coast (Kim & Andreae 1992; Xie & Moore 1999). These data indicate CS₂ concentrations from 13 pM to 35 pM, broadly similar to those found around the British Islands. Nevertheless, our understanding of the geographical variability of CS₂ concentrations remains limited and is further compounded by the lack of seasonal coverage. In particular, it is worth noting that the seasonal pattern of CS₂ remains unknown, owing to the lack of time series measurements and the unavailability of data from the winter months of November to March. In view of these constraints, further studies are required to improve our knowledge of the geographical and seasonal variability of CS₂ in European shelf waters.

Estuarine systems.

Average CS₂ concentrations of European estuarine systems varied from 36 pM to 508 pM (Jørgensen & Okholm-Hansen 1985; Moret *et al.* 2000; Sciare *et al.* 2002; Watts 1991), approximately ten fold higher than CS₂ concentrations on the adjacent shelves. In the western European estuaries of the Rhine, Ems, Scheldt, and Gironde rivers, CS₂ concentrations were lowest near the freshwater-saline interface (2–22 pM), and generally displayed highest levels at high salinities (ca. 80 pM, Sciare *et al.* 2002). Interestingly, axial CS₂ profiles were distinct from those simultaneously recorded for COS, indicating that the estuarine concentrations of these two trace gases are controlled by contrasting biogeochemical processes. In contrast, shallow coastal water bodies with low freshwater inputs showed average CS₂ concentrations ranging from 179 pM to 508 pM (Jørgensen & Okholm-Hansen 1985; Moret *et al.* 2000; Watts

1991), significantly higher than those observed in western European estuaries. The only available data on seasonal variability are from a study in the shallow lagoon of Venice in the northern Adriatic, which provides near-complete seasonal cover extending from March to November 1997 (Moret *et al.* 2000). CS_2 concentrations showed pronounced short-term variability with lowest levels in November (ca. 50 pM) and maxima exceeding 1000 pM during May, July and September. Background levels appeared highest during July and August (> 500 pM), and remained above 200 pM for most of the year. Interestingly, no CS_2 maxima were observed during the phytoplankton spring bloom, indicating that processes other than algal production were dominant.

CS_2 emissions from intertidal areas were studied in Norsminde Fjord, Denmark, and the north-eastern Wadden Sea (Bodenbender *et al.* 1999; Jørgensen & Okholm-Hansen 1985). In Norsminde Fjord, flux rates were around 50 nmol m⁻² d⁻¹, similar to flux rates from shelf waters (Table 8). In contrast, flux rates in the north-eastern Wadden Sea were significantly higher throughout the whole year (362 nmol m⁻² d⁻¹). It is worth noting that CS_2 emissions from spartina alterniflora dominated salt marshes may be significantly higher (1700 to 8560 nmol m⁻² d⁻¹, Aneja *et al.* 1979) than emissions from the Wadden Sea. However, no data are available for European salt marshes. Nevertheless, our data compilation in Table 8 suggests persistently high CS_2 concentrations in estuarine waters and elevated flux rates from some intertidal areas, suggesting that estuarine systems are probably locally important sources of atmospheric CS_2 .

CS₂ emission estimates – major uncertainties and constraints.

The geographical coverage of CS_2 measurements around Europe remains comparatively poor and displays a clear bias towards shelf waters around the British Islands (Table 8). As for COS, inadequate geographical coverage is compounded by pronounced concentration differences between shelf waters (11 pM to 52 pM) and estuarine systems (36 pM to 508 pM). In addition, estuarine systems show widely different CS_2 concentrations, evidently increasing the uncertainty of CS_2 concentration and flux estimates for these environments. Furthermore, seasonal coverage is mainly restricted to summer months, particularly in shelf areas. This lack of seasonal cover is arguably one of the most important constraints, especially since preliminary time series measurements from one estuarine system indicate summer/winter ratios of approximately 2.5 for sea surface CS_2 (Moret *et al.* 2000).

Although inadequate seasonal cover still precludes the application of winter/summer scenarios, available data are sufficient to allow separate emission estimates for shelf waters and estuarine systems. We therefore derived mean, annual CS_2 concentrations for European shelf waters and estuarine systems by equally weighting each of the study areas in our data compilation (Table 8). We also calculated CS_2 saturation ratios (SR), using temperature and salinity dependent solubility data from Elliott (1989) and average atmospheric mixing ratios for shelves (20 ppt) and estuaries (69 ppt) from Kim and Andreae (1987). Salinity and temperature values were the same as those used for DMS (Table 4.).

Our mean, annual CS_2 concentrations (saturation ratios) for European shelf waters and estuarine systems were 27.9 pM (13) and 158 pM (69), respectively, indicating strong supersaturation with respect to ambient atmospheric levels (Table 9). It is worth noting that estuarine CS_2 concentrations are approximately six times higher than those on the adjacent shelves. Our average, estuarine CS_2 concentration is almost three times higher than a previous estimate for US east coast estuaries (57 pM, Kim & Andreae 1992), mainly due to the inclusion of recent data from highly productive estuarine systems (Jørgensen & Okholm-Hansen 1985; Moret *et al.* 2000; Watts 1991; Watts 2000).

However, our average for European shelf waters (27.9 pM) is in close agreement with previous work (Kim & Andreae 1992; Xie & Moore 1999). These results indicate that CS₂ emissions from estuarine systems may be significantly more important than believed previously.

5.5 Oxygenated volatile organic chemicals (OVOC)

Oxygenated volatile organic chemicals (OVOC) in the atmosphere have an indirect climate effect through their influence on the atmospheric lifetime of species like methane (through OH) and on the concentration of tropospheric ozone, which is a climate gas, and particulate matter. Based on airborne measurements over the Pacific (TRACE-P Spring 2001 experiment) and model calculations, Singh *et al.* (2003) found that the surface waters of the Pacific Ocean are greatly supersaturated with acetaldehyde and propanal and therefore a source to the troposphere of these gases, and a modest sink of methanol and acetone. Assuming the marine surface mixed layer to be 50-100 m thick, it is concluded that the oceanic reservoir of OVOC is one order of magnitude larger than the atmospheric reservoir. Sunlight initiated reactions can decompose organic matter in surface oceans to form a variety of oxygenated chemicals. The role of oceans in the global OVOC budget is largely unexplored, however, and only little data is available according to Singh *et al.*, 2003, who do not discuss the contributions from coastal regions to the ocean-atmosphere OVOC fluxes compared to the open ocean fluxes.

5.6 Concluding remarks

The coastal ocean is a source of trace gases to the atmosphere. The most important trace gases emitted in appreciable amounts from the coastal ocean include methane, nitrous oxide, DMS and COS. The behaviour of carbon dioxide in estuaries is more complex. The production of these trace 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. The vast majority of efforts to explain the production and water to air transport has 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 CO₂ from the surface water to the atmosphere are higher for the coastal areas than for the open sea, for some gases the differences are up to several orders of magnitude. A comparison of these flux rates for the coastal zone and the open ocean is presented in Table 21 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 and CO₂. This information is also presented in Table 21.. Limited information on flux rates for methane, nitrous oxide, DMS, COS, and CO₂ 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 indicates that on a global scale the estuaries will contribute a few percent to the total emissions of methane, DMS and COS, and a bit more to the total emissions of nitrous oxide and CO₂. This suggestion, however, should be considered as a crude approximation and would need new studies for refinement.

The flux rates of methane, nitrous oxide, DMS, COS, and carbon dioxide 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 21 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 21. 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.

Despite the fact that our knowledge on the distribution of N_2O and CH_4 in coastal areas is still limited, a general impact assessment of various parameters which may influence current and future emissions of these gases from European coastal water shown in Table 10.

• 6. Ocean ecosystems under global warming

Global warming will affect ocean ecosystems in general and coastal margins in particular, affecting the atmosphere-ocean exchange of e.g. carbon dioxide, nutrients and halogens. Sarmiento *et al.* (2004) examined the ocean biological response to climate warming between the beginning of the industrial revolution and 2050 on the basis of several coupled climate model simulations. They found that climate warming leads to a contraction of the highly productive marginal sea ice biome by 42% in the Northern Hemisphere and 17% in the Southern Hemisphere, and leads to an expansion of the low productivity permanently stratified subtropical gyre biome by 4.0% in the Northern Hemisphere and 9.4% in the Southern Hemisphere. The low-latitude (mostly coastal) upwelling biome area was found to change only modestly. Vertical stratification was found to increase, which would be expected to decrease nutrient supply everywhere, but increase the growing season length in high latitudes. Three different primary production algorithms were used to estimate the response of primary production to climate warming and were found to give a global increase in primary production of 0.7% at the low end to 8.1% at the high end, with very large regional differences. The main cause of both the response to warming and the variation between algorithms is the temperature sensitivity of the primary production algorithms.

Gregg *et al.* (2003) found on the basis of satellite in-situ blended ocean chlorophyll records that global ocean annual primary production has declined more than 6% since the early 1980's. Nearly 70% of the global decadal decline occurred in the high latitudes. In the northern high latitudes, these reductions in primary production corresponded with increases in sea surface temperature and decreases in atmospheric iron deposition to the oceans. These results indicate that ocean photosynthetic uptake of carbon may be changing as a result of climatic changes and suggest major implications for the global carbon cycle. The reduction in marine primary productivity may represent a reduced sink of carbon via photosynthesis, with implications for the atmospheric budget of carbon dioxide, nutrients and other trace species that affect the atmospheric composition of direct or indirect greenhouse gases. The halogens belong to the latter. With their high reactivity they influence the oxidation capacity of the atmosphere and consequently the atmospheric lifetime of GHGs that undergo chemical transformation in the atmosphere, like methane and ozone.

• 7. Future changes of fluxes of trace gases in the coastal zone

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 CO₂ to the sea. These precursors include organic matter, nitrates, ammonium, sulphates 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 extent 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.

• 8. Future research needs

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, sulphur and contaminants and the production of trace gases from their precursors.

Concerning measurements, the following future activities can be defined:

- time series measurements of dissolved and atmospheric concentrations along the salinity gradients in selected coastal and estuarine systems (intertidal estuaries, fjords, lagoons, upwelling etc.) in order to resolve the seasonality,
- time series measurements of N_2O and CH_4 formation processes along the salinity gradients in selected estuarine systems (intertidal estuaries, fjords, lagoons etc.) in order to reveal the major formation pathways,
- implementation of obligatory station grids in the North, Mediterranean and Black Seas (there is already one existing for the Baltic Sea) in order to facilitate comparison of various measurements and to avoid "patchwork" surveys,
- measurements of CH_4 emissions from shallow geological sources (natural seepages) in order to quantify the contribution by geological CH_4
- No DMS data are as yet available for the large shelf areas of the Barents, Greenland and Norwegian Seas (except very few measurements around Iceland), the Caspian and Azov Seas, the Adriatic and large areas of the Baltic Sea. Considering the large area coverage (about 50% of European shelf area) their contribution to coastal European DMS emissions is likely to be important and requires further study.
- development of an obligatory standard protocol to measure trace gases in the water and in the atmosphere. These measurements should be performed with standards which have to be intercalibrated against internationally accepted standard scales,
- development of a GIS (geographical information system) database where trace gas measurements as well as associated parameters such as temperature, salinity, wind speed, oxygen nutrients etc. are archived,
- development of an obligatory standard protocol to compute and extrapolate emissions on a regional (European) scale, and
- development of autonomously operating measurement systems to be used on ferry lines or ships of opportunity to gain a high temporal and spatial resolution of the distribution of trace gases in surface waters.

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 modelling. This environmental modelling 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 modelling 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.

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Table 1: Areal extent and trophic status of European coastal shelves (adopted from Walsh 1988)

Region	Area / 10^5 km ²	Type	Trophic Status
Northwestern European shelf			
Barents Sea	7.3	Wide shelf	Phototrophic system
Greenland-Norwegian Seas	2.8	Narrow shelf	Phototrophic system
North and Irish Seas	8.7	Wide shelf	Eutrophic system
Bay of Biscay	2.7	Narrow shelf	Eutrophic system
Western Iberian *	0.4	Narrow shelf	Eastern boundary current
European Enclosed Seas			
Baltic Sea	3.9	Brackish, anoxic bottom waters	Eutrophic system
Northern Mediterranean	2.9	High salinity	Eutrophic system
Black Sea and Sea of Azov	1.6	Brackish, anoxic bottom waters	Eutrophic system
Caspian Sea	1.5	Brackish inland sea	Eutrophic system
Total Area	31.8		

* Estimated as 50% of Portugal-Morocco shelf in WALSH (1988)

Table 2: Drivers, pressures and Impacts: Present trends assessed for the Baltic Sea (B, b), Black Sea (BS, bs), Mediterranean (M, m), North Sea (N, n) and Atlantic coast (A, a). Capital letters symbolize a very significant impact, small letters a significant impact, no letter means no significant impact.

Drivers	Impacts	Contamination related impacts	coastal squeeze and habitat loss	species composition	salinisation	land subsidence	flood risk change	decreased sedimentation/coastal erosion	increased sedimentation	landscape/amenities	fisheries loss	loss of water resources
climate change			b, n	m, N, A			b, bs, m, n, a	b, n, m				
agriculture/forestry	B, BS, m, n		bs, n		M, bs	m, n		M				bs, M
urbanisation	b, BS, m, n	b, BS, m, n	B, BS, M, N, A	b	B, bs, M	m, n	m					
Tourism	b, bs, m	m, bs	b, BS, M, n, a	B, m	B, m			m		b, BS, M, n, a	M	
industry and trade	b, bs	b, bs, m, n, a	b, bs, m, n	b, BS, m, n, a				b, m, n		b, BS, n, a		
fishery and shell fish fishery	b, m, a	a	B, BS, M, N, A	B, BS, M, N, A							B, BS, M, N, A	
Energy		b, bs, m, n, A				n		BS				bs

[illegible]

<i>Urbanisation</i>	b, BS, m, n	b, BS, m, n	B, BS, M, N, A	B, BS, M, N, A	b	B, BS, M, N, A	b	B, BS, M, N, A	b, bs, m	m	m	bs, m, n	M	BS, M	bs	BS, m			
scenario 1	B, bs, M, n	B, bs, M, n	B, BS, M, N, A	B, BS, M, N, A	b	B, BS, M, N, A	b	B, BS, M, N, A	b, bs, m	m	bs, m, n	M		BS, M	bs	BS, m			m
scenario 2	bs, m		BS, M	BS, M		b, BS, M		b, BS, M	bs, m	m	bs, m			BS, m		bs			
scenario 3	bs, m		bs, M	bs, M		b, bs, M		b, bs, M	bs, m	m	bs, m			BS, m		bs			
Tourism	b, bs, m	b, bs, m	bs, M	bs, M		b, bs, M		b, bs, M	bs, m	m	bs, m			M		b, BS, M, n, a			
scenario 1	B, M	B, BS, M, n	B, BS, M, N, A	B, BS, M, N, A	b	B, BS, M, N, A	b	B, BS, M, N, A	b, bs, m	m	bs, m			M	BS	B, BS, M, N, A			BS, m
scenario 2	m	bs	BS, m, n, a	BS, m, n, a	m	b, bs, m, n, a	m	b, bs, m, n, a	bs, m					m		b, BS, m, n, a			bs
scenario 3	b, m	b, bs, n, a	b, BS, m, n, a	b, BS, m, n, a	m	b, bs, m, n, a	m	b, bs, m, n, a	b, m					m		b, bs, m, n, a			
industry and trade	b, bs, m	b, bs, m				b, bs, m, n, a		b, bs, m, n, a	b, BS, m, n, a					B, m, n		b, BS, n, a			
scenario 1	bs, m	B, BS, M, n, a	bs	bs		b, BS, M, n, a		b, BS, M, n, a	b, BS, m, N, A					b, m, N	BS	b, BS, n, a			
scenario 2		BS, m	bs	bs		BS		BS	BS, n, a					b, n	bs	b, BS			
scenario 3		b, bs, m	bs	bs		BS		BS	bs					b		b, BS			
Fishery and aquaculture	b, m	a				B, BS, M, N, A		B, BS, M, N, A	B, BS, M, N, A									B, BS, M, N, A	
scenario 1	bs, m, A	A				b, BS, M, N, A		b, BS, M, N, A	b, BS, m, N, A					a		a		B, M, N, A	
scenario 2	a	a				b, BS, M, n, a		b, BS, M, n, a	b, bs, M, n, a									m, n, a	
scenario 3	a	a				b, bs, M, n, a		b, bs, M, n, a	b, bs, M, n, a									b, m, n, a	
Energy		b, bs, m, n, A				n, a		n, a			n			BS					bs
scenario 1	bs	B, bs, m, n, A	b	bs		bs		b, bs, n	b, bs, n	n						bs, N			
scenario 2	bs	b, bs						b, n								m			
scenario 3		b, bs				b, bs		b, n								n			b

Table 4: Compilation of average N_2O surface saturations in European shelf waters (excluding estuarine systems and river plumes, see Table 5).

Region	Date	Avg. N_2O (range or sd), Reference nmol L^{-1}	
Baltic Sea			
Baltic Proper	1977-1980*	127** (111 – 138)	Rönner (1983)
Bothnian Sea	Jun 1980	119** (101 – 130)	Rönner (1983)
Bothnian Bay	Jun 1980	116** (109 – 120)	Rönner (1983)
Gotland Deep	1986-1987*	112**	Brettar and Rheinheimer (1991)
North Sea			
German Bight	1991-1992*	100 (99 – 101)	Bange et al. (1996b)
German Bight	Jul 1987	130	Law and Owens (1990)
Central North Sea	Sep 1991	104 ± 1	Bange et al. (1996b)
Central North Sea	Jul 1987	102	Law and Owens (1990)
Mediterranean Sea			
Northern Aegean Sea	Jul 1993	106 ± 2	Bange et al. (1996a)
Eastern Ionian Sea	Jul 1993	107 ± 3	Bange et al. (1996a)
Gulf of Lions	Jun 1998	86** (0 – 197)	Marty et al. (2001)
Gulf of Thermaikos	Apr 1998	171** (84 – 309)	Marty et al. (2001)
Adriatic Sea	Aug 1996	93** (85 – 100)	Leip (1999)
Black Sea			
Northwestern shelf	Jul 1995	112	Amouroux et al. (2002)
Average		113 ± 21	

sd stands for standard deviation.

* study with a seasonal/interannual coverage, for details see reference.

** values estimated based on the information given in the reference.

Table 5: Compilation of average N_2O surface saturations in European estuarine systems and river plumes.

Region	Date	Avg. N_2O (range or sd), Reference $nmol\ L^{-1}$	
Baltic Sea			
Bodden waters	1994-1997*	108** (100 – 120)	<i>Bange et al. (1998a)</i>
North Sea			
Colne	1993-1994*	2645** (100 – 5190)	<i>Robinson et al. (1998)</i>
Scheldt	1997-1998*	710	<i>De Bie et al. (2002)</i>
Humber	1995-1996*	452 (100 – 4250)	<i>Barnes and Owens (1998)</i>
Tweed	1996-1997*	100 (96 – 110)	<i>Barnes and Owens (1998)</i>
Humber Wash plume	May 1995	113* (100 – 125)	<i>Barnes and Owens (1998)</i>
NE Atlantic			
Gironde	Nov 1992	132 (106 – 165)	<i>Bange et al. (1996b)</i>
Tamar	1988-1990*	215** (100 – 330)	<i>Law et al. (1992)</i>
Mediterranean Sea			
Amvrakikos Bay	Jul 1993	103 \pm 2	<i>Bange et al. (1996a)</i>
Sacca di Goro	1996-1997*	490 (0 – 6635)	<i>Leip (1999)</i>
Rhone plume	1997*	398** (226 – 555)	<i>Marty et al. (2001)</i>
Black Sea			
Danube plume	Jul 1995	112	<i>Amouroux et al. (2002)</i>
Average		465 \pm 716	

sd stands for standard deviation.

* study with a seasonal/interannual coverage, for details see reference.

** values estimated based on the information given in the reference.

Table 6: Estimate of the annual N_2O emissions from European shelf and estuarine areas.

	Area ¹ , 10 ¹² m ²	Avg. saturation ² , %	ΔC ³ , nmol L ⁻¹	Emissions ⁴ (LM86), Tg N yr ⁻¹	Emissions ⁴ (W92), Tg N yr ⁻¹
Shelf	3.18	113	1.1	0.08	0.15
Estuaries	0.17	465	34	0.13	0.25

¹ G. Uher, personal communication.

² see Table 4 and Table 5.

³ ΔC stands for the concentration difference across the ocean/atmosphere interface and was calculated as $DC = (\text{saturation}/100 \cdot C_{\text{air}}) - C_{\text{air}}$. C_{air} was calculated with the Bunsen coefficient of *Weiss and Price* [1980] for a water temperature of 15°C and salinities of 35 and 15 for shelf and estuaries, respectively. We applied a mean atmospheric N_2O dry mole fraction of 308 ppb (i.e. the mean for the period 1980-1998 corresponding to the dates of the listed measurements)

⁴ LM86 stands for the model approach of *Liss and Merlivat* [1986]. W92 stands for the model approach of *Wanninkhof* (1992) for climatological wind speeds. We applied a mean wind speed of 7 m s⁻¹. N_2O Schmidt numbers were calculated with the mean water temperature and salinities as given in footnote 3.

Table 7: Compilation of average CH_4 surface saturations in European shelf waters (excluding estuarine systems and river plumes, see Table 8).

Region	Date	Avg. CH_4 (range or sd), Reference saturation, %	
Arctic Sea			
Barents Sea	Aug 1991	120 (115 – 125)	Lammers et al. (1995)
Baltic Sea			
Baltic Proper	1992*	254 (113 – 395)	Bange et al. (1994)
North Sea			
Southern North Sea	Nov 1980	140	Conrad and Seiler (1988)
German Bight	Sep 1991	126 \pm 8	Bange et al. (1994)
Southern Bight	Mar 1989	113 (95 – 130)	Scranton and McShane (1991)
Central North Sea	May 1994	215 (120 – 332)	Rehder et al. (1998)
Southern North Sea	Aug 1993	338 (118 – 701)	Upstill-Goddard et al. (2000)
Off UK east coast	1995-1999	129 (112 – 136)	Upstill-Goddard et al. (2000)
NE Atlantic			
Bay of Biscay	Nov 1980	100	Conrad and Seiler (1988)
Mediterranean Sea			
Adriatic Sea	Aug 1996	425* (420 – 450)	Leip (1999)
Eastern Ionian Sea	Jul 1993	148 \pm 22	Bange et al. (1996a)
Northern Aegean Sea	Jul 1993	231 \pm 32	Bange et al. (1996a)
Black Sea			
Northwestern shelf	Jul 1995	567	Amouroux et al. (2002)
Average		224 \pm 142	

sd stands for standard deviation.

* study with a seasonal/interannual coverage, for details see reference.

** values estimated based on the information given in the reference.

Table 8: Compilation of average CH_4 surface saturations in European estuarine systems and river plumes.

Region	Date	Avg. CH_4 (range or sd), Reference saturation, %	
Baltic Sea			
Randers Fjord	2000*	6840** (1640 – 13,380)	<i>Abril and Iversen (2002)</i>
Bodden waters	1994-1997*	7802** (105 – 15,500)	<i>Bange et al. (1998a)</i>
Eckernförde Bay	1993-1994*	838** (793 – 7803)	<i>Bussmann and Suess (1998)</i>
North Sea			
Humber	1995-1996*	4436 (238 – 21,048)	<i>Upstill-Goddard et al. (2000)</i>
Tyne	Jan 1996	5843 (450 – 20,000)	<i>Upstill-Goddard et al. (2000)</i>
Elbe	Apr 1997	580 (130 – 29,800)	<i>Middelburg et al. (2002)</i>
Ems	Jul 1997	3150 (9200 – 13,100)	<i>Middelburg et al. (2002)</i>
Thames	Feb 1999	570 (150 – 6700)	<i>Middelburg et al. (2002)</i>
Rhine	1996-1998*	8400 (140 – 49,700)	<i>Middelburg et al. (2002)</i>
Scheldt	1996-1998*	3210 (380 – 3210)	<i>Middelburg et al. (2002)</i>
NE Atlantic			
Loire	Sep 1998	660 (340 – 23,100)	<i>Middelburg et al. (2002)</i>
Gironde	1996-1998*	580 (70 – 13,400)	<i>Middelburg et al. (2002)</i>
Douro	Sep 1998	3610 (620 – 5720)	<i>Middelburg et al. (2002)</i>
Sado	Sep 1998	5900 (940 – 158,000)	<i>Middelburg et al. (2002)</i>
Mediterranean Sea			
Amvrakikos Bay	Jul 1993	522 ± 177	<i>Bange et al. (1996a)</i>
Black Sea			
Danube plume	Jul 1995	5340	<i>Amouroux et al. (2002)</i>
Average		3643 ± 2814	

sd stands for standard deviation.

* study with a seasonal/interannual coverage, for details see reference.

** values estimated based on the information given in the reference.

Table 9: Estimate of the annual CH_4 emissions from European shelf and estuarine areas.

	Area ¹ , 10 ¹² m ²	Avg. saturation ² , %	ΔC ³ , nmol L ⁻¹	Emissions ⁴ (LM86), Tg C yr ⁻¹	Emissions ⁴ (W92), Tg C yr ⁻¹
Shelf	3.18	224	3.1	0.09	0.17
Estuaries	0.17	3643	99.5	0.16	0.31

¹ G. Uher, personal communication.

² see Table 7 and Table 8.

³ DC stands for the concentration difference across the ocean/atmosphere interface and was calculated as $\text{DC} = (\text{saturation}/100 \times C_{\text{air}}) - C_{\text{air}}$. C_{air} was calculated with the Bunsen coefficient of *Wiesenburg and Guinasso* (1979) for a water temperature of 15°C and salinities of 35 and 15 for shelf and estuaries, respectively. We applied a mean atmospheric CH_4 dry mole fraction of 1.83 ppm (i.e. the mean for the period 1980-2000 corresponding to the dates of the listed measurements)

⁴ LM86 stands for the model approach of *Liss and Merlivat* (1986). W92 stands for the model approach of *Wanninkhof* (1992) for climatological wind speeds. We applied a mean wind speed of 7 m s⁻¹. CH_4 Schmidt numbers were calculated with the mean water temperature and salinities as given in footnote 3.

Table 10: *Impact assessment of various parameters which might influence today's and future N₂O and CH₄ emissions from European coastal waters. Classification scheme: – = minor; + = moderate; ++ = high; ? = unknown.*

	N ₂ O	CH ₄
Eutrophication	++	++
Coastal upwelling	+	–
Release from natural seepages	n.a.	++
Fish farming	–	?
Ecosystem shifts due to climate change	?	?

n.a. stands for not applicable.

Table 11: Overview of DMS measurements in European coastal and adjacent open ocean waters. Coastal and open ocean data have not been separated here, unless otherwise stated. Please note that data ranges given in brackets may refer to individual measurements or to averages from data subsets, depending on the original report.

Region	Date	Comments	DMS / nM	Flux / $\mu\text{mol m}^{-2} \text{d}^{-1}$	Source
Northwestern European shelf and adjacent open ocean					
Barents Sea off North Norway	13 – 29 May 1993	Includes no shelf data	n.a. (2.8 – 25.3)	n.a.	Matrai and Vernet (1997)
N North Sea	16-26 Jun 1999	Coccolithophore bloom	3.2 (2.3 – 4.7)	8.1 (6-10.2)	Burkall et al. (2002) Archer et al. (2002)
N Atlantic, UK to Iceland	13 – 29 Jun 1991	Coccolithophore bloom	16.9 (1 – 45)	26.9	Holligan et al. (1993)
N and S Atlantic starting from Iceland	Oct 1996	Only Iceland shelf data shown here	n.a. (0.16 – 0.26)	n.a.	Belviso et al. (2000)
Off Western Ireland	8 Jun – 2 Jul 1996		4.2 (0.2 – 42.6)	Ca. 1.0 (0 – 6.6)	Locarnini et al. (1998)
Off Western Ireland	12 – 31 May 1997		5.5 (0.1 – 46.4)	n.a. (0 – 38)	Baker et al. (2000)
Around Great Britain	1984 - 1987	Flux based on data from April to September	4.8 (0.8 – 90.0)	32	Turner et al. (1989)
Around Great Britain	Jan and Jul – Aug 1985	North & Irish Seas, English Channel	6.9 (0.1 – 34.3)	14.8 (0.5 – 29.1)	Turner et al. (1988)
S North Sea	Aug – Sep 1989; May, Sep – Oct '90	Only water column DMS shown here	5.2 (May '90) 0.15 (Sep '90)	n.a.	Nedwell et al. (1994)
S North Sea	Feb – Oct 1989	Data as in Turner et al.	3.9 (0.13 – 25.0)	3.8 (0.2 – 16.4)	Turner et al. (1996); Liss et al. (1993)
SW North Sea, off Great Yarmouth	May – Aug 1983	DMS and CS ₂ not separated	0.4 – 15.6 nM S (DMS+CS ₂)	n.a.	Turner and Liss (1985)
English Channel	Jun 1984	Ushant frontal system	n.a. (1.4 – 24.3)	n.a.	Holligan et al. (1987)
NE Atlantic	Sep 1994; Jul 1995	Means (ranges) for all data	5.0 (0.6 – 38.5)	10.5 (6.6 – 16.7)	Uher et al. (2000)
N & S Atlantic; Sargasso Sea	Oct–Nov 1980; Sep 1981	Includes S North Sea, English Channel	2.6 (all data) 8.0 (shelf)	n.a. (7.9 – 13.1, all)	Andreae and Barnard (1984); Barnard et al., (1982)

Table 11: *continued*

Region	Date	Comments	DMS / nM	Flux / $\mu\text{mol m}^{-2} \text{d}^{-1}$	Source
Northwestern European shelf and adjacent open ocean					
Atlantic, NW Mediterranean, Indian Ocean	Mar 1977 – May 1978		0.9 (0.2 – 18.1)	4.1	Nguyen et al. (1978)
N and S Atlantic	Mar – Apr 1987	Concentrations for 28W, 30N to 14W, 47N only	2.5 (0.8 – 8.5)	5.8 - 6.6 (all data)	Bürgermeister et al., (1990)
N and S Atlantic	12 Sep – 2 Oct 1998	Incl. data from English Channel and Celtic Sea	2.0 (0.2 – 5.9)	6.0 (0.0 – 43.4)	Kettle et al. (2001)
N and S Atlantic (1988-1990), Arctic (Jul-Aug 1990)	Sep – Oct 1988; Aug – Sep 1989; Oct – Nov 1990	Includes S North Sea, English Channel	0.9 (1988) 4.4 (1989) 2.2 (1990) 3.1 (Arctic)	n.a. (4.0 – 9.5)	Staubes and Georgii (1993); Staubes- Diederich (1992)
Baltic Sea					
NE Baltic Sea, Kattegat/Skager- rak, NE North Sea	July 1988		n.a. (2.1 – 4.7)	n.a. (4.7 – 23.7)	Leck and Rodhe (1991)
E Baltic Sea	Jan 1987 – Jun 1988		n.a. (0.06 – 6.2)	n.a.	Leck et al. (1990)
Mediterranean Sea					
Ligurian Sea, NW Mediterranean,	May 1990	Also data from NE Atlantic	4.6 (Ligurian only)	n.a.	Belviso et al. (1993)
NW Mediterranean	Jun 1993; Apr & Jul 1994		n.a. (0.1 – 24.0)	11.2 (shelf) 2.5 (open sea)	Simó and Grimalt (1998); Simó et al. (1997); Simó et al. (1995)
Around Greece	July 1993		3.7 (0.2 – 18.1)	n.a.	Rapsomanikis, unpublished, as in Kettle et al. (1999)
Black Sea					
Around Turkey (SE Black Sea, Aegean & Mediterranean)	Oct 2000	Highest concn near sewage outfall	2.0 (0.6 – 7.0)	17.6 (all data)	Besiktepe et al. (2004)
NW Black Sea	18 Jul – 2 Aug 1995	Includes data from Danube plume	7.8 (3.0 – 11.9)	5.2 (1.6 – 11.9)	Amouroux et al. (2002)

Table 11: *continued*

Region	Date	Comments	DMS / nM	Flux / $\mu\text{mol m}^{-2} \text{d}^{-1}$	Source
Estuarine systems					
6 W European estuaries	Jul 1996 – May 1998	Mean of means of all estuaries	1.3 (0.02 – 10.0)	n.a.	Sciarc et al. (2002)
Norsminde Fjord, Denmark	Jun – Sep 1984	Flux data are for intertidal areas	2.2 (0.6–3.6)	37.1 (0.5 – 335.3)	Jørgensen and Okholm-Hansen (1985)
Oosterscheldt, The Netherlands	1 – 17 May 1985	Former estuary of River Scheldt	7.0 (1.5 – 22.7)	n.a.	Turner, unpublished as, in Kettle et al. (1999)
W Wadden Sea, Marsdiep, The Netherlands	Nov 1991 – Nov 1992; Jan – Jun 1993	Incl. Phaeo-cystis spring bloom data	2.9 (<0.5 – 18)	n.a. (0 – 18)	Kwint and Kramer (1996)
W Wadden Sea, Marsdiep, The Netherlands	Mar – Jun 1995	Incl. Phaeo-cystis spring bloom data	n.a. (<1 – 40)	n.a.	van Duyl et al. (1998)
Ria de Aveiro, Portugal	45 surveys over one year	mud flat data excluded here	4.1 (2.9 – 5.3)	0.7 (0.1 – 1.1)	Cerqueira and Pio (1999)
Toulon Bay, NW Mediterranean	Jan – Dec 1997		9.8 (3.6 – 21.0)	n.a.	Desplau et al. (2002)
Venice lagoon, N Adriatic	3 Jun 1996 – 26 Nov 1997		4.6 (0.4 – 16.3)	0.3 (0.1 – 0.7)	Moret et al. (2000)
NE German Wadden Sea	Jun 1991 – May 1994	Intertidal mud flat data only	n.a.	1.3 (0.1 – 1.7)	Bodenbender et al. (1999)
Cole Estuary, SE England	Jul 1988 – Jul 1989	Saltmarsh creek, pan & vegetated	Porewater: 3.7 – 7.8 nmol mL^{-1} sediment	n.a. (1.2 – 2.5)	Hamison et al. (1992)

Table 12: Arithmetic means of DMS concentrations on European shelves and adjacent open ocean waters. The data are extracted from the subset of the global DMS database from Kettle et al. (1999) shown in Figure 9. The numbers of individual measurements are given in brackets. For comparison, the annual mean for European estuarine systems is also listed. The mean, estuarine DMS concentration is calculated from averages in Table 11, which are based on annual coverage except the data from Sciare et al. (2002), which only have partial annual coverage.

Region	DMS / nM Winter (October to March)	DMS / nM Summer (April to September)	DMS / nM Annual
Shelf	0.76 (n = 410)	8.43 (n = 1519)	4.6
Open ocean	1.86 * (n = 84)	6.20 § (n = 1287)	4.0
Estuarine systems	n.a.	n.a.	4.4

* from measurements in October in the northeastern Atlantic only

§ biased towards midsummer (see text for details)

Table 13: DMS emissions from European shelves and estuarine systems. The DMS emissions are reported as averages of estimates from two air-sea gas exchange models (Liss and Merlivat 1986; Wanninkhof 1992). For a detailed description of calculations, please see Uher et al. (2000). We used mean values of sea surface temperature (10.2°C), salinity (32.9), and wind speed (9.7 ms⁻¹) from the subset of the global DMS database from Kettle et al. (1999) shown in Figure 9. See section 'European coastal zone' for details on area cover.

Region	Area km ²	DMS / nM	DMS emission / Gmol a ⁻¹
Shelf	3.18 x 10 ⁶	4.6	21.0
Estuarine systems (area from this work)	0.17 x 10 ⁶	4.4	1.1
Estuarine systems (area from EU CORINE project)	0.025 x 10 ⁶	4.4	0.16

Table 14: Overview of COS measurements in European coastal and adjacent open ocean waters. Coastal and open ocean data have not been separated here, unless otherwise stated. SR denotes the saturation ratio with respect to ambient atmospheric concentration and is given in brackets below the respective mean concentrations. Please note that flux ranges reported in brackets may refer to individual measurements or to averages from data subsets, depending on the original report.

Region	Date	Comments	COS / pM (SR)	Flux / nmol m ⁻² d ⁻¹	Source
Northwestern European shelf and adjacent open ocean					
SE North Sea and outer Elbe estuary	Apr 1994	COS highest in outer Elbe	118 (5.6)	100	Ulshöfer and Andreae (1998)
SE North Sea; NE Atlantic	Sep 1992	Only SE North sea data reported here	49 (3.2)	95	Uher and Andreae (1997a)
SW North Sea, off Great Yarmouth	May – Aug 1983	SR is sum of COS and H ₂ S	65 - 170 (4.6)	n.a.	Turner and Liss (1985)
S North Sea and English Channel	Sep 1989 – May 1990		142 (n.a.)	n.a.	Watts (1991)
N and NW French Coast	1987 – 1989 (summer)		n.a. (9.0)	n.a.	Mihalopoulos et al. (1992)
NE Atlantic	Apr – May 1992; Jan 1994; Sep '94	Mostly open ocean data	Jan: 5.3 (0.5) Apr-May: 14.9 (1.3) Sep: 46 (2.1)	Jan: 51 Apr-May: 9 Sep: 30	Ulshöfer et al. (1995)
N and S Atlantic; SE North Sea	Sep – Oct 1988, Aug – Sep '89, Oct – Nov '90; Jul – Aug '90; May 1988 & Apr '89	Data for 40-80°N only. Incl. S North Sea, English Channel	102 (1.1 - 3.3)	248	Staubes et al. (1990); Staubes-Diederich (1992)
N and S Atlantic	Oct/Nov 1997; May/Jun 1998	Shelf data, digitised from Xu et al. (2001)	Oct-Nov: n.a. (1.3) May-Jun: n.a. (5.9)	n.a.	Xu (2001); Xu et al. (2001)
N and S Atlantic	12 Sep – 2 Oct 1998	Incl. data from English Channel and Celtic Sea	21.7 (14.7 – 18.1)	19.3 (-0.07 – 2.2)	Kettle et al. (2001)

Table 14: *continued*

Region	Date	Comments	COS / pM (SR)	Flux nmol m ⁻² d ⁻¹	Source
Mediterranean Sea					
NW Mediterranean off Villefranche	Jun 1994		n.a. (7.0)	n.a.	Mihalopoulos et al. (1992)
Around Greece	Jul 1993		Shelf: 43 (5.2) Open Sea: 21 (2.6)	Shelf: 56 Open Sea: 52	Ulshöfer et al. (1996)
Estuarine systems					
4 W European estuaries	Jul 1996 – May 1998	Mean of means of all estuaries	309 (n.a.)	n.a.	Sciare et al. (2002)
Norsminde Fjord, Denmark	Jun – Sep 1984		255	n.a.	Jørgensen and Okholm-Hansen (1985)
Off Great Yarmouth, SE England	Apr - Nov 1990		775 (n.a.)	n.a.	Watts (1991)
NE German Wadden Sea	Jun 1991 – May 1994	Intertidal mud flat data only	n.a.	890 (180 – 1500)	Bodenbender et al. (1999)
Colne Estuary, SE England	Jul 1988 – Jul 1989	Saltmarsh creek & intertidals	515	850 (intertidal only)	Harrison et al. (1992)

Table 15: Arithmetic means of COS concentrations in European shelf waters and estuarine systems, calculated from data in Table 14. Saturation ratios (SR), calculated as described in Ulshöfer et al. (1995), are given in brackets (see text for details).

Region	COS / pM Winter (October March)	COS / pM to Summer (April September)	COS / pM to Annual
Shelf	15.7 (0.9)	93.0 (5.1)	54.3 (3.0)
Estuarine systems	234 (13)	476 (26)	355 (20)

Table 16: COS emissions from European shelves and estuarine systems. The COS emissions are reported as averages of estimates from two air-sea gas exchange models (Liss and Merlivat 1986; Wanninkhof 1992). For a detailed description of calculations, please see Ulshöfer et al. (1995). We used mean values of sea surface temperature (10.2°C), salinity (32.9), and wind speed (9.7 ms⁻¹) from the subset of the global DMS database from Kettle et al. (1999) shown in Figure 9. The mean atmospheric mixing ratio was 606 ppt and was calculated from atmospheric measurements on the European shelf (see references in Table 14). See section 'European coastal zone' for details on area cover.

Region	Area km ²	COS nM	COS emission Gmol a ⁻¹
Shelf (excluding estuarine systems)	3.01 x 10 ⁵	54.3	0.19
Estuarine systems (area from this work)	0.17 x 10 ⁵	355	0.10
Estuarine systems (area from EU CORINE project)	0.025 x 10 ⁵	355	0.014
Total			0.20 – 0.29

Table 17: Overview of CS₂ measurements in European coastal and adjacent open ocean waters. Coastal and open ocean data have not been separated here, unless otherwise stated.

Region	Date	Comments	CS ₂ pM	Flux nmol d ⁻¹	Source
Northwestern European shelf and adjacent open ocean					
NE North Sea	July 1988		11	50	Leck and Rodhe (1991)
SW North Sea, off Great Yarmouth	July 1983		16	n.a.	Turner and Liss (1985)
S North Sea and English Channel	Sep 1989 – May 1990		49	n.a.	Watts (1991)
SE North Sea	Apr 1989		16	n.a.	Staubes-Diederich (1992)
Off western Ireland	July 1973		36	n.a.	Lovelock (1974)
Off western Ireland	Jun – Jul 1996	Only coastal data reported here	13.6	13.4	Xie and Moore (1999)
N and S Atlantic	Sep – Oct 1988		52	167	Staubes et al. (1990)
N and S Atlantic	12 Sep – 2 Oct 1998	Incl. data from English Channel and Celtic Sea	10.9	19.3	Kettle et al. (2001)
Baltic Sea					
NE Baltic Sea, Kattegat/Skagerrak	July 1988		11	28	Leck and Rodhe (1991)
Estuarine systems					
4 W European estuaries	Jun 1997 – May 1998	Mean of means of all estuaries	36	n.a.	Sciara et al. (2002)
Norsminde Fjord, Denmark	Jun – Sep 1984	Flux data are for intertidal areas	179	50	Jørgensen and Okholm-Hansen (1985)
Off Great Yarmouth, SE England	Apr - Nov 1990		263	n.a.	Watts (1991)
Venice lagoon, N Adriatic	3 Mar – 26 Nov 1997		508	43	Moret et al. (2000)
NE German Wadden Sea	Jun 1991 – May 1994	Intertidal mud flat data only	n.a.	362	Bodenbender et al. (1999)

Table 18: Arithmetic means of CS₂ concentrations in European shelf waters and estuarine systems, calculated from data in Table 17. Saturation ratios (SR) are given in brackets (see text for details).

Region	CS ₂ / pM Winter (October March)	CS ₂ / pM to Summer (April September)	CS ₂ / pM Annual to
Shelf	n.a.	27.9	27.9
	n.a.	(13)	(13)
Estuarine systems	n.a.	158	158
	n.a.	(76)	(76)

Table 19: CS₂ emissions from European shelves and estuarine systems. The CS₂ emissions are reported as averages of estimates from two air-sea gas exchange models (Liss and Merlivat 1986; Wanninkhof 1992). For a detailed description of calculations, please see Xie and Moore (1999). We used mean values of sea surface temperature (10.2°C), salinity (32.9), and wind speed (9.7 ms⁻¹) from the subset of the global DMS database from Kettle *et al.* (1999) shown in Figure 9. Atmospheric mixing ratios for shelves (20 ppt) and estuaries (69 ppt) were taken from Kim and Andreae (1987). See section 'European coastal zone' for details on area cover. Region Area / km² CS₂ / nM CS₂ emission / Gmol a⁻¹ Shelf (excluding estuarine systems) 3.01 x 10⁶ 27.9 0.11 Estuarine systems (area from this work) 0.17 x 10⁶ 158 0.04 Estuarine systems (area from EU CORINE project) 0.025 x 10⁶ 158 0.005 Total 0.12 – 0.15

Region	Area km ²	CS ₂ nM	CS ₂ emission / Gmol a ⁻¹
Shelf (excluding estuarine systems)	3.01 x 10 ⁶	27.9	0.11
Estuarine systems (area from this work)	0.17 x 10 ⁶	158	0.04
Estuarine systems (area from EU CORINE project)	0.025 x 10 ⁶	158	0.005
Total			0.12 – 0.15

Table 20: Overview of CS₂ measurements in European coastal and adjacent open ocean waters. Coastal and open ocean data have not been separated here, unless otherwise stated.

Region	Date	Comments	CS ₂ pM	/ Flux nmol m ⁻² d ⁻¹	/ Source
Northwestern European shelf and adjacent open ocean					
NE North Sea	July 1988		11	50	Leck and Rodhe (1991)
SW North Sea, off Great Yarmouth	July 1983		16	n.a.	Turner and Liss (1985)
S North Sea and English Channel	Sep 1989 – May 1990		49	n.a.	Watts (1991)
SE North Sea	Apr 1989		16	n.a.	Staubes-Diederich (1992)
Off western Ireland	July 1973		36		Lovelock (1974)
Off western Ireland	Jun – Jul 1996	Only coastal data reported here	13.6	13.4	Xie and Moore (1999)
N and S Atlantic	Sep – Oct 1988		52	167	Staubes et al. (1990)
N and S Atlantic	12 Sep – 2 Oct 1998	Incl. data from English Channel and Celtic Sea	10.9	19.3	Kettle et al. (2001)
Baltic Sea					
NE Baltic Sea, Kattegat/Skagerrak	July 1988		11	28	Leck and Rodhe (1991)
Estuarine systems					
4 W European estuaries	Jun 1997 – May 1998	Mean of means of all estuaries	36	n.a.	Sciare et al. (2002)
Off Great Yarmouth, SE England	Apr – Nov 1990		263	n.a.	Watts (1991)
Venice lagoon, N Adriatic	3 Jun 1996 – 26 Nov 1997		508	43	Moret et al. (2000)
NE German Wadden Sea	Jun 1991 – May 1994	Intertidal mud flat data only	n.a.	362	Bodenbender et al. (1999)

Table 21: 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	310 ^a	64 ^a	up to 75% ^c	1.4 - 2.2 ^e
N ₂ O	~ 100	300 ^b	60 ^b	up to 1% ^d	0.7 - 44 ^f
DMS	1 - 3	60 (as S)	1.0 ^{*1}	up to 10%	2.0 ^{*1}
COS	10 - 100			up to 50%	
CO ₂	~ 10	30-60 x 10 ⁶	2 - 4		0.4 - 0.8

^{*1}Contribution to the total European or global emissions of sulfur

^a see Table 9

^b see Table 6

^c Bange *et al.* (1994)

^d Bange *et al.* (1996)

^e IPCC (2001), Bange *et al.* (1994)

^f IPCC (2001), Nevison *et al.* (2004)

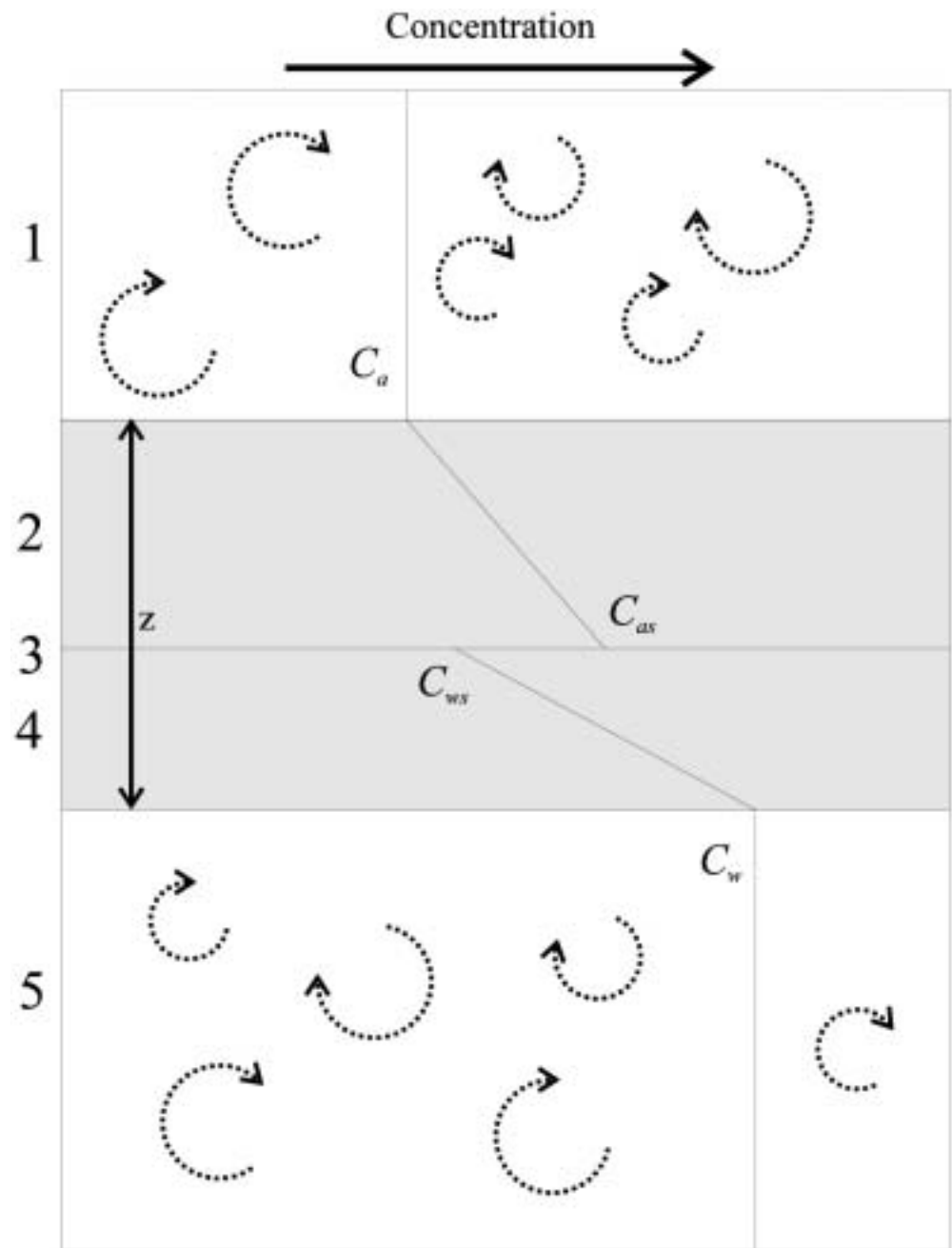


Figure 1: An idealised steady-state air-water interface; regions 1 and 5 are turbulent boundary layers in air and water, with respective gas concentrations C_a and C_w ; regions 2 and 4 are the diffusive sub-layers, and region 3 is the air-water interface. C_{as} and C_{ws} are gas concentrations at the air-side and water-side respectively, of the air-water interface. The concentration discontinuity across the interface exists for relatively insoluble gases such as CH_4 but not for more soluble gases such as CO_2 .

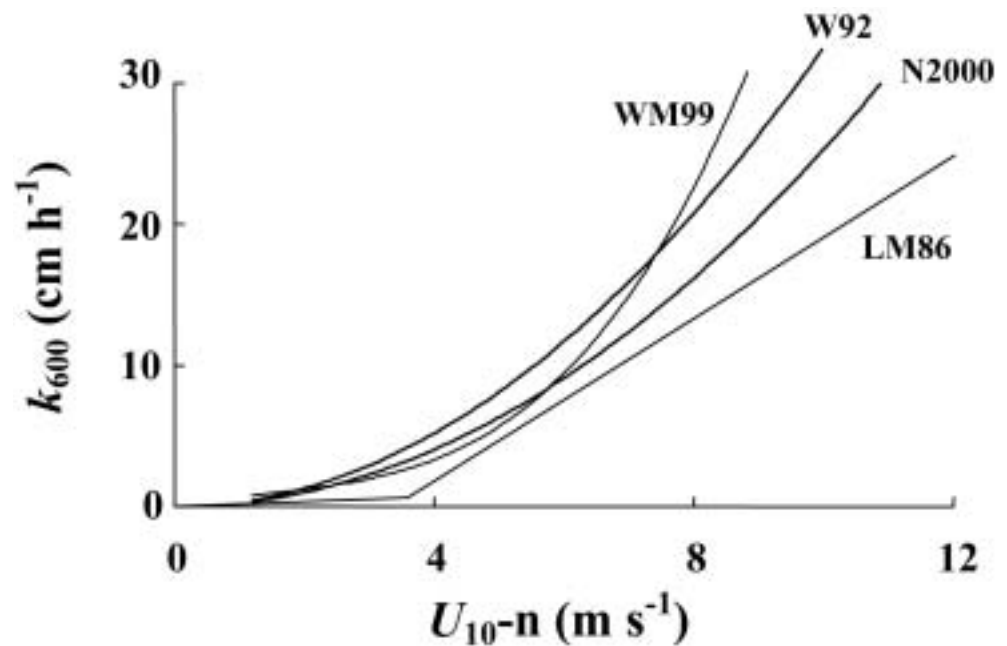


Figure 2: Some contemporary transfer velocity vs wind speed parameterizations. The parameter k_{600} is the value of k_w normalized to $Sc = 600$, being the value for CO_2 in freshwater at $20^\circ C$, and U_{10-n} is the value of U_{10} normalized to a uniform atmospheric stability to remove the effects of buoyancy-induced turbulence associated with thermal stability (Large and Pond, 1982). LM86 is the (Liss and Merlivat, 1986) curve, W92 is the relationship of (Wanninkhof, 1992) for instantaneous winds, N2000 is a best fit to North Sea dual tracer data (Nightingale et al., 2000), and WM99 is a cubic relationship (Wanninkhof and McGillis, 1999).

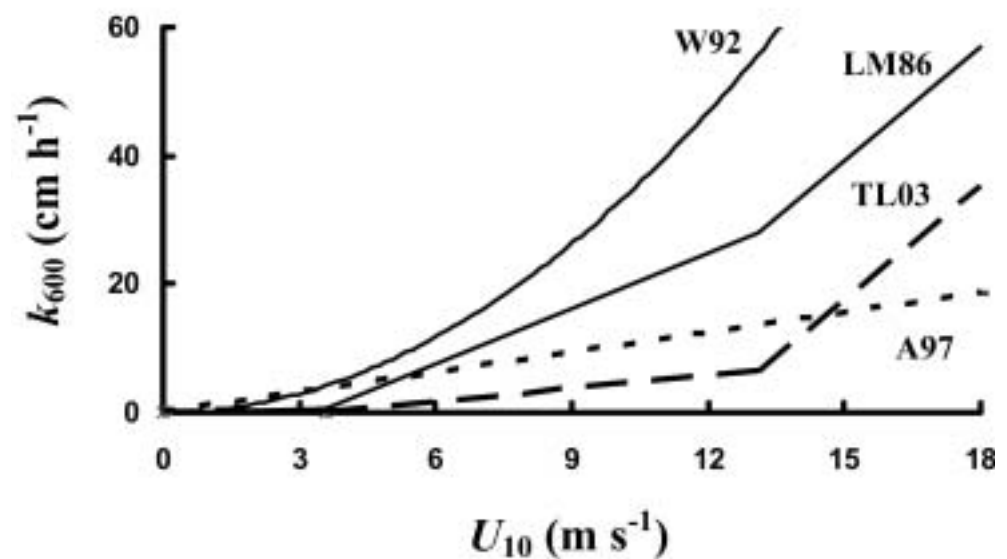


Figure 3: Gas transfer velocity (k_{600}) versus U_{10} for clean and surfactant covered ocean waters. LM86 is the (Liss and Merlivat, 1986) curve, W92 is the relationship of (Wanninkhof, 1992) for instantaneous winds, A97 is the linear relationship of (Asher, 1997) for surfactant covered waters, and TL03 is the relationship of (Tsai and Liu, 2003), based adjusting the "rough surface" and "smooth-surface" regimes of (Liss and Merlivat, 1986) for surfactant effects.

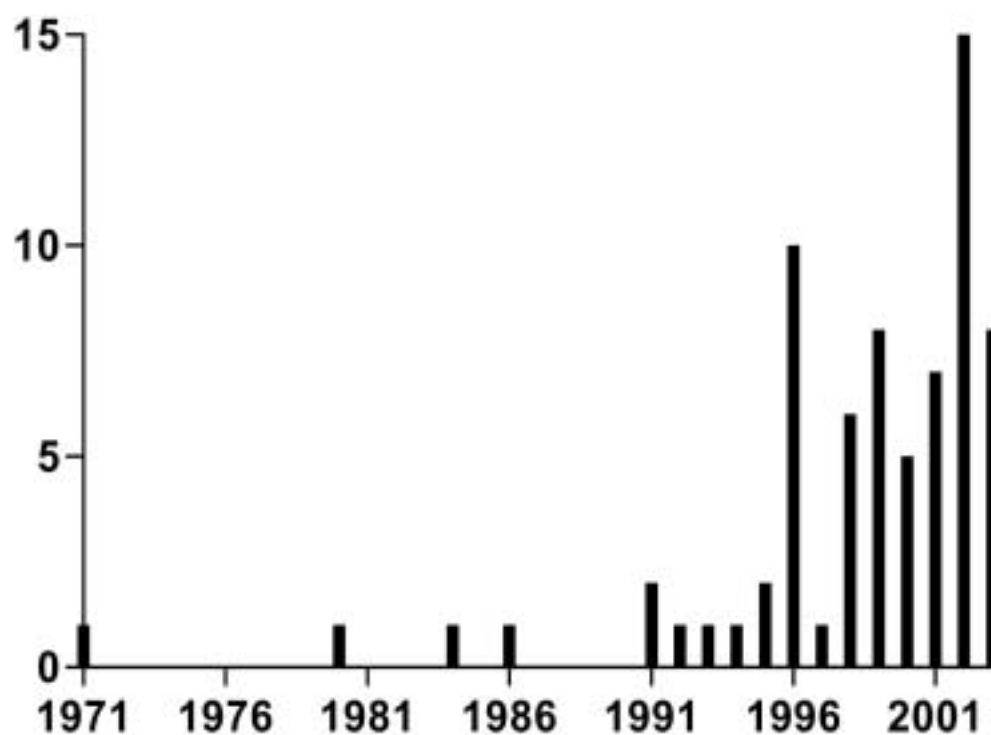


Figure 4: Evolution of the number of publications that report $p\text{CO}_2$ variations in coastal environments during the last 30 years.

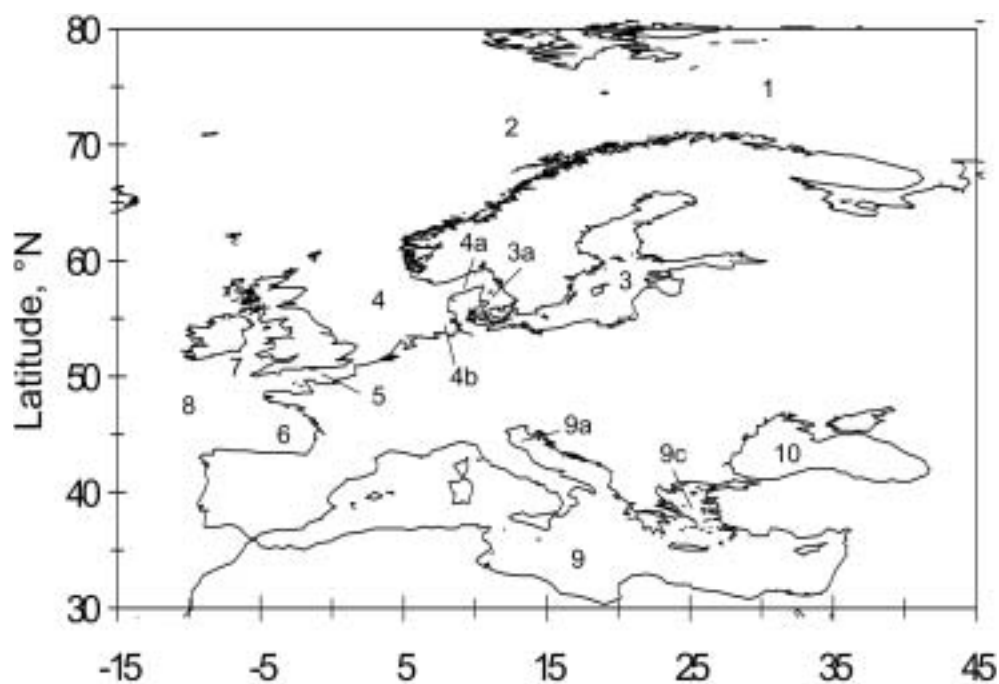


Figure 5: Map with European marginal seas indicated: 1 – Barents Sea; 2 – Norwegian Sea; 3 – Baltic Sea; 3a – Kattegat; 4 – North Sea; 4a – Skagerrak; 4b – German Bight; 5 – English Channel; 6 – Bay of Biscay; 7 – Celtic (Irish) Sea; 8 – NE Atlantic; 9 – Mediterranean Sea; 9a – Adriatic Sea; 9b – Aegean Sea; 10 – Black Sea.

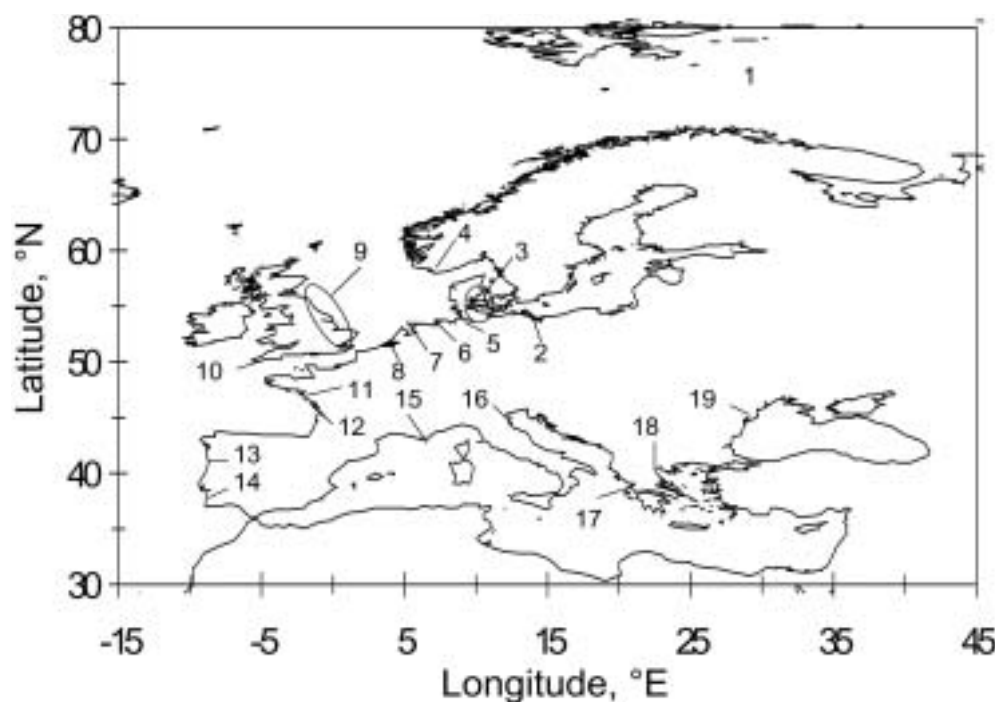


Figure 6: Locations of prominent coastal areas, estuaries, fjords and other features mentioned in the text. 1 – pockmark field; 2 – Bodden waters/Oder River estuary; 3 – Fjords along the east coast of Jutland, Denmark (Norsminde Fjord, Limfjorden, Randers Fjord, Marianger Fjord) and northern Germany (Eckernförde Bay, Kiel Harbour); 4 – Framvaren Fjord; 5 – Elbe River; 6 – Ems River; 7 – western Wadden Sea; 8 – Scheldt River, Rhine River; 9 – Estuaries along the English east coast (Tyne River, Colne River, Humber Estuary, Thames River); 10 – Tamar River; 11 – Loire River; 12 – Gironde estuary; 13 – Douro River; 14 – Sado River; 15 – Rhone River, Gulf of Lions; 16 – Po River delta, Sacca di Goro; 17 – Amvrakikos Bay; 18 – Gulf of Thermaikos; 19 – Danube River Delta.

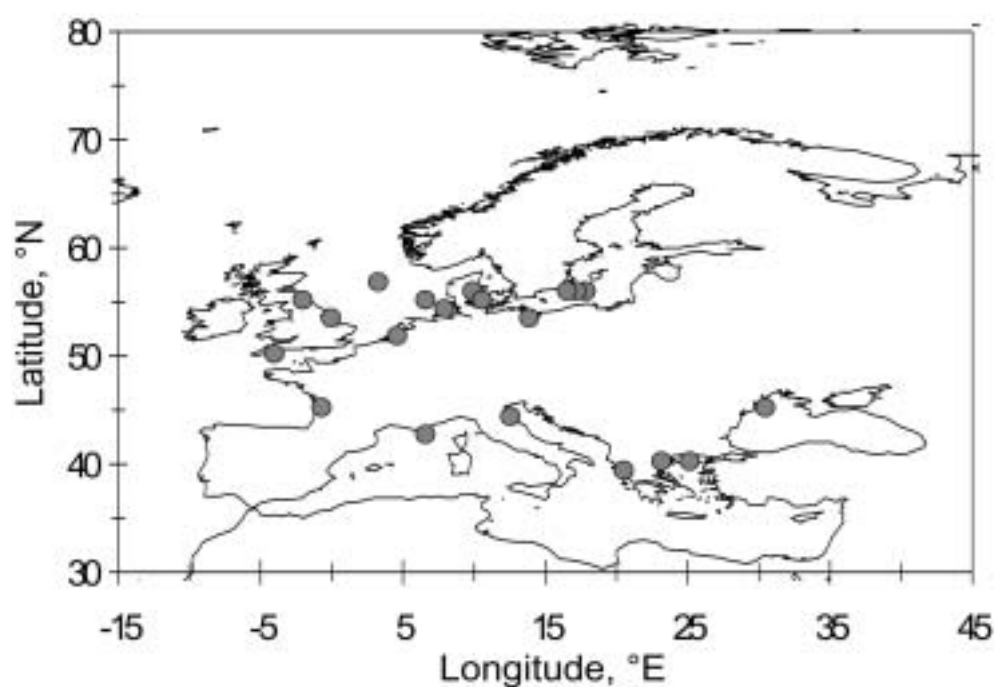


Figure 7: Locations of studies of N_2O in European coastal waters.

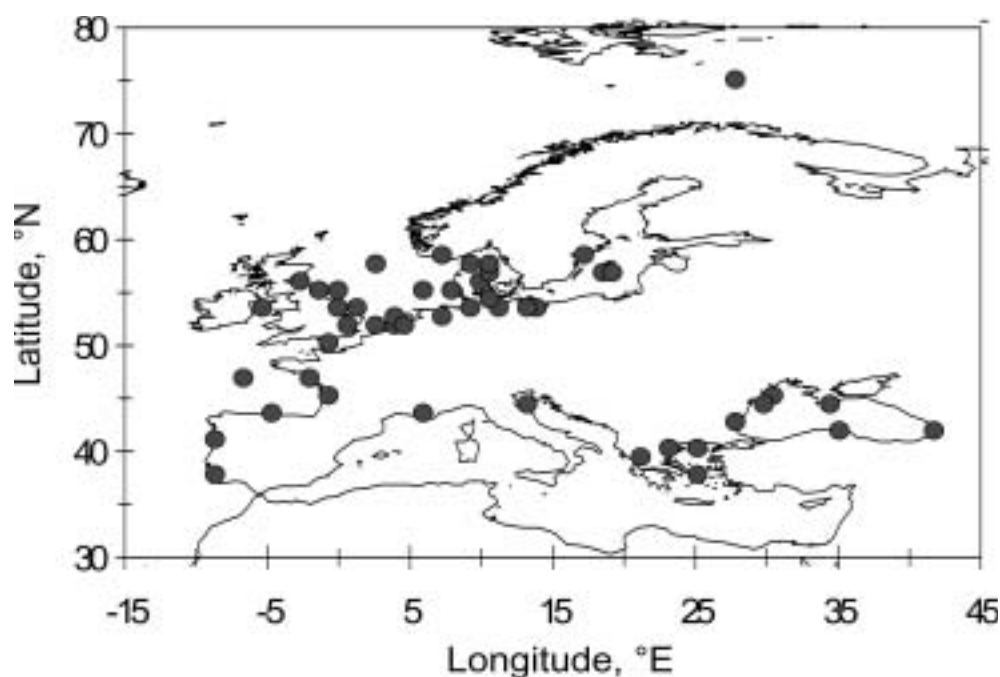


Figure 8: Locations of studies of CH_4 (incl. observations of CH_4 bubble plumes and CH_4 enriched sediments) in European coastal waters.

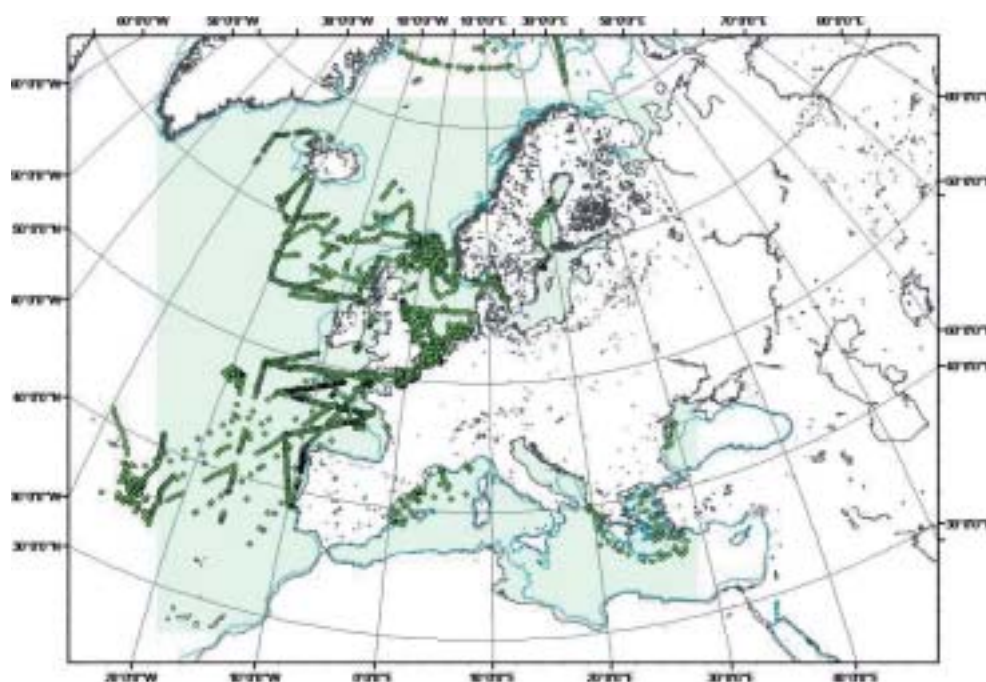


Figure 9: Geographical cover of DMS measurements around Europe from the recent data compilation in Kettle a (1999). The sampling locations shown (green diamonds) fall within an area extending from 30°W to 60°E and 34 to 77°N, selected to cover all European shelf areas including those of the Black and Caspian Seas. The high resolution coastline (black) is from Wessel and Smith (1996). The 200 meter depth contour (blue) was interpolated from ETOPO2 two minute resolution bathymetry data obtained from the U. S. NOAA National Geophysical Data Center, Boulder, Colorado, USA (<http://www.ngdc.noaa.gov/mgg/image/2minrelief.html>). The shaded area indicates the spatial extent of the EU CORINE Land Cover project. See text for more details.

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