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Spatial and temporal variability of dissolved sulfur compounds in European estuaries

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Abstract. The spatial and temporal distribution of Dimethylsulfide (DMS), Dimethylsulfoniopropionate (DMSP) – its precursor –, Dimethylsulfoxyde (DMSO) – one of its oxidation products – Carbonyl sulfide (COS) and Carbonyl disulfide (CS_2) were investigated during nine oceanographic cruises carried out in six major tidal European estuaries between July 1996 and May 1998. Low levels of DMS were recorded (mean of 0.6 nM, standard deviation (σ) 0.3 nM) during these 9 cruises. Positive correlations between DMS and salinity were frequently observed, with the highest DMS concentrations in the plume of estuaries, which could be explained by change in phytoplankton speciation from estuarine to shelf waters. Strong correlation between DMSP and DMS was reported for most of the estuaries denoting a simple conservative mixing of riverine and marine waters controlled by tide. In contrast to DMS, significant levels of COS and CS_2 with mean concentrations of 220 ± 150 (pM; pM = 10^{-12} M) and 25 ± 6 pM respectively were recorded in four estuaries, indicating that estuaries could be a significant source of these compounds.

Introduction

Dimethylsulfide (DMS) is produced by some marine phytoplankton species, and once released in the atmosphere could have – through its oxidation products – direct and indirect effects on climate (Charlson et al. 1987; Andreae et al. 1995). DMS is produced in seawater by the cleavage of beta Dimethylsulfoniopropionate (DMSP) that is associated in most of the cases with bacteria (Kiene 1990, 1992). Yield of the DMS production from DMSP cleavage is highly variable and reported to vary between 12 to 66% (Kiene 1996). DMSP is produced by some classes of marine phytoplankton and is dependent on taxonomic groups (Liss et al. 1997 and references therein). Ventilation to the atmosphere as well as bacterial consumption, photodegradation and downward mixing have been identified as the major sinks for DMS in seawater. Whether DMSO has been firmly identified as a major DMS oxidation product in seawater from photodegradation and/or microbial and anaerobic processes, its biotic production in oxic waters remains unclear. Production and fate of DMSO in seawater is an important issue since DMSO can in its turn act as a source of DMS from bacteria reduction.

Ocean margins have been identified as a significant source of DMS (Andreae 1986; Leck & Rhode 1991; Turner et al. 1996) and several results suggest that estuaries (Iverson et al. 1989) and corresponding plumes in the open sea (Turner et al. 1996; Simo et al. 1997) could represent an important source of atmospheric DMS. However, up to now the only detailed studies on the importance of estuaries as a source of DMS originate from the work of Iverson et al. (1989) conducted in several Northern American estuaries and Cerqueira and Pio (1999) in a Portuguese canal. The role of the tidal European estuaries by far remains unclear.

Besides DMS, estuaries have been also identified as a significant source of various sulfur compounds (S-compounds) and especially Carbonyl sulfide (COS) and Carbon disulfide (CS_2) (Watts 2000 and references therein).

COS is the most abundant sulfur compound in the atmosphere and is considered as a dominant source of SO_2 and subsequently sulfate aerosol in the stratosphere because of its long residence time in the atmosphere (Engel & Schmidt 1994). These sulfate aerosol plays a significant role in the global radiation budget (Zepp et al. 1995). Open and coastal oceanic areas could represent 20–25% of the total COS source in the atmosphere (Andreae & Crutzen 1997; Watts 2000). The photochemical production of COS in seawater can result from the photosensitized reaction of organosulfur compounds. Because natural photosensitizers are more prevalent in coastal than in the open ocean waters (Zepp & Andreae 1994), sea-to-air fluxes of COS from estuaries could play an important role in the oceanic COS budget (Watts 2000). However, the only available data set existing in the literature originate from one estuary (Cheasapeake Bay, US, Cutter & Radford-Knoery 1993; Zhang et al. 1998).

CS_2 is a precursor of both COS and SO_2 and thus represents an interesting aspect of the natural sulfur cycle. Based on the budget estimates presented by Chin and Davis (1993) and Watts (2000), CS_2 emissions from estuaries could compare with those from the open ocean and both could account for about 30% of its budget. However, based on the most recent budget estimate presented by Watts (2000), the estimation of CS_2 fluxes from the estuaries is highly uncertain since only 5 analysis have been reported for CS_2 concentrations in the estuaries.

This paper presents the spatial and temporal distributions of DMS, DMSP, DMSO, COS and CS_2 obtained during nine cruises performed in six major tidal European estuaries as part of the BIOGEST (BIOGas transfer in ESTuaries) program. To our best knowledge this is the first attempt to characterise the role of tidal European estuaries as a source of biogenic sulfur species.

Methodology

Analysis of DMS, COS, CS_2

DMS, COS and CS_2 measurements in seawater were performed onboard of the ships of the BIOGEST program, immediately after the collection. The collection was performed using either NISKIN bottles (sampling at 1-m depth) and/or the pump of the ship. Simultaneous tests performed using these sampling systems showed non-significant difference in the measured concentrations of the biogenic sulfur gases. Water samples were taken via a syringe and filtered through GF/F filter while being injected into the extraction vessel. To minimize cell damage during filtration, a very gentle positive pressure was applied by hand. Several tests have been performed during the different campaigns to check the stability of filtered DMS samples. It was found that DMS stability in these samples (stored at room temperature) could not exceed half an hour: depending on the estuary (e.g. different bacteria and chlorophyll concentrations, DMSP concentrations, etc) DMS could significantly increase (by a factor of 4 in the Gironde estuary) or decrease (by a factor of 2 in the Scheldt estuary) after a storage of one hour. Thus particular attention has been paid to analyse DMS samples within the 15 minutes following their collection through the whole cruises.

DMS, COS and CS_2 extraction was conducted for 10 minutes under helium flow of 150 ml/min and concentrated on a "Tenax GC" trap immersed in liquid nitrogen. Extraction yield after 10 minutes of helium bubbling was found to be close to 100% for all compounds even considering the low density of some samples (influencing the size of helium bubbles). After trapping, the sulfur gases were introduced in a packed column (Chromosil 310) by heating the trap with boiling water (90 °C). The analysis was made using a Shimadzu Gas chromatograph (GC) equipped with a Sulfur Chemiluminescence Detector (Sievers 355 SCD), which provides a linear response for all the S-compounds. Time program was used to separate DMS, COS and CS_2. The detection limit was 0.1 ng for all the compounds of interest. DMS quantification was performed by the mean of a permeation tube (WAFER type, Metronics, Santa Clara) maintained at 30 °C and calibrated against liquid standards of DMSP as described by Belviso et al. (1993). This technique has been adapted from the GC-FPD technique described by Nguyen et al. (1990) and has been successfully used in many other field experiments (see for example Sciare et al. 1999). The similar response of the detector to other S species has been checked by injection of COS standards generated as described at Mihalopoulos et al. (1992). Considering the linear response of the Sievers detector, injection of both 1 ng of DMS or COS provides similar areas on chromatrograms. Based on this result, CS_2 measurements were calibrated from the DMS permeation tube. Injections of DMS standards were performed after each analysis with no visible drift in the calibration. Regular checks of the reproducibility of the analysis showed that it was systematically better than 5%. In addition to DMS samples, seawater samples have been collected for dissolved and total (e.g. non dissolved) DMSP analysis (noted as $DMSP_d$ and $DMSP_t$ respectively) and for dissolved DMSO ($DMSO_d$).

Analysis of DMSP

For $DMSP_t$ analysis seawater samples were conditioned with addition of 1 ml of NaOH (10M) in 60-ml glass vials. $DMSP_d$ samples were derived from seawater filtered on GF/F filter and conditioned as well as the $DMSP_t$ samples. Analyses of both $DMSP_t$ and $DMSP_d$ were conducted back the laboratory using the technique described above for DMS.

Analysis of $DMSO_d$

$DMSO_d$ samples were also obtained from seawater filtration on Whatmann GF/F filters and conditioned with 1 ml of HCl (fuming acid) in 60-ml plastic vials following the recommendation made by Andreae (1980). A technique based on an in-situ reduction of DMSO to DMS using sodium borohydride ($NaBH_4$) was used to determine DMSO in seawater. Produced DMS was subsequently preconcentrated using the previously described purge-and-cryotrap technique and GC-FPD analysis. More details on the analysis of DMSO are reported at Sciare and Mihalopoulos (2000). Presence of DMS in the sample as well as the quantitative reduction of $DMSP_d$ by $NaBH_4$ in the samples were taken into account (Andreae 1980), thus the reported DMSO corresponds to the difference of the measured DMS (after the reduction by $NaBH_4$ minus ($DMS+DMSP_d$)).

Results and discussion

The spatial distribution of S-compounds was investigated from the results of 9 oceanographic cruises performed in 6 different tidal European estuaries

Table 1. Spatial and temporal distribution of S-compounds and chlorophyll a in the investigated tidal European estuaries (Salinity 0 to 30)

Estuary	Period	DMS (nM)	$DMSP_d$ (nM)	COS (pM)	CS_2 (pM)	Chl-a* (μg/l)
Scheldt	05/1998	(0.4–1.2), **0.6**, n = 16		(60–470), **190**, n = 44	(9–50), **21**, n = 20	1.4–83.5
	07/1996	(0.3–1.3), **0.5**, n = 13	(0.4–2.3), **1.2**, n = 11	(90–330), **190**, n = 12		4–224
	12/1996	(< 0.02–2.4), **0.4**, n = 13	(0.5–1.6), **0.9**, n = 11			0.1–6.7
Gironde	06/1997	(0.05–1.7), **0.7**, n = 18	(0.2–7.0), **2.2**, n = 10	(110–440), **180**, n = 31	(2–81), **32**, n = 27	0.7–4.1
	09/1997	(0.03–1.0), **0.2**, n = 17	(0.1–3.0), **1.0**, n = 12	(110–270), **170**, n = 19	(2–44), **24**, n = 17	0.6–2.8
Rhine	07/1997	(0.4–10.0), **4.2**, n = 14	(0.5–27.2), **7.2**, n = 15	(160–1010), **500**, n = 28	(14–117), **67**, n = 12	0.5–2.8
Elbe	04/1997	(0.1–2.5), **0.9**, n = 50				2–15
Ems	07/1997	(0.03–1.4), **0.2**, n = 16	(0.9–19.1), **3.1**, n = 12	(200–790), **370**, n = 15	(6–93), **37**, n = 16	2–11
Loire	09/1998	(0.4–3.8), **1.3**, n = 20				3–74

Note: Range (in parenthesis) and mean concentrations (in bold) are reported for each S-compound. Mean concentrations are calculated using the average derived for every 5 degrees of salinity. Total number of measurements (n) for each S-compound is also reported.
*from Lemaire et al. (2002)

(Scheldt, Gironde, Rhine, Ems, Elbe, Loire). Time and location of these campaigns are reported in Table 1 together with range and mean values of DMS, $DMSP_d$, COS and CS_2. To avoid bias from non-homogeneous sampling along the salinities, S-compounds mean concentration for each investigated estuary was calculated as the average of sub means of DMS concentrations obtained every 5-degree of salinity (Table 1). All the measurements were performed during daytime within the same day and tide except for the Scheldt estuary where measurements were obtained during 3–4 consecutive days due to the size of its estuary. However, several profiles obtained during 3 consecutive days in the Rhine estuary showed that changes in the mean concentration for all S-compounds were less than 15% (see for example Figure 1(e)) and thus could not affect significantly the levels reported for these compounds. To be consistent with previous measurements of S-compounds performed in estuaries (Iverson et al. 1989), we separated them in two parts: the inland or inner part (most of the time with salinity between 0 to 30) and the outer part (out of the mouth of the estuary and separated from shelf waters with salinity below 34). Location of the mouth of estuary can dramatically influence the levels of S-compounds (see the later discussion), for that reason its location was indicated in Figure 1 for each investigated estuary. More details concerning these estuaries are given by Frankignoulle & Middelburg (2002).

Spatial and temporal distribution of seawater DMS in estuaries

Complementary to our measurements of surface seawater DMS and DMSP, spatial and temporal distribution of phytoplankton pigments was studied in the frame of the BIOGEST program (Lemaire et al. 2002). These pigments can be used as biomarkers of particular classes of phytoplankton, for example, fucoxanthin for diatoms, peridinin for dinoflagellates, and 19-‘hexanoyloxyfucoxanthin (19’-HEX) for prymnesiophytes (Liss et al. 1997; Claustre 1994). Of particular interest is the class of prymnesiophytes such as *Phaeocystis pouchetti*, which is known to produce much higher DMSP than diatoms (Malin et al. 1993; Keller et al. 1989). Diatoms dominate in the low salinities of the investigated estuaries (Lemaire et al. 2002) whereas *Phaeocystis* is reported to develop in the Northern Sea, and thus off of the mouth of the Scheldt, Ems, Elbe, and Rhine estuaries (Turner et al. 1996). It is generally accepted that freshwater phytoplankton species dominate estuarine environments for salinities not exceeding 5 (Ahel et al. 1996) whereas for salinities exceeding 15, marine species develop. Thus diatoms from the low salinities and *Phaeocystis* from the sea might influence both the DMS and DMSP levels in the previous estuaries. All the concentrations of pigments and chlorophyll a (chl-a), which are discussed later in this manuscript, refer to the paper presented by Lemaire et al. (2002). Seawater DMS concentrations as function of salinity are discussed below for each of the six investigated estuaries. DMS seasonal variation is discussed only for the Scheldt and Gironde estuaries.

Scheldt estuary

Seawater DMS concentrations in the Scheldt estuary (0 to 30 in salinity) average 0.6 nM in May 1998, 0.5 nM in July 1996 and 0.4 nM in December 1996 (Table 1). DMS profiles versus salinity along the Scheldt estuary are reported in Figure 1(a) for these 3 periods. A first maximum of DMS of the order of 1 nM is recorded in summer toward the freshwaters at the maximum of turbidity zone (MTZ, salinity 1.9). This maximum is consistent with the highest concentrations of diatoms and chl-a (above 200 mg/m^3) which occurred around this salinity (report to Figure 2(a)). This maximum of DMS is shifted towards lower salinities in December 1996 with a maximum

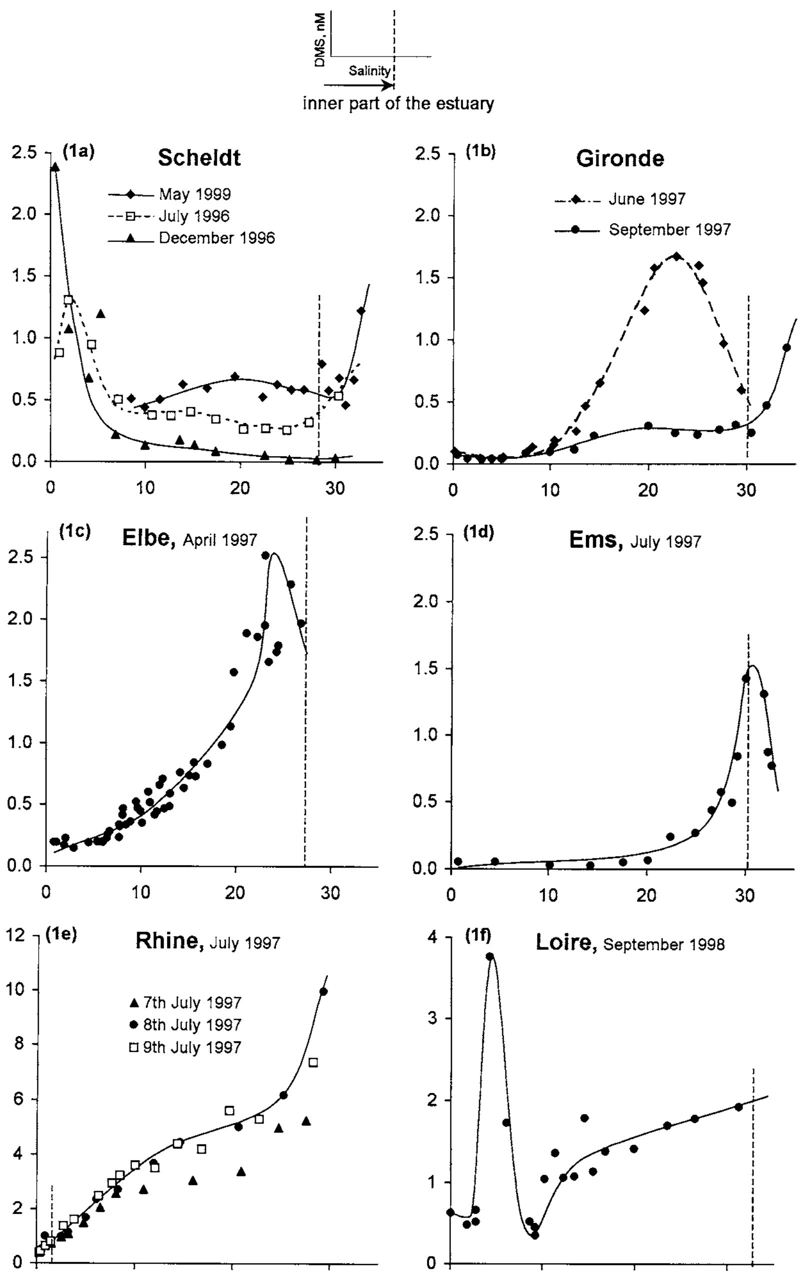

Figure 1. Salinity profiles of seawater DMS in 6 tidal European estuaries. Dashed lines correspond to the limits between inner part and mouth of estuary.

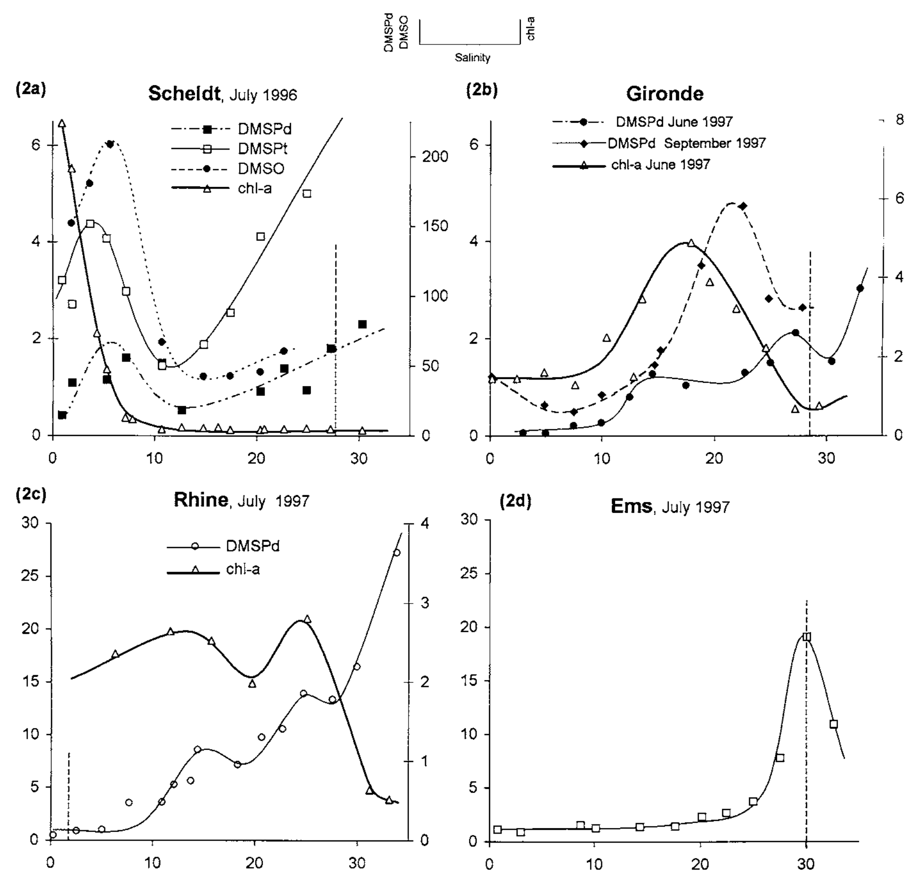

Figure 2. Salinity profiles of $DMSP_d$ and Chl-a in 4 tidal European estuaries.

of 2.4 nM at salinity 0.44, still consistent with the maximum in chl-a. The small maximum of DMS reported for salinity 20 in May 1998 also coincides with an increase in chl-a and diatoms reported for this salinity. These results denote that the DMS-origin of the Scheldt estuary, for salinities below 30 is linked to the diatoms population. Outward from the mouth of the Sheldt estuary (Figure 1(a)), DMS concentrations increase in July 1996 and May 1998 to reach values above 1 nM whereas chl-a remained stable. Production of DMS from species other than diatoms is needed to explain such increase. As we mentioned before, *Phaecosystis pouchetti*, which is known to be a high DMSP-producer (higher than diatoms) and identified off of the mouth of the Scheldt estuary (Turner et al. 1996) could explain this DMS increase.

The seasonal variation of DMS concentration observed at this estuary (higher values during May compared to December) is also clearly linked to the phytoplankton community and chl-a concentrations. Based on the phytoplankton data presented by (Lemaire et al. 2002) higher concentrations of chl-a and diatoms have been measured during May compared to December.

Gironde estuary

Seawater DMS concentrations in the Gironde estuary (0 to 30 in salinity) average 0.7 nM in June 1997 and 0.2 nM in September 1997 (Table 1), i.e. same order of magnitude to that reported for the Scheldt estuary. DMS profile versus salinity for June (Figure 1(b)) is not consistent with that of chl-a, which shows a maximum of 2 μg/L between 10 and 14 in salinity. Changes in phytoplanktonic speciation can explain the location of DMS maximum. Indeed, the DMS maximum of 1.7 nM observed at salinity 22.5 corresponds to the maximum in the concentration of the pigments 19'-HEX and peridinin. These pigments are indicators of phytoplanktonic classes "Phaeocystis" and "dinoflagellates", both known to be high producers of DMSP and DMS (see also Figure 2(b); Liss et al. 1997). The maxima in DMS and pigments clearly decreased 3 months later (September 1997, Figure 1(b)). Note however that the slight increase in DMS observed at this period (9/97) between salinity 15–20 coincides with a smaller bloom of dinoflagelattes and is also consistent with the $DMSP_d$ profile reported in Figure 2(b). Interestingly is also the sharp increase of DMS out of the mouth of the estuary during September and thus consistent with the results reported during May and July for the Scheldt estuary. These results suggest a significant source of DMS out of the mouth of the estuary probably due to the shift in phytoplaktonic population from the less DMS producers like diatoms inside the estuary to high DMS producers like "Phaeocystis" at its mouth.

The observed seasonal variation of DMS with higher levels during June compared to September is due to the changes in phytoplanktonic communities population (bloom of dinoflagellates during June; Lemaire et al. 2002).

Elbe estuary

Seawater DMS concentrations in the Elbe estuary (0 to 30 in salinity) average 0.9 nM in April 1997 (Table 1). The DMS profile recorded for this estuary reach a slight maximum at salinity 23 (Figure 1(c)), which is consistent with a maximum in chl-a and diatoms between 22 and 25 in salinity. As will be discussed later (see Figure 4), the DMS levels found here are closely related to the salinity, which in turns depends on the tide.

Complementary to this study, several seawater DMS measurements were performed in and out of the mouth of the Elbe estuary in order to estimate the impact of its plume on the marine DMS production. The highest DMS levels were recorded in the mouth of the Elbe estuary with concentrations ranging from 3.4 nM to 8.7 nM (mean 4.2 ± 2.4 nM, n = 5). By contrast, open sea/shelf DMS levels measured in the German bight ranged from 2.0 to 4.0 nM (mean 3.2 ± 0.8 nM, n = 4). This mean of 3.2 nM compares well with that of 2.5 nM reported by Turner et al. (1996) for the DMS surface waters in the same area during April 1989. The above results are in line with those presented for the estuaries of Scheldt and Loire and indicate a clear enhancement in DMS concentrations within the plume of the estuary. Additional work is clearly needed to understand the enhancement in DMS in the plume compared to the inner and shelf waters.

Ems estuary

Seawater DMS concentrations in the Ems estuary (0 to 30 in salinity) average 0.2 nM in July 1997 (Table 1) and thus the lowest DMS mean concentration reported for estuarine waters during summer. The corresponding seawater DMS profile reported in Figure 1(d) follows quite well the salinity reaching a maximum of 1.4 nM at the mouth of the estuary (Salinity of 30–31). Following this maximum, DMS decreases at higher salinities. Even though DMS levels along the estuary follow very well those of $DMSP_d$ (see the later discussion), its profile is in contrast with the maximum of chl-a and diatoms reported at the maximum of turbidity zone around salinity 1. As proposed by Lemaire et al. (2002), the Ems estuary belongs to those estuaries for which the pigment distribution can be described by a simple conservative mixing of the riverine and marine communities. Given the fact that in almost all the estuaries DMS presented a maximum at the mouth of estuary the DMS profile at Ems could be explained by assuming, similarly to pigments, a simple dilution of this DMS maximum towards the less saline waters.

Rhine estuary

Due to its important flow rate, the mixing of riverine and sea waters occurred in the mouth of the estuary with changes in salinity roughly from 3 to 33 within several hundred of meters. Thus strictly speaking DMS levels recorded for salinities higher than 3 were more representative of the plume of the Rhine river than of its estuary. Probably for that reason, seawater DMS levels (Figure 1(e)) were by far the highest reported for the investigated European estuaries. The highest DMS concentrations of 9–10 nM were attained at the highest salinities. These values compare well with the values of 8–16 nM reported by Turner et al. (1996) offshore of the Rhine estuary in July 1989. The existence of *Phaeocystis* bloom found at the waters with salinity 30 together with a simple conservative mixing of riverine and marine waters could explain the DMS profile and levels found at this estuary.

Loire estuary

Seawater DMS concentrations in the Loire estuary (0 to 30 in salinity) average 1.3 nM in September 1998 (Table 1). The corresponding seawater DMS profile reported in Figure 1(f) exhibits a significant maximum before 5 in salinity, consistent with a maximum in chl-a, fucoxanthin (e.g. diatoms) and 19'-HEX (e.g. *Phaeocystis*; Lemaire et al. 2002). Since Loire estuary belongs to the same category with Rhine and Ems regarding the phytoplankton distribution (Lemaire et al. 2002), the linear increase in DMS for salinities higher than 15 might be explained by assuming a simple dilution of the DMS maximum observed at the mouth of the estuary towards the less saline waters (down to 15 of salinity).

Processes controlling the cycling of DMS in estuarine

Distribution of DMS, DMSP$_t$, DMSP$_d$ and DMSO, case of the Scheldt estuary

The Profiles of DMSP$_d$, DMSP$_t$, DMSO$_d$ and chl-a versus salinity are reported in Figure 2a for the Scheldt estuary (July 1996). The profiles of DMS precursors (DMSP$_t$ and DMSP$_d$) are consistent with that reported for DMS (Figure 1a) with a first maximum at low salinities (below 5) and a significant increase towards the open sea. They are thus consistent with the previous observations on the distribution of diatoms and *Phaeocystis* in the Scheldt estuary and with chl-a profile reported in Figure 2a.

The DMSO$_d$ profile reported in Figure 2a is consistent with those of DMSP$_t$, DMSP$_d$, and DMS with a maximum of 20–25 nM for salinities between 0 and 5. The decrease of DMSO beyond the salinity 5, as also observed for its precursors is most probably due to dilution than any change in production/consumption since all these compounds decrease almost at the same rate (70–80% decrease within 10 degrees in salinity, see also the later discussion).

The (DMS/DMSO$_d$) molar ratio is of the order of 5% throughout the estuary, in good agreement with the median value of 9% calculated from the results reported by Simo et al. (1995) for the western Mediterranean Sea. Hence, it is in agreement with the work reported by Wolfe and Bates (1993), which suggests a DMS oxidation into dissolved material. High levels of DMSO$_d$ (up to 30 nM) were also measured in parts of the other investigated estuaries and allow us to conclude that DMS oxidation into DMSO$_d$ is a non negligible process in estuarine waters and could compare with that in the open sea (Simo et al. 1995; Hatton et al. 1998).

DMS versus DMSP$_d$

Production and consumption of DMSP$_d$ and DMS can proceed through different pathways (Groene 1995). Of particular interest is to understand what are the factors controlling these pathways along estuaries since parameters such as salinity, bacteria, turbidity and phytoplankton species do vary along these estuaries.

For comprehensive reasons, we reported in Figures 2(a), (b), (c), (d) the DMSP$_d$ and chl-a profiles for the Scheldt, Gironde, Rhine and Ems estuaries. In all these estuaries, consistencies were found between the DMS, DMSP$_d$ and chl-a profiles (Figures 1 and 2 respectively).

Four profiles of the DMS/DMSP$_d$ molar ratio (R) versus salinity are reported in Figure 3, for the Gironde, Ems and Rhine estuaries. The very good correlation coefficients r^2 (from 0.92 to 0.99) show that the distribution between DMS and DMSP$_d$ remains identical through these estuaries. A simple conservative mixing of riverine and marine waters controlled by tide can account for the observed significant correlation coefficients and indicates a conservative processes controlling production and consumption of these compounds through these estuaries. This assumption is in agreement with the previous hypothesis to explain the distribution of DMS along these estuaries. For the Scheldt estuary, the DMS/DMSP$_d$ molar ratios calculated for both summer and wintertime decrease from nearly 100% for salinities below 5 (at the maximum of turbidity and diatoms) to 10–20% for higher salinities. The low levels of DMSP$_d$ compared to DMS in the low salinities might be due to the important reduction of grazing due to oxygen stress at the maximum of turbidity zone (Kromkamp et al. 1995; Muylaert & Sabbe 1999).

The slopes reported in Figure 3 are quite different even within a week period and for the same area (Ems and Rhine estuaries). DMSP$_d$ values between these 2 estuaries are comparable only at salinity 30, once these rivers reached the shelf. On the other hand, DMS levels are a factor of 10 lower in the Ems, which could not be explained by chl-a or diatoms concentrations since they were even higher compared to the Rhine estuary. Suspended matter measurements performed in both estuaries give a mean value of 240 mg/l for the Ems estuary, that is 25 times higher than in the Rhine and comparable to the Gironde (200 mg/l in June 1997 and 315 mg/l in September 1997). Uptake of DMS and further oxidation into particles (as reported by Wolfe & Kiene 1993 for estuarine waters) could be higher in the Ems and Gironde and thus partly explain the lower DMS/DMSP$_d$ slopes observed at these estuaries compared to the Rhine (Figure 3).

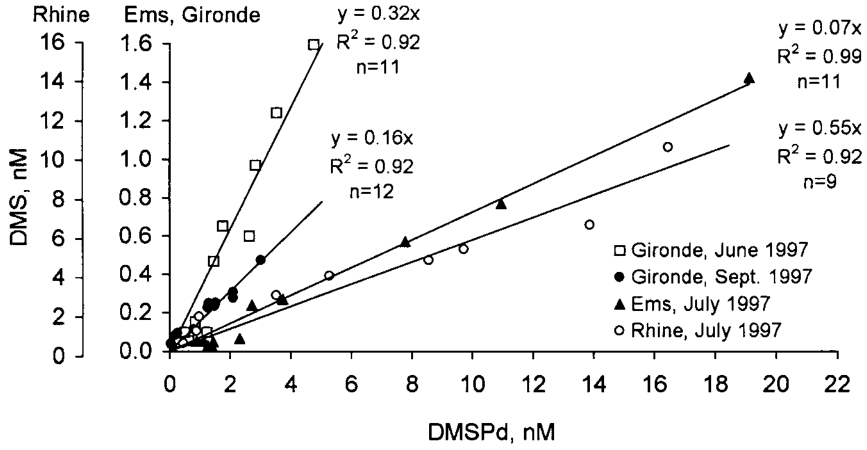

Figure 3. Correlation between DMS and DMSP$_d$ in 3 European estuaries (Gironde, Ems and Rhine) for the salinity range 0 to 30.

Diurnal variation of DMS in estuaries

Understanding the process controlling the short-time variation of DMS and DMSP may help to understand the distribution of DMS in estuarine waters (see later Table 2). Several 24-hour cycles were performed in the Elbe estuary for that purpose. Figure 4 presents the variation of DMS, DMSP$_d$ and salinity versus local time during one of the 24-hour experiments. As displayed in this figure, tidal influence, as shown by the salinity profile, is responsible for the short-time variations of both DMS and DMSP$_d$. This result is once more in agreement with the previous conclusion that a conservative mixing of riverine and marine waters controlled by tide can account for the distribution of these compounds in most of the studied estuaries.

Comparison with other estuaries

Our previous results suggest, most of the time, an important positive correlation between DMS, DMSP$_d$ levels and salinity. They also suggest a different DMSP production with low DMSP-producer phytoplankton species in the low salinities (diatom-dominated communities) and higher DMSP-producer phytoplankton species in higher salinities. All these results are consistent with those reported for Northern American estuaries (Iverson et al. 1989). Hence, good agreement was found between our DMS and DMSP$_d$ values and those reported by Iverson et al. (1989) (Table 2), suggesting that our low DMS levels found in European estuaries are at least representative of mid-latitudes estuaries.

Table 2. Comparison of seawater concentrations of DMS, COS and CS_2 in open ocean, coastal, shelf and estuaries

Area	DMS (nM)	COS (pM)	CS_2 (pM)	References
Open Ocean				
(surrounding Western Europe)				
N. Atlantic Ocean (summer)	2.5			Berresheim et al. (1991)
Global (winter)	3.3			Andreae (1990)
(summer)	9.0			
N. Atlantic Ocean		5–19		Ulshofer et al. (1995)
N. Atlantic Ocean			8 ± 4	Kim and Andreae (1987)
Shelf / coastal				
Southern North Sea (December/May)	1.8–5.9			Turner et al. (1996)
North Atlantic Shelf			17 ± 4	Kim and Andreae (1987)
Mediterranean Sea		18–23		Mihalopoulos et al. (1991)
Ionian Sea				Ulshofer et al. (1996)
N. Sea, English channel		142 ± 90		Watts (2000)
N. American coastal waters	2.43–3.58			Iverson et al. (1989)
Estuarine				
6 tidal European estuaries	(< 0.02–10) **0.6**	(60–1010) **220**	(2–117) **25**	*This work*
Yarmouth, UK		130 775	263	Watts (2000 and references therein)
Eastern seaboard USA			120	Bandy et al. (1982)
Canal de Mira (Portugal)	2.9–5.3			Cerqueira and Pio
(Winter/Summer)			(1999)	
N. American estuaries	0.31–1.67	61–1466		Iverson et al. (1989) Zhang et al. (1998)

Spatial and temporal distribution of COS and CS_2 in estuarines

COS

The distribution of carbonyl sulfide has been examined in 4 estuaries: Rhine, Ems, Gironde and Scheldt (Figure 5). The distribution of COS in the Gironde and Scheldt has been examined during two seasons: summer (June) and autumn (September) in the Gironde; spring (May) and summer (July) in the

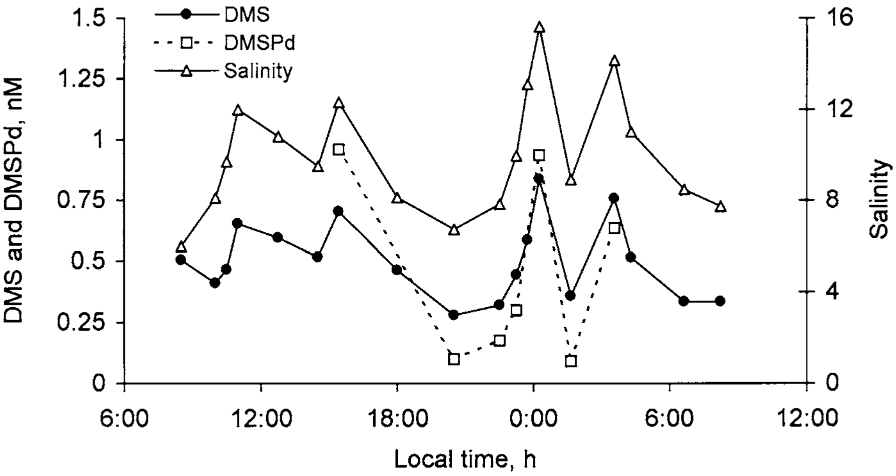

Figure 4. Temporal variation of DMS, $DMSP_d$ and salinity in the Elbe estuary (April 1997).

Scheldt. Table 1 summarizes the location, period, number of the performed measurements, as well as the mean concentrations derived as for the DMS (average for each 5 degree of salinity). COS levels are highly variable and range from 60–1010 pM (220 ± 90 n = 149). The above mean is within the range of the values reported for the Yarmouth estuary, which represents the only data set available in literature (Watts 2000 and references therein). The above mean value is a factor of 2–15 and 5–60 higher when it is compared to the mean values reported for the coastal and open ocean respectively (Table 2) and indicates a clear production of COS from the estuaries.

The detailed distribution of COS versus salinity for four of the six studied estuaries are presented in Figure 5. From these profiles, the following remarks can be drawn:

- The highest COS concentrations have been measured in the Rhine estuary in July. As displayed in Table 1, the mean COS concentration calculated for the Rhine is a factor of 2–3 higher compared to the other estuaries. This picture is in agreement with the DMS concentrations, also a factor of 2–3 higher in the Rhine compared to the other estuaries. Such difference might originate from the fact that the measurements performed in the Rhine estuary are more representative of its plume (report to the previous discussion).
- A clear COS maximum has been observed in all studied estuaries in the low salinity waters. The high contents of chl-a in these waters can account for this maximum.
- Apart from the Rhine estuary, the other studied estuaries present a COS minimum associated with the presence of the maximum turbidity

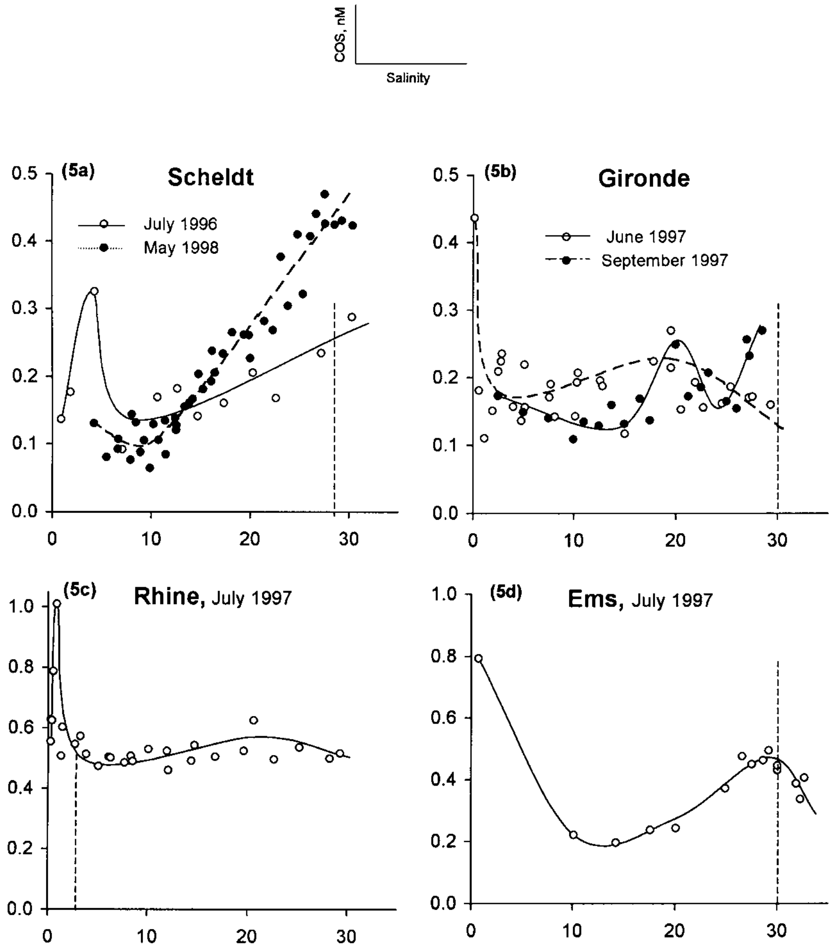

Figure 5. Salinity profiles of COS in 4 tidal European estuaries.

zone, which inhibits the light penetration and thus the COS production from the photosensitized reactions of organosulfur compounds (Zepp & Andreae 1994).

– Finally the distribution of COS as a function of salinity observed for the Ems, Gironde and Scheldt estuaries follow that of DMSP, indicating that at least for these estuaries a common process for the production of DMSP and COS occurs.

CS_2

The distribution of carbonyl disulfide has been examined in 4 estuaries: Rhine, Ems, Gironde and Scheldt (Figure 6). The distribution of CS_2 in the

Gironde has been examined during two seasons: summer (June) and autumn (September). Range, mean concentration and total number of measurements are reported in Table 1. CS_2 levels are highly variable and range from 2–117pM (25 ± 6 n = 92). Compared to the values reported in the literature (Watts 2000 and references therein) the above mean falls within their lower range. However, as pointed out in the introduction very few measurements have reported for CS_2 concentrations in the estuaries. Although no measurements have been performed in the open sea during these cruises the above mean value is 3–7 times higher compared to the value reported in the literature (Table 2), indicating a clear enhancement in the CS_2 concentration in the estuaries compared to the open sea.

The detailed distribution of carbonyl disulfide along the salinity gradient for all the studied estuaries is presented in Figure 6. No clear pattern can be derived from the above measurements. However, the distribution of CS_2 is in very good agreement with that observed for DMS and DMSP at least for the Ems, Gironde and Scheldt estuaries. In these estuaries carbonyl disulfide follows quite well the DMS distribution presenting maxima at the same salinity levels, indicating that at least for these estuaries a common process for the production of both biogenic sulfur compounds occurs.

Significance of estuaries as a source of biogenic sulfur compounds

A complete picture of the DMS levels in estuarine waters is hard to obtain since estuarine environment is complex and depends upon many characteristics, which may significantly influence the DMS concentrations and further process studies are clearly needed to better determine the factors controlling the S-compounds turnover in these estuaries. Even the salinity criteria (0 to 30) applied to define estuaries is not suitable to describe all of them since, for instance, the mixing of the Rhine freshwaters with shelf waters occurred in the mouth of its estuary. Probably for that reason, the DMS levels found in this estuary (3 to 33 in salinity) are more representative of the shelf (Turner et al. 1996) than of estuarine waters (Tables 1, 2). The DMS levels reported for the other estuaries (Scheldt, Loire, Ems, Gironde and Elbe) do not exceed 1–2 nM even during summer. These values are 5–10 times lower than those observed in the surrounding shelf waters (Turner et al. 1996, Table 2) and even lower than observed in the open ocean (Table 2). Considering the surface area occupied by estuaries (more than 1000 times lower than coastal and shelf ocean, Watts, 2000), the role of inner estuaries as source of atmospheric DMS appears to be insignificant. On the other hand, significantly high DMS levels have been observed in the plumes of the estuaries compared to the open sea and shelf (Elbe, Ems, Rhine). This finding agrees well with the significant DMS levels reported also for the plumes of Rhone, Ebro (Western Medi-

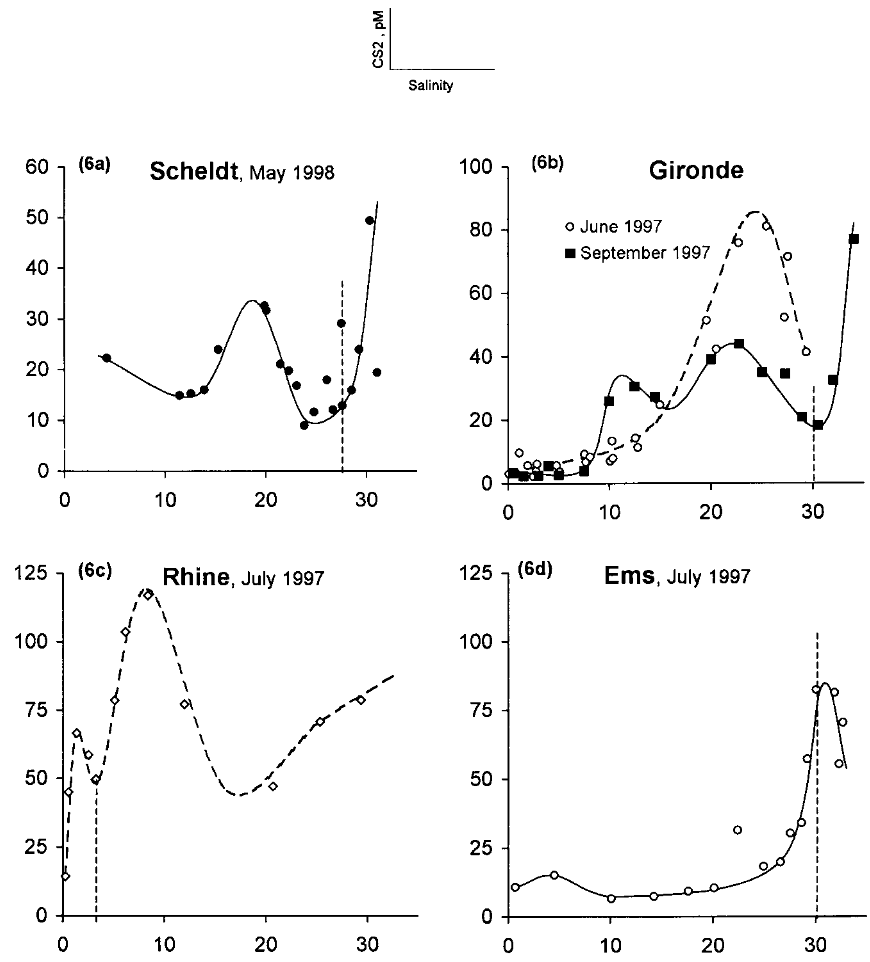

Figure 6. Salinity profiles of CS_2 in 4 tidal European estuaries.

terranean sea, Simo et al. 1997) and Northern American estuaries (Iverson et al. 1989). Seawater DMS distribution in the estuarine plumes could be spatially and temporally significant compared to the shelf and thus could play a significant role in terms of DMS emission into the atmosphere on a local basis.

On the other hand, as shown in Table 2, significant levels of both COS and CS_2 are reported in all the investigated estuaries. The observed COS levels are a factor of 2–50 higher than observed both in coastal and open sea, indicating that estuaries can play an important role as a source of COS in the atmosphere. Although the CS_2 levels fall in the low range of the values reported for the estuaries, they are still comparable to the values reported for the coastal areas and a factor of 3 higher to those reported for the open ocean.

The up to date works dealing with the biogenic S-compounds distribution in estuaries are performed in mid-latitudes and concern relatively small rivers with high anthropogenic forcing. In addition little is known on the distribution of these compounds in the plumes of the estuaries. To obtain a more precise picture on the importance of estuaries and corresponding plumes as a global source of S-compounds, work under various conditions representative of the diversity of estuaries on a global scale is clearly needed.

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