Seasonal and interannual variability of volatile reduced sulfur compounds (VRSC) in a marine coastal environment: the Bay of Quiberon (Brittany, France).

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Abstract

Seasonal and annual variability of hydrogen sulfide (H_2S), carbonyl sulfide (COS), methane thiol (MeSH), dimethylsulfide (DMS) and dimethyldisulfide (DMDS) concentrations and supporting parameters (e.g., phytoplankton cells density) were investigated in a coastal marine environment, the Bay of Quiberon (Brittany, France) from July 2004 to August 2006. The sampling was conducted in the water column above the sediment water interface (SWI). Minimum and maximum values were <0.1-1.6 nmol L^{-1} for H_2S, <0.1-4.2 nmol L^{-1} for COS, <0.1-7.8 nmol L^{-1} for MeSH, <0.1-17.5 nmol L^{-1} for DMS and <0.1-1.7 nmol L^{-1} for DMDS. Vertical carbonyl sulfide distribution showed seasonal variations with lower concentrations near the SWI during the winter and significant enrichments near sediments for the summer period. Vertical hydrogen sulfide distribution did not influenced by the shallow sediments. The seasonal variability of MeSH, DMS and DMDS concentrations was explained by the dinophyceae presence.

Keywords: Sulfide – Coastal environment – Sediment Water Interface – Phytoplankton – Dimethylsulfide

1. Introduction

Over the last decades, the distribution and the biogeochemistry of sulfur compounds such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), methane thiol (MeSH, CH_3SH) dimethylsulfide (DMS, CH_3SCH_3) and dimethyldisulfide (DMDS, CH_3SSCH_3) in marine environments have received growing attention (Cutter and Radford-Knoery 1993; Zhang et al. 1998; Yang et al. 2005) because of their high reactivity and significant contribution to the atmospheric sulfur budget. Since the 1970s, DMS has generated much interest with its possible role in the biological regulation of the climate (CLAW hypothesis) (Lovelock et al. 1972; Charlson et al. 1987; Andreae 1990). Dimethylsulfide (DMS) is the most abundant form of volatile sulfur in the ocean (Andreae 1990). Kettle and Andreae (2000) showed that DMS may be responsible for up to 60% of the biogenic sulfur emissions; 15 to 33 Tg (S).yr^{-1} leave the oceans to the atmosphere. DMS is produced by the enzymatic cleavage (i.e., DMSP-lyase role) of dimethylsulfoniopropionate (DMSP), which is an abundant compound in phytoplankton (Challenger, 1951; Ackman et al., 1966). It is widely accepted that DMSP is an osmolyte and a cryoprotectant for marine algae (Vairavamurthy et al. 1985; Dickson and Kirst 1987; Kirst et al. 1991; Karsten et al. 1992). DMSP is one of the most abundant forms of reduced sulfur found in the euphotic zone of oceans, with concentrations (dissolved plus particulate forms) ranging from few to several nmol L^{-1} (Malin et al. 1993). DMSP is released during phytoplankton grazing by zooplankton, phytoplankton virus infection and phytoplankton cells senescence (Keller et al. 1989; Simo et al. 2002). Recent studies also show that DMSP and its degradation products (DMS, DMSO) could have antioxidant properties for marine phytoplankton (Steinke et al. 2002;

Sunda et al. 2002; Van Rijssel and Buma 2002). In marine environments, DMS concentration range is between 0.4 and 16 nmol L^{-1} (Turner et al. 1988; Moret et al. 2000; Amouroux et al. 2002; Andreae et al. 2003). Studies suggest that a relatively small portion (<30%) of DMSP degradation is converted to DMS (Belviso et al. 1990). Thus, the major part of DMSP is demethylated and further degraded to methane thiol (Kiene and Taylor 1988) which is also produced from DMS (Kiene et al. 2002). Another sulfur compound, dimethyldisulfide, is synthesized from the DMSP (Tanzer and Heumann 1992) but it also results from the oxidative dimerization of the methane thiol by polysulfides (Gun et al. 2000). In anoxic marine environments like marine sediments or in water column with restricted ventilation, dissolved hydrogen sulfide is produced by bacterial sulfate reduction. H_2S concentration occurs from micromolar level in anoxic environments and sediments to nanomolar level in oxic areas (e.g., open oceans). In open oceans, one source of H_2S is the COS hydrolysis (Elliot et al. 1989) and a direct production by phytoplankton cells (Walsh et al. 1994). H_2S is a significant compound of the marine sulfur budget (Andreae 1990) with average coastal concentrations about 0.4 to 2.5 nmol L^{-1} (Cutter and Krahforst 1988; Luther and Tsamakis 1989; Radford-Knoery and Cutter 1994). COS is the most abundant and probably the most long-lived sulfur gas in the atmosphere (Ulshöfer and Andreae 1998). Dissolved COS is produced by several processes; *i)* photochemical degradation of dissolved organo-sulfur compounds (Zepp and Andreae 1994) and *ii)* non-photochemical production from dissolved organo-sulfur compounds (e.g., methane thiol degradation; Ulshöfer et al. 1996). The COS concentration in surface waters of open oceans averages 0.03 nmol L^{-1} (Johnson and Harrison 1986) whereas its coastal concentrations range from 0.07 nmol L^{-1} (Rasmussen et al. 1992) to 1.2 nmol L^{-1} (Jorgensen and Okholm-Hansen 1985).

In this paper, the five sulfur compounds were called VRSC for Volatile Reduced Sulfur Compounds according to their common properties of volatilisation and oxidation. We examined these VRSC in a coastal environment to highlight the complexity of relationships between these sulfur species. The sediment-water interface (SWI) was considered because it is the place of chemical and microbiological transformations which are responsible for cycling biogenic constituents between water and sediments (Ni et al. 2002; Viollier et al. 2003). Although reduced sulfur compounds and particularly H_2S, have been studied in porewaters (Klump and Martens 1989), their distribution at the 10^{-2} to 10^{-1} m scale above the SWI (i.e., bottom water column) is yet unknown in nearshore environments. Fuelled by OM supply, nebulous statement bacteria activity causes chemical interactions between water column and sediments (Anschutz et al. 2000). Thus, the SWI which plays a significant role on the distribution of chemical compounds (e.g., sulfur compounds) in sediments may also influence the bottom water column.

Over a 25 month-period (i.e., from July 2004 to August 2006), one sampling into the 2-m water column above the SWI was lead to estimate seasonal and interannual variability of VRSC concentrations in a temperate coastal marine environment, the Bay of Quiberon. A part of the originality of this work was the simultaneous study of VRSC concentrations and phytoplankton density to determine the role of two phytoplankton groups (i.e., dinophyceae and bacillariophyceae) on the VRSC production.

2. Materials and Methods

2.1. The Sampling area: the bay of Quiberon

The bay of Quiberon is a semi-closed Bay in the south-west of Brittany (Morbihan, France) which opened onto the bay of Biscay at 47°32N. The western bay of Quiberon covers an area of 150 km^2 with a 9-m average depth and it is regularly exposed to waves and tidal action. Dominant winds are S-SW and N-NW onto an annual scale but between the end of winter and spring, they are NE or S. The swell is residual and comes into the bay with a 15 km-fetch. This coastal zone is also submitted to tidal currents whose maximum speed is between 0.18 km h^{-1} (neap tide) and 0.37 km h^{-1} (spring tide) (www.shom.fr) in the middle of the bay (47°29N, 3°02W) while the spring tidal range is about 4.6 meters (source: www.shom.fr). The major part of sediments is sandy muds (63-80 µm; Lemoine 1989 unpubl.). The water is saturated with oxygen throughout the entire water column, there is no anoxia.

Sampling was conducted over a 25-month period (n=11) and only one sampling occurred for winter period (i.e., adverse weather conditions). The monitored station (Men Er Roué, 47°32N, 3°05W) was considered as the best representative zone of the whole bay of Quiberon. The station was near the bay mouth and had a depth about 7.5 meters with sandy muds sediments (Figure 1).

2.2. Phytoplankton density and abiotic parameters

The phytoplankton density was monitored through the REPHY (i.e., French network to survey the phytoplankton and phycotoxins densities on coastal environments); one

measurement was lead every week from May to September and one each two weeks for the rest of the year. Assessments were carried out as following; 1 L of water was taken from the sea surface at Men Er Roué and immediately, an acid lugol solution was added to fix the algal cells (i.e., 2 to 10 ml L^{-1} according to the phytoplankton density). Less than 36 h later, the cell density of each phytoplankton groups was determined using the Untermöhl technique (Paxinos and Mitchell, 2000). Hydrographical parameters were monitored from June 2004 to August 2006. They were not presented in this article to not overload it. Temperature and salinity were measured continuously (i.e., one measurement per hour) with a Micrel probe and just above the SWI (i.e., 7-m depth); the daily means were presented here (Figure 2A). Turbidity was weekly measured *in situ* with a specific probe (WTW Turb550IR). Precipitations and insolation were also available for the whole sampling period (www.meteofrance.com). Monthly measurements were calculated to show the seasonal trends (Figure 2B). Unfortunately, data concerning the wind strength were unavailable in the Bay of Quiberon but no important storm event was recorded for the sampling period.

2.3. Sampling, conservation and analyses

The epibenthic sampler, Susane (Knoery et al. unpubl.) was used to acquire water samples and to reveal sulfur gradients in the water column above the SWI. Briefly, it is a syringe sampler with fine scale and high vertical resolution. Susane was put down on sediments by a scuba diver, and using a vertical rod, up to sixteen samples could be simultaneously collected at altitudes ranging from 1 cm to 200 cm above the seabed. To the proper water column sampling, the syringes thoroughly cleaned. To minimize sample degradation and

for example, the production of COS via photolysis (Ferek and Andreae 1983), the subsampling was as rapidly as possible (i.e., < 5min) into transfer syringes. Water samples were refrigerated in the dark until analysis (i.e., less than 2 hours) to prevent the DMSP degradation (Jean et al. 2004). The analytical technique used to determine the VRSC concentrations was the purge and trap extraction followed by a gas chromatography separation and pulsed flame photometric detection. Detection limits were 0.07 nmol L^{-1} for H_2S, 0.03 nmol L^{-1} for COS, 0.01 nmol L^{-1} for MeSH, 0.1 nmol L^{-1} for DMS and 0.03 nmol L^{-1} for DMDS. Precision values were 6.0% for H_2S, 4.1% for COS, 5.6% for MeSH, 4.9% for DMS and 8.4% for DMDS (Cozic-Houly et al. pers. comm.).

One 30 cm-sediment cores were sampled to analyse hydrogen sulfide concentrations in the first 10-cm porewaters (i.e., Men Er Roué station). To avoid sulfide degradation, the cores were refrigerated in the dark (i.e., icebox) until analysis (i.e., < 2h). Rhizons were used to sample seepage water in sediment cores (Seeberg-Elverfeldt et al. 2005). They were connected to syringes and a colorimetric analysis (i.e., methylene blue method) was lead. Its detection limit was about 0.32 µmol L^{-1} for hydrogen sulfide. Unfortunately, no similar method exists for others VRSC and the very low volume (i.e., less than 5 ml) of seepage water did not permit chromatographic analysis of these samples.

For some sampling days, more water heights were sampled (e.g., 15 in June 2006). The sampling step was smaller within the first 10-cm layer to specify the variability of VRSC concentrations near SWI. In the upper column (i.e., above +70 cm), the sampling resolution was smaller because the water column was expected to be more homogeneous (Lemoine 1989, unpubl.).

3. Results

3.1. Abiotic parameters

The seawater temperature was 5-6°C during winter (Figure 2A). From March on, it increased progressively to reach a maximum value in August (ca. 20°C). Interannual variations were not significant between the three summers sampled with a summer mean temperature about 16 and 18°C. The salinity was relatively constant over the 26-months sampling with a mean value of 33.7±1.4 (Figure 2A). The turbidity showed seasonal variations with higher monthly values during the winter (Figure 2A). Indeed, from mid-September to march, the 3-years mean turbidity was 13.4±1.5 and from April to mid-September, it was 10.5±0.2. Precipitations also showed seasonal variations with an increase from the autumn period (Figure 2B). From mid-September to march, the 3-years mean of monthly precipitations was 63.3±9.2 mm and from April to mid-September, it was 46.6±13.8 mm. The insolation (number of hours per month) occurred clear variations through the year with a consistent increase from winter to summer period (Figure 2B). Indeed, from mid-September to march, the 3-years mean insolation was 111.6±12.3 hours and from April to mid-September, it was 229.6±5.3 hours.

3.2. Phytoplankton

In order to describe the role of phytoplankton on the VRSC distribution, the density of two main algal groups (i.e., dinophyceae and bacillariophyceae) were monitored for the sampling period. Dinophyceae and bacillariophyceae accounted for more than 92% of the phytoplankton whatever the season. Dinophyceae are different from bacillariophyceae

because they synthesize significant amounts of DMSP (Turner et al. 1988). As expected, the variations of algal density were seasonal and interannual (Figure 3). Two annual phytoplankton blooms were observed in 2004 (June and September), 2005 (March and May) and 2006 (May and July). To clarify the description, the weekly survey of bacillariophyceae and dinophyceae densities were presented by lines whereas the weekly survey of total phytoplankton was presented by an area (Figure 3).

3.2.1. Bacillariophyceae

The distribution showed a seasonal feature with higher algal density from May to September (Figure 3). For example, from March to September 2005, the mean value of the bacillariophyceae density was $(3.29\pm4.93)x10^5$ cell L^{-1} (n=23) with a maximum in the end of march. In winter, the algal density decreased considerably to low values (e.g., $0.03x10^5$ cell L^{-1} in 2005). Summer density was highly variable with large density swings. In 2004, the bacillariophyceae density was highest in the beginning of June and September whereas in 2006, it was in May and July. In 2005, after the maximum observed in March, the density decreased in the end of June.

3.2.2. Dinophyceae

The dinophyceae cells density was usually lower than that of the Bacillariophyceae (Figure 3) but seasonal variations also occurred with high values during the summer period. During 2004, the dinophyceae density showed the same features as the Bacillariophyceae density with two maxima, in the beginning of June ($5.05x10^5$ cell L^{-1}) and in the end of September ($0.30x10^5$ cell L^{-1}). In 2005, the cell density increased by a factor of ten between March ($0.37x10^5$ cell L^{-1}) and June ($4.15x10^5$ cell L^{-1}). In 2006 only one maximum was noted in

April ($1.91x10^5$ cell L^{-1}). Moreover, at least two dinophyceae blooms occurred per year with a time span between the blooms of 2 to 3 months; June and September 2004, March and May 2005, June 2006 (no available data from September).

3.3. Suprabenthic distribution of VRSC

The VRSC profiles collected in the suprabenthic layer (i.e., from zero to ca. 200 cm above the SWI) are presented in Figure 4. Only one water sample – 1st of February – was lead for the winter. But, within this important limitation, it was attempted to describe seasonal variations in VRSC concentrations.

Several H_2S profiles showed a trend of concentration increase close to the SWI (Figure 4). In addition, a layer exhibiting a minimum was present at 30 to 60 cm above the SWI. COS showed an identical trend with a smoother increase close to the bottom. The MeSH profiles did not show evidence of increase at the SWI but rather a maximum zone between 10 and 60 cm above the sediment-water interface. The DMS profiles occurred a higher concentration in the top of water column sampled (i.e., beyond one meter above sediments). An increase of DMS concentration was apparent into the first centimetres above the SWI for some summer profiles. In addition, some DMS profiles showed a minimum concentration at 30 or 50 cm above sediments. The DMDS concentration like the one of DMS showed a higher concentration above 1-m altitude but no clear vertical variations except in some summer profiles (Figure 4).

3.3.1. Seasonal variations of VRSC concentrations

The H_2S concentration was maximum at the beginning of spring (April 2006) with 0.57±0.06 nmol L^{-1} (n=8); it was generally higher during the summer (Figure 4). Vertical variations were greater for the spring (e.g., June 2005) and the beginning of summer. From the end of summer to winter, the H_2S concentration started to decrease and it was below the detection limit (0.07 nmol L^{-1}, pers. comm.) above +30 cm (22 September 2004). In winter, (February 2005), it was less than the summer period and never greater than to 0.07 nmol L^{-1}.

Carbonyl sulfide showed a stronger vertical concentration gradient than H_2S for the summer periods, and exhibited larger variations in the 50-cm layer above the SWI (Figure 4). During the early 2005-summer period, the maximum concentration was often observed near +30 to +50 cm. In addition, its summer concentration was from twice to twenty times (e.g., 4.20 nmol L^{-1} observed in June 2006) greater than observed during the winter.

The MeSH concentration showed significant seasonal variations with summer values ten-fold greater than the winter values (Figure 4). Clear variations are also observed in the 50-cm layer above the SWI. MeSH was undetectable or very low levels in the winter. The MeSH concentration increased during the summer period and maximum values occurred between +10 and +50 cm above sediments. At the end of summer 2005, there was five-fold less MeSH (0.78 nmol L^{-1}) than in June and vertical variations were less important. During the last summer sampled, MeSH concentration began to increase with 4.15 nmol L^{-1} measured in June.

Dimethylsulfide concentration was either constant (summer 2006) into the 2 m-water column sampled or very variable (summer 2005). Its concentration was lowest in winter

with less than 0.20 nmol L^{-1} and it increased clearly like MeSH, during summer to reach several nmol L^{-1}. The highest concentration was measured in spring (April 2006) with 15 nmol L^{-1} at +180 cm.

For DMDS, no clear repeated and vertical variations were apparent in winter and spring. A clear maximum value was observed only in June 2005, August 2005 and June 2006; it was respectively 1.69 nmol L^{-1} (at +50 cm), 1.36 nmol L^{-1} (+90 cm) and 1.29 nmol L^{-1} (+1cm). Thus, like for DMS, an increase was noted from the spring to the end of summer. For example, the maximum DMDS concentration was 0.04 nmol L^{-1} in winter 2005 whereas it reached 1.36 nmol L^{-1} in August (Figure 4).

3.3.2. Interannual variations of VRSC concentrations

During the 3 summer-sampling, interannual variations were obtained for each sulfur gas. It was interesting to highlight similarities between summers but also the variability linked to biotic factors (e.g., phytoplankton density).

No clear interannual variations of sulfide concentration were observed with 0.17±0.36 nmol L^{-1} (n=24) measured in 2004, 0.05±0.08 nmol L^{-1} (n=41) in 2005 and 0.07±0.03 nmol L^{-1} (n=24) in 2006. The summer H_2S concentration was often higher near the SWI than in the upper water samples. This feature was apparent for summer 2004, June 2005 and summer 2006 with significant variations into the 20-cm layer above the SWI (Figure 4). The maximum values occurred near sediments and they were followed by a rapid decrease, itself followed by another increase. The best example is observed in June 2005 with a minimum value (0.06 nmol L^{-1}) detected from +32 to +50 cm. The opposite trend was recorded in February 2005 and April 2006 with a maximum value between two minimum zones in the 20-cm layer above the SWI.

No interannual variations were apparent for COS concentration between summer 2005 (0.30±0.18 nmol L^{-1}; n=41) and summer 2006 (0.55±0.82 nmol L^{-1}; n=24) whereas in 2004, it was lower with 0.08±0.06 nmol L^{-1} (n=24). During the summer period, COS concentration increased from the beginning to the middle of summer and a decrease phase was observed later (Figure 4). Into the 2-m water column sampled, clear variations were observed into the 50 cm above sediments; in the top of water column sampled, COS concentration was relatively constant. Some profiles (e.g., 1 September 2004, July 2005, and June 2006) showed an increase of COS concentration just above the SWI and a minimum value near +15 cm. The profiles of July 2004 and June 2005 showed another trend; COS concentration increased from the SWI to +10 cm and it decreased rapidly until a given altitude (+32 cm in 2004 and +20 cm in 2005) before to increase again (Figure 4).

Three different features were observed for the MeSH concentration. Interannual summer variations were detected; 0.18±0.17 nmol L^{-1} (n=24) in 2004, 1.95±1.34 nmol L^{-1} (n=41) in 2005 and 3.61 ±1.99 nmol L^{-1} (n=24) in 2006 (Figure 4). All summer profiles showed a sharp decrease just above the SWI, overlain by a clear maximum at +50 cm (0.56 nmol L^{-1}) in July 2004, +15 cm (4.17 nmol L^{-1}) in July 2005 and +8 cm (7.83 nmol L^{-1}) in June 2006. Out of summer period, MeSH concentration slightly varied (except in June 2005). During summer, MeSH profiles were consistent with an increase until the middle of summer followed by a decrease to winter (Figure 4).

The DMS profiles occurred less variability than all VRSC but clear interannual summer variations were observed; with 1.03±0.79 nmol L^{-1} (n=24) in 2004, 6.79±2.98 nmol L^{-1} (n=41) in 2005 and 4.00±0.58 nmol L^{-1} (n=24) in 2006. During the early summer, it was about nine-fold more concentrated at the beginning of summer than in September. Next year, DMS concentration showed two increase periods; one from June to the beginning of

July 2005 and another from the end of July to August. In summer 2006, DMS concentration did not vary so much between June and August. The maximum DMS concentration was often observed above +100 cm and sometimes, high DMS concentration was also recorded near the SWI (Figure 4). For example, in summer 2005 (e.g., 28 July), DMS concentration was 7.09 nmol L^{-1} in the 50-cm layer above the SWI, 3.65 nmol L^{-1} (minimum value) at +90 cm and 10.80 nmol L^{-1} (maximum value) at +190 cm.

Dimethyldisulfide also showed interannual variations with summer concentrations of 0.15±0.10 nmol L^{-1} (n=24) in 2004, 0.50±0.36 nmol L^{-1} (n=41) in 2005 and 0.27±0.26 nmol L^{-1} (n=24) in 2006 (Figure 4). For most of the profiles, the vertical DMDS distribution was uniform (e.g., July 2004, August 2006). But for some profiles, clear variations occurred like in the beginning of September 2004 with a minimum (0.13 nmol L^{-1}) at +50 cm and 0.24±0.03 nmol L^{-1} (n=11) over the whole profile. It was important to note there were also variations of DMDS concentration during a specific summer with no clear trend for the date of the maximum (Figure 4).

3.4. Porewater sulfide concentration

To ascertain the presence of a permanent oxygenated sediment layer in this oligotrophic bay (Soletchnik et al., 2007) and negate the possibility of a seasonal sulfide sedimentary source, we examined porewaters H_2S concentration in 30-cm long cores collected at the same time as the water column depth profiles. For this report, we presented only the evolution of H_2S concentration near the SWI and in the 3-cm layer of sediments (Figure 5).

Near the SWI (altitude zero), the sulfide concentration was often less than one micromolar but, given the analytical detection limit of 0.32 µmol L^{-1} for the colorimetric method that

was used, only few results were significantly different from non-detectable levels. H_2S concentration was undetectable (<0.32 µmol L^{-1}) in February, June and at the end of July 2005 and very low in spring and August 2006. The highest concentrations near the SWI occurred at the beginning of summer; 0.65 µmol L^{-1} in July 2004, 0.73 µmol L^{-1} in July 2005 and 0.46 µmol L^{-1} in June 2006. Porewaters H_2Sconcentration showed relatively the same feature with higher values for summertime. Seasonal variations were greater than interannual variations with values measured in the upper 3-cm sediments remained two to three orders of magnitude greater than those recorded in the water column samples.

4. Discussion

There are many data available on the distribution of volatile reduced sulfur gases in the marine environment. Table 1 shows concentrations in different settings and highlights the increase of VRSC concentrations shoreward or in areas with increased productivity. The water column data we report here are consistent with the literature data on dissolved H_2S, COS, MeSH and DMS for comparable coastal environments (Table 1). Our 2-year sampling campaign gives the following concentration ranges ; up to 1.6 nmol L^{-1} for H_2S, up to 4.2 nmol L^{-1} for COS, up to 7.8 nmol L^{-1} for MeSH, from 0.1 to 17.5 nmol L^{-1} for DMS and up to 1.7 nmol L^{-1} for DMDS (Figure 4).

To simplify the discussion of the VRSC concentration evolution, the different sulfur species were placed in two groups. H_2S and COS are studied together because they are directly issued from compounds as sulfate or dissolved organo-sulfur compounds (Dyrssen, 1985; Elliot et al. 1989; Zepp and Andreae 1994). Methane thiol, DMS and DMDS, on the other hand, can have the same origin, DMSP (Kiene and Taylor 1988; Dacey et al. 1998). The

first hypothesis was whether the SWI plays an important role on the VRSC distribution in the bottom water column. The second hypothesis was the following; does the phytoplankton distribution in the water column influence the VRSC distribution?

4.1. Hydrogen sulfide (H_2S) and carbonyl sulfide (COS)

For several vertical profiles, H_2S and COS show the same general trend, an increase of concentrations toward the seabed which suggests a higher production near sediments than in the upper water column sampled (Figure 4). Moreover, H_2S was sometimes measured in pore waters near the SWI (Figure 5). Therefore, water column sulfide could have a sedimentary origin or it could be produced in the bottom water column. No diffusive gradients were calculated on account of the lack of data. But, for the following years sampled, a temporal decoupling (e.g., summer 2005) appears to exist between H_2S presence in the water column and sediments suggesting that the sediment was not essential as a source for the H_2S. By default, sulfide may likely have originated from the water column itself.

The lower water column could be favourable to H_2S production because of special conditions. Alldredge et al. (1998) showed that the phytoplankton cells are present in marine snow which is exported to the seafloor. These marine snow aggregates are enriched in microbial communities taking important part in phytoplankton degradation (Alldredge 2000). Therefore, the important phytoplankton sedimentation (i.e., degradation of organic matter) may create anoxic micro zones near the seabed and thus, H_2S may be produced in the first cm above sediments and remain undetected either by sediment pore waters studies or water column studies conducted using pumps or large bottles. We also note that the maximum H_2S concentration in the 10-cm layer above the SWI (Figure 5; September 2004,

June 2005 and April 2006) occurred during blooms (Figure 3). This relation between the high density of phytoplankton cells and high sulfide levels encountered near the SWI is consistent with high organic matter flux (i.e., post bloom event) and subsequent rapid degradation releasing directly or inducing anoxic micro zones where sulfate reduction may occur.

The possible direct release from phytoplankton cells like the cause of the higher H_2S concentration near sediments can be evaluated as follows. Wollast et al. (1993) showed that the elemental composition of the particulate organic matter (POM) is $C_{106}H_{263}O_{110}N_{16}S_{1.7}P_1$. Thus, the sulfur content in POM (e.g., phytoplankton cell) is not negligible (i.e., 0.34% S). Considering a spherical phytoplankton (from $1.4x10^{-5}$ to $3.4x10^{-5}$ µl with a ratio of 0.1 between the dry weight and the fresh weight), we obtained a phytoplankton sulfur concentration between 6.2 $x10^2$ and $2.5x10^2$ nmol L^{-1} during September 2004 (i.e., bloom with $16.9x10^5$ cell L^{-1}). Therefore, the concentration of phytoplankton sulfur determined in the water column is one order of magnitude greater than the H_2S concentration into the 10-cm layer above the SWI (0.24 nmol L^{-1}; Figure 5). Thus, a low turnover of phytoplankton cells may become a significant source of reduced sulfur and its decay in the water column could contribute to the increasing of H_2S concentration near the SWI.

Cutter and Radford-Knoery (1993) studied COS concentrations surface waters on the shelf of the western North Atlantic. They showed that pore waters are 200 times enriched compared to the water column. Thus, COS produced in marine sediments, may diffuse through the SWI. Cutter and Zhang (1997) studied the COS sediment-water fluxes in the Chesapeake Bay during 3 years. They showed highest values during the summer periods because the sedimentary COS production (i.e., dark production) was coupled to a higher

rate of microbial sulfate reduction, more important for summer. In the 3-years sampling in the Bay of Quiberon, the COS concentration was twice as elevated near the SWI as in the shallow water column for every summer period (Figure 4). However, the opposite trend (i.e., an increasing with the altitude) was recorded for the winter period, spring and sometimes at the end of summer (Figure 4).

The principal source of COS in oceans is photochemical production from chromophoric dissolved organic matter (CDOM; Ferek and Andreae 1984; Kettle et al. 2001). The magnitude of the photoproduction is related to the irradiance, seawater absorption and CDOM content (Ulshöfer and Andreae 1998). In the euphotic zone, the DOM concentration is often correlated with the phytoplankton cells density. Mihaloupoulos et al. (1992) showed a positive correlation between the monthly average oceanic COS concentration and the monthly average of the daily insolation period. Therefore, the higher COS concentration analysed in Bay of Quiberon during the warm periods may be explained by a higher sun insolation (Figure 2) and an increase of phytoplankton cells density (Uher and Andreae 1997).

So, sediments appear to be a source of COS or neutral, given the shape of the water column gradient. During winter, photolytic production was the major source of COS in the water column (Cutter and Zhang 1997) whereas sediments were neutral. In opposite, in summer, sediments appeared to be a COS source (Kettle et al. 2001) which it explains the highest concentration observed near the SWI (Figure 4).

4.2. Dimethyl sulfide (DMS), methane thiol (MeSH) and dimethyl disulfide (DMDS)

DMS, MeSH and DMDS are produced directly or indirectly by bacterial degradation of DMSP (Kiene and Taylor 1988; Tanzer and Heumann 1992; Simo et al. 2002) and a significant production is confined to few classes of marine phytoplankton, mainly the dinophyceae (Keller et al. 1989). Therefore, a strong correlation may exist between the taxonomic position of the phytoplankton and the density of these VRSC in the bay of Quiberon.

The dinophyceae cell density showed seasonal and annual variations with blooms (i.e., generally two per year) during the warm period (Figure 3). For winter, the dinophyceae concentration was much lower than during the summer periods. The higher concentrations of DMS, MeSH and DMDS were always recorded during the summertime (Figure 4) but various features existed for each of these VRSC during each summer monitored. Dinophyceae blooms were recorded in May 2005 and April 2006, two months before the highest summer MeSH concentrations which occurred at the end of July in 2005 and in June 2006. A time span between dinophyceae cells density and DMDS maximum occurred with higher values observed in the beginning of July 2005 and in June 2006. Concerning DMS, a time span of 2 months was only observed during the summer 2005 with highest concentration analysed in July. In 2006, the maximum DMS concentration observed in April is contemporaneous with the dinophyceae bloom (Figure 3). Therefore, in 2006, the production of DMS is faster than the previous year and the MeSH and DMDS productions. The DMS concentration is always higher than MeSH and DMDS concentrations even in winter (Figure 4). The absence of MeSH (except at +50 cm) and DMDS in winter 2005 can be explained by a lower dinophyceae density. Indeed, there is as much DMDS as DMS in

the end of September but five months later, there is about ten times more DMS than DMDS. This is consistent with an additional winter production of DMS whereas methane thiol and dimethyl disulfide may be only produced for the warm period.

So, there exists a correlation between the time series of phytoplankton density and the levels of MeSH, DMS and DMDS. The DMSP-producers and VRSC synthesizers density may explain the distribution of these VSRC into the 2-m water column sampled and near the SWI. Methane thiol and DMDS concentrations are twice to four times higher in the 50-cm layer above the SWI in summer, whereas the DMS profiles show this feature only in the middle of summer. A hypothesis is purposed to explain the different features observed for these VRSC, in the 2-m water column, through the summer period. This increase of VRSC concentrations near the SWI may be linked to more abundant decomposing fragments of dinophyceae cells (Sorensen 1988). The DMS synthesis appears faster than those of MeSH and DMDS because in June (Figure 4), there is always more DMS in the upper water column than in the 50-cm layer above the SWI. The DMS may be produced by the decay of dinophyceae coming from the first bloom. These algae cells fall into the water column and are degraded near the SWI to give MeSH and DMDS in the beginning of summer. Along the summer period, the VRSC synthesis may continue into the 50-cm layer above the SWI. At the end of summer (i.e., August), the opposite trend (i.e., highest concentration above +50 cm) occurs for the three VRSC and it may indicate a moving towards the upper water column of the DMSP-producers. During, the spring period, no gradients are observed into the 2-m water column sampled and the concentrations are 0.47 nmol L^{-1} for MeSH (weighed average over the entire profile), 12.44 nmol L^{-1} for DMS and non-detectable levels for DMDS. This absence of vertical gradients may be linked to the mixing of the

water column (i.e., unstratified water column) according to the possible strong winds affecting the Bay and the 7-m depth (Lemoine 1989, unpubl.).

Considering MeSH concentrations into the 2-m water column more in detail, a maximum is measured at a given altitude ; it is +20 cm in the spring period (2.6 nmol L^{-1}), +15 cm at the beginning of summer (4.2 nmol L^{-1}) and +50 cm for the middle of summer (5.8 nmol L^{-1} ; Figure 4). This same trend is also observed for DMDS at the end of summer 2005 with a maximum concentration at +90 cm (1.4 nmol L^{-1}) whereas the MeSH concentration is constant over the entire profile. Lomans et al (1997) showed MeSH can be produced in sediments when H_2S is present in significant quantity. For example, in July 2005, H_2S shows a concentration above the detection limit near the SWI and in the 3-cm layer beneath it (Figure 5) whereas no sulfide is analysed near the SWI in June. Thus, a sedimentary origin of MeSH may be possible in July 2005 but it not appears to exist in June. The opposite phenomenon (i.e., a clear minimum concentration depth) is observed for DMS in June 2005 (Figure 4). The hypothesis advanced to explain this minimum DMS concentration layer is the following. The high concentration observed near the SWI may be induced by the decay of the first dinophyceae bloom (March) and the higher concentration measured on the top of water column sampled may be linked to the second bloom (May). Concerning DMDS concentration, in September 2004 and June 2006, there is also a given altitude where it is lowest. Moreover, in June 2006, the altitude of the lowest DMDS concentration corresponds to the maximum of MeSH concentration.

These variations of VRSC concentrations into the 2-m water column are very complex and an unequivocal link between these three sulfur compounds is not really established on the base of our data. We can just conclude discrete altitudes exist where higher VRSC concentrations are more favoured and that these altitudes vary during the warm period.

Decay of dinophyceae cells in the 2 m above the seabed may exist at various altitudes according to the DMSP-producers density.

5. Conclusion

This 3-summer survey of the volatile reduced sulfur compounds concentrations in a marine coastal environment highlighted interactions between the water column, the sediments, the phytoplankton and the VRSC distribution. The very tight sampling in the first centimetres above sediments made it possible to demonstrate that the SWI can play a key role on the VRSC distribution. Concerning COS, its seasonal concentration variations are linked to the balance between its sinks and sources. During winter, the major source of COS appears to be the photolytic production from CDOM (vertically uniform in the water column), whereas in the summer, sediments appear to be the main COS source which explains highest concentrations measured near the seabed. The variations of MeSH, DMS and DMDS concentrations may be directly linked to the seasonal variations of dinophyceae density because blooms increase the available organic matter to the DMSP-producers and so, the production of these biogenic sulfur compounds. The observations of a 2-month time span between the dinophyceae density and the maximum of MeSH and DMDS may be explained by a slower transformation of DMSP in these sulfur compounds in opposite to the DMS production which appears faster. The vertical variations of MeSH, DMS and DMDS concentrations may be linked to the spatial repartition of DMSP-producers in the 2-m water column. Concerning H_2S inventory which is greater near the SWI, it is likely linked to anoxic microzones from the decay of organic matter (e.g., phytoplankton cells). These zones may be found above and below the SWI and so H_2S analyzed does not seem to have a

consistent sedimentary origin. Other processes of sulfide could be the direct release by phytoplankton cells in the first meter above the SWI.

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No conflict of interest exists.

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1 **Tables**

2 Table 1 - Comparison between seawater concentrations of H2S, COS, MeSH, DMS and DMDS

3 and the values observed in the Bay of Quiberon.

Volatile Reduced Sulfur Compound	**References**	**Bay of Quiberon Concentration range**
Hydrogen Sulfide H_2S	0.4 – 2.5 nmol L^{-1} Cutter and Krahforst 1988 ; Luther and Tsamakis 1989 ; Knoery and Cutter 1994	0 – 1.6 nmol L^{-1}
Carbonyl Sulfide COS	0.08 – 0.73 nmol L^{-1} Mihalopoulos et al. 1992 ; Ulshöfer et al.1996 ; Cutter and Knoery 1993 ; Von Hobe et al. 2001 ; Cutter et al. 2004	0.02 – 4.2 nmol L^{-1}
Methane Thiol MeSH	3 – 76 nmol L^{-1} Lomans et al., 1997	0 – 7.8 nmol L^{-1}
Dimethyl Sulfide DMS	0.4 – 16 nmol L^{-1} Turner et al. 1988 ; Moret et al. 2000 ; Amouroux et al. 2002 ; Andreae et al. 2003	0.1 – 17.5 nmol L^{-1}
Dimethyl Disulfide DMDS	>0.15 nmol L^{-1} Tanzer and Heumann, 1992	0 – 1.7 nmol L^{-1}

4

Figures legends

Figure 1 - White point on mini map marks, which part of France is shown. Red point marks the city Quiberon on the peninsula of Quiberon. The grey star locates the Men Er Roue station. In the east of the peninsula there is the bay of Quiberon and in the south, a part of Belle-île Island is shown.

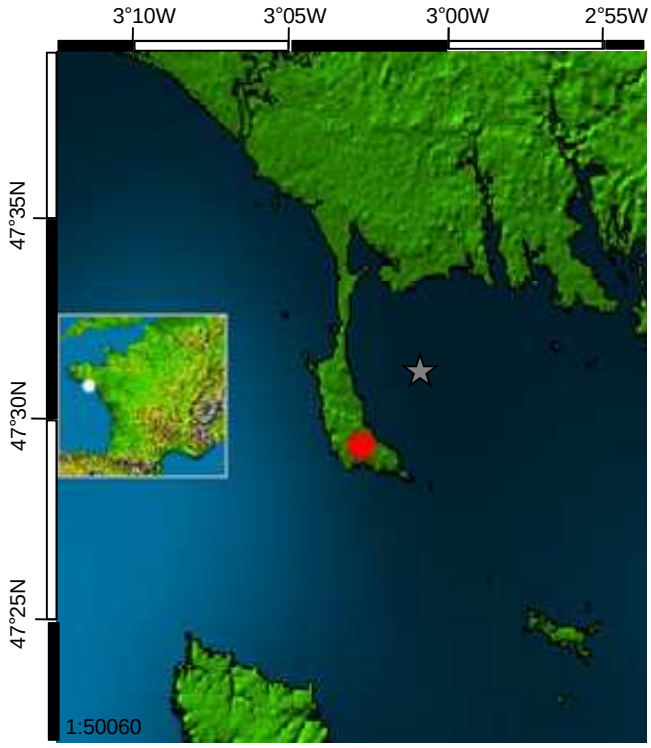
Figure 2 – Evolution of hydrographical parameters in the Bay of Quiberon from May 2004 to August 2006; A - SST (tiny dotted line), turbidity (large dotted line), salinity (middle dotted line) ; B – Precipitations (dark) and insolation (white).

Figure 3 - Evolution of phytoplankton density from May 2004 to August 2006; (A) Bacillariophyceae, (B) Dinophyceae. Monthly variations (gray areas); weekly variations (black lines). All densities are given in $x10^5$ cell L^{-1}.

Figure 4 - Evolution of the VRSC concentrations in the Bay of Quiberon (Men Er Roué station) from July 2004 to August 2006. All concentrations are given in nmol L^{-1}.

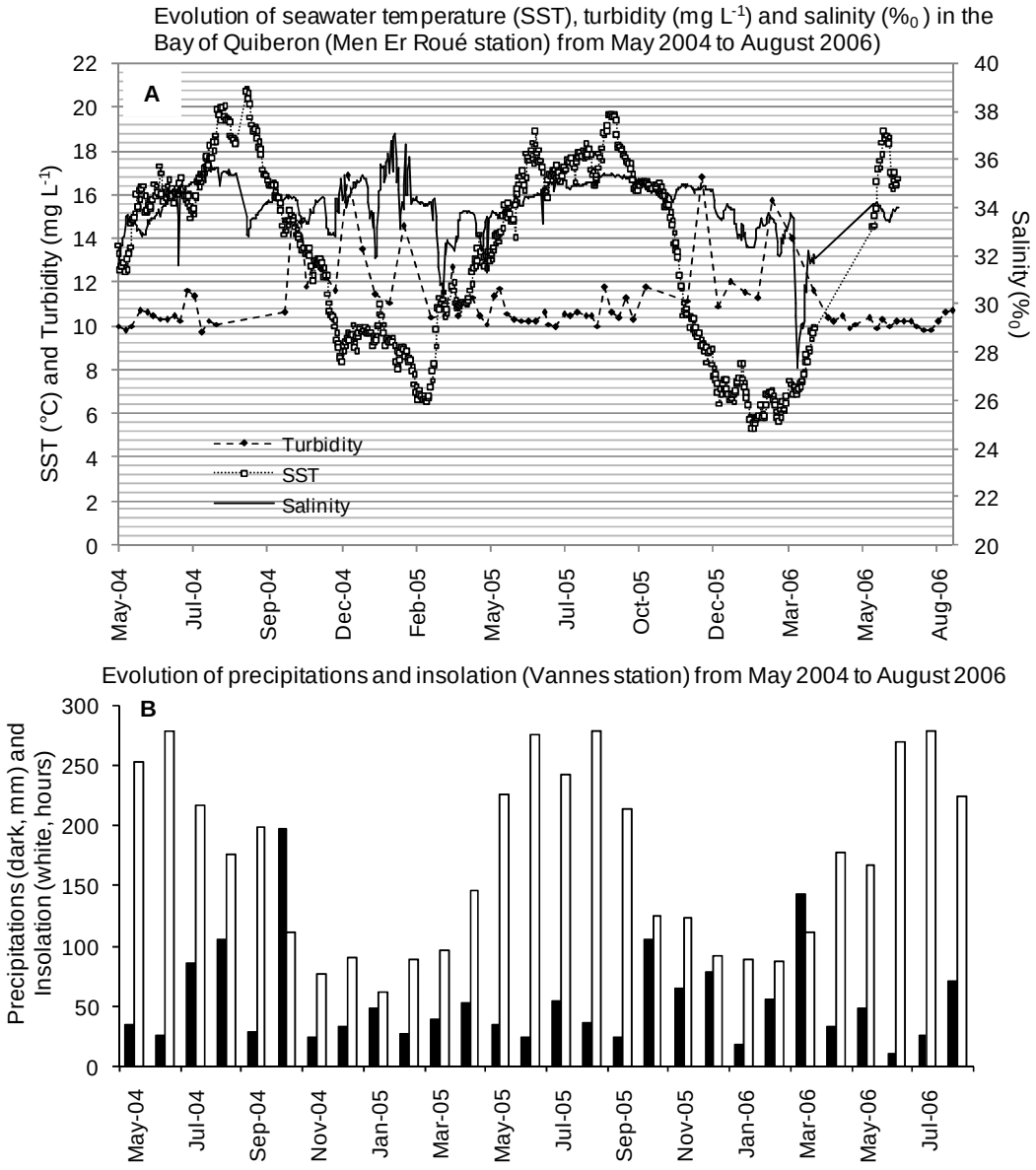
Figure 5 - Evolution of hydrogen sulfide concentration near the sediment water interface. The detection limits are 0.07 nmol L^{-1} for the chromatographic method and 0.32 µmol L^{-1} for the colorimetric method; precisions are respectively 10% and 6%.

1 Figure 1 –



2

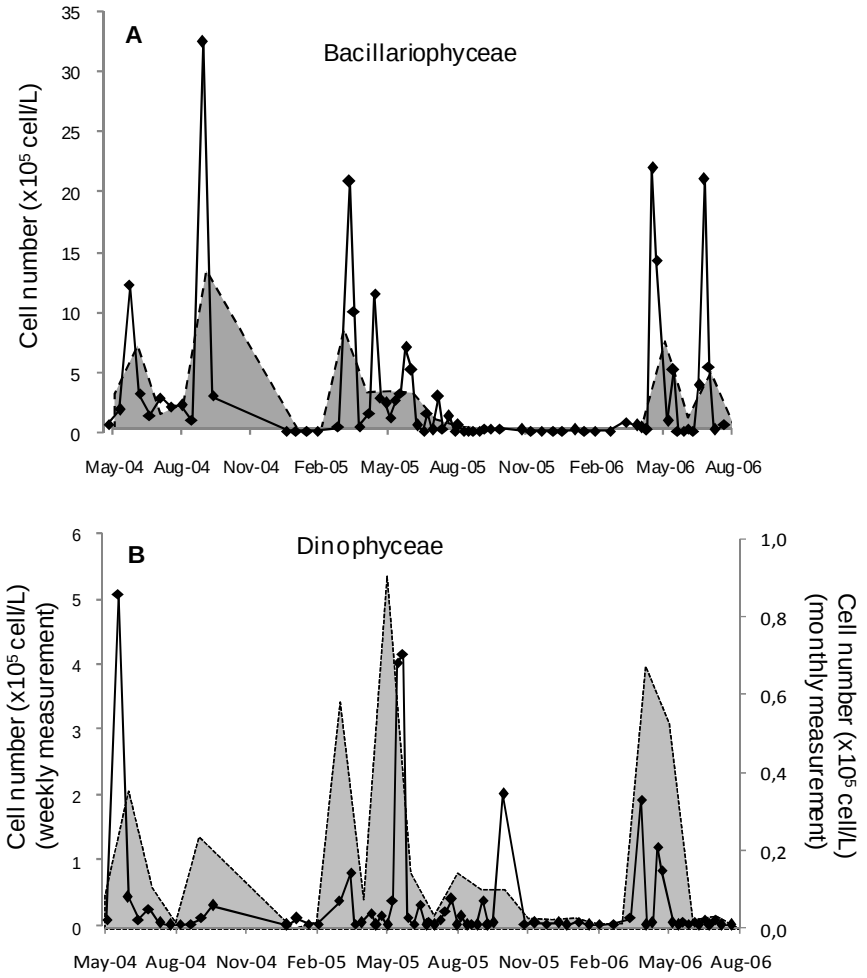
1 Figure 2 –


Evolution of seawater temperature (SST), turbidity (mg L-1) and salinity (‰) in the Bay of Quiberon (Men Er Roué station) from May 2004 to August 2006)
A
SST (°C) and Turbidity (mg L-1)
Salinity (‰)
Turbidity
SST
Salinity
May-04
Jul-04
Sep-04
Dec-04
Feb-05
May-05
Jul-05
Oct-05
Dec-05
Mar-06
May-06
Aug-06
Evolution of precipitations and insolation (Vannes station) from May 2004 to August 2006
B
Precipitations (dark, mm) and Insolation (white, hours)
May-04
Jul-04
Sep-04
Nov-04
Jan-05
Mar-05
May-05
Jul-05
Sep-05
Nov-05
Jan-06
Mar-06
May-06
Jul-06

2

3

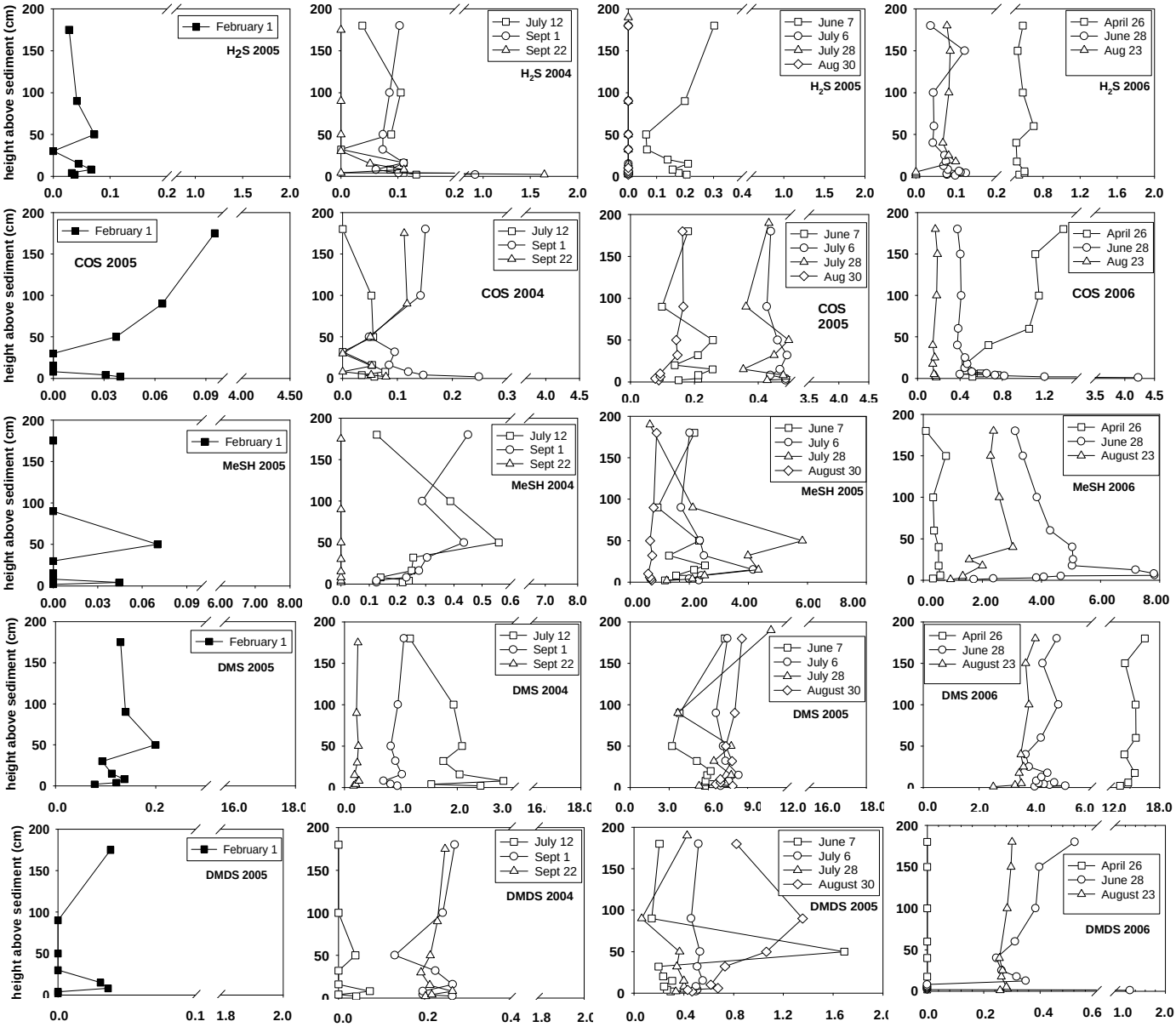
1 Figure 3 –


A
Bacillariophyceae
Cell number (x10⁵ cell/L)
35
30
25
20
15
10
5
0
May-04 Aug-04 Nov-04 Feb-05 May-05 Aug-05 Nov-05 Feb-06 May-06 Aug-06
B
Dinophyceae
Cell number (x10⁵ cell/L) (weekly measurement)
Cell number (x10⁵ cell/L) (monthly measurement)
6
5
4
3
2
1
0
1,0
0,8
0,6
0,4
0,2
0,0
May-04 Aug-04 Nov-04 Feb-05 May-05 Aug-05 Nov-05 Feb-06 May-06 Aug-06

2

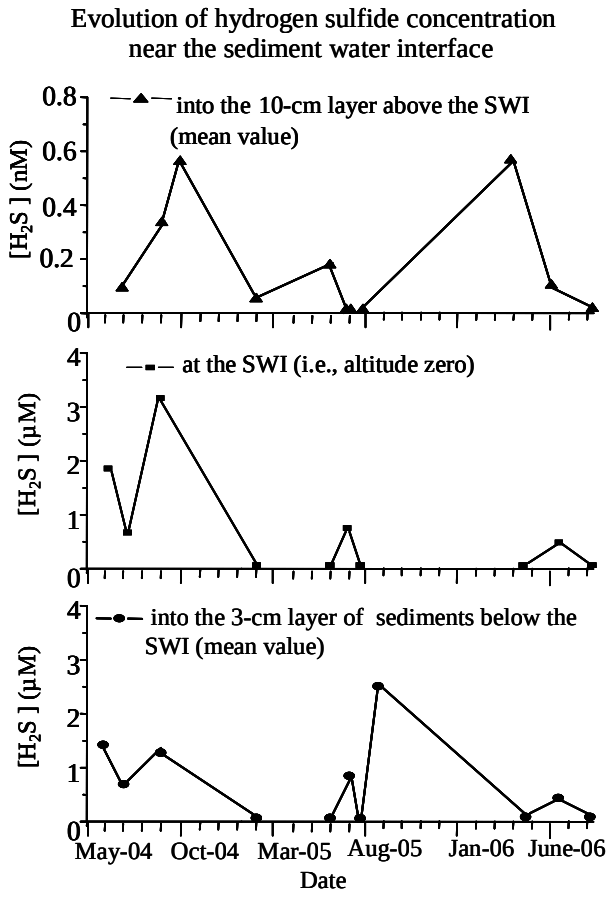
3

1 Figure 4 –


height above sediment (cm)
February 1
H2S 2005
July 12
Sept 1
Sept 22
H2S 2004
June 7
July 6
July 28
Aug 30
H2S 2005
April 26
June 28
Aug 23
H2S 2006
COS 2005
COS 2004
COS 2005
COS 2006
MeSH 2005
MeSH 2004
August 30
August 23
MeSH 2005
MeSH 2006
DMS 2005
DMS 2004
DMS 2005
DMS 2006
DMDS 2005
DMDS 2004
DMDS 2005
DMDS 2006

2

1 Figure 5 –


Evolution of hydrogen sulfide concentration
near the sediment water interface
into the 10-cm layer above the SWI
(mean value)
[H2S] (nM)
0.8
0.6
0.4
0.2
0
at the SWI (i.e., altitude zero)
[H2S] (µM)
4
3
2
1
0
into the 3-cm layer of sediments below the
SWI (mean value)
[H2S] (µM)
4
3
2
1
0
May-04
Oct-04
Mar-05
Aug-05
Jan-06
June-06
Date

2