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

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Abstract

Seasonal and annual variability of hydrogen sulfide (H_2S), carbonyl sulfide (OCS), methane thiol (MeSH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) concentrations and supporting parameters (e.g., phytoplanktonic cells abundance) 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, within two meters of 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 OCS, <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 concentration near the SWI in winter and bottom enrichments near sediments in summer. Vertical sulfide distribution not seems to be influenced by the shallow sediments. The likely influence of Dinophyceae abundance on the MeSH, DMS and DMDS concentrations was evident for the 3-summer monitored period.

1 Introduction

Over the last decades, the distribution and biogeochemistry of sulfur compounds such as hydrogen sulfide (H_2S), carbonyl sulfide (OCS), methane thiol (MeSH, CH_3SH) dimethyl sulfide (DMS, CH_3SCH_3) and dimethyl disulfide (DMDS, CH_3SSCH_3) in the marine environment have received growing attention (Cutter and Radford-Knoery, 1993; Zhang et al., 1998; Yang et al., 2005). Interest in these chemical compounds is linked to their important reactivity and their significant contribution to the atmospheric sulfur budget. Kettle and Andreae (2000) showed that DMS may be responsible for up to 60% of the biogenic sulfur emissions with 15 to 33 Tg (S) yr^{-1} which leave the oceans to the atmosphere. In terms of sea-air exchange, dimethyl sulfide (DMS) is the major sulfur gas released from the oceans (Andreae, 1990). It is produced from the enzymatic cleavage, from dimethylsulfoniopropionate (DMSP, a regulator of the internal osmotic pressure produced by phytoplankton. 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 nmol L^{-1} to several (Malin et al., 1993). DMSP is released during phytoplanktonic grazing by zooplankton, phytoplanktonic viruses infection and phytoplanktonic cells senescence (Keller et al., 1989; Simo et al., 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 only 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, dimethyl disulfide, 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 a water column with restricted ventilation, dissolved hydrogen sulfide is produced by bacterial sulfate reduction. In such anoxic environments and sediments, the sulfide concentration can be in micromolar levels, whereas in oxic areas (e.g., open oceans), H_2S always occurs at nanomolar levels. In the open ocean, one of the H_2S sources appears to be the hydrolysis of carbonyl sulfide (Elliot et al., 1989). Phytoplankton also are able to produce hydrogen sulfide when they are subject to environmental stress (Walsh et al., 1994). Hydrogen sulfide is also 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; Knoery and Cutter, 1994).

Carbonyl sulfide is the most abundant and probably the most long-lived sulfur gas in the atmosphere (Ulshöfer and Andreae, 1998). Dissolved OCS is produced by a number of processes: photochemical degradation of dissolved organo-sulfur compounds (Zepp and Andreae, 1994), non-photochemical production from dissolved organo-sulfur compounds (e.g., methane thiol degradation; Ulshöfer et al., 1996). Diffusion out of sediments certainly could be a source of MeSH (Flock and Andreae, 1996). Its concentration decreases due to hydrolysis of dissolved OCS (Johnson and Harrison, 1986) and air-sea exchange (Ulshöfer et al., 1996). The concentration of OCS in the surface waters of the open ocean averages 0.03 nmol L^{-1} (Johnson and Harrison 1986) whereas coastal concentrations range from 0.07 nmol L^{-1} (Rasmussen et al., 1992) to 1.2 nmol L^{-1} in a eutrophic estuary (Jorgensen and Okholm-Hansen, 1985).

In this paper, we collectively call these five compounds VRSC for Volatile Reduced Sulfur Compounds according to their common properties of volatilisation and oxidation.

We examined these VRSC in a coastal environment because of the complex relationships between these sulfur species. Also, the proximity of the sediment-water interface (SWI), a significant zone of enhanced organic matter (OM) degradation, may be a source of these compounds. The SWI is the locus where enhanced chemical and microbiological transformations are responsible for cycling biogenic constituents between water and sediments (Ni et al., 2002; Viollier et al., 2003). Although reduced sulfur compounds and principally H_2S, have been studied in porewaters (Klump and Martens 1989), their distribution at the centimeter to decimeter scale above the SWI and into the bottom water column is yet unknown in the nearshore environments. Fuelled by OM supply, nebulous statement bacteria activity there 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 the sediment, may also influence the water column just above it.

Over a 26 month-sampling period of the 2-m water column above the SWI, VRSC concentrations are measured in order to estimate possible seasonal and interannual variations. Our purpose was to survey these five volatile reduced sulfur compounds during several months (i.e., from July 2004 to August 2006) in a temperate coastal marine environment, the Bay of Quiberon. A part of the originality of this work was to study simultaneously H_2S, OCS, MeSH, DMS and DMDS.

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) which opened onto the Bay of Biscay at 47°32 N. The Western Bay of Quiberon covers an area of 150 km^2 with a 9 m average depth and 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 subject to tidal currents whose maximum speed is between 0.1 (neap tide waters) and 0.2 (spring tide waters; source: www.shom.fr) knot in the middle of the Bay (47°29 N, 3°02 W) while the spring tidal range is about 4.6 m (source: http:shom.fr). The major part of sediments are sandy muds (63–80 μ; Lemoine, 1989, unpublished[1]). The water is saturated with oxygen throughout the entire water column, there is no anoxia.

Sampling was conducted over an 24-month period (n=11) and only one time for the winter months because of adverse weather conditions. The monitored station (Men Er Roué, 47°32 N, 3°05 W) was considered the best representative zone of the whole Bay of Quiberon. The station was near the Bay mouth and had a depth about 7.5 m with sandy muds sediments (Fig. 1).

2.2 Ancillary parameters

The phytoplankton density for our sampling period 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 the rest of year time. Assessments were carried out as

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[1] Lemoine, G.: Etude sédimentaire de la Baie de Quiberon: la zone ostréicole en eau profonde et ses abords, La Trinité-sur-Mer, France, 102, unpublished, 1989.

follows; one liter of water was taken from the sea surface at Men Er Roué and immediately, an acid lugol (i.e., 2 to 10 ml L^{-1} according to the phytoplankton density) solution is added to fix the algal cells. Less than 36 h later, the cell density of each phytoplanktonic species was determined using a Malassez cell and an inverted microscope.Hydrographic parameters were also monitored from June 2004 to August 2006. They were not presented in this article in order 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). Turbidity was weekly in situ measured with a specific probe (WTW Turb 550IR). Therefore, to increase the clarity of the Fig. 1a no tick marks was indicated. Precipitations and insolation were also available for the whole sampling period (http:meteofrance.com). Monthly measurements were calculated to show the seasonal trends. 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., unpublished[2]) was used to acquire water samples in order to reveal concentration gradients in the water column above the SWI. Briefly, it is a simple, lightweight and relatively inexpensive syringe sampler with fine scale and high vertical resolution. The 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. For proper water column sampling, collection syringes thoroughly cleaned. To minimize sample degradation and for example, the production of OCS via photolysis (Ferek and Andreae, 1983), subsampling into transfer syringes was done as quickly as possible (less than

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[2] Knoery, J., Cozic-Houly, A., Averty, B., Sarazin, G., and Jouin J. C.: The suprabenthic sampler for nearshore enviro nmol Lents (Susane), a new device to collect simultaneously closely-spaced water samples immediately above the sediment water interface, unpublished.

five minutes) on the deck of a small boat. Water samples were refrigerated in the dark until analysis and less than 2 h to prevent a possible DMSP degradation (Jean et al., 2004). The analytical technique used to determine the VRSC concentrations in the water column samples was a purge and trap extraction, followed by gas chromatography separation and pulsed flame photometric detection. The detection limit of this method was 0.07 nmol L^{-1} for H_2S, 0.03 nmol L^{-1} for OCS, 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 OCS, 5.6% for MeSH, 4.9% for DMS and 8.4% for DMDS (Cozic-Houly et al., personal communication[3]).

One 30 cm-sediment core was taken, near the location where the water samples were collected, in order to analyse hydrogen sulfide concentrations in the top 10 cm of porewaters. To avoid degradation, sediment cores were also refrigerated in the dark (i.e., icebox) until analysis (i.e., <2 h). Extraction of H_2S from the porewaters was based on the use of rhizons which are often 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 μM for hydrogen sulfide. Unfortunately, no similar method exists for the other VRSC studied and the very low volume (i.e., less than 5 ml) of seepage water did not permit a chromatographic analysis of these samples.

For some sampling days, more water heights were sampled (e.g., 15 June 2006). The sampling step was smaller within the 10 first centimeters above the SWI because we wanted to show preferentially the VRSC concentrations variations close to the 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, unpublished[1]).

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[3] Cozic-Houly, A., Knoery, J., Averty, B., and Viollier, E.: Simultaneous analysis of five volatile reduced sulfur compounds by purge and cryogenic trapping/gas chromatography separation in natural waters, personal communication, unpublished, 2009.

3 Results

3.1 Hydrography

The seawater temperature reached 5–6°C during winter (Fig. 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 (Fig. 2a). The turbidity showed seasonal variations with higher monthly values during the winter (Fig. 2a). Indeed, from mid-September to March, the 3-years mean trubidity 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 (Fig. 2b). From mid-September to march, the 3-years mean monthly precipitations were 63.3±9.2 mm and from April to mid-September, they were 46.6±13.8 mm. The insolation (number of hours per month) occurred clear variations through the year with a consistent increase from the winter to the summer period (Fig. 2b). Indeed, from mid-September to March, the 3-years mean insolation was 111.6±12.3 h and from April to mid-September, it was 229.6±5.3 h.

3.2 Phytoplankton

In order to describe the role of phytoplankton species variability for the VRSC distribution, the variations of the two main algae families (i.e., dinophyceae and diatomae) were monitored for the sampling period. Dinophyceae and diatomae accounted for more than 92% of the phytoplankton cells present at all seasons. Dinophyceae are different from the diatomae because the former one known to synthesize significant amounts of DMSP (Turner et al., 1988). As expected, the algal density varied seasonally and interannually (Fig. 3). Two annual phytoplankton blooms were observed in 2004 (June and September), 2005 (March and May) and 2006 (May and July). In order to clarify the description, the weekly survey of diatomae and dinophyceae densities were presented by lines whereas the weekly survey of total phytoplankton was presented by a shaded area (Fig. 3).

3.2.1 Diatomae

More specifically, diatomae distribution showed a seasonal feature (Fig. 3) with higher algal density from may to september. For example, from March to September 2005, the mean value of the diatomae density was $(329 \pm 493) \times 10^3$ 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., 3×10^3 cell L^{-1} in 2005). Summer abundances were highly dymanic with large density swings. In 2004, the diatomae density was maximum in the beginning of June and September whereas in 2006, it was maximum 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 diatomae (Fig. 3) but seasonal variations also occurred with high values during the summer period. During 2004, the dinophyceae cells density showed the same features as the diatomae density with two maxima, in the beginning of June (505×10^3 cell L^{-1}) and in the end of September (30×10^3 cell L^{-1}). In 2005, the cell density increased by a factor of ten between march (37×10^3 cell L^{-1}) and June (415×10^3 cell L^{-1}). In 2006 only one maximum was noted in April (191×10^3 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 VSRC profiles collected in the suprabenthic layer (i.e., from zero to ca. 200 cm above the SWI) are presented in Fig. 4. Only one water sample –1st of February– was conducted during the winter. But, within thisimportant 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 (Fig. 4). In addition, a layer exhibiting a relative concentration minimum was present at 30 to 60 cm above the SWI. With smoother concentration increase close to the bottom, OCS showed a nearly identical trend. MeSH profiles did not show evidence of concentration increase at the SWI but rather a zone of concentration maximum 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). A feature of concentration increase into the first centimetres above the SWI was apparent for DMS in some summer profiles. In addition, some DMS profiles also showed a minimum concentration at 30 or 50 cm above sediments. DMDS, like DMS, showed a higher concentration above 1 m altitude and did not occur clear vertical variations except in some summer profiles (Fig. 4).

3.4 Seasonal variations of VRSC concentrations

The hydrogen sulfide concentration was maximum at the beginning of spring (April 2006) with about 0.57 ± 0.06 nmol L^{-1} ($n=8$) and was generally higher during the summer. Moreover, vertical variations in the 2 m-water column were greater for the spring (e.g., June 2005) and the beginning of summer. From the end of summer into winter, H_2S concentration started to decrease to below the detection limit (0.07 nmol L^{-1}, personal communication) 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. 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 OCS concentration decreased progressively during the winter.

The MeSH concentrations showed significant seasonal variations with summer values ten times greater than winter values and also clear variations in the 50 cm layer above the SWI. It 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 times less MeSH (0.78 nmol L^{-1}) than in June and the vertical variations were less important. During the last summer sampled, MeSH concentration began to increase to reach until 4.15 nmol L^{-1} in the end of June.

Dimethyl sulfide concentrations were uniform (summer 2006) in the 2 m-water column sampled or very variable (summer 2005). Concentrations were lowest in the winter with less than 0.20 nmol L^{-1} and increased substantially during the summer period, like MeSH, to reach several nanomolar. The highest concentration was measured in spring (April 2006) with about 15 nmol L^{-1} at +180 cm.

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

3.4.1 Interannual variations of VRSC concentrations

During the 3 summer-sampling campaign, interannual variations were obtained for each sulfur gas. It was interesting to highlight similarities between the summers but also variability which could be linked to those of other parameters.

No clear interannual sulfide variations were apparent through the 3-summers survey with 0.17±0.36 nmol L^{-1} (n=24) 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 hydrogen sulfide concentration was often more elevated near the SWI than in the upper water samples. This feature was apparent for summer 2004, June 2005 and summer 2006 with significant variations of the sulfide concentration in the 20-cm layer above the SWI. The maximum values usually occurred near sediments and they were followed by a rapid decrease, itself followed by another increase. The best example of this behaviour 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 in the concentration of OCS between the summers of 2005 and 2006 whose the carbonyl sulfide concentrations were respectively, 0.30±0.18 nmol L^{-1} (n=41) and 0.55±0.82 nmol L^{-1} (n=24). In summer 2004, the OCS concentration was lower with 0.08±0.06 nmol L^{-1} (n=24). During the summer period, the OCS concentration varied with an increase from the beginning of summer reaching in the middle of summer a maximum which was followed by a decrease. In the 2-m water column sampled, clear variations were observed only in the 50 cm immediately above the while sediments; in the top of water column sampled, OCS concentrations were relatively constant. Some profiles (e.g., 1 September 2004, July 2005, June 2006) showed an increase of OCS concentration just above the SWI and a minimum value near ca. +15 cm. The profiles of July 2004 and June 2005 showed another trend in the 2-m water column sampled. From the SWI, the OCS concentration increased until ca. +10 cm and then, it decreased rapidly until a given altitude (+32 cm in 2004 and +20 cm in 2005) before to increase again.

Three different features were also observed for methane thiol concentration during the 3 summers surveyed. 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. Moreover, all summer profiles showed a sharp concentration decrease immediately 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 the summer period, MeSH concentrations slightly varied in the 2-m water column sampled (except in June 2005). Concerning the evolution of MeSH concentration during summer, profiles were consistent with an increase until the middle of summer followed by a decrease to winter values.

Dimethyl sulfide profiles occurred less depth variations than all VRSC but clear interannual summer variations 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 times 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 concentrations were often observed above +100 cm and sometimes, higher DMS concentrations were also recorded near the SWI. For example, in summer 2005 (e.g., 28 July), the 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.

Dimethyl disulfide 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. For most of the profiles, the vertical DMDS distribution was uniform in the 2-m water column (e.g., July 2004, August 2006). But for some profiles, clear variations occurred. It was the case in the beginning of September 2004 with a minimum (0.13 nmol L^{-1}) at +50 cm whereas the DMDS concentration was 0.24±0.03 nmol L^{-1} (n=11) over the entire profile. It was important to note there also existed variations of DMDS concentration during a given summer with no clear trend for the date of the maximum.

3.5 Porewater sulfide concentration

In order to ascertain the presence of a permanent oxic sediment layer in this eutrophic bay and negate the possibility of a seasonal sulfide sedimentary source, we examined porewater 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 the H_2S concentration near the SWI and in a ca. 3-cm layer of sediments (Fig. 5).

Near the SWI (altitude zero), the sulfide concentration was often less than one micromolar but, given the analytical detection limit of $0.32\,\mu\text{mol}\,\text{L}^{-1}$ for the colorimetric method that was used, only few results were significantly different from non-detectable levels. Hydrogen sulfide concentrations were undetectable ($<0.32\,\mu\text{mol}\,\text{L}^{-1}$) 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; $0.65\,\mu\text{mol}\,\text{L}^{-1}$ in July 2004, $0.73\,\mu\text{mol}\,\text{L}^{-1}$ in July 2005 and $0.46\,\mu\text{M}$ in June 2006. Porewater sulfide concentrations 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 litterature data on dissolved H_2S, OCS, MeSH and DMS for comparable coastal environments (Table 1). Our 2-year sampling campaign gives the following concentration ranges; up to $1.6\,\text{nmol}\,\text{L}^{-1}$ for H_2S, up to $4.2\,\text{nmol}\,\text{L}^{-1}$ for OCS, up to $7.8\,\text{nmol}\,\text{L}^{-1}$ for MeSH, from 0.1 to $17.5\,\text{nmol}\,\text{L}^{-1}$ for DMS and up to $1.7\,\text{nmol}\,\text{L}^{-1}$ for DMDS (Fig. 4).

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Interactive Discussion

To simplify the discussion of the VRSC concentration evolution, the different sulfur species were placed in two groups. H_2S and OCS 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 (OCS)

For several vertical profiles, H_2S and OCS 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 (Fig. 4, subperiod a). Moreover, H_2S was sometimes measured in porewaters near the SWI (Fig. 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 phytoplanktonic 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 microzones near the seabed and thus, sulfide may be produced in the first centimeters above sediments and remain undetected either by sediment porewaters 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 (Fig. 5, September 2004, June 2005 and April 2006) occurred during blooms (Fig. 3, subperiods a, c and e). 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 microzones where sulfate reduction may occur.

The hypothesis that direct release from phytoplankton cells is responsible for 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., phytoplanktonic cell) is not negligible (i.e., 0.34% S). Considering a spherical phytoplanktonic (from 1.4×10^{-5} to 3.4×10^{-5} μl with a ratio of 0.1 between the dry weight and the fresh weight), we obtained a phytoplanktonic sulfur concentration between 6.2×10^2 and 2.5×10^2 nmol L^{-1} during September 2004 (i.e., bloom with 16.9×10^5 cell L^{-1}). Therefore, the concentration of reduced, intracellular phytoplanktonic sulfur determined in the water column is one order of magnitude greater than the hydrogen sulfide concentration into the 10-cm layer above the SWI (0.24 nmol L^{-1}; Fig. 5). Thus, a modest 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 sulfide concentration near the SWI.

Cutter and Knoery (1993) studied OCS concentrations surface waters on the shelf of the western North Atlantic. They showed that porewaters are 200 times enriched compared to the water column. Thus, OCS produced in marine sediments, may diffuse through the SWI. Cutter and Zhang (1997) studied the OCS sediment-water fluxes in the Chesapeake Bay during 3 years. They showed highest values during the summer periods because the sedimentary OCS 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 OCS concentration was twice as elevated near the SWI as in the shallow water column for every summer period (Fig. 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 (Fig. 4).

The principal source of OCS 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 phytoplanktonic cells density. Mihaloupoulos et al. (1992) showed a positive correlation between the monthly average oceanic OCS concentration and the monthly average of the daily insolation period. Therefore, the higher OCS concentration analysed in Bay of Quiberon during the warm periods may be explained by a higher sun insolation (Fig. 2) and an increase of phytoplanktonic cells density (Uher and Andreae, 1997).

So, sediments appear to be a source of OCS or neutral, given the shape of the water column gradient. During winter (Fig. 4, subperiod b), photolytic production was the major source of OCS in the water column (Cutter and Zhang, 1997) whereas sediments were neutral. On the contrary, in summer (Fig. 4, subperiods a, c and e), sediments appeared to be a OCS source (Kettle et al., 2001) which it explains the highest concentration observed near the SWI.

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 abundance 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 (Fig. 3, subperiods a, c and e).

For winter (subperiods b and d), the dinophyceae concentration was much lower than during the summer periods. The higher concentrations of DMS, MeSH and DMDS were always recorded during the subperiods a, c and e (Fig. 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 2005 and in June 2006. A time span between Dinophyceae cells abundance 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 (Fig. 3, subperiod e). Therefore, in 2006, the production of DMS is faster than the previous year and than the MeSH and DMDS productions. The DMS concentration is always higher than MeSH and DMDS concentrations even in winter (Fig. 4). The absence of MeSH (except at +50 cm) and DMDS in winter 2005 (subperiod b) 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 abundance may explain the distribution of these VSRC in 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. An 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 (Fig. 4, subperiod c), 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) observed for the three VRSC, may indicate a moving towards the upper water column of the DMSP-producers. During, the spring period, no gradients are observed in 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., non-stratified water column) according to the possible strong winds affecting the Bay and the 7-m depth (Lemoine, 1989).

Considering MeSH concentrations in 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}; Fig. 4, subperiod c). 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 hydrogen sulfide is present in significant quantity. For example, in July 2005, H_2S shows a concentration markedly above the detection limit near the SWI and in the 3-cm layer beneath it (Fig. 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 (Fig. 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, subperiod c) 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 minimum. Moreover, in June 2006, the altitude of the lowest DMDS concentration corresponds to the maximum of MeSH concentration.

These variations of VRSC concentrations onto 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 there exists discrete altitudes 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 abundance.

5 Conclusions

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 centimeters above sediments made it possible to demonstrate that the SWI can play a key role on the VRSC distribution. Concerning OCS, its seasonal concentration variations are linked to the balance between its sinks and sources. During winter, the major source of OCS appears to be the photolytic production from CDOM (vertically uniform in the water column), whereas in the summer, sediments appear to be the main OCS 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 Dinophyceae density and MeSH and DMDS maximum 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 the sulfide inventory that is greater near the SWI, it is likely linked to anoxic microzones from the decay of organic matter (e.g., phytoplanktonic 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. Another processes of sulfide could be the direct release by phytoplanktonic cells in the first meter above the SWI.

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Table 1. Comparison between seawater concentrations of H_2S, OCS, MeSH, DMS and DMDS 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 OCS	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}

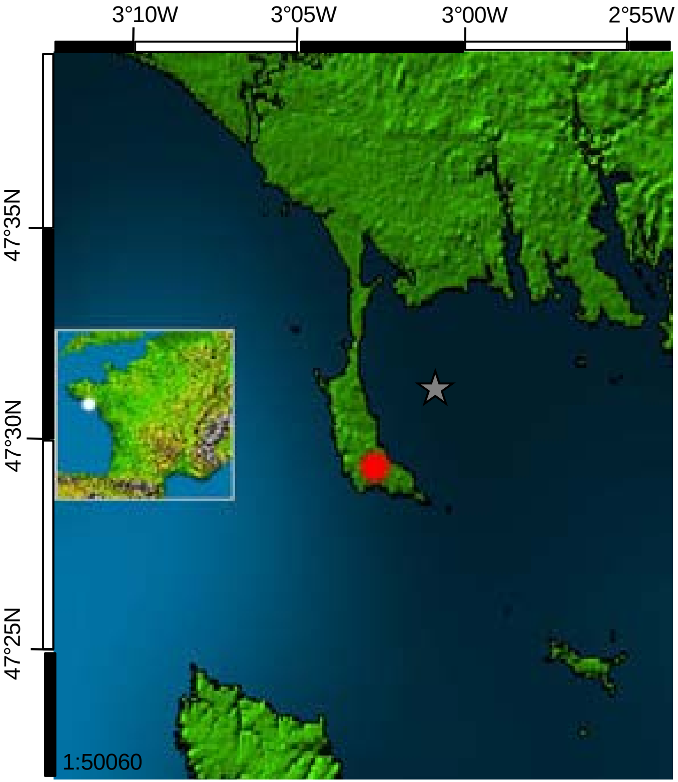

Fig. 1. White point on mini map marks, which part of France is shown. Red point marks the city Quiberon on the peninsula of Quiberon. The grey star locates the Men Er Roué station. In the east of the peninsula there is the bay of Quiberon and in the south, a part of Belle île island is shown.

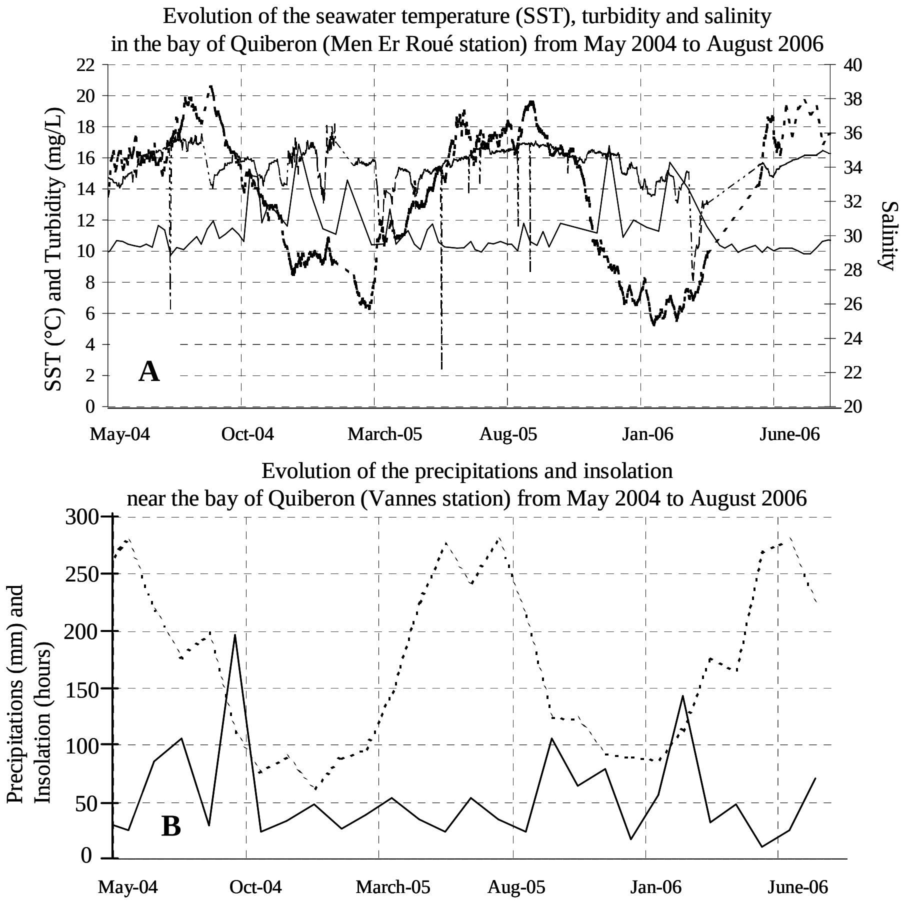

Fig. 2. Evolution of hydrographical parameters in the Bay of Quiberon from May 2004 to August 2006; **(A)** Temperature (regular dotted line), Turbidity (filled line), Salinity (irregular dotted line); **(B)** Precipitations (filled line) and Insolation (regular dotted line).

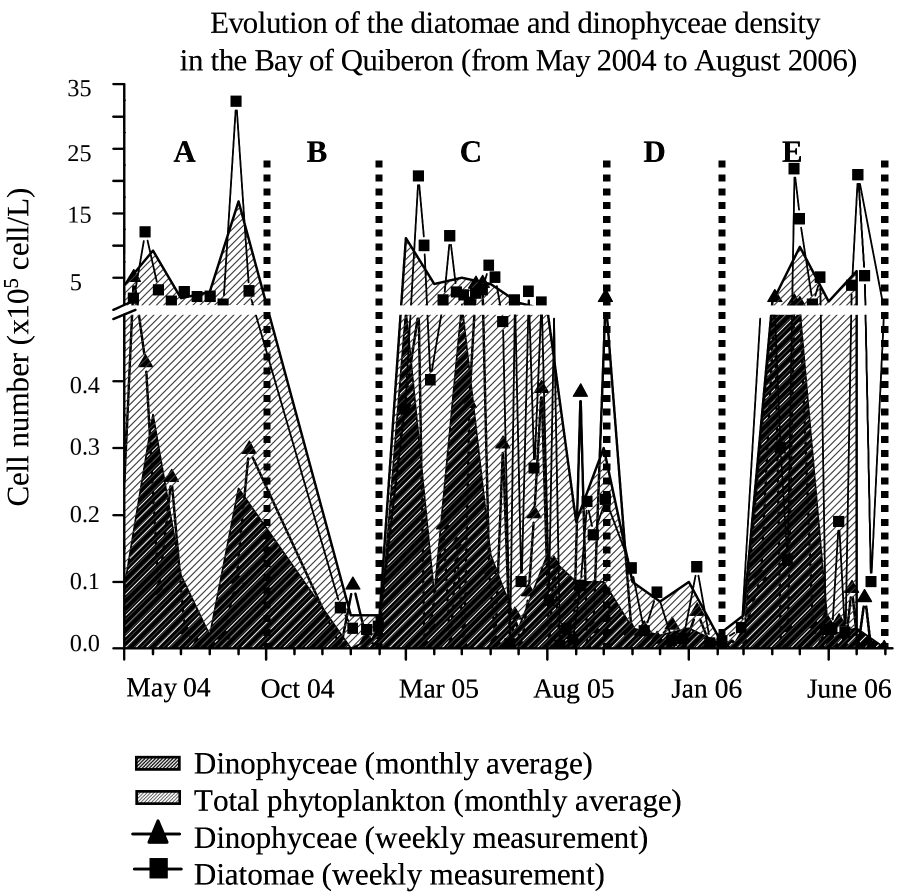

Fig. 3. Evolution of phytoplanktonic cells density from May 2004 to August 2006. (Total phytoplankton is the sum of Dinophyceae cells density and Diatomae cells density). The sampling period is divided in several subperiods **(A)** to **(E)**.

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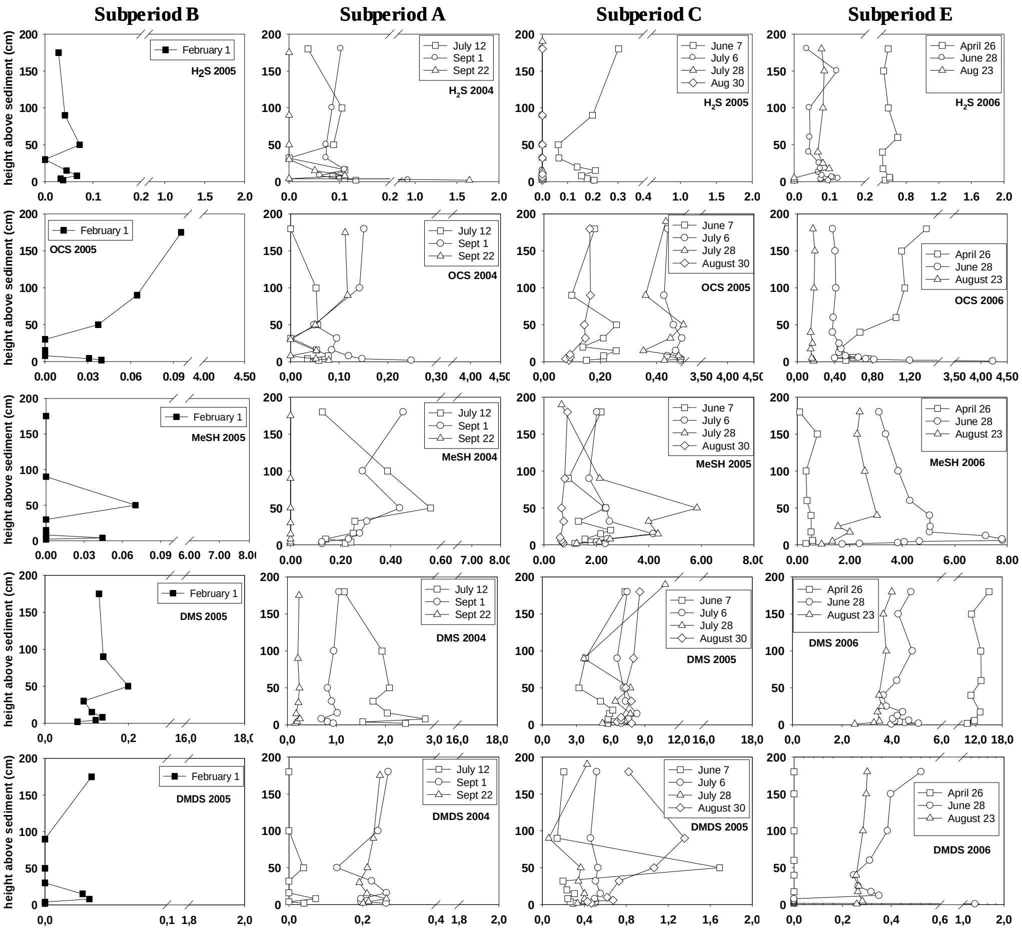

Fig. 4. Evolution of the VRSC concentrations in the Bay of Quiberon (Men Er Roué station) from July 2004 to August 2006. All concentrations are given in nmol L^{-1}.

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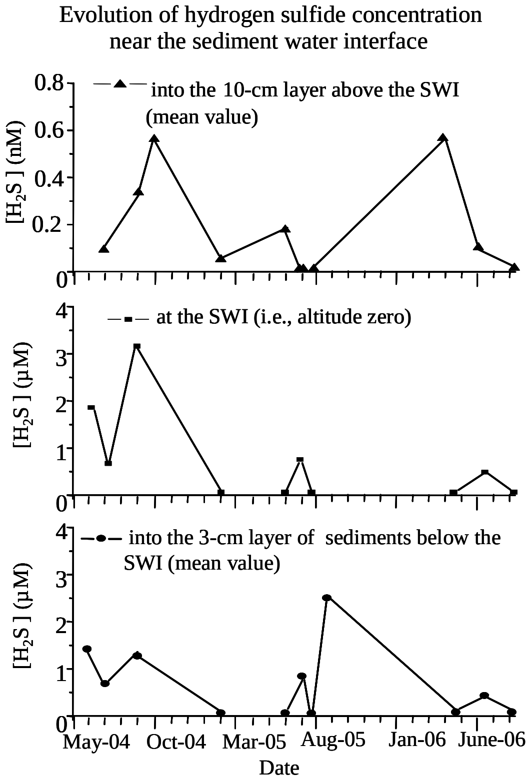

Fig. 5. Evolution of hydrogen sulfide concentration near the sediment water interface. The detection limit is 0.07 nmol L^{-1} for the chromatographic method and 0.32 μmol L^{-1} for the colorimetric method. The precision of these methods are respectively 10% and 6%.