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Seasonal Variations in Sediment Sulfur Cycling in the Ballastplaat Mudflat, Belgium

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ABSTRACT: Sulfate reduction rate (SRR) and pools of reduced inorganic sulfur, acid volatile sulfide (AVS), chromium reducible sulfur (CRS), and elemental sulfur (S°), were studied from June 1990 till March 1992 at two locations on the Ballastplaat mudflat in the Scheldt estuary. The sediment composition at station A was mainly sand with low organic content whereas sediments at station B were dominated by silt and clay with high organic content. SRR was positively related to temperature; more pronounced at station B ($Ea = 190$ kJ mol^{-1}) than at station A ($Ea = 110$ kJ mol^{-1}). The maximum SRR values observed equalled 14 μmol cm^{-3} d^{-1} at station B and 1 μmol cm^{-3} d^{-1} at station A. AVS was the dominant radiolabelled end product of the sulfate reduction reaction, except in surface sediments where pyrite and S° were more dominant. However, CRS was the predominant reduced inorganic sulfur pool in the sediments. Both AVS and CRS pools showed temporal variations out of phase with SRR. SRR peaked in summer, while the concentrations of AVS and CRS were highest in fall. The accumulation of AVS and CRS started late summer after depletion of oxidants, which had accumulated during winter and spring. The estimated annual SRR and thus sulfide production in the upper 15 cm of station B was of the order of 100 mol m^{-2} yr^{-1}, and at station A of the order of 12 mol m^{-2} yr^{-1}. The sulfur mass balance shows that only a very small fraction, if any, of the produced sulfide is retained as reduced inorganic sulfur in the sediment.

Introduction

Sulfate is the dominant electron acceptor for oxidation of organic carbon via dissimilatory sulfate reduction in oxygen depleted marine environments (Goldhaber and Kaplan 1974; Postgate 1979). Aquatic sediments are largely anaerobic beneath a shallow, oxic layer, which is usually only a few millimeters deep (Revsbech et al. 1980). Decomposition of organic matter in marine sediments is therefore a function of aerobic metabolism in this narrow surface layer together with anaerobic decomposition which proceeds below the oxic layer. Anaerobic decomposition relies upon the interactions of a complex community of anaerobic bacteria, each of which brings about partial oxidation of the organic substrates leading to simpler organic molecules, acetate being the most important. In the terminal stages the sulphate respiring bacteria are responsible for the ultimate conversion of organic carbon to carbon dioxide (Abram and Nedwell 1978; Nedwell 1984). The reason for their importance is that seawater contains approximately 26 mM sulphate, providing abundant electron acceptors for this group of bacteria. In Long Island Sound, about 11% of the net primary production in the top 10 cm of the sediment is broken down by sulfate reducers (Aller and Yingst 1980). It has been demonstrated that in coastal marine sediments 10% to 50% of the organic matter mineralization is driven by sulphate respiration with the balance due to aerobic metabolism (Jørgensen 1982). Mackin and Swider (1989) reported that 65% to 85% of organic carbon in coastal marine sediments is decomposed by sulfate reduction. In the muddy sediments of the Ballastplaat (the sampling area in this study), Elskens et al. (1991) found that less than 20% of the electron flux involved in the anaerobic degradation of the organic matter relates to Fe(III) reduction, the remaining and major part resulting from sulfate reduction. Skyring (1987) reviewed the sulfate reduction rates and noted that they vary seasonally and between sediment types. High sulfate reduction rates are usually found in sediments containing a high amount of organic matter.

The H_2S produced from the organic matter oxidation process is partially lost through atmospheric emission or reoxidation into sulfate in oxidized environments (King 1988; Luther et al. 1991), while the other part reacts with reactive metals in anaerobic environments to form insoluble metal sulfides (Salomons and Forstner 1984; Morse 1994). Iron monosulfide (FeS) and pyrite (FeS_2)

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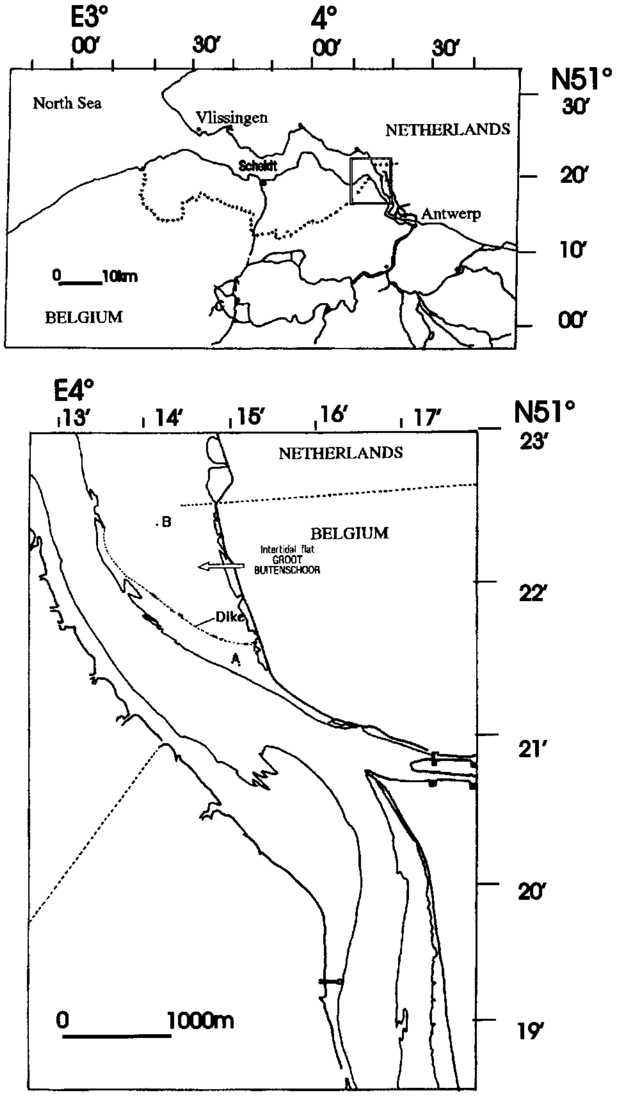

Fig. 1. Map A shows the Ballastplaat intertidal mudflat area as a part of the Scheldt estuary. Map B shows the sampling sites A and B on the Ballastplaat mudflat.

generally represent the major reduced inorganic sulfur pools in marine sediments (Berner 1984; King et al. 1985; Thamdrup et al. 1994). The retention of freshly produced sulfide varies from one system to another. Jørgensen et al. (1990) estimated that only about 10% of the produced sulfide is buried in coastal marine sediments, while Chanton et al. (1987) found that up to 77% is retained in rapidly accumulating sediments. The role of benthic bioturbation as a loss process for sulfide and pyrite was reported by Berner and Westrich (1985).

During a study on the geochemical behavior of heavy metals in sediments of the Ballastplaat mudflat (Fig. 1), it became clear that reduced inorganic sulfur (RIS) pools played an important role on the mobility of the metals in these sediments (Panutrakul and Baeyens 1991). Therefore, more information about the sulfur cycle and the seasonal variations in RIS-pools in these mudflat sediments was needed.

Sampling Area

The Ballastplaat, a 250 hectares mudflat, is located in the Scheldt estuary near the Belgium-Dutch border, about 60 km from the river mouth. Details about the physical and hydrodynamical characteristics of the Scheldt, which is one of the most polluted estuaries in Europe, can be found elsewhere (Baeyens et al. 1998). It is, however, worthwhile to note that the dissolved oxygen content in the Scheldt estuary near the Belgium-Dutch border varies seasonally from close to zero in summer to almost saturated in winter (Somville and De Pauw 1982; Baeyens et al. 1998). Two sampling stations (stations A and B) representing a sandy and a muddy type of sediment were chosen according to their sediment characteristics. Sediments at station A consist of about 85% sand (grain size > 63 μm), while sediments at station B contain about 85% silt and clay (grain size < 63 μm). Results from a preliminary study on the geochemical behavior of Fe, Mn, Cd, and Pb in the sediments of the Ballastplaat are reported by Baeyens et al. (1991). In addition, redox profiles at stations A and B were shown: at the sediment surface at station A the redox potential equals 350 mV, smoothly decreases to 250 mV at 5 cm depth and then rapidly falls down to -100 mV at 10 cm depth, while at the sediment surface at station B the redox potential equals 80 mV and then rapidly falls down to -200 mV at 2.5 cm depth.

Microbial Description of the Sampling Stations

In the upper layer of the sandy sediment (station A), oxygen is apparently the terminal electron acceptor. Substantial numbers of aerobic chemoheterotrophic bacteria (most of which were gram-negative) have been enumerated by a classical plate count method (Elskens et al. 1991). As oxygen is consumed, conditions become locally anaerobic and fermentative organisms develop. The products of fermentation then diffuse to regions in which oxygen is still present or they may be oxidized anaerobically by organisms able to reduce nitrates, sulfates, or carbonates. Reduction of iron and sulfate was already detected close to the subsurface of the sediment. The FeS ($+FeS_2$) profile increased slowly with depth below the upper 1-cm slice, but most of the iron remained in the ferric form. Small concentrations of reduced sulfur were detected in the interstitial water (Panutrakul 1993).

The higher organic matter content of the muddy sediment (station B) resulted in a rapid exhaustion of the dissolved oxygen. For this reason, particulate organic matter (POM) degradation is most probably first mediated by *Clostridia* and other fermentative anaerobes with the formation of CO_2, H_2, NH_3, organic acids, and alcohols (Elskens et al. 1991). Other electron acceptors are subsequently involved in the oxidation of the fermentative products: successively nitrate, iron (and manganese), and sulfate are reduced.

Materials and Methods

Sulfate reduction rate (SRR) and reduced inorganic sulfur pools (RIS); acid volatile sulfide ($AVS = FeS + H_2S + HS^- + S^{2-}$), chromium reducible sulfur ($CRS = FeS_2 + S°$) and elemental sulfur (S°) were determined in mudflat sediments during 7 samplings: June 1990 (RIS), November 1990 (RIS), January 1991 (RIS), April 1991 (RIS, SRR), August 1991 (RIS, SRR), December 1991 (RIS, SRR), and March 1992 (RIS, SRR).

The radiotracer technique described by Fossing and Jørgensen (1989) was used to determine SRR. A whole core was incubated for 5 h in a water bath at the ambient field temperature, than the solid fraction was extracted for AVS and CRS following Fossing and Jørgensen (1989) and elemental sulfur according to Trøelsen and Jørgensen (1982). Radioactivity in the sediment extract was measured by liquid scintillation counting (Beckman LS 7500). Sulfur pools in the sediment (AVS, CRS, and S°) were determined spectrophotometrically after an extraction procedure similar as the one used for SRR. Sulfide concentrations (AVS and CRS) were determined by the methylene blue technique (Cline 1969), while S° was measured at 460 nm after cyanolysis (Troelsen and Jørgensen 1982). Further details about these procedures can be found in Panutrakul (1993).

Pore water was obtained from duplicate sediment cores (4 cm diam and 30 cm length). After slicing the cores, sections of 1 cm (up to 5 cm depth) and 2 cm (up to 20 cm depth), were squeezed through 0.45 μm Millipore filters under nitrogen pressure, using a modified Reeburgh pore water squeezer (Reeburgh 1967). All sediment handling was performed under N_2 in a glove box. Pore water for sulfide analysis was preserved with 1 ml of 5% zinc acetate until analysis as mentioned above. Samples for sulfate analysis were stored frozen until analysis by the methylthymol blue technique (Merks and Sinke 1981) using an AutoAnalyzer II (Technicon).

The water content of sediment samples was determined as weight loss after drying at 105°C for 12 h. Sediment density was calculated from the weight of a known volume. Organic carbon content in the sediments was determined by a CN analyzer (Carlo Erba NA 1500) after acidification with a few drops of 0.5 M HCl and eliminating inorganic carbon.

Results

SULFATE REDUCTION RATES

Preliminary experiments on sulfate and iron reduction rates were carried out on muddy sediment samples of station B (Elskens et al. 1991). Sediment slices from appropriate depth intervals were homogenized in sterile conditions with a 5 g l^{-1} NaCl solution to provide a slurry with a water content of 60–80%. In these experiments the half-life period of sulfate in this layer was estimated at 72 h. In the deeper layers, sulfate reduction could be limited by the low concentration of the electron acceptor, but this limitation might also be due to the higher refractory nature of the organic matter. The major part of the sulfide produced was precipitated under the form of a metal complex, so that the pore water concentration remained very low. No sulfate reducing activity occurred in the sterilized reference sample. The iron reducing experiments (Elskens et al. 1991) gave similar results as for sulfate, however, the amount of iron reduced in the upper layer after 10 d was rather small; (3 mg Fe(II) g dry weight^{-1}). This value, which represents only 11% of the total Fe(III) quantity present in sediments, is understandable when looking at the sequential extraction results (Baeyens et al. 1991). About 75% of the iron content belongs to the residual phase and can only be liberated through strong acid attack.

In the period from 1990–1992 seasonal variations in SRR were assessed with the procedure previously described. Depth profiles of SRR at station A showed the highest rates in August 1991 (0.8 to 1.05 μmol cm^{-3} d^{-1}) between 2 and 7 cm depth (Fig. 2). During other periods, SRR was less than 15% of this value with a more or less similar depth pattern, except for December showing very low rates in the upper 8 cm. At station B, SRR generally increased with depth presenting a broad maximum between 5 and 12 cm. The highest rates were found in August 1991 (a depth average of 4.5 μmol cm^{-3} d^{-1} with maxima between 10 and 14 μmol cm^{-3} d^{-1} at 10 to 12 cm of depth), about 10 times higher than in April. In December and March, SRR remained below 0.30 μmol cm^{-3} d^{-1} at all depths.

Depth integrated SRR from 0 to 15 cm (ΣSRR) in different sampling periods varied from 10 to 80 mmol m^{-2} d^{-1}, at station A and from 17 to 680 mmol m^{-2} d^{-1} at station B (Table 1). In general,

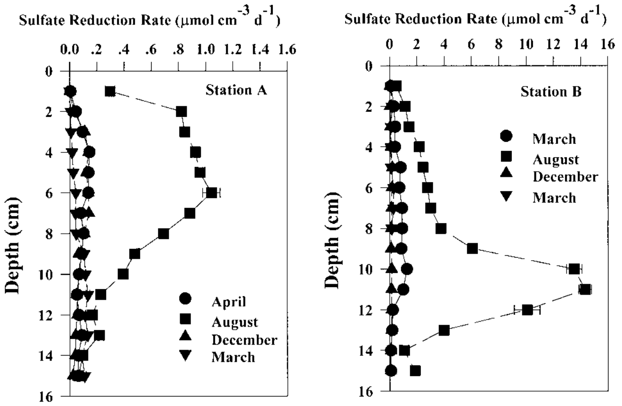

Fig. 2. Depth profiles of sulfate reduction rates (µmol cm^{-3} d^{-1}) at stations A and B during the 4 sampling periods.

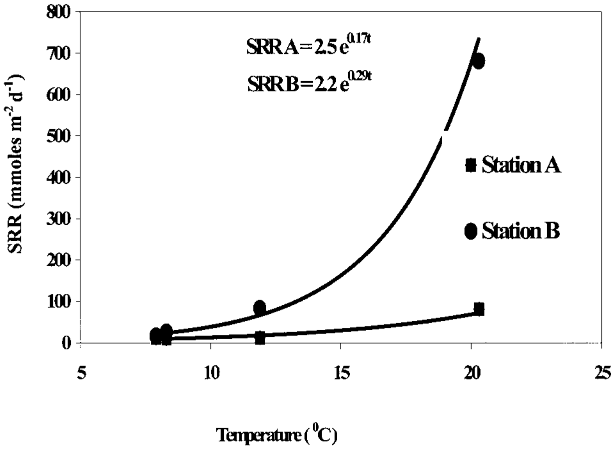

Fig. 3. Depth integrated sulfate reduction rate (mmol m^{-2} d^{-1}) versus temperature.

SRR was positively related to temperature according to an exponential pattern (Fig. 3). The effect of temperature on SRR was more pronounced at station B, which contained 1% to 5% organic carbon, than at station A, which contained 0.2% to 0.8% organic carbon (Table 2). However, at temperatures below 10°C, SRR measured at both stations were within the same range. The ratios of SRR (t + 10°C) to SRR (t), with t the temperature, or Q_{10}-values, in stations A and B were 5.5 and 18, respectively. This means that the temperature dependency of SRR is more pronounced at station B than at station A. Activation energy (Ea) at stations A and B, calculated using the Arrhenius equation, are 110 kJ mol^{-1} and 190 kJ mol^{-1}, respectively. The value obtained at station A compares, for example, with those reported by Vosjan (1974) for sediments of the Wadden Sea (92 kJ mol^{-1}) and Goldhaber et al. (1977) for sediments of Long Island Sound (104 kJ mol^{-1}). The temperature dependence of the SRR at station B is much higher but this may be an indirect effect of the higher amount of labile organic substrates available in summer (elevated temperature) than in winter. In contrast, at station A there might be a shortage of labile organic substrates in summer. The annual sulfate reduction rate (ASRR) in the upper 15 cm of the sediments, was estimated (order of magnitude): station A = 12 mol m^{-2} yr^{-1} and station B = 100 mol m^{-2} yr^{-1}. This estimation is based on the temperature dependency curve of SRR (see Fig. 3) and the average river water temperature at that site.

REDUCED END PRODUCTS OF SULFATE REDUCTION

The predominant end product of reduced ^{35}S formed during the incubation was generally AVS, with the exception of the surface sediments, where ^{35}S-pyrite and ^{35}S-S° were more dominant (Fig. 4). At all other depths, ^{35}S-AVS represented about 70% to 80% of the reduced $^{35}SO_4^{2-}$. Only 15% to 30% of the injected $^{35}SO_4^{2-}$ was recovered as pyrite, and 0% to 5% was recovered as S° in the deeper layers. The thickness of the more oxidized surface layer, where ^{35}S-pyrite and ^{35}S-S° were the predominant radiolabelled end products, varied seasonally. It was almost absent in August, when the SRR was highest. During winter and spring, seasons corresponding to low metabolic activity, the surface layer increases in thickness to a maximum of 5 cm (station B) and 8 cm (station A) in March.

REDUCED INORGANIC SULFUR POOLS

Although AVS was found to be the predominant end product of ^{35}S reduced pools during the short term incubation experiments, pyrite was the predominant RIS pool, while S° is almost negligible

TABLE 1. Sulfate reduction rats (∫SRR) at stations A and B between April 1991 and March 1992.

Date	Temp (°C)	Range of volume specific SRR (nmol cm^{-3} d^{-1})		Depth integrated SRR (mmol m^{-2} d^{-1})	
		Station A	Station B	Station A	Station B
Apr-1991	11.9	6–146	90–1,270	12.4	83.0
Jul-1991	20.3	62–1,040	505–14,300	809	681
Dec-1991	7.9	2–140	25–198	11.5	16.8
Mar-1991	8.3	1–132	86–296	10.0	25.9

TABLE 2. Organic content (mg g^{-1}) at stations A and B between April 1991 and March 1992.

Date	Organic content mean (SD) (mg g^{-1})	
	Station A	Station B
Apr-1991	5.1 (1.4)	33 (12)
Jul-1991	5.3 (1.9)	33 (8)
Dec-1991	4.5 (1.7)	31 (12)
Mar-1992	4.7 (1.3)	27 (7)

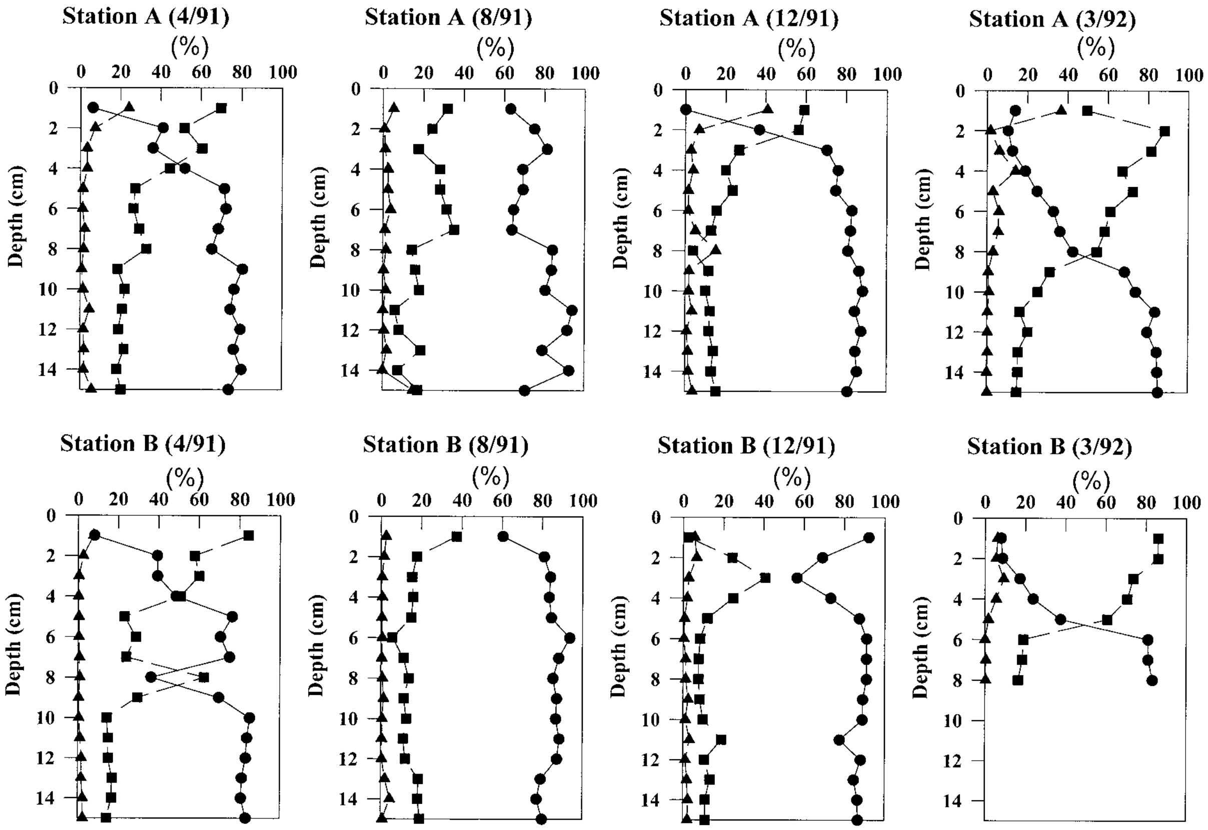

Fig. 4. Depth distribution of radiolabelled end-products from SRR incubations (%) in sediment from stations A and B. AVS (●), pyrite (■), and elemental sulfur (▼).

except in the surface layer in summer (Fig. 5). The following concentration ranges could be observed: AVS from 0.02 to 31.7 μmol g^{-1} at station A, and from 1.38 to 174 μmol g^{-1} at station B; CRS from 9.95 to 49.5 μmol g^{-1} at station A and from 65.8 to 482 μmol g^{-1} at station B; S° from detection limit to 0.58 μmol g^{-1} at station A and from 0.24 to 6.31 μmol g^{-1} at station B. In relative terms, AVS accounted for 0.1% to 6% and 1% to 13% of the RIS pool in surface sediments (0–5 cm) at stations A and B, respectively. Below this depth, AVS increased to about 30%. S° usually accounted for less than 1% of the RIS pool, except at the surface, where it could reach up to 5%. Pyrite comprised up to 95% of the RIS pool at the surface at both stations but decreased to 60–70% at a depth of 5 cm at station B and 10 cm at station A.

At station A both AVS and CRS reached a maximum level during winter and decreased to a minimum level in spring and early summer. At station B the following results (averages over depth) were observed (expressed in μmol g^{-1}): in winter AVS was equal to 79.5 (December) and 103 (January) while in spring values decreased to 35.3 (March) and 27.0 (April). In winter CRS was equal to 311 (December) and 204 (January) and in spring to 153 (March) and 119 (April). At station A, a similar trend was observed: in winter AVS was equal to 13.3 (December) and 17.0 (January) and in spring and early summer to 7.93 (March), 7.92 (April), 5.87 (June), and 7.08 (July). In winter, CRS was equal to 41.2 (December) and 34.9 (January) and in spring and early summer to 26.3 (March), 18.7 (April), 20.0 (June), and 26.2 (July). No clear temporal trend was evident for S°, whereas at station B a maximum accumulation occurred at the surface during summer.

It is very difficult to estimate how much of the annually generated sulfide (12 mol m^{-2} yr^{-1} at station A and 100 mol m^{-2} yr^{-1} at station B) is retained in the sediment. For example, the difference in the reduced inorganic sulfur content in the upper 15 cm of the sediment between April 1991 and March 1992 equalled 590 mmol m^{-2} yr^{-1} at station A and 960 mmol m^{-2} yr^{-1} at station B. Hence, the percentage of produced sulfide, calculated on a yearly basis, that was retained in the upper 15 cm of the sediments, was very small (4.9% at station A and 0.93% at station B). In fact most of the sulfide, if not all, produced in these

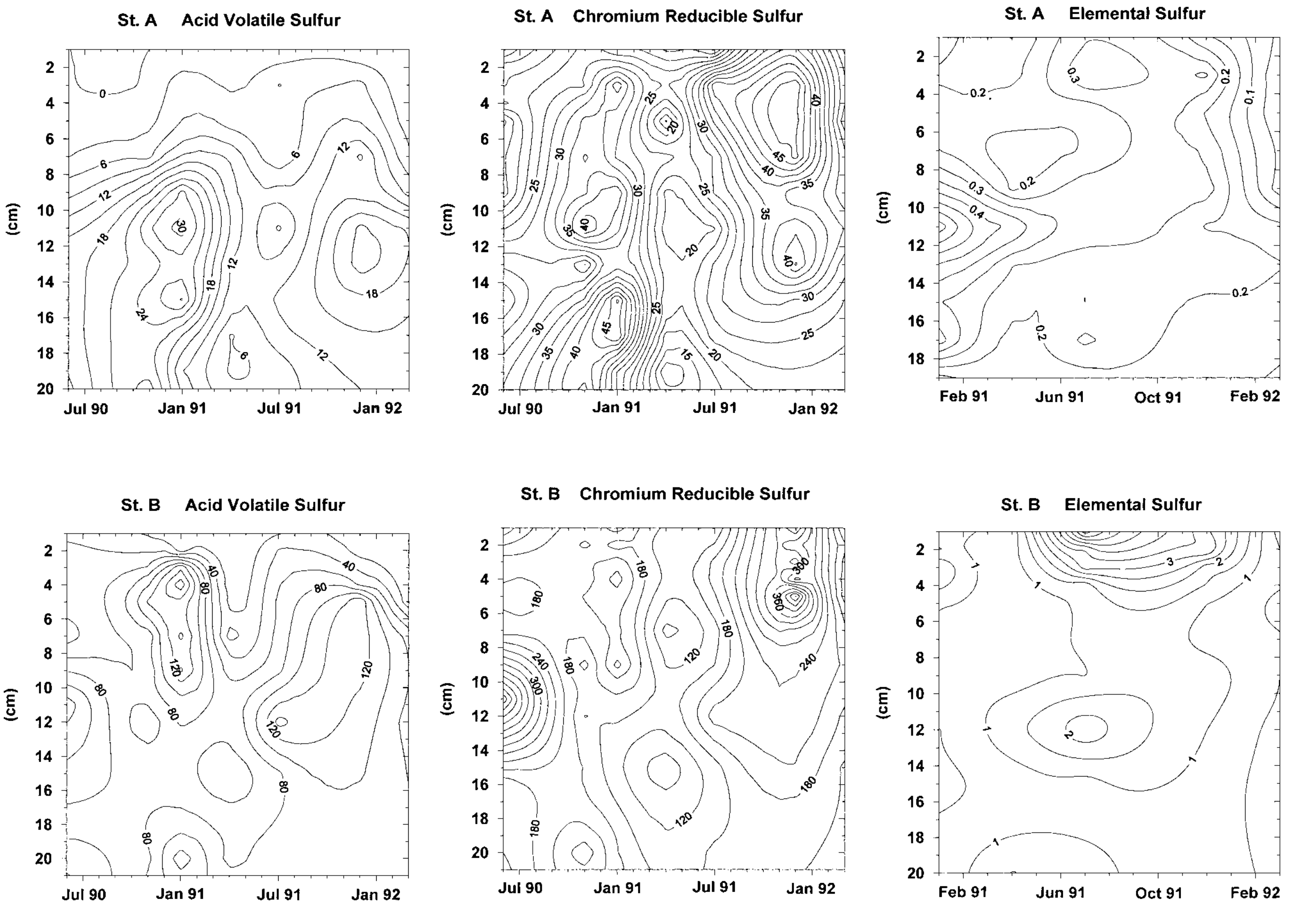

Fig. 5. Isocline plots of acid volatile sulfide (AVS), chromium reducible sulfur, and elemental sulfur (EleS) (μmol g^{-1}) at stations A and B as a function of depth (cm) and time (mo).

sediments is either reoxidised or emitted to the atmosphere/overlying water. Sulfide may also be retained in sediments in other forms such as humic or organic sulfur which results from reactions between organic matter and H_2S or its oxidation products (François 1987; Ferdelman et al. 1991).

Discussion

The values of SRR found in this study are within the range reported from other ecosystems (Skyring 1987). However, it should be noted that the maximum SRR observed in muddy sediments at station B is one order of magnitude higher than in sandy sediments at station A. The lower SRR at station A, may be due to a shortage of labile organic substrates. This is not the case at station B, where a high supply of organic carbon takes place. A sulfate reduction rate of 3.3 μmol cm^{-3} d^{-1} was obtained when an anaerobic incubation experiment was carried out on sediment from station B, enriched in organic matter by adding 50 mg l^{-1} of yeast extract (unpublished results) at 20°C. This rate is close to the maximum depth-averaged SRR (4.5 μmol cm^{-3} d^{-1}) found at station B in summer.

SRR showed a seasonal variation pattern with low rates in winter and high rates in summer. A similar temperature dependence of SRR, has also been reported by other authors (King 1988; Westrich and Berner 1988; Swider and Mackin 1989; Moeslund et al. 1994; Thampdrup et al. 1994). Jørgensen (1977) concluded in his work that seasonal variations in sulfate reducing activity is not a simple temperature effect but also reflects variation in the amount of labile organic substrate available for anaerobic decomposition. Thamdrup et al. (1994) and Moeslund et al. (1994) found that the sulfate reduction rate in Åarhus Bay, Denmark, strongly increased after the spring phytoplankton bloom has sedimented. Seasonal variation of SRR in the sediments of the Ballastplaat may therefore not only depend on temperature variations but also on the quality and quantity of organic carbon in that sediment.

During short incubation experiments (5 h) AVS was found to be the predominant end product of the various ^{35}S reduced pools. AVS, which is not stable and can be released through acidification, is composed of amorphous iron sulfide, and is responsible for the black color of anoxic sediments, mackinawite, and maybe greigite (Goldhaber and Kaplan 1974). Under reducing conditions ferrous ion is generated and can react with hydrogen sulfide to form a variety of iron sulfide minerals, including amorphous FeS (Allen et al. 1993). Pyzik and Sommer (1981) found that the pathway of FeS formation passes via the reduction and dissolution of goethite and the subsequent reaction of iron hydroxide with bisulfide. In relatively sulfide rich environments, environments with ppm or greater total dissolved sulfide concentrations, a standing concentration of $Fe(SH)_2$ will be present and may constitute an important component in further reactions, such as pyrite formation (Rickard 1995). In contrast in sulfide-poor systems, the H_2S pathway, involving direct formation of FeS, dominates in all environments with $pH < 8$.

The dissolved sulfide content in the pore waters of sediments of the Ballastplaat was found to be below the detection limit of Cline's (1969) method (1 μM) throughout the sampling period despite the very high SRR. Outgassing during the squeezing step was checked and appeared not to be the cause of the low dissolved sulfide content. Using exactly the same procedure, various dissolved sulfide levels could be determined in a sample set from Åarhus Bay, Denmark (Panutrakul 1993). The high amounts of reactive iron (about 2 and 7 mg-Fe g^{-1} sediment were extracted at $pH = 2$ in the surface sediment at station A and B, respectively) suggest that there is always enough reactive Fe to scavenge the newly produced dissolved sulfide. According to Rickard (1995), the H_2S pathway, involving the direct formation of FeS, should thus dominate in the sediments of the Ballastplaat.

In addition to AVS, ^{35}S-pyrite and ^{35}S-S° were also formed during the short-term radiolabelled sulfate incubation experiments but their relative importance was highest in the suboxic surface layer of sediments. In addition, both reduced sulfur species were dominant in spring (both stations) and winter (station A). Although FeS and S° can react to produce pyrite, the reaction rate in natural conditions is very slow (e.g., Berner 1970, 1984; Middelburg 1991). Recently Rickard (1997) reported pyrite formation by H_2S oxydation of FeS in aqueous solutions; the rates described were by far the most rapid of the pyrite-forming reactions identified hitherto. In natural systems therefore the H_2S process will tend to be favored in strictly anoxic environments. However, in transitional suboxic environments, with limited molecular oxygen contents, pyrite formation through the polysulfide pathway (e.g., Rickard 1975; Luther 1991) or a solid state process (e.g., Schoonen and Barnes 1991) may become more important. Although isotopic exchange reactions of the reduced ^{35}S-pools do not allow to quantify the specific formation rate of each of the end products on the basis of the observed partition of ^{35}S (Thode-Andersen and Jørgensen 1989; Fossing et al. 1992), it appears that the ^{35}S-pyrite and ^{35}S-S° production were linked to the redox condition of the sediment (transitional environment). Thode-Andersen and Jørgensen (1989) also observed ^{35}S-S° formation in more oxidized, surface, or subsurface sediments.

On a longer seasonal time scale, redox conditions also play an important role. Sulfide produced by sulfate reduction lowers the redox potential of the sediment during the summer months. As temperature decreases in autumn and winter, less sulfide is produced and the sediment will gradually shift into a more oxidized state; the SRR and change in redox conditions are, however, out of phase. Accumulation of RIS pools in the mud flat shows temporal variations according to the changing redox conditions. King (1988) reported a similar dynamic pattern of sulfur in a South Carolina salt marsh, although we must be careful when comparing marshes and mud flats; organic C and oxygen inputs are in general very different. King (1988) found a maximum SRR in August whereas the dissolved sulfide concentration reached its maximum in fall. The distribution (percentages) of the different sulfur species within the RIS pool is, on a seasonal scale, different from that on a short-term scale (incubations lasted 5 h). On a seasonal scale, pyrite is the dominant species, especially in surface sediments, whereas AVS is only significant in the deeper layers where it can reach up to 30–40%. In the radiolabelled short-term incubation experiments pyrite was the dominant species in surface sediments, but AVS accounted for 70–80% (about twice as high as the accumulation on a seasonal time-scale) of the RIS end products in the deeper layers. These observations are not in contradiction with the pyrite formation kinetics reported by Rickard (1997); he observed up to 50% pyrite formation in one day but this value is pH dependent. For example a pH increase from 6 to 7.5 halves the rate constant. Our radiolabelled experiments were carried out at a pH of 7.5 and lasted 5 h; hence a further conversion of AVS into pyrite, in agreement with long-term observations (sediment stocks of RIS-species) seems acceptable.

The accumulation of RIS pools started in summer when strong anoxic sediments were created and reached their maximum contents in winter (December and January). During spring (March–

April), the RIS pools in the sediments were diminished due to the combined effect of a long term low SRR, and high oxygen content in the water column. Jørgensen (1977) and Sorensen and Jørgensen (1987) also found a seasonal delay of FeS accumulation compared to SRR. Jørgensen (1977) showed that the redox condition of Limfjorden, Denmark, sediments became strongly reduced during fall (September to November) but not in summer. He also suggested that sulfide produced during early summer was oxidized and that accumulation of RIS was only noticeable at a later moment when the sediment became sufficiently anoxic.

Conclusions

SRR in sediments of the Ballastplaat exponentially increased with increasing temperature. The increase of sulfate reducing activity due to increasing temperature, can be limited by the availability (qualitative and quantitative) of organic carbon in the sediments. AVS was found to be the predominant radiolabelled end product of inorganic reduced sulfur, formed during short-term incubations in laboratory, with an exception of the surface sediments where pyrite and elemental sulfur were more dominant. The predominant species of RIS in sediments of both sampling stations is pyrite. The apparent contradiction between short-term (5 h incubation) results, with a dominance of AVS, and long-term observations, with a dominance of pyrite, can be explained on the basis of the pyrite formation kinetics established by Rickard (1997). The reduced inorganic sulfur pools AVS, pyrite, and S° showed a seasonal variation. The maximum AVS and pyrite contents in sediments at the Ballastplaat, were found in winter, in contrast with the maximum SRR values which were observed in summer. The sulfur mass balance shows that in the upper 15 cm interval, very little if any of the produced sulfide is retained.

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