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Inorganic sulfur turnover in oligohaline estuarine sediments

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Abstract. Inorganic sulfur turnover was examined in oligohaline (salinity < 2 g kg^{-1}) Chesapeake Bay sediments during the summer. Cores incubated for < 3 hr exhibited higher sulfate reduction (SR) rates (13—58 mmol m^{-2} d^{-1}) than those incubated for 3—8 hr (3—8 mmol m^{-2} d^{-1}). SR rates (determined with $^{35}SO_4^{2-}$) increased with depth over the top few cm to a maximum at 5 cm, just beneath the boundary between brown and black sediment. SR rates decreased below 5 cm, probably due to sulfate limitation (sulfate < 25 μM). Kinetic experiments yielded an apparent half-saturating sulfate concentration (K_s) of 34 μM, ≈ 20-fold lower than that determined for sediments from the mesohaline region of the estuary. Sulfate loss from water overlying intact cores, predicted on the basis of measured SR rates, was not observed over a 28-hr incubation period. Reduction of $^{35}SO_4^{2-}$ during diffusion experiments with intact core segments from 0—4 and 5—9 cm horizons was less than predicted by non-steady state diagenetic models based on $^{35}SO_4^{2-}$ reduction in whole core injection experiments. The results indicate that net sulfate flux into sediments was an order of magnitude lower than the gross sulfur turnover rate. Solid phase reduced inorganic sulfur concentrations were only 2—3 times less than those in sediments from the mesohaline region of the Bay, despite the fact that oligohaline bottom water sulfate concentrations were 10-fold lower. Our results demonstrate the potential for rapid SR in low salinity estuarine sediments, which are inhabited by sulfate-reducing bacteria with a high affinity for sulfate, and in which sulfide oxidation processes replenish the pore water sulfate pool on a time scale of hours.

Abbreviations: AVS — acid-volatile sulfide; NAVS — nonacid-volatile sulfide; SR — sulfate reduction; SRB — sulfate-reducing bacteria.

Introduction

Sulfate reduction (SR) dominates organic carbon mineralization in anaerobic sediments where sulfate is present at non-limiting concentrations (Martens & Berner 1974; Winfrey & Zeikus 1977; Oremland & Taylor 1978) and

amounts of microbially reducible iron and manganese oxides are low (Lovley & Phillips 1987). Rates of sulfate turnover in surficial lake sediments (Smith & Klug 1981; Ingvorsen et al. 1981; Lovley & Klug 1983; Herlihy & Mills 1985; Bak & Pfennig 1991) indicate that SR contributes significantly to carbon oxidation even at relatively low ($\leqslant$ 0.1 mM) sulfate concentrations. Freshwater sulfate reducing bacteria (SRB) possess highly efficient sulfate uptake systems, with half-saturation constants on the order of 5 μM (Ingvorsen & Jørgensen 1984). These observations and the presence of substantial quantities of reduced inorganic sulfur in lake (King & Klug 1982; Davison et al. 1985; Rudd et al. 1986; Carignan & Tessier 1988; White et al. 1989; Bak & Pfennig 1991) and low-salinity estuarine sediments (Martens & Goldhaber 1974) verify that SR can be significant in freshwater sedimentary environments.

Estuaries and their tributaries along the central and northern Atlantic coast of the US receive some of the highest acidity, highest sulfate content acid rain in the United States (Likens et al. 1979), suggesting that sulfur cycling could be of particular importance in low-salinity sediments in the upper reaches of these estuarine systems. Little comparative information is available concerning sulfur transformations in oligohaline estuarine sediments. In this study we measured sulfate concentrations, turnover rates, and solid phase reduced inorganic sulfur in sediments from the $<$ 2 g kg^{-1} salinity zone of the Chesapeake Bay. Our results suggest that a combination of efficient bacterial sulfate uptake systems and rapid sulfide oxidation is responsible for a high rate of sulfur turnover, which is comparable to rates in shallow coastal marine and eutrophic freshwater ecosystems.

Materials and methods

Study site and sampling procedure

Sediments at a site (39°26′30″ N, 76°02′00″ W) in the oligohaline region of Chesapeake Bay were sampled during June to August 1987 and 1988. The water depth was 5 m. Box cores (136 cm^2 area, $\approx$ 25 cm depth) were obtained with a Bouma corer. Communities of the bivalve *Rangia cuneata* were sometimes observed in dense patches, within which undisturbed cores could not be obtained. Such patches were therefore avoided during core collection, although *Rangia* were still frequent in cores from outside the patches. The sediments had a $\approx$ 4-cm deep brown surface layer, below which the sediment was black. We refer to the transition from

brown to black sediment as the redox discontinuity boundary (RDB), although sediment redox potentials were not determined.

Sulfate reduction in sediment cores

Subcores for SR measurements were sampled from box cores with 2.5 cm diameter tubes having silicone-filled injection ports at 2-cm intervals. The subcores were held at *in situ* temperature prior to and following injection with 2—4 μCi of carrier-free (40 Ci mmol^{-1}) $Na_2^{35}SO_4$ (ICN Radiochemicals, Irvine, CA) at 2—3 cm intervals from 1 to 11—13.5 cm. Incubations conducted aboard ship (1—8 hr) were terminated by freezing (−20 °C) intact subcores. Whole core time course incubations (0.4—5 hr) were terminated by sectioning the cores (2—3 cm intervals) and acidifying the slices (see below).

Subcores for pore water sulfate analysis were taken from box cores with 7.3-cm ID polycarbonate tubes. The cores were sectioned aboard ship at 1—3 cm depth intervals and the sediments transferred to 50 ml centrifuge tubes. The tubes were either packed full or flushed with N_2 before being frozen. Back at the laboratory, the samples were quickly thawed, centrifuged, and the pore waters passed by syringe through glass fiber (GF/C, Whatman) filters into vials for storage prior to analysis by ion chromatography. Because we could not detect an odor of free sulfide in the sediments during sectioning or after centrifugation, pore waters were not fixed with Zn^{2+}.

SR rates were calculated as the product of the fraction of added $^{35}SO_4^{2-}$ activity recovered as reduced ^{35}S (see below) per unit time and the whole sediment sulfate concentration at the appropriate depth in the sediment. All SR rates were corrected for time-zero blanks determined for the reduced sulfur extraction procedures described below.

Kinetics of sulfate reduction

The dependence of SR rate on sulfate concentration was examined in sediments from 5—10 cm depth (just below the brown surface layer), collected in sterile canning jars which were completely filled to exclude O_2 penetration. Sediment homogenates were pre-incubated for 1—2 weeks to deplete pore water sulfate (< 6 μM) prior to conducting the kinetic studies. Portions of sediment (50 ml) were amended with small volumes of sulfate stock solutions and mixed while gassing with O_2-free N_2, yielding a range of sulfate concentrations of 0.1—10 mmol L^{-1} (high sulfate range) or 0.01—1 mmol L^{-1} (low sulfate range). Five ml portions of sediment

were then distributed to cut-off syringes. The syringes were sealed with serum stoppers and held at 30 °C (high sulfate range) or 22 °C (low sulfate range) for ≈ 1 hr prior to injection with 1—10 μCi of carrier-free $^{35}SO_4^{2-}$. The samples were incubated for 1—4 hr (high sulfate range) or 5—30 min (low sulfate range). Incubations were terminated by acidification with 10 ml of 6N HCl/1M $TiCl_3$. $^{35}SO_4^{2-}$ turnover constants for each concentration level were calculated as the average (n = 3—4) of individual rate constants (zeroth order) determined for samples incubated for different lengths of time.

The dependence of SR rate on sulfate concentration was also determined in mesohaline (salinity 15—20 g kg^{-1}) Chesapeake Bay sediments. Sediments from both the sulfate-rich (> 10 mM) 0—4 cm and sulfate-depleted (< 1 mM) 12—16 cm depth intervals were examined. The sediments were pre-incubated in the laboratory until the sulfate concentration in sediment pore fluids was < 10 μM. Portions of homogenized sediment (3 ml) were transferred inside an anaerobic chamber to 15 ml serum vials. The vials were amended with 0.3 ml of sterile, O_2-free $Na_2SO_4^{2-}$ solutions to yield a range of added sulfate concentrations of 0.01 to 20 mmol L^{-1}. One to 10 μCi of $Na_2{}^{35}SO_4^{2-}$ was added to each vial 1 min after addition of unlabeled SO_4^{2-}. The vial contents were well mixed before and after the addition of $^{35}SO_4^{2-}$. Duplicate vials were used for each concentration level, and duplicate unamended control vials were injected with O_2-free distilled water prior to addition of $^{35}SO_4^{2-}$. Incubation times varied from 15 min to 4 hr for the different sulfate levels; short incubations were required at low sulfate concentrations due to rapid consumption of $^{35}SO_4^{2-}$. Incubations were terminated by addition of 3 ml of 20% zinc acetate. Turnover constants for $^{35}SO_4^{2-}$ were calculated as the average of duplicate rate constant (zeroth order) determined for each sulfate level.

Sulfate flux experiments

Sulfate flux was determined using duplicate 7.3 cm ID cores incubated in the laboratory for 25—30 hours at 22 °C. Overlying water samples (2 ml) were collected for sulfate analysis at 4—6 hr intervals. The cores were incubated undisturbed, except that the water overlying the cores was gently mixed (avoiding sediment resuspension) prior to each sampling. Following the incubation period, the cores were sectioned at 1—3 cm intervals, the slices centrifuged, and pore waters filtered through glass fiber (GF/C, Whatman) filters into plastic vials for sulfate analysis.

An experiment to examine the simultaneous diffusion and reduction of $^{35}SO_4^{2-}$ was performed with whole sediment segments (2.5 cm ID cores) from the 0—4 and 5—9 cm depth intervals. For each interval, one segment

was injected with $NaMoO_4$ (final concentration 4 mmol L^{-1}) and pre-incubated (16 hr) prior to addition of $^{35}SO_4^{2-}$, whereas a duplicate section was not treated with molybdate. For 0—4 cm sediment sections, the experiment was started by adding 10.8 μCi of $^{35}SO_4^{2-}$ to 1 cm (depth) of overlying water. For the 5—9 cm sections, the top 5 cm of sediment was extruded and sliced off while gassing with O_2-free N_2, and the experiment started by dispensing 5.4 μCi of $^{35}SO_4^{2-}$ (contained in 0.5 ml of degassed pore water from 5—10 cm) onto a 0.45 μm membrane filter placed on the top of the core segment. The 5—9 cm sections were then sealed with rubber stoppers (under N_2) to maintain anaerobiosis. Cores from both depth intervals were incubated at 22 °C for 3 days, during which time the $^{35}SO_4^{2-}$ diffused downward into the sediment. The cores were then sectioned at 0.5 cm intervals, and the segments (8 per core) transferred to O_2-free N_2-gassed centrifuge tubes containing 5 ml of boiled out and O_2-free N_2-gassed distilled water. The tubes were sealed, vortexed, and centrifuged. A 1-ml portion of the supernatant was collected for determination of residual $^{35}SO_4^{2-}$ just prior to resuspension of the pellet, and subsequent distillation with 5 ml of 6N HCl/1M $TiCl_3$.

Analytical methods

Reduced inorganic sulfur in SR cores sampled in 1987 was extracted in a boiling solution of 1M reduced chromium (30 ml) and concentrated HCl (15 ml) (Zhabina & Volkov 1979), whereby all forms of reduced inorganic sulfur were recovered in a single distillation. SR cores obtained in 1988 were analyzed first by room temperature acid distillation with 20 ml of 6N HCl/1M $TiCl_3$, followed by boiling reduced chromium reduction. Samples from the SR kinetics and $^{35}SO_4^{2-}$ diffusion/reduction experiments were analyzed by room temperature acid distillation only. Acid distillation recovers dissolved sulfide and iron-monosulfides, which are referred to as acid-volatile sulfide (AVS) compounds. $TiCl_3$ was included in these distillations to prevent oxidation of H_2S by ferric iron that may be released by acidification (Albert 1984). Partially oxidized inorganic reduced sulfur (S^o, FeS_2) recovered by chromium reduction after acid distillation is termed nonacid-volatile sulfide (NAVS).

The H_2S evolved during each of the above distillations was carried by an O_2-free N_2 stream into 10% zinc acetate traps, where it precipitated as ZnS. The concentration of unlabeled ZnS in the traps was determined colorimetrically (Truper & Schlegel 1964) with a precision of $\approx$ 10%. Recoveries of reagent grade FeS (Aldrich Chemicals) by acid distillation and FeS_2 by reduced chromium distillation were 97 $\pm$ 4% (n = 3) and 100 $\pm$ 6% (n = 6), respectively. The amount of $Zn^{35}S$ activity in the

traps was determined by mixing 2-ml portions of trap solution with 7 ml of Instagel scintillation cocktail (Packard Instrument Co., Downers Grove, IL) and counting the samples in a Packard Model 4330 liquid scintillation spectrometer operated in the DPM mode. Quench corrections were made by the external standard channels-ratio method. Time zero blanks for the acid and reduced chromium distillations were determined by adding a known quantity of $^{35}SO_4^{2-}$ to 10 ml of sediment and immediately beginning the distillation. The two distillation procedures exhibited blanks amounting to 0.05 ± 0.03% (n = 3) and 0.145 ± 0.049% (n = 12) of total added $^{35}SO_4^{2-}$ activity, respectively.

Pore water sulfate concentrations were determined with a Dionex (Sunnyvale, CA) Model 2020i ion chromatograph. The detection limit for sulfate was 1 μM. At sulfate concentrations < 10 μM, distilled water blanks run between analyses remained below the detection limit and the precision of replicate determinations was 10—20%. At 50 to 500 μM sulfate, blanks were ⩽ 2 μM and precision was ⩽ 5%.

Results and Discussion

Water column sulfate concentrations

Summer water column sulfate concentrations in the upper Bay ranged from ≈ 0.5 to 1.7 mM (Table 1). Sulfate concentrations predicted from conservative mixing of seawater with a sulfate-free freshwater input were lower than measured values, indicating a substantial external sulfate input.

Table 1. Bottom water salinity and sulfate concentration in upper Bay study area during the summer.

Date	Measured salinity (g kg^{-1})	Sulfate (mM)		Estimated riverwater sulfate[2] (mM)
		Measured	Predicted[1]	
6/22/88	0.10	0.46	0.0	0.46
7/21/87	0.70	1.27	0.47	0.74
8/24/88	1.77	1.73	1.33	0.28

[1] Calculated as: $[(S_m - S_{rw})/S_{sw}] \times C_{sw}$, where S_m = measured salinity; S_{rw} = average salinity of riverwater* (0.110 g kg^{-1}); S_{sw} = average salinity of seawater* (35.5 g kg^{-1}); and C_{sw} = average seawater sulfate concentration* (28.4 mM) (*from Drever 1982).

[2] Calculated as: $(C_m - fC_{sw})/(1 - f)$, where C_m = measured bottom water sulfate concentration, and $f = (S_m - S_{rw})/(S_{sw} - S_{rw})$.

Estimated riverine end-member sulfate concentrations (0.28—0.74 mM; Table 1) exceeded average riverwater sulfate concentrations (0.09—0.12 mM; Drever 1982) several-fold, suggesting that the Susquehanna river may be sulfate-enriched (possibly from acid mine drainage). In addition to riverine input, weathering of nearby shoreline or marsh soils could also provide a source of sulfate to upper Bay waters.

Sulfate reduction rates

Sediments incubated for < 3 hr yielded significantly higher areal SR rates than those incubated for 3—8 hr (Table 2). As discussed below, SR rates measured in highly sulfate-depleted sediments ($\leqslant$ 10 μmol L^{-1}) below 6 cm depth may be unreliable due to difficulty in specifying the pool size of sulfate which was actively turning over in the sediment. SR rates integrated over the entire 0—15 cm sampling interval therefore represent maximum values. However, for cores incubated for < 3 hr, these rates are no more than 25% higher than those integrated over the upper 6 cm of sediment (Table 2).

Table 2. Depth-integrated SR rates in upper Bay cores incubated for < 3 or > 3 hr (25 °C). Error terms refer to the standard deviation of the mean. Numbers in parentheses are the number of cores analyzed.

Incubation period (hours)	Sulfate reduction rate (mmol m^{-2} d^{-1})	
	0—15 cm	0—6 cm
< 3	28.6 ± 19.0 (5)	23.6 ± 19.8 (5)
	19.9 ± 1.5 (4)[1]	14.8 ± 3.4 (4)[1]
> 3	7.5 ± 2.4 (5)	4.1 ± 3.0 (5)

[1] Excludes core incubated for 0.43 hr, which yielded a SR rate of 63 mmol m^{-2} d^{-1}.

SR rates typically increased with depth over the upper few cm to a maximum just below the RDB, where rapid turnover of a relatively small pool of sulfate (25—50 μM) was evident (Fig. 1). The highest areal SR rate ($\approx$ 60 mmol m^{-2} d^{-1}) was measured in a core incubated for 0.43 hr, in which very rapid SR occurred within the brown surface layer at 3 cm depth and just below it at 5 cm (data not shown). The high variability of SR estimates above and in the vicinity of the RDB may have resulted from a heterogeneity of redox microenvironments in this layer. Similar results were reported for the oxidized surface layer (0—1 cm) of littoral Lake Constance sediments (Bak & Pfennig 1991).

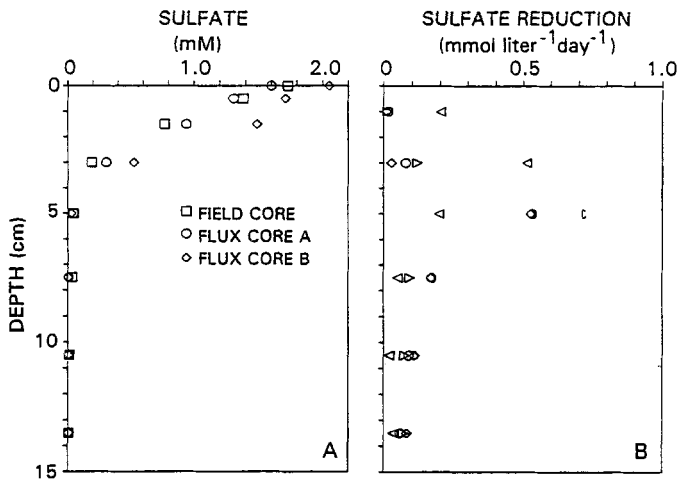

Fig. 1. (A) Pore water sulfate concentrations in upper Bay sediments measured during August. The 'field' core was sectioned at the time of sampling. The 'flux' cores were sectioned at the end of sulfate flux core incubations (see Fig. 5). (B) SR rates in upper Bay sediments measured during August (25 °C). Rates are based on total inorganic reduced ^{35}S recovery in cores incubated for 0.85—2.4 hr.

Areal SR rates in upper Bay sediments are in the mid-range of values reported for freshwater systems (Table 3), and are comparable to those typical of shallow water (< 20 m) coastal marine sediments (Jørgensen 1982). The upper Bay SR rates are about half the average summer sediment SR rates found in the mesohaline portion of the Bay (Roden &

Table 3. Areal SR rates (determined with $^{35}SO_4^{2-}$) in various freshwater environments.

Location	Temperature (°C)	SR rate (mmol m^{-2} d^{-1})	Reference
Upper Chesapeake Bay	25	14.8	this study
Lake Washington	10	0.12	Kuivila et al. 1989
Lake Vechten	6	1.7	Hordijk et al. 1985
Wintergreen Lake	10	15.3	Smith & Klug 1981
Lake Constance	25	20	Bak & Pfennig 1991
Little Rock Lake	4	1.5—5.2	Urban et al. 1993
Lake Anna	26	13.5	Herlihy & Mills 1984
"	26	32.4	"
Contrary Creek	26	39.2	"
"	26	226	"
Big Run Bog	17	88.3	Weider et al. 1990
Buckles Bog	17	144	"

Tuttle 1993). Our results suggest that low salinity estuarine sediments can be important sites of sulfur transformation, especially in shallow productive environments such as the Chesapeake Bay. Confirmation of this hypothesis will require SR rate measurements in other oligohaline systems of varying hydrography and productivity.

$^{35}SO_4^{2-}$ turnover in intact cores

Initial rates of $^{35}SO_4^{2-}$ reduction were rapid beneath the RDB (Fig. 2), corresponding to sulfate turnover times of < 3 hr. Similarly rapid rates of $^{35}SO_4^{2-}$ reduction have been reported in other freshwater sediments (Smith & Klug 1981; Ingvorsen et al. 1981; Kelly & Rudd 1984; Hordijk et al. 1985; Weider & Lang 1988; Bak & Pfennig 1991). A pattern of reduced ^{35}S accumulation and subsequent loss was evident at depths of 5 cm and below. In contrast, complete and permanent reduction of carrier-free $^{35}SO_4^{2-}$ occurred within 1 hr in sulfate-depleted sediment that had been held for several months at 22 °C (data not shown). Less than complete reduction of $^{35}SO_4^{2-}$ (after a 4-hr incubation) below 4 cm depth could, therefore, be indicative of *in situ* sulfide oxidation. This oxidation, superimposed on a rapid rate of $^{35}SO_4^{2-}$ consumption, may have been responsible for systematic underestimation of SR rates in cores incubated for longer than a few hours.

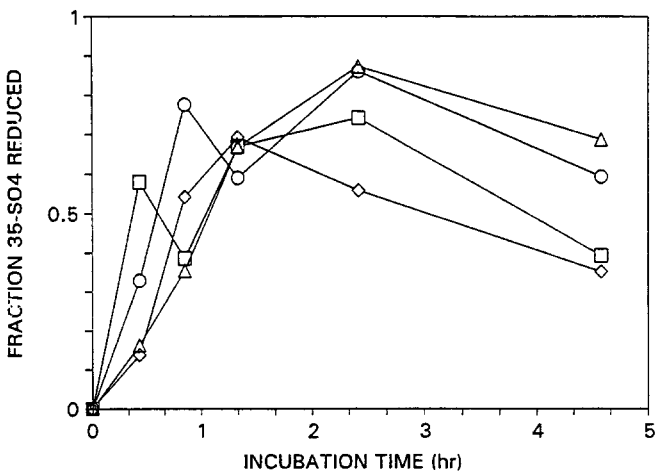

Fig. 2. Time course of $^{35}SO_4^{2-}$ reduction measured at different depths in intact upper Bay cores in August. Reduction of $^{35}SO_4^{2-}$ was calculated from total inorganic reduced ^{35}S accumulation. The different symbols refer to the following depths of $^{35}SO_4^{2-}$ injection: □, 5 cm; ○, 7.5 cm; ◇, 10.5 cm; △, 13.5 cm.

A recent study demonstrated oxidation of sulfide in freshwater sediment via a thiosulfate shunt pathway (Jørgensen 1990a). Some of the thiosulfate produced was oxidized to sulfate, some reduced back to sulfide, and some disproportionated to sulfate and sulfide. Recycling of sulfur through these reactions could ultimately lead to complete oxidation of sulfide to sulfate (Jørgensen 1990b). Thus, a mechanism exists for sulfur recycling in anoxic sediments, although the electron acceptor(s) for sulfide oxidation have not been directly identified. Oxidation of reduced sulfur back to sulfate coupled to reduction of added manganese oxides has been demonstrated in anoxic salt marsh (Aller & Rude 1988) and intertidal sediments King (1990). Such compounds could presumably serve as *in situ* electron acceptors for sulfide oxidation in freshwater sediments.

An alternative explanation for the apparent loss of reduced inorganic ^{35}S activity over time in upper Bay sediments (Fig. 2) is that ^{35}S was being incorporated into one or more organic sulfur fractions which are not recovered by acid or reduced chromium distillation. Several studies have shown that organic sulfur is an important product of $^{35}SO_4^{2-}$ reduction in freshwater sediments (Brown 1986; Rudd et al. 1986; Baker et al. 1989; Marnette et al. 1992). We cannot evaluate this possibility directly because we did not determine $^{35}SO_4^{2-}$ incorporation into organic sulfur; nor can we evaluate it indirectly by examining the difference between total $^{35}SO_4^{2-}$ consumption and total reduced inorganic ^{35}S recovery (cf. Marnette et al. 1992), because we did not measure the amount of $^{35}SO_4^{2-}$ activity remaining after incubation. Thus we cannot rule out formation of organic S as an explanation for the loss of reduced inorganic ^{35}S over time during the whole core incubations (Fig. 2). However, regardless of the nature of the end products of sulfate reduction, as discussed below there is strong evidence for rapid S recycling (i.e. an internal source of sulfate) in these sediments. Mineralization of organic sulfur compounds could contribute to S recycling (as has been suggested for other freshwater sediments; King & Klug 1980, 1982; Marnette et al. 1992), although Weider & Lang (1988) have argued convincingly that even in organic S-rich freshwater peat sediments S cycling is dominated by flux through inorganic S pools.

Sulfate reduction kinetics

The nearly complete depletion of sulfate below 4 cm depth in intact cores suggested that SR was sulfate-limited within and/or below this layer. We measured SR rates over a range of sulfate concentrations in homogenized sediment from 5—10 cm depth to test this hypothesis. SR rates were independent of sulfate at added sulfate concentrations of 0.1 to 10 mmol

L^{-1} (data not shown). In a subsequent experiment we decreased the range of sulfate concentrations 10-fold and included an unamended control. Reduction of $^{35}SO_4^{2-}$ was very rapid (1.6-hr turnover time) in unamended sediments (Fig. 3b), in which a residual sulfate concentration of 5 μmol L^{-1} was measured two days before and on the day of the $^{35}SO_4^{2-}$ reduction experiment. The calculated SR rate in the unamended homogenized sediments (75 μmol L^{-1} d^{-1}) exceeded rates at 10—50 μmol added sulfate L^{-1} (Fig. 3a). Similar results were obtained with mesohaline Bay sediments (see Figs. 4a, c). Given the low and unchanging sulfate pool in these sediments, such high rates SR rates seem improbable, and could be sustained only by rapid replenishment of pore water sulfate from an

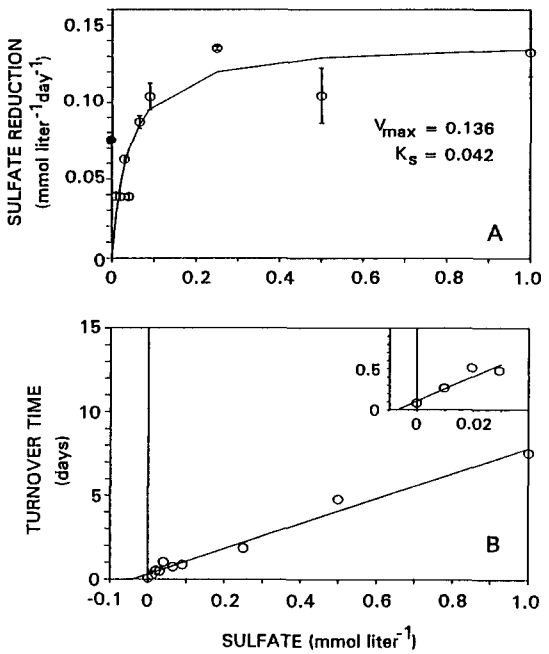

Fig. 3. (A) SR rates in upper Bay sediments at sulfate concentrations of 0.01 to 1.0 mmol L^{-1}; error bars show 1 standard deviation. Open symbols indicate rates calculated based on concentrations of sulfate *added* to sulfate-depleted sediments. The solid symbol indicates the SR rate calculated for unamended sediment containing a residual sulfate concentration of 5 umol L^{-1}. The solid line is a non-linear least squares regression fit of the data to the equation $R(C) = V_{max}[C/(K_s + C)]$, where R(C) is the rate of SR at sulfate concentration C, V_{max} is the maximum rate of SR, and K_s is the half-saturating sulfate concentration. (B) Wright-Hobbie (1965) plot of $^{35}SO_4^{2-}$ turnover in samples shown in panel A. Inset shows data for the 0—0.03 mmol L^{-1} concentration range. Solid lines are linear least square regression fits of the data.

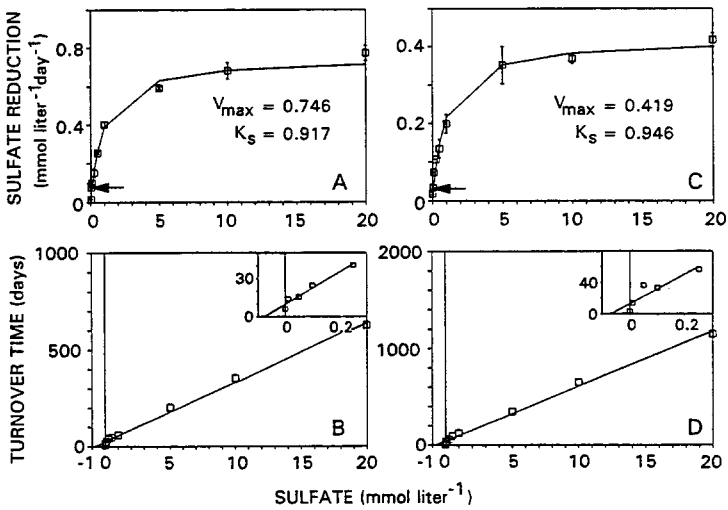

Fig. 4. (A) SR rates in mesohaline Bay sediments, collected from the 0—4 cm depth horizon, at sulfate concentrations of 0.01 to 20 mmol L^{-1}; error bars show 1 standard deviation. (B) Wright-Hobbie (1965) plot of $^{35}SO_4^{2-}$ turnover in samples shown in panel A. (C) SR rates in mesohaline Bay sediments, collected from the 12—16 cm depth horizon, at sulfate concentrations of 0.01 to 20 mmol L^{-1}; error bars show 1 standard deviation. (D) Wright-Hobbie (1965) plot of $^{35}SO_4^{2-}$ turnover in samples shown in panel C. Open symbols in panels A and C indicte rates calculated based on concentrations of sulfate *added* to sulfate-depleted sediments. Arrows in panels A and C indicate SR rates calculated for unamended sediments containing a residual sulfate concentration of 5 umol L^{-1}. Insets in panels B and D show $^{35}SO_4^{2-}$ turnover data for the 0—0.25 mmol L^{-1} concentration range.

internal source of sulfate. Reoxidation of reduced inorganic sulfur is an unlikely explanation because a complete and permanent reduction of $^{35}SO_4^{2-}$ was observed during other experiments with the same sediments (data not shown). Alternatively, mineralization of organic sulfur (e.g. sulfate ester hydrolysis) could have provided a source of sulfate. Although this process could have been occurring, there is no reason to expect that SR rates in excess of those measured at 10—50 μmol added sulfate L^{-1} would occur in unamended sediments. Instead, it is more likely that the measured pool of pore water sulfate did not reflect that which was available for reduction by the SRB.

The rapid uptake of carrier-free $^{35}SO_4^{2-}$ observed in unamended homogenized sediments and at depth in intact cores (Figs. 2 and 3b) indicates that the measured sulfate levels did not represent a 'threshhold' concentration as defined by Ingvorsen et al. (1984), i.e. the sulfate concentration below which no reduction of carrier-free $^{35}SO_4^{2-}$ occurs due to inherent limitations of a microorganism's sulfate uptake system. Other investigators

(Smith & Klug 1981; Kelly & Rudd 1984; Hordijk et al. 1985; Weider & Lang 1988; Bak & Pfennig 1991; Marnette et al. 1992; Urban et al. 1993) have similarly observed rapid reduction of $^{35}SO_4^{2-}$ at depth in lake and wetland sediments where residual sulfate concentrations of 5—20 μM were present. The fact that our carrier-free $^{35}SO_4^{2-}$ solution (and presumably those of other investigators) contained < 1 μM total sulfate implies that the true threshold sulfate concentration in freshwater sediments is much lower than measured residual concentrations. This is not surprising considering that freshwater SRB possess sulfate uptake systems with half-saturation constants on the order of 5 μM, and are capable of decreasing sulfate concentrations to well below 1 μM in washed cell suspensions (Ingvorsen & Jørgensen 1984). Together these findings argue strongly against a limitation of SRB sulfate uptake systems as the explanation for the $\approx$ 5 μM residual sulfate pool found in Chesapeake Bay sediment pore waters. These findings also argue against SRB being outcompeted for electron donors by other bacteria (e.g. methanogens; Lovley & Klug 1986) as the explanation for this substantial residual sulfate pool.

Bak & Pfennig (1991) suggested the possibility that the residual pool of sulfate observed at depth in Lake Constance sediments was present in a complexed form that was unavailable to the SRB. Based on the unlikelihood of other explanations for our results with unamended sediments, we propose that such a pool of microbially unavailable sulfate (possibly associated with dissolved organic matter) was also present in Chesapeake Bay sediment pore waters. Because the size of this sulfate pool (relative to the pool of sulfate that may have been actively turning over) is unknown, we could not specify the SR rate in unamended homogenized sediment samples, or at depth in intact upper Bay core samples. For this reason the latter rates must be considered unreliable, and rates of SR in sulfate-amended homogenized sediments were calculated on the basis of *added* sulfate concentrations.

A maximum SR rate (V_{max}) of 136 μmol L^{-1} d^{-1} and a half-saturating sulfate concentration (K_s) of 42 μmol L^{-1} of whole sediment (34 μM in pore water) were determined from a non-linear least squares regression fit of the rate data in Fig. 3a to a hyperbolic kinetic function. These values are indistinguishable from the V_{max} and ($K_s + S_n$) parameters determined by linear transformation (Wright & Hobbie 1965) of the data (Fig. 3b). Pore water sulfate concentrations in upper Bay sediments ranged from 24—48 μM at 4—6 cm and from 5—10 μM below 6 cm in August (Fig. 1d). Thus, SR was sulfate-limited below the RDB, especially considering that some portion of the measured sulfate pools were likely unavailable to the sulfate-reducing bacteria.

The non-linear fit in Fig. 3a passes through the origin in accordance

with the assumption that the rate of activity approaches zero as the substrate concentration goes to zero. We note, however, that measured SR rates (40—66 μmol L^{-1} d^{-1}) were essentially constant in the 10 to 50 μmol added sulfate L^{-1} range. This result is likely due to experimental error in determining SR rates at very low sulfate concentrations rather than to an independence of SR rate with respect to sulfate in this concentration range. Despite the scatter of the data, the potential for significant rates of SR at added sulfate concentrations as low as 10 μmol L^{-1} was clearly demonstrated.

Diversity in the sulfate affinity of sulfate-reducing bacteria

The estimated K_s for SR in oligohaline Chesapeake Bay sediments is comparable to that determined for lake sediments (66 μM, Smith & Klug 1981; 20—30 μM, Urban et al. 1993), and consistent with the independence of SR rate and sulfate concentration in freshwater sediments having pore water sulfate concentrations greater than 60—100 μM (Ingvorsen et al. 1981; Weider et al. 1990; Bak & Pfennig 1991; this study). In contrast, the upper Bay-sediment K_s value is about 20-fold lower than that determined for mid-salinity Chesapeake Bay sediments (Fig. 4a, c). These findings demonstrate that SRB in low salinity estuarine sediments have considerably greater affinity for sulfate than SRB inhabiting sediments in the more saline region of the estuary. The similarity of K_s values for SR determined in surficial (typically sulfate-rich) and deep (typically sulfate-depleted) mesohaline sediments suggests that selection for SRB with higher sulfate affinity does not occur with depth in these sediments.

Freshwater species of *Desulfovibrio* exhibit lower K_s values than the marine strain, *D. salexigens* (Ingvorsen & Jørgensen 1984). However, the K_s value determined for *D. salexigens* ($\approx$ 80 μM) is several-fold lower than that found for the acetate-oxidizing marine strain *Desulfobacter postgatei* (Ingvorsen et al. 1984), and at least an order of magnitude lower than K_s values determined in experiments with marine and estuarine sediments (Boudreau & Westrich 1984; Ingvorsen & Jørgensen 1984; this study). These observations support the suggestion that populations of SRB with different K_s values coexist in natural sediments (Ingvorsen & Jørgensen 1984). SR kinetic experiments with natural sediments therefore integrate the response of the SRB community.

The range of variation with respect to K_s is important in determining the kinetic response of mixed microbial populations at concentrations in the limiting range (Williams 1973). The model results of Williams (1973) suggest that linear transform (Wright & Hobbie 1965) plots of kinetic data

obtained for mixed populations of organisms having different K_s values should show a break from linearity at concentrations approaching K_s. Our results with upper Bay sediments are suggestive of this effect (Fig. 3d). When only the first four data points (0—30 μmol L^{-1} sulfate range) were used to extrapolate ($K_s + S_n$) (Fig. 3d inset), a value of 7 μmol L^{-1} was obtained. This value is 6 times lower than the ($K_s + S_n$) estimate derived from all the data points.

A similar break in linearity was evident in Wright-Hobbie plots of mesohaline sediment SR kinetic data (Fig. 4b, d). When data from the 0—0.25 mmol L^{-1} sulfate range were used to extrapolate ($K_s + S_n$) for the two experiments (Fig. 4b, d insets), values of 67 and 78 μmol L^{-1} were obtained. These values are an order of magnitude lower than the ($K_s + S_n$) estimates derived from all the data points, as well as the K_s value derived from non-linear regression analysis of the rate vs concentration data (Fig. 4a, c).

The above results indicate that a diversity of SRB with differing K_s values are present in both oligohaline and mesohaline estuarine sediments. Thus, even though the kinetic response of the overall SRB community did not change with depth in mesohaline sediments (Fig. 4a, c), the presence of a diversity of strains allows SR to occur at low sulfate concentration at depth in the sediment. Similarly, the presence of SRB with very high sulfate affinity permits substantial SR rates in oligohaline sediments having sulfate concentrations as low as 10 μmol L^{-1}. It is interesting that the K_s value of $\approx$ 70 μmol L^{-1} for 'high sulfate affinity' mesohaline SRB is still $\approx$ 2-fold higher than that for the overall SRB community in oligohaline sediment, suggesting that a community-wide selection for increased sulfate affinity occurs in oligohaline estuarine sediments.

Sulfate flux and sulfur recycling

Time course assays of $^{35}SO_4^{2-}$ reduction in intact cores (Fig. 2) suggested that the end products of SR were subject to oxidation on a time scale of hours. If such rapid sulfur recycling occurs *in situ*, the net flux of sulfate into the sediment must be less than the gross rate of SR. To test this hypothesis, we estimated sulfate flux into subcores obtained from the same box cores (collected in August) subsampled for $^{35}SO_4^{2-}$ reduction measurements. Although sulfate depletion from overlying waters was predicted based on SR reduction rates, measured sulfate concentrations failed to decrease over a 30-hr incubation period (Fig. 5). At the end of the incubations, pore water sulfate concentration profiles were similar to the one measured in the field at the time of sampling (Fig. 1a), indicating that the

sulfate pool remained in an approximately steady state during the incubation interval.

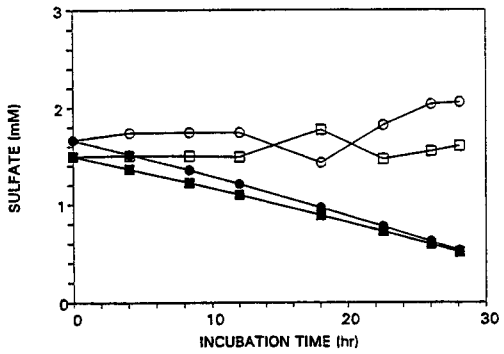

Fig. 5. Measured and predicted sulfate concentrations in water overlying upper Bay cores collected in August. Open symbols: sulfate concentrations measured in water overlying 7.3 cm ID cores incubated in the laboratory for ≈ 30 hours prior to sectioning. Closed symbols: overlying water sulfate concentrations predicted from the average areal SR rate measured in the upper 6 cm of parallel cores (Table 4). The predictions accounted for the volume of overlying water (2 ml) removed at each sampling interval.

An average of 86 ± 12% of total area SR occurred within the upper 6 cm of sediment in August; sulfur cycling thus took place mainly in the upper 6 cm. The average short-term SR rate in this layer exceeded the estimated diffusive flux of sulfate across the sediment-water interface by nearly an order of magnitude (Table 4). This discrepancy cannot be explained by enhanced sulfate transport into the sediment, because overlying water sulfate concentrations remained constant during intact core incubations (Fig. 5). Neither can it be attributed to a change of sediment pore water sulfate concentration, because concentration profiles in the incubated cores were similar to the profile measured at the time of sampling (Fig. 1a). Therefore, an internal source of sulfate and/or rapid sulfur recycling is implicated. If AVS oxidation were the source of sulfate, turnover of < 3% of the total AVS pool per day (Table 4) would have been required to resupply the sulfate consumed by SR. Alternatively, the sulfate pool may have been resupplied by oxidation of a relatively small pool of reduced sulfur that turned over on a time scale of hours. Sulfur recycling may be associated with sediment particle surfaces, where sulfide could be directly exposed to manganese oxides and lithotrophic bacteria, which are required to catalyze oxidation of sulfide to sulfate in anoxic sediments (Aller & Rude 1988).

Table 4. Inorganic sulfur pool sizes and turnover rates in upper Bay sediments (0—6 cm) during August. Numbers in parentheses are the number of cores analyzed; S.D. refers to standard deviation of the mean. Sulfate reduction cores were incubated for 0.85—2.4 hr.

	Pool size				Turnover constant	
	SO_4^{2-}	AVS	Diffusive SO_4^{2-} flux	SO_4^{2-} reduction	[1]SO_4^{2-}	[2]AVS
	(mmol m^{-2})		(mmol m^{-2} d^{-1})		(day^{-1})	
Mean:	30.0	566	1.98	14.8	0.49	0.026
S.D.:	5.7 (3)	392 (3)	0.20 (3)	4.3 (3)		

[1] SO_4^{2-} reduction rate × SO_4^{2-} pool $size^{-1}$.
[2] SO_4^{2-} reduction rate × AVS pool $size^{-1}$.

We evaluated the importance of sulfur recycling above and below the RDB on the time scale of a few days by following $^{35}SO_4^{2-}$ diffusion downward into 2.5-cm ID core segments from the 0—4 and 5—9 cm sediment horizons. About 90% of added radiolabel, virtually all as $^{35}SO_4^{2-}$, was recovered from molybdate amended cores from both sediment horizons. The amount of added $^{35}SO_4^{2-}$ radioactivity recovered as sulfate from unamended cores was 19 and 55% lower than from molybdate amended cores for the 0—4 and 5—9 cm intervals, respectively. Only 20% of the 'missing' $^{35}SO_4^{2-}$ in the 0—4 cm segment could be accounted for by $AV^{35}S$ accumulation. The remainder of the missing radiolabel was assumed to be partitioned into a NAVS or organic S pool.

The 5—9 core segments consisted entirely of black sediment from below the RDB. $AV^{35}S$ accounted for 62% of total $^{35}SO_4^{2-}$ reduced in the unamended core, 2.5 times greater than observed in the 0—4 cm segment. Estimates of SR in intact cores indicated that $^{35}SO_4^{2-}$ reduction below the RDB was sufficiently rapid to cause complete reduction of the added label within the 5 to 6 cm interval in less than 12 hr. In contrast, only 55% of added $^{35}SO_4^{2-}$ was reduced in the unamended core, and $^{35}SO_4^{2-}$ penetrated well below 2 cm into the sediment over the 3-day incubation (Fig. 6c).

Profiles of $^{35}SO_4^{2-}$ in molybdate inhibited cores (Fig. 6a, c) yielded sulfate diffusion coefficients of 0.42 and 0.34 cm^2 d^{-1} for the 0—4 and 5—9 cm intervals, respectively. These values were employed in transient state models of $^{35}SO_4^{2-}$ diffusion and reduction in which $^{35}SO_4^{2-}$ reduction was assumed to occur according to the average $^{35}SO_4^{2-}$ turnover constant profile (Fig. 6d, inset). Formulation of the 0—4 cm sediment horizon model is given in the Appendix. A similar model (not shown) was used for the 5—9 cm horizon. The lower boundary condition in both models assumed a zero $^{35}SO_4^{2-}$ gradient at depth (Fig. 6a, c). For the 0—4 cm

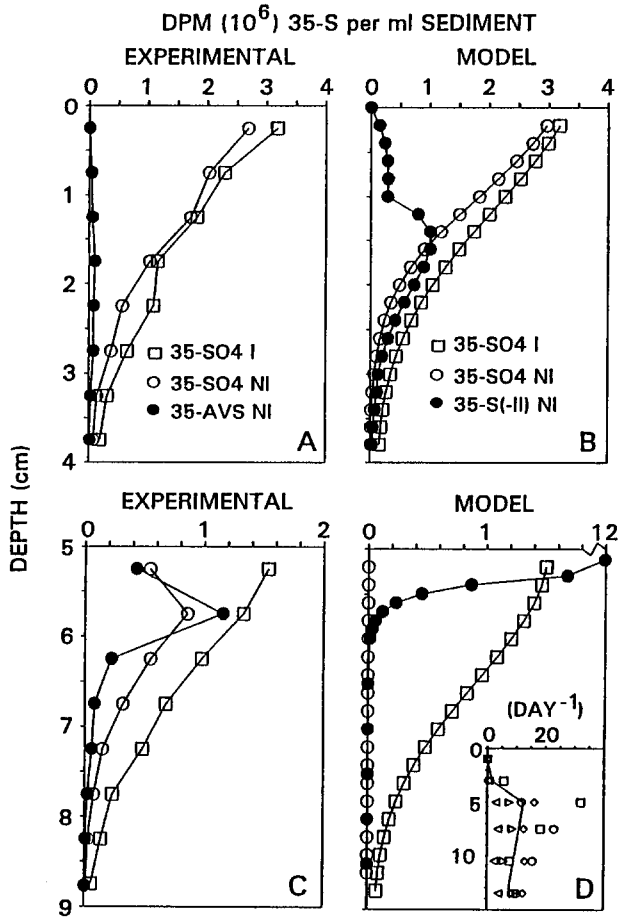

Fig. 6. Measured and model-predicted depth distributions of $^{35}SO_4^{2-}$ (35-SO4) and reduced ^{35}S (35-AVS, 35-S(-II)) in the 0—4 cm (A, B) and 5—9 (C, D) sections of upper Bay sediment cores at the end of the $^{35}SO_4^{2-}$ diffusion/reduction experiment. The abbreviation I refers to molybdate inhibited cores; NI refers to uninhibited cores. Model formulation is given in the Appendix and discussed in the text. Inset in panel D shows $^{35}SO_4^{2-}$ turnover constants as a function of depth in intact upper Bay cores collected in August (solid line represents the fit of the data used in the diffusion/reduction models; the $^{35}SO_4^{2-}$ turnover constant between 0 and 1 cm was assumed equal to the average value measured at 1 cm (0.022 day^{-1})).

model, we adopted a surface boundary condition depicting balance between overlying water $^{35}SO_4^{2-}$ concentration change and diffusive exchange with the sediment. For the 5—9 cm model, we assumed a zero $^{35}SO_4^{2-}$ gradient at the stoppered surface of the core. The matrix expressions in the

Appendix were solved at each time step by multiplying the inverse of coefficient matrix **A** (obtained by a modified Gauss-Jordan algorithm) by the right side of each equation.

The 0—4 cm model predicted 30% greater consumption of $^{35}SO_4^{2-}$ (29.6% of total ^{35}S) than was observed in the unamended experimental core (19.4%). A depth-independent, first order ^{35}S(-II) oxidation constant (k) of $\approx$ 0.8 d^{-1} was incorporated into the model in order to obtain agreement between predicted and observed inventories of $^{35}SO_4^{2-}$ at the end of the incubation period. The magnitude of this oxidation constant is comparable to the average turnover time of the sulfate pool in the top 6 cm (Table 4). The 5—9 cm model (without ^{35}S(-II) oxidation) predicted complete consumption of $^{35}SO_4$ within the topmost cm of the unamended core segment (Fig. 6d). A ^{35}S(-II) oxidation constant of $\approx$ 10 d^{-1} was required to give approximate agreement with the observed $^{35}SO_4^{2-}$ profile and depth-integrated $^{35}SO_4^{2-}$ inventory. This is within the range of *in situ* $^{35}SO_4^{2-}$ turnover constants measured at $\geqslant$ 5 cm depth (Fig. 6d, inset), a result which parallels that found above the RDB except that the time scale of sulfur turnover is an order of magnitude shorter below the RDB.

Because the diffusion/reduction experiments were not repeated with replicate cores, we cannot comment on the variability of $^{35}SO_4^{2-}$ diffusion and ^{35}S(-II) oxidation rate estimates. However, the similarity in estimated time scales of reduced sulfur production and oxidation is indicative of tight coupling between these two processes in oligohaline sediments. Although the quantitative nature of this coupling remains to be defined rigorously, it appears to take place on the order of a day or less. Steady state diffusion-reaction models (based on measured sulfate concentrations and reduction rates) show that without rapid sulfide oxidation (i.e. sulfate regeneration), sulfate would be totally depleted within the upper 1 cm of sediment (data not shown). This result is attributable to the relatively high rates of SR observed even within the brown surface layer. Thus, rapid sulfide oxidation appears to be fundamental in permitting high rates of SR in these sediments. Similar conclusions have been drawn from measurements of sulfate distributions and SR rates in freshwater lake (Bak & Pfennig 1991; Urban 1993; Urban et al. 1993) and peatland sediments (Marnette et al. 1992; Weider et al. 1990).

Although the cores used for our rate and flux measurements were not subject to the direct influence of bioturbation by *Rangia* or other macrofauna, the burrowing and/or respiratory activity of such organisms in the upper 5—10 cm of sediment is probably important in maintaining conditions favorable for sulfide oxidation beneath the sediment surface. In particular, bioturbation may be responsible for renewal of sediment

particle coatings of metal oxides, which can in turn serve as electron acceptors for sulfide oxidation in the absence of oxygen. Bioturbation could also increase sulfate *input* to the sediment by enhancing solute exchange across the sediment-water interface (Aller 1980; Emerson et al. 1984). However, because this was not a factor in our experiments, our results demonstrate the importance of sulfide oxidation as a mechanism for sulfate replenishment.

Inorganic reduced sulfur concentrations

AVS concentrations in upper Bay sediment cores (the same cores used for SR rate measurements) increased across the RDB and remained relatively constant below it (Fig. 7a). NAVS concentrations were several-fold higher than AVS concentrations in the top few cm, but increased only slightly with depth in the upper 6 cm, suggesting that most NAVS formation takes place near the sediment surface. The fraction of reduced ^{35}S recovered as NAVS was maximal (35—85%) in the topmost 2 cm of sediment collected in August 1988, and averaged $\approx$ 25% between 2 and 10 cm depth (data not shown). Below 10 cm, an average of less than 10% of reduced ^{35}S was recovered as NAVS. The partitioning of a large portion of reduced ^{35}S into NAVS in the upper few cm of sediment in whole core injection and in $^{35}SO_4^{2-}$ diffusion/reduction experiments is consistent with the suggestion

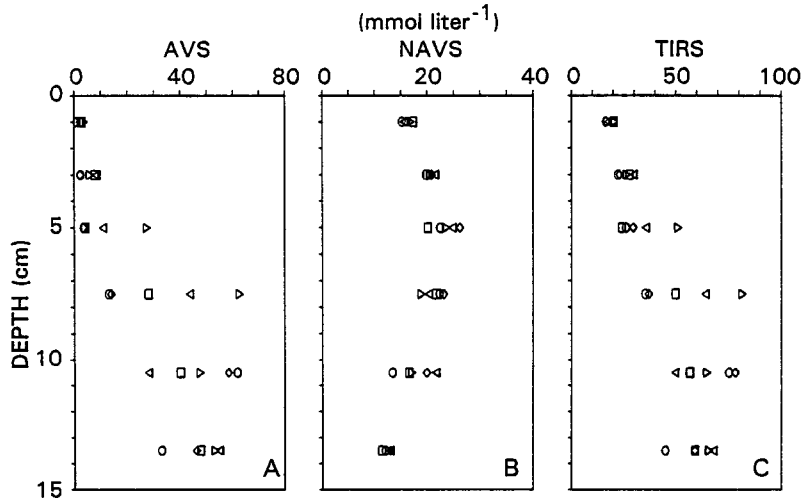

Fig. 7. Whole sediment concentrations of AVS, NAVS and total inorganic reduced sulfur (TIRS) measured in upper Bay cores collected in August. The different symbols represent individual cores used for $^{35}SO_4^{2-}$ reduction measurements.

that pyrite and/or elemental sulfur formation dominates inorganic reduced sulfur accumulation within this interval.

Whole sediment concentrations of total inorganic reduced sulfur at depth (Fig. 7c) were only 2—3 fold lower than typically observed in sediments from the mid-Bay region, where bottom water sulfate concentrations are at least an order of magnitude higher (Roden & Tuttle 1993). On a dry weight basis, however, the inorganic reduced sulfur content of upper Bay sediments (0.2—0.4%) was 5—10 fold lower than that of mid-Bay sediments. The low dry weight reduced sulfur content of upper Bay compared to mid-Bay sediments may be attributable to the relatively coarse nature of upper Bay sediments ($>$ 50% silt and sand; Hill 1988), whereas most of the reactive iron in aquatic sediments is associated with clay size ($<$ 2 μm) particles (Shultze 1988), which comprise $\geqslant$ 70% of sediments in much of the mid-Bay region (Hill 1988).

Martens & Goldhaber (1974) measured significant quantities (0.5—1.2% dry weight) of solid-phase inorganic reduced sulfur in sediments from the freshwater region of the White Oak River estuary, North Carolina. They suggested that the formation of this material had taken place sometime in the past, when there was greater penetration of seawater into the estuary, and therefore greater sulfate availability. Our results suggest an alternative explanation, i.e. that rapid SR at low ambient sulfate concentration ($\leqslant$ 1 mM) can account for the accumulation of substantial reduced sulfur in low salinity estuarine sediments. Such high rates of SR at low sulfate concentration are permitted by the presence of SRB with a relatively high affinity for sulfate, and by sulfide oxidation processes that replenish the pore water sulfate pool on a time scale of hours.

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Appendix

Formulation of a transient state model of $^{35}SO_4^{2-}$ diffusion and reduction in the 0—4 cm layer of upper Bay sediment cores.

$C(x, t) = {}^{35}SO_4^{2-}$ concentration; $S(x, t) = {}^{35}S(-II)$ concentration (DPM cm^{-3})

Model equations (x = h to z):

Overlying water: $\delta C(x, t)/\delta t = [D_s \delta C(x, t)/\delta x]/h$

Sediment: without $^{35}SO_4^{2-}$ reduction: $\delta C(x, t)/\delta t = D_s \delta^2 C(x, t)/\delta x^2$

with $^{35}SO_4^{2-}$ reduction: $\delta C(x, t)/\delta t = D_s \delta^2 C(x, t)/\delta x^2 - k(x)\, C(x, t)$

$\delta S(x, t)/\delta t = k(x)\, C(x, t)$

where: h = overlying water height (1 cm)

z = lower boundary depth in the sediment (4 cm)

$D_s = {}^{35}SO_4^{2-}$ diffusion coefficient (0.42 $cm^2\ d^{-1}$)

$k(x) = {}^{35}SO_4^{2-}$ reduction rate constant at depth x (d^{-1})

Numerical Approximations: $\delta C(x, t)/\delta t \cong [C(x_i, t_{j+1}) - C(x_i, t_j)]/dt$

$\delta C(x, t)/\delta x \cong [C(x_{i+1}, t_{j+1}) - C(x_i, t_{j+1})]/dx$

$\delta^2 C(x, t)/\delta x^2 \cong [C(x_{i+1}, t_{j+1}) - 2C(x_i, t_{j+1}) + C(x_{i-1}, t_{j+1})]/(dx)^2$

where: dt = time increment (0.02 d)

dx = depth increment (0.1 cm)

Boundary Conditions: $x = 0$: $[C(0, t_{j+1}) - C(0, t_j)]/dt$

$- D_s [C(dx, t_{j+1}) - C(0, t_{j+1})]/(hdx) = 0$

$x = z$: $[C(z, t_{j+1}) - C(z - dx, t_{j+1})]/dx = 0$

Simultaneous Equations:

$x = 0$: $(1 + b_1)\, C(0, t_{j+1}) - b_1 C(dx, t_{j+1}) = C(0, t_j)$

$x = dx$ to $(z - dx)$: $-D_s b_2 C(x_{i-1}, t_{j+1}) + (1 + 2D_s b_2) C(x_i, t_{j+1}) - D_s b_2 C(x_{i+1}, t_{j+1})$

$= C(x_i, t_j)$ (without $^{35}SO_4^{2-}$ reduction)

$= C(x_i, t_j) - k(x_i) C(x_i, t_j) dt$ (with $^{35}SO_4^{2-}$ reduction)

$x = z$: $C(z, t_{j+1}) - C(z - dx, t_{j+1}) = 0$

where: $b_1 = D_s dt/(hdx)$

$b_2 = dt/(dx)^2$

Matrix expressions: $\mathbf{A}\mathbf{C}_{j+1} = \mathbf{C}_j$ (without $^{35}SO_4^{2-}$ reduction)

$\mathbf{A}\mathbf{C}_{j+1} = (\mathbf{C}_j - \mathbf{k}\mathbf{C}_j dt)$ (with $^{35}SO_4^{2-}$ reduction)

$\mathbf{S}_{j+1} = \mathbf{S}_j + \mathbf{k}\mathbf{C}_j dt$

where: $\mathbf{C}_{j+1}$ = vector of $C(x_i, t_{j+1})$ values

$\mathbf{C}_j$ = vector of $C(x_i, t_j)$ values

$\mathbf{S}_{j+1}$ = vector of $S(x_i, t_{j+1})$ values

$\mathbf{S}_j$ = vector of $S(x_i, t_j)$ values

$\mathbf{k}$ = vector of $^{35}SO_4^{2-}$ reduction rate constants ($k(x_i)$)

dt = scalar

$\mathbf{A}$ = coefficient matrix

with $\mathbf{A}(1, 1) = (1 + b_1)$; $\mathbf{A}(1, 2) = -b_1$

$\mathbf{A}(n, n) = 1$; $\mathbf{A}(n, n - 1) = 1$

for $i = 2$ to $n - 1$, $\mathbf{A}(i, j - 1) = \mathbf{A}(i, j + 1) = -D_s b_2$

$\mathbf{A}(i, j) = 1 + 2D_s b_2$

all other elements of $\mathbf{A} = 0$

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