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Sulfate reduction and sediment metabolism in Tomales Bay, California

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Abstract. Sulfate reduction rates (SRR) in subtidal sediments of Tomales Bay, California, were variable by sediment type, season and depth. Higher rates were measured in near-surface muds during summer (up to 45 nmol cm^{-3} h^{-1}), with lower rates in sandy sediments, in winter and deeper in the sediment. Calculations of annual, average SRR throughout the upper 20 cm of muddy subtidal sediments (about 30 mmol S m^{-2} d^{-1}) were much larger than previously reported net estimates of SRR derived from both benthic alkalinity flux measurements and bay wide, budget stoichiometry (3.5 and 2.6 mmol m^{-2} d^{-1}, respectively), indicating that most reduced sulfur in these upper, well-mixed sediments is re-oxidized. A portion of the net alkalinity flux across the sediment surface may be derived from sulfate reduction in deeper sediments, estimated from sulfate depletion profiles at 1.5 mmol m^{-2} d^{-1}. A small net flux of CO_2 measured in benthic chambers despite a large SRR suggests that sediment sinks for CO_2 must also exist (e.g., benthic microalgae).

Introduction

Sulfate reduction (SR) on average accounts for at least half of the total carbon respiration in organic-rich sediments of coastal embayments and estuaries, and is the dominant anaerobic pathway (Jørgensen 1982; Canfield 1989b). In these anoxic environments, rates of sediment deposition and organic matter mineralization are typically high (Berner 1978, 1989; Canfield 1991), and H_2S and by-products of SR (iron monosulfides, pyrite) are formed (Goldhaber et al. 1977; Howarth & Jørgensen 1984; Chanton et al. 1987; Thode-Andersen & Jørgensen 1989). Because of re-oxidation, however, reduced sulfur compounds accumulate in shallow sediments at much slower rates than H_2S is produced (Howarth 1984).

Sulfate reduction rates (SRR) in estuaries have been measured almost exclusively in the upper 30 cm of sediments (Skyring 1987; Jørgensen et al. 1990), where relative to deeper sediments the amounts of sulfate and labile organic matter are high (Westrich & Berner 1984; Boudreau 1991; Burdige 1991; Hansen & Blackburn 1992). SR in deeper sediments is limited by low concentrations of both suitable organic substrates and the terminal electron acceptor. However, in regions characterized by lower sedimentation rates, e.g., continental shelf and some estuarine environments, sulfate reduction rates are lower and thus sulfate may extend over several meters (Goldhaber & Kaplan 1975; Canfield 1989b; Jørgensen et al. 1990).

Tomales Bay, California, is a shallow estuary where rates of sediment deposition are high, 1–2 cm y^{-1} (Snidvongs et al. submitted). Since a positive correlation exists between sedimentation and sulfate reduction rates (Berner 1989; Canfield 1989b), we would also expect high SRR in the sediments. Using results from benthic flux chambers and stoichiometric arguments, Dollar et al. (1991) estimated that carbon metabolism by sulfate reduction represented about one-third of total benthic metabolism, and thus SR was a significant component of total respiration of Tomales Bay (see also Smith et al. 1991). Unlike many of the estuaries that have been studied, however, free sulfides or distinct zones of concentrated iron monosulfide deposition have rarely been detected in subtidal sediments of Tomales Bay (Chambers pers. obs.). If net SRR predicted from benthic flux measurements and budget stoichiometry are realistic (Dollar et al. 1991; Smith et al. 1991), then physical resuspension and bioturbation of sediments must supply O_2 to re-oxidize a large portion of sulfides and sulfide minerals produced in these anaerobic sediments. As a result of extensive sediment mixing, the depth to which SR contributes to net biogeochemical fluxes measured at the sediment-water interface could be substantial (Jørgensen et al. 1990).

The objective of the present study was to determine rates of sulfate reduction in subtidal sediments of Tomales Bay, California. We compared SR in short cores by season and sediment type, and calculated integrated SRR 1) in the upper sediments where sulfate was not depleted (< 20 cm), and 2) in the deeper zone of sulfate depletion (below 30 cm). To determine the extent of sulfide re-oxidation, SRR measurements were then compared with rates of net SR and carbon metabolism predicted from benthic flux measurements and budget stoichiometry (Dollar et al. 1991), and with the observed distribution of reduced sulfur compounds.

Methods

Site description

Tomales Bay is one of five estuaries in the Land Margin Ecological Research (LMER) program, initiated to determine the role of bays and estuaries in nutrient exchange between land and ocean. The estuary, located about 40 km north of San Francisco, California, is long and narrow; it is formed at the coastal juncture of the North American and Pacific tectonic plates (Fig. 1). Average water depth is about 3 meters. Two subtidal sedimentary environments are distinguished by relative location and sediment source: 1) the outer

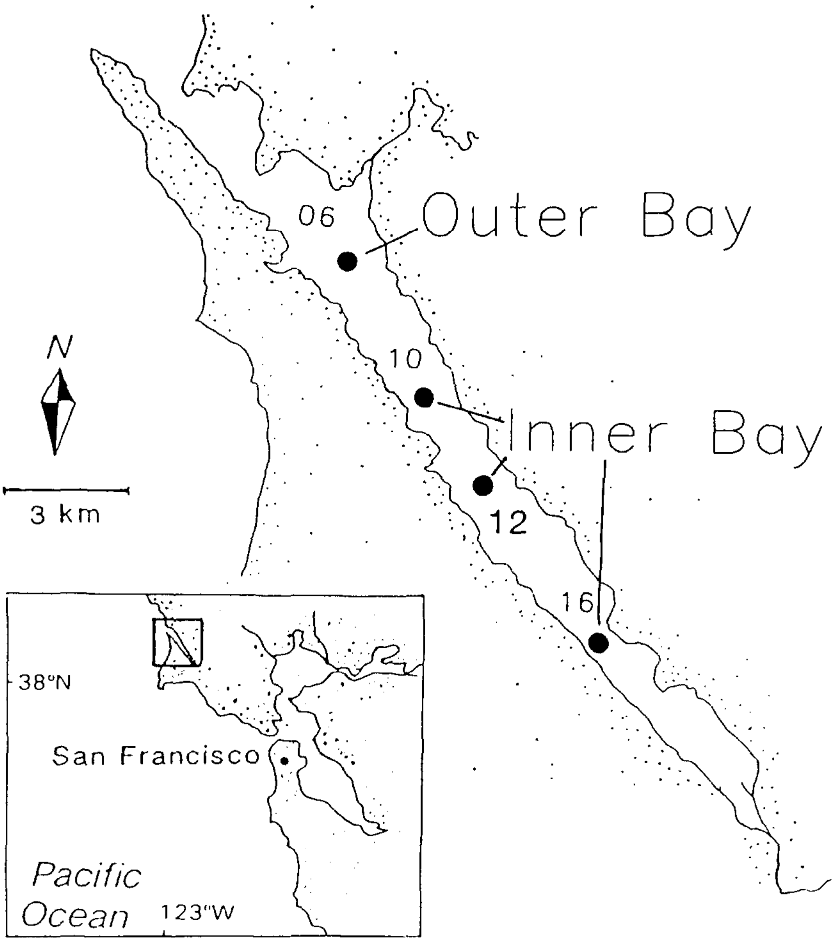

Fig. 1. Tomales Bay site map, showing location of inner bay (Stns 10, 12, 16) and outer bay (Stn 06) sampling stations.

bay, where sandy sediments are deposited by coastal ocean currents; 2) the inner bay, where muddy silts are eroded, transported and deposited from the surrounding watershed. Because of the local Mediterranean-type climate, Tomales Bay receives freshwater runoff during the November–March rainy season, although 6 years of extended drought occurred from 1987–1992. Average surface water temperatures in Tomales Bay fluctuate annually from 8 to 20 degrees (Smith et al. 1987)

Inorganic sulfur profiles

Using a 4-inch diameter piston corer (Sansone et al. submitted), sediment cores were collected by divers from an outer bay site (Stn 06) in March and

September 1991, and from two inner bay sites (Stns 12, 16) in March 1993 (Fig. 1). All cores were capped immediately and transported to the field laboratory for processing. Sets of horizontal sub-cores were removed at selected depths from the sediment cores for physical and chemical analyses. One set was used for determining the bulk properties of the sediments. A known volume of sediment was weighed wet, after drying at 80 °C and after ashing for 6 hours at 450 °C for determinations of porosity, dry bulk density, and ash-free dry weight.

Porewater was extracted from a second set of sub-cores by centrifugation or sediment squeezing, then frozen for transport to the University of Hawaii laboratory. Analysis of porewater for dissolved sulfate was completed using ion chromatography. Concentrations of free sulfides in porewater extracted by sediment squeezing under a nitrogen atmosphere were undetectable either by smell or by immediate chemical analysis (Cline 1969) (Chambers pers. obs.).

A third set of collected sediment sub-cores was capped with butyl rubber stoppers to exclude oxygen, then frozen and transported to the Tiburon Center laboratory. Inorganic sulfur determinations were completed using sequential extractions for acid-volatile sulfur (AVS: free sulfides, iron monosulfides) and chromium-reducible sulfur (CRS: elemental sulfur and pyrite). One mL of sediment was placed in a nitrogen-purged reaction vessel, and 15 mL of 1 N HCl was added. Hydrogen sulfide liberated at room temperature (AVS fraction, Cornwell & Morse 1987) was collected by running the gas train through vials containing 5 mL 0.2 N NaOH (Herlihy et al. 1988; Elsgaard & Jørgensen 1992). After 1 hour, the vials were replaced, then 10 mL concentrated HCl and 15 mL 1 N reduced chromium solution, specific for extraction of inorganic sulfur compounds (Canfield et al. 1986) were added to the reaction vessel. Reactants were heated to boiling for 1 hour, and liberated sulfides were trapped in collection vials. AVS and CRS concentrations were determined spectrophotometrically (Cline 1969) against prepared sulfide standards (Hines et al. 1989). Organic sulfur is not extracted with these methods (Canfield et al. 1986).

Sulfate reduction rates in shallow sediments

To determine seasonal rates of sulfate reduction in shallow sediments, cores up to 20 cm long were collected at inner (Stns 10, 16) and outer (Stn 06) bay locations every two months between March 1991 and January 1992 (Fig. 1). Depth-specific sulfate reduction rates (SRR) were determined using ^{35}S-labelled sulfate as a tracer (Jørgensen 1978). Open-end, 5-mL glass syringes served as subcorers and sediment incubation tubes. Intact subcores, usually in replicate, were collected at 3–4 cm depth intervals and injected with a solution of $Na_2{}^{35}SO_4$ (carrier-free, approximately 1 μCi in 10 μL solution), using a long needle to distribute the label evenly along the central axis of the core. Following injection, the cores were capped with butyl rubber stoppers and incubated at the ambient sediment temperature for 24 hours, a period of time over which incorporation was linear (see below).

Incubation was terminated by freezing. Inorganic sulfur compounds (dissolved sulfides, sulfide minerals, elemental sulfur) were then extracted using a single-step chromium reduction procedure (Fossing & Jørgensen 1989). An N_2 stream was used to flush H_2S into 0.2N NaOH traps which were then counted. Sulfate reduction rates were calculated as a rate of label incorporation relative to the amounts injected, multiplied by the porewater concentration of sulfate (Fossing & Jørgensen 1989).

Initial tests of injection and extraction methodologies were completed with well-mixed sediments, stirred with a plastic spatula to decrease heterogeneity among test groups. We compared sulfate reduction rates in triplicate subsamples of mixed sediments for which label was injected in ambient air, or in N_2-filled glove bags; we also compared SRR measurements using two-step or single-step sulfide extraction techniques (Fossing & Jørgensen 1989). Although the two-step extraction method yielded higher average SRR (1.04 ± 0.62 vs 0.52 ± 0.20 nmol cm^{-3} h^{-1}), there were no statistically significant differences among injection or extraction techniques (2-way ANOVA, $p > 0.05$). On the basis of smallest variance among replicates and ease of processing, we chose to 1) inject samples under ambient atmospheric conditions, and 2) extract inorganic sulfur using the single-step method.

To determine an appropriate incubation time, replicate samples of well-mixed sediment were injected with $Na_2{}^{35}SO_4$ and incubated for periods of 0, 1, 2, 4, 8, 16, and 24 h. At time 0 very little label was incorporated into the sulfide pool, and average label incorporation over the entire 24 h was essentially linear (Fig. 2). Subsequent sediment subcores were therefore

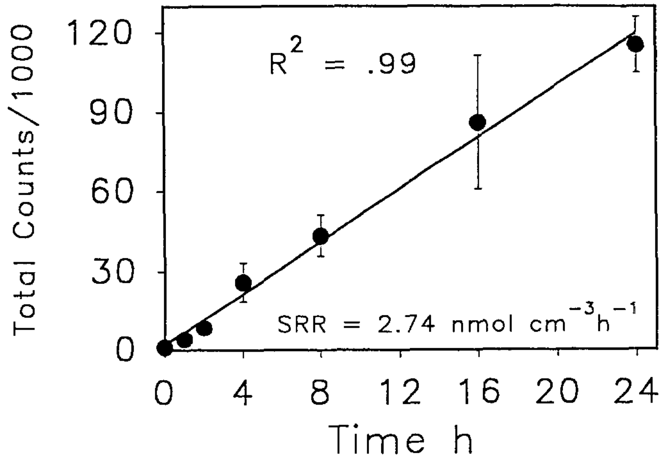

Fig. 2. Time-course incorporation of ^{35}S by sulfate reduction. Mixed sediments were injected with label and incubated up to 24 hours. Inorganic sulfur extractions were completed using a one-step method, after Fossing & Jørgensen (1990). The regression of label incorporation vs time was determined using the replicate averages (± SE, $N = 2$) at each incubation time.

injected and incubated for 24 h before freezing. Throughout the year of sampling, the incorporation of ^{35}S in time 0 controls was consistently as low as experimental blanks, obtained by direct injection of ^{35}S-labelled sulfate into the single-step extraction procedure.

Sulfate reduction in deep sediments

Two long sediment cores to 300 cm were collected at inner bay sites (Stns 12, 16) to obtain complete profiles of sulfate reduction below the bioturbated zone, estimated to be 30–50 cm (see Fig. 3; discussion). Long cores from sandy sediments at the outer bay site (Stn 06) could not be collected because of an impenetrable shell layer at ≈ 35 cm.

Three different methods were used to calculate SRR below the bioturbated zone. First, the linear range of sulfate depletion below 30 cm was used to estimate net SRR (after Canfield 1991):

$$\text{Rate} = \phi D_s \frac{dC}{dx} + \phi_{\text{upper}}\, w\, C_{\text{upper}} - \phi_{\text{lower}}\, w\, C_{\text{lower}}$$

where ϕ is the depth-averaged porosity, D_s is an estimate of diffusivity which takes into account tortuosity (Berner 1980 after Li & Gregory 1974), dC/dx is the sulfate concentration gradient in the zone of sulfate depletion, ϕ_{upper}, C_{upper} and ϕ_{lower}, C_{lower} are the porosities and sulfate concentrations at the upper

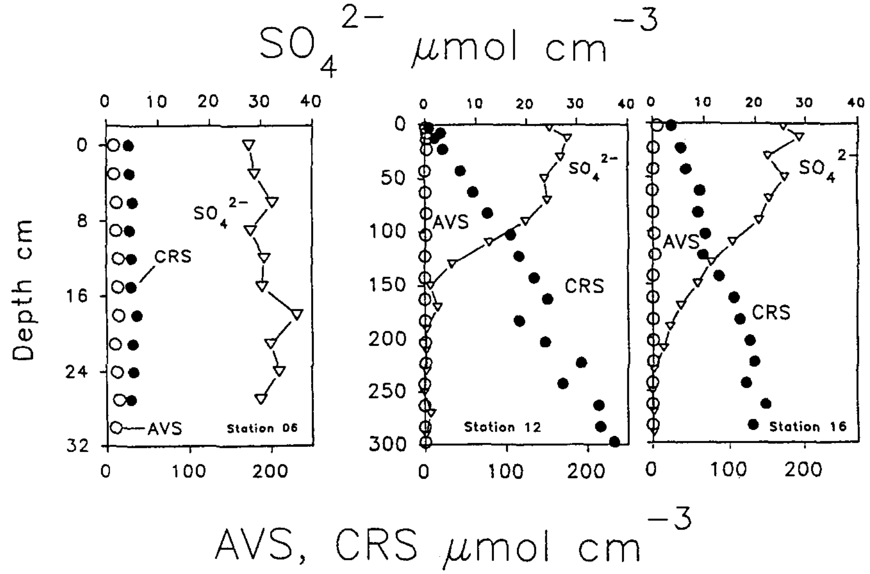

Fig. 3. Average (± SE) acid-volatile sulfide (AVS) and chromium-reducible sulfide (CRS) profiles from outer bay (Stn 06), and inner bay (Stns 12, 16) sediments. Note difference in vertical scale. Dissolved sulfate concentrations were determined from porewater samples; sulfide concentrations were determined from sediment + porewater samples.

and lower boundaries of sulfate depletion, respectively, and w is the sedimentation rate. Second, the profile of extracted inorganic sulfur accumulated in the zone of sulfate depletion was used to calculate a rate of burial of sulfides with depth (and, by proxy, time), under the assumption that all reduced sulfur produced was preserved in dissolved sulfide and inorganic minerals. Finally, using the methodology described above, depth-specific sulfate reduction rates were determined in sediment subcores at 20 cm intervals the entire length of the cores (single measurements at each depth), then integrated through the zone of sulfate depletion to calculate a daily rate of gross sulfate reduction.

Results

Inorganic sulfur profiles

Profiles of inorganic sulfur from outer bay sediments (Stn 06) varied only slightly and exhibited no major trends by depth (Fig. 3) The AVS fractions contributed less than 5 percent to the total inorganic sulfur at this site, averaging less than 1 μmol cm^{-3}. Sulfate was not depleted with depth into the sediment, and the CRS fraction was relatively constant, between 10–15 μmol cm^{-3}. Similarly, the AVS pool in inner bay sediments (Stns 12, 16) was very small relative to the CRS pool (Fig. 3). Chromium-reducible sulfides generally increased from 5 μmol cm^{-3} at the surface to over 150 μmol cm^{-3} at 300 cm. Sulfate concentrations in porewater varied between 20 and 30 μmol cm^{-3} in the upper 50 cm of sediment, and were depleted in deeper sediments to 150–250 cm.

Sulfate reduction in shallow sediments

Sulfate reduction rates measured in Tomales Bay were highly variable in both outer and inner bay sediments (Fig. 4). No consistent patterns of sulfate reduction by depth were obvious in shallow sediments from the outer bay, and annually the depth-specific rates varied between 0 and 12 nmol cm^{-3} h^{-1}. The highest rates of SR in these sediments were measured in March and September 1991. For all other months the measured rates of sulfate reduction were < 5 nmol cm^{-3} h^{-1}. Similarly, SRR measured in the upper 20 cm of sediments from the inner bay were typically < 5 nmol cm^{-3} h^{-1} and exhibited a general trend of decreasing rate with depth (Fig. 4). Rates in July 1991, however, were much higher than in any other month, up to 45 nmol cm^{-3} h^{-1} near the sediment surface and decreasing to 9.6 nmol cm^{-3} h^{-1} at 18 cm. Measured rates in September were lower than in July, but still higher than those measured during other times of the year (Fig. 4).

Depth-specific rate measurements were used to calculate seasonal, depth-integrated rates of sulfate reduction through the upper 20 cm of sediment (Table 1). The annual average rate of sulfate reduction (six dates, March 1991

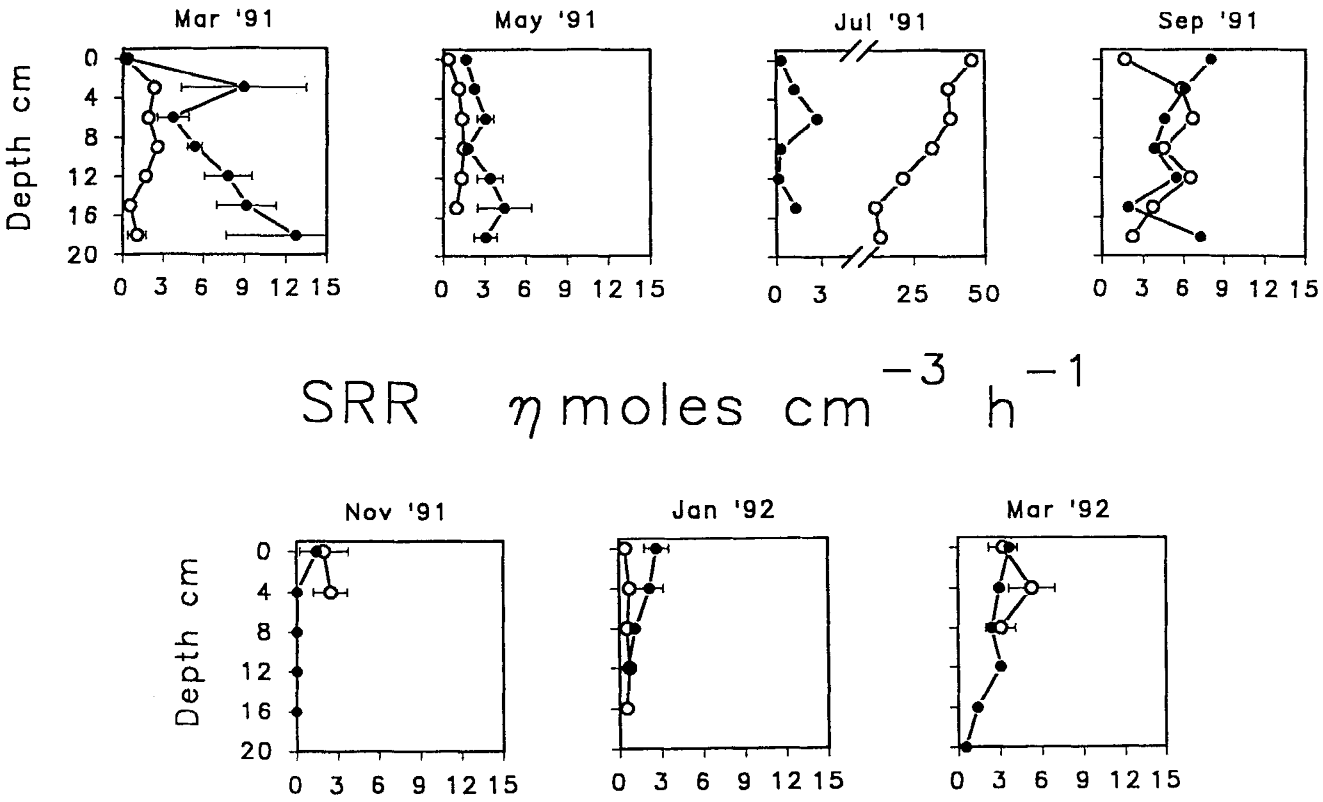

Fig. 4. Profiles of sulfate reduction rates in outer bay (●) and inner bay (○) sediments. Each point represents the mean of 2 or 3 samples ± SE, except during March, July and September, 1991, when single cores were measured.

Table 1. Seasonal, depth-integrated rates of sulfate reduction (SRR), in mmol m^{-2} d^{-1}, from inner (Stations 10, 16) and outer (Station 06) regions of Tomales Bay, California. Twenty-centimeter integrated averages were calculated directly from measured SRR profiles (± SE).

Site	Mar 91	May	July	Sept	Nov	Jan 92	Annual mean
Outer Bay, Station 06:	33	13.5	4.9	25.5	1.6	7.9	14.4
Upper 20 cm	(10.3)	(3.3)	(1.8)	(3.5)	(1.0)	(2.9)	(3.8)
Inner Bay, Stations 10, 16 averaged:	7.7	5.2	136	21.3	10.8	2.8	30.6
Upper 20 cm	(0.8)	(0.7)	(22)	(3.4)	(7.1)	(0.6)	(5.8)

through January 1992) was 30.6 mmol S m^{-2} d^{-1} from inner bay sediments, and 14.4 mmol S m^{-2} d^{-1} from outer bay sediments. Inclusion of the high rates measured from a single core in July from the inner bay tripled the estimated annual rate; the mean, depth-integrated sulfate reduction rates from outer and inner bay sediments were similar the rest of the year (16 vs 10 mmol m^{-2} d^{-1}, respectively).

Sulfate reduction in deep sediments

Depth-specific SR rates from the inner bay (measured using ^{35}S) were highest near the sediment surface and had decreased to near zero by 100 cm. (Fig. 5). With the exception of higher rates measured at 160–180 cm at Stn 16, the rates remained low to 300 cm.

From these measured sulfate reduction rates, sediments in the zone of sulfate depletion account for an integrated SRR of about 4.5 mmol S m^{-2} d^{-1} (Table 2). For comparison, net SRR for deep sediments obtained using the sulfate depletion profile (Fig. 3), with sediment porosities of 0.7, and a sediment deposition rate of 1.6 cm y^{-1} (Snidvongs et al. submitted) yielded a lower estimate, about 1.5 mmol S m^{-2} d^{-1}, a rate almost identical to one calculated using the HCO_3^- profile from the same cores, which assumes that all DIC production is coupled to sulfate reduction (F.J. Sansone pers. comm.). Finally, the gradient of reduced sulfur accumulation (Fig. 3) was combined

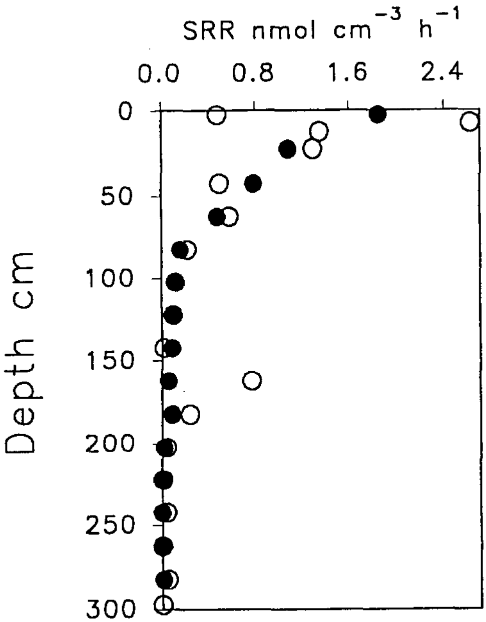

Fig. 5. Comparison of sulfate reduction rates in deep cores from inner bay sediments, Stn 16 (○) and Stn 12 (●), March 1993.

Table 2. Comparison of estimates of SRR within the zone of sulfate depletion (deep sediments below the bioturbation zone), in mmol S m^{-2} d^{-1}.

Source	Station 12	Station 16
SRR by SO_4^{2-} depletion[a] (Fig. 3)	1.7	1.3
SRR by CRS accumulation[a] (Fig. 3)	3.1	2.9
SRR by ^{35}S (Fig. 5)	3.2	5.8
SRR by HCO_3^- accumulation[b]	1.7[c]	1.3[c]
Depths for measurements	70–150 cm	50–190 cm

[a] Method after Canfield (1991)

[b] Data from FJ Sansone (pers. comm.)

[c] $D_S(HCO_3^-) = 9.8 \times 10^{-6}$ cm^2 sec^{-1} (Berner 1980)

with sedimentation rate to calculate an intermediate SRR of about 3.0 mmol S m^{-2} d^{-1}.

Discussion

Sulfate reduction in shallow sediments

Depth-specific rates of gross sulfate reduction, as high as 45 nmol cm^{-3} h^{-1} in Tomales Bay during July (Fig. 4), are high relative to SRR in other estuarine environments (Skyring 1987). In San Francisco Bay sediments, however, Oremland & Silverman (1979) obtained similar rates using an electrical impedance technique (35–75 nmol cm^{-3} h^{-1}). Fossing & Jørgensen (1989) measured rates between 1 and 35 nmol cm^{-3} h^{-1} in marine sediments of the North Sea, and high rates have similarly been obtained for highly organic sediments of salt marshes (Howarth & Merkel 1984; Howes et al. 1984; Hines et al. 1989) and microbial mats (Canfield & Des Marais 1991; Fründ & Cohen 1992; Visscher et al. 1992). For most of the year, however, the rates in Tomales Bay were less than 5 nmol S cm^{-3} h^{-1}, which are typical of shallow estuarine environments, but high relative to coastal oceanic sediments (Christensen 1989; Canfield 1991).

Sulfate reduction rates were also generally higher during warm months in the inner bay and lower during cold months (Fig. 4; Table 1). With warmer temperatures the rates of reactions proceed more rapidly (Hines et al. 1982; Crill & Martens 1987; Westrich & Berner 1988; Jørgensen et al. 1990). There was less variation in SRR at the outer bay site (Fig. 4), where seasonal fluctuations in temperature are smaller (Smith et al. 1987). Temperature, however, is not the only factor which changes over seasons. In some estuaries, the supply of labile organic matter is elevated during warmer seasons (Klump & Martens 1989; Hansen & Blackburn 1992), so other variables which influence SRR could obscure a direct effect of temperature.

As in other studies of sulfate reduction in marine sediments (Hines et al. 1982; Crill & Martens, 1987), measured rates in Tomales Bay were quite variable by depth and sediment type. Although we have demonstrated that some variability is introduced methodologically, perhaps by unequal distribution of label throughout cores (Fig. 2), much of the variation in ^{35}S incorporation may be due to heterogeneity in sulfate reducer activity in intact sediment subcores. In subcores, microscale differences in porewater residence times could influence turnover/exchange rates of constituents affecting the sulfur cycle (Harvey 1992; Canfield 1989a), and labile organic matter is undoubtedly distributed non-uniformly in sediments, even within a particular depth. At a larger scale, Dollar et al. (1991) documented great within-site differences in Tomales Bay sediment metabolism measured in benthic flux chambers covering 2000 cm^2; for comparison, syringe cores have a total sediment volume of only 5 cm^3. Benthic metabolism in Tomales Bay sediments appears to vary at spatial scales which may be strongly influenced by the degree of sediment mixing of oxidants and reductants (see below).

The zone of sulfate reduction in many other estuarine environments typically is more shallow than in Tomales Bay (Goldhaber et al. 1977; Chanton et al. 1987; Skyring 1987), where sediment mixing is hypothesized to extend to 30 cm or greater. Since sulfate reduction occurs in this zone where sulfate concentrations are relatively constant, the amounts of sulfide re-oxidation must be substantial. In Mississippi delta sediments, Canfield (1989a) found that high concentrations of reactive iron oxides effectively buffered sulfide concentrations to very low levels, and iron sulfide minerals were continuously re-oxidized by sediment mixing. Tomales Bay sediments are high in total iron (Smith et al. 1991) and are physically mixed by tidal and wind-driven currents. A large and active infaunal population of polychaetes and other invertebrates also irrigates the sediment via bioturbation (Chambers pers. obs.). We suspect that the cycling of iron oxides and perhaps other reactive species (Aller & Rude 1988; King 1990; Dalsgaard & Bak 1992) are important to the re-oxidation of reduced sulfur compounds in shallow Tomales Bay sediments, a feature which may be typical of iron-rich, well-mixed sediments of West Coast estuaries.

Vertical sulfate reduction profiles in sediments of Tomales Bay are more typical of deeper waters where sedimentation rates are lower (Jørgensen et al. 1990). Among marine environments, a positive correlation exists between sedimentation and sulfate reduction rates (Berner 1989; Canfield 1989b). We measured high depth-integrated rates of sulfate reduction in a high depositional environment, although net SRR is apparently much smaller (Dollar et al. 1991). Most terrestrially-derived sediment is transported to Tomales Bay during the rainy winter, with mostly autochthonous inputs to the sediments during warm summer months. In other estuaries, perhaps the supply of labile organic matter occurs year-round, so that oxygen exchange across the sediment-water interface is seasonally limited (S.V. Smith, pers. comm.). Sulfate reduction would therefore be concentrated in the most recentlydeposited sediments, with rates decreasing rapidly (and concomitantly with sulfate concentrations) with sediment depth. As a shallow, high depositional environment, Tomales Bay may be different from other estuaries that have been studied because sulfate reduction is sustained throughout an actively mixed sediment profile that extends the zone of sulfate reduction down as far as 200 cm (Fig. 5).

Sulfate reduction in deep sediments

Because oxidative and reductive sulfur cycling may occur simultaneously (Elsgaard & Jørgensen 1992), it is not surprising that sulfur storage in shallow sediments is not always linked tightly to sulfate reduction (Giblin 1988). In deep sediments below the zone of bioturbation, however, sulfate reduction and sulfur storage should be closely correlated. In Tomales Bay, SRR measured by ^{35}S is only slightly greater than estimates of SRR using a diffusion-based model of either sulfate depletion or DIC accumulation, and at one site (Stn 12) almost identical to the rate of sulfide burial (Table 2). Given the observed variability in SR (Dollar et al. 1991; Table 1), we consider these estimates to be in fairly close agreement. Although sulfides could also be incorporated into organic sulfur compounds or reactive intermediates such as thiosulfate or polysulfides, these sulfur species are usually found in low concentrations in marine sediments (Luther et al. 1986; Jørgensen 1990; Jørgensen & Bak 1991).

Sulfate reduction and sediment metabolism

Depth-integrated rates of gross sulfate reduction measured in this study were much higher than previous estimates of net sulfate reduction in Tomales Bay. Assuming that 2 moles of organic carbon are oxidized to CO_2 for every mole of sulfate reduced, then the annual mean rates of sulfate reduction are 61 and 28 mmol C m^{-2} d^{-1} for the upper 20 cm of inner and outer bay sediments, respectively. These rates are much higher than either 1) benthic flux measurements of total alkalinity used to calculate net sulfate reduction in Tomales Bay (7 mmol C m^{-2} d^{-1}; Dollar et al. 1991), or 2) estimates of net sulfate reduction derived by a hydrographic/stoichiometric model (5.1 mmol m^{-2} d^{-1}; Smith et al. 1991), and suggest that 80–90% of the sulfides produced are re-oxidized, a typical amount of re-oxidation in bioturbated sediments (Howarth 1984).

The measured rates of sulfate reduction are also about half as large as the estimated annual average of primary production by phytoplankton in Tomales Bay, approximately 75 mmol C m^{-2} d^{-1} (Cole 1989). If 20–30% of the organic carbon produced by phytoplankton in Tomales Bay is deposited and respired in the sediment (Dollar et al. 1991), then only 15–23 mmol C m^{-2} d^{-1} is supplied to sulfate reducers from phytoplankton production. Additional organic carbon sources other than phytoplankton must be available to sulfate reducers in the sediments to support the measured SRR. Terrestrial and oceanic organic carbon, deposited with autochthonous organic carbon and inorganic sediments at rates greater than 1.5 cm y^{-1} in Tomales Bay (Snidvongs et al. submitted), are allochthonous sources which must contribute to sulfate-reducing metabolism in sediments and satisfy the apparent carbon demand. At a conservative sedimentation rate of 1 cm y^{-1}, a mean sediment porosity of 0.7 and an average organic carbon content of 6% in particulate material transported in creekwater draining into Tomales Bay (S.V. Smith, pers. comm.), we estimate that the annual mean deposition of terrestrial carbon would contribute about 100 mmol C m^{-2} d^{-1} to the sediments of Tomales Bay. Organic carbon supply is sufficient to support the measured high rates of sulfate reduction.

Since 80–90% of the alkalinity produced through gross sulfate reduction must be titrated by re-oxidation of sulfides, suitable electron acceptors must also be available. The net benthic flux of oxygen into the sediments, measured *in situ* over 24 h in transparent domes, is only about 10 mmol m^{-2} d^{-1} in Tomales Bay (Dollar et al. 1991), not enough to support the predicted high rates of sulfide oxidation. Although other electron acceptors (iron and manganese oxides, nitrate) are available in the sediments, they also must eventually be regenerated to allow continuous sulfide oxidation. Total oxygen exchange between the water column and sediments may be underestimated in 24-h flux dome incubations which preclude both large-scale physical reworking by storm-generated waves and currents (Grant 1983) and sediment-disturbance activities of bottom-feeding fishes like rays (Thrush et al. 1991), which are abundant in Tomales Bay (Hopkins 1993). These physical processes occur patchily in space and time, however, and their contribution to oxygen exchange may be small relative to advective exchange mediated by infauna.

The extent of sulfide oxidation predicted by the 80–90% difference in measured and net rates of sulfate reduction requires a larger supply of oxygen than has been measured in transparent, benthic flux domes (Dollar et al. 1991). Also, the measured CO_2 flux in these domes is much smaller than the CO_2 flux which would be predicted from our measurements of sulfate reduction. Given a large SRR (this study) and smaller net SRR, net O_2 and net CO_2 fluxes (Dollar et al. 1991), then the general requirements to support the predicted dynamics of sulfur cycling in Tomales Bay sediments are 1) a large CO_2 sink in the sediments to offset CO_2 production by sulfate reduction, and 2) a large O_2 source in the sediments to replenish reactive oxides for sulfide oxidation (Table 3).

A possible resolution of this budgetary problem is that contributions of benthic microalgae have not been included in estimates of either carbon or oxygen dynamics in these sediments. Since the measured fluxes of oxygen into the sediment are net, then it is possible that a much larger production of oxygen occurs due to photosynthesis by surface microalgae. Fixation of CO_2 by photoautotrophs (Howarth 1984) would remove CO_2 generated by sulfate reduction, and subsequent production of photosynthetic oxygen *in situ*

Table 3. Comparison of annual mean carbon and oxygen fluxes measured or estimated in Tomales Bay sediments. The CO_2 sink and O_2 source rates are calculated to satisfy the net CO_2 and O_2 fluxes measured in benthic domes (Dollar et al. 1991).

Carbon fluxes	Rate mmol m^{-2} d^{-1}	Oxygen fluxes	Rate mmol m^{-2} d^{-1}
Net CO_2 flux[a]	20	Net O_2 flux[a]	–10
Net sulfate reduction[a]	7	–	–
80% sulfide re-oxidation[b]	35	80% sulfide re-oxidation[b]	–35
Denitrification[c]	3	Nitrification[c]	–4
CO2 sink to balance carbon budget	–25	O2 source to balance oxygen budget	29

[a] Dollar et al. 1991.
[b] This study.
[c] Joye et al. submitted.

could be used (directly or indirectly) in chemical oxidation of reduced sulfur compounds.

How significant is benthic primary production in Tomales Bay sediments? Benthic microalgal production in shallow estuaries can be as large as water column phytoplankton production on a meter-squared basis (Murray 1983; Rizzo 1986; Rizzo et al. 1992). To be consistent with observed DIC and O_2 fluxes, however, the production rates would have to be net production, since any respired algal production would be a DIC source and an O_2 sink. A preliminary light model of benthic photosynthesis in Tomales Bay is being developed; examinations of dissolved carbon and oxygen fluxes across the sediment/water interface in light and dark domes should help determine the importance of benthic microalgal production to the sediment sulfur cycle.

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