Sulfide release from estuarine sediments underlying anoxic bottom water

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Abstract

Independent measurements of dissolved sulfide (DS) production in and release from mesohaline Chesapeake Bay sediments underlying anoxic bottom water were made during summer. DS accumulated under benthic chambers at a rate of 27.3±8.2 mmol m⁻² d⁻¹. Rates of DS release ranged from 60 to 80% of depth-integrated (0–12 cm) sulfate reduction (SR) rates (average 39.0±9.0 mmol m⁻² d⁻¹) determined with ³⁵SO₄²⁻. The balance between DS production, accumulation in pore waters, and sediment–water exchange was examined by steady state and transient state transport-reaction modeling, with a DS sediment diffusion coefficient derived from that determined for sulfate by the instantaneous source technique. The results indicate that DS transport is influenced by processes other than vertical molecular diffusion, most likely gas bubble ebullition driven by methane production beneath the SR zone. Although such processes may significantly reduce pore-water DS accumulation (i.e. promote DS release), the models show that most (65–95%) DS formation during summer is not stored in the DS pool regardless of the transport processes occurring. The observed rates of DS production and release correspond to a potential oxygen demand of 1–2 g O₂ m⁻² d⁻¹, equal to or greater than estimated rates of eddy-diffusive bottom-water reaeration during summer stratification. Thus, sulfur cycling alone can maintain anoxia in these subpycnocline waters during summer under quiescent water conditions.

Anoxic sediment metabolism is a quantitatively significant component of the carbon cycle in shallow-water aquatic ecosystems (Jørgensen 1983), and sulfate reduction (SR) is the principal terminal microbial process in anoxic sediments where sulfate is abundant (Capone and Kiene 1988). The reoxidation of reduced sulfur formed by SR influences oxygen balance in shallow coastal systems, accounting for at least half of sediment oxygen consumption (SOC) under waters <20 m deep (Jørgensen 1982). In coastal systems subject to vertical water stratification, SOC linked to sulfur cycling contributes to the onset of bottom oxygen depletion, and it is the emergence of dissolved sulfide, DS (= S²⁻ + HS⁻ + H₂S), from the sediments that finally drives bottom waters anoxic; subsequent oxidation of DS at the pycnocline retards bottom-water reaeration, thereby helping to maintain anoxic conditions once they have become established (Tuttle et al. 1987).

Recent studies in the mesohaline region of Chesapeake Bay (Tuttle et al. 1987) indicate that sediments are the dominant source of DS in anoxic bottom waters. Thus, sediment SR is implicated as a major driving force in the maintenance of summer deep-water anoxia in the midbay. In the present study, we estimated the contribution of sediment sulfur metabolism to oxygen balance in the midbay during summer by making independent measurements of DS production in and release from central channel sediments under anoxic bottom-water conditions. The relationship between DS production and its exchange across the sediment–water interface (SWI) was examined by transport-reaction modeling, and the magnitude of DS flux compared with estimated bottom-water reaeration rates and SOC rates by other midbay sediments.


Acknowledgments

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**Methods**

**DS flux measurement**—Direct measurements of DS release from central channel slope sediments (stations R64 and R64E, Fig. 1) were made during late summer anoxia by determining DS accumulation under benthic chambers. The chambers (volume, 33.5 liters; area, 0.29 m²) were carefully emplaced by divers to prevent disturbance of flocculent surficial sediments. Water underlying the chambers was recirculated with a submersible pump, which maintained currents of 10–15 cm s⁻¹ at 6 cm above the sediment surface. Samples were collected at 0.5–1-h intervals for 2–4 h from a tubing line connected to a hand-operated vacuum pump and analyzed immediately for DS content as described below.

**Pore fluid DS concentration**—DS concentrations in sediment pore fluids were measured in cores (6.7-cm i.d.) subsampled from box cores. Cores were sectioned inside an anoxic (N₂ atmosphere) glove bag or quickly sectioned into N₂-gassed centrifuge tubes. After centrifugation (20–40 min at 5,000 x g), the supernatant was immediately removed with an N₂-gassed syringe and filtered through an in-line GF/C filter (Whatman) into a preweighed vial containing 0.5 ml of 10% Zn-acetate. Duplicate 100–500-μl portions of the resulting ZnS suspension were analyzed for sulfide as described below. The remaining pore water was then diluted with 5 ml of distilled water, filtered again through a GF/C filter, and the filtrate stored at 4°C for sulfate analysis.

The DS concentrations of anoxic bottom waters, sediment pore waters (fixed with Zn²⁺), and water underlying benthic chambers and overlying sediment box cores were determined by a methylene blue colorimetric method similar to that described by Cline (1969), except that the N,N-dimethyl-p-phenylenediamine and ferric chloride solutions were added to samples as separate solutions rather than as a mixed reagent. Calibration curves for the reagents were prepared with sodium sulfide solutions standardized by iodometric titration.

A sediment diffusion coefficient for sulfate in the upper 5 cm of R64E sediments was determined by the ³⁵S°₄²⁻ instantaneous source technique as described by Jørgensen (1978b). The sediment diffusion coefficient for DS was derived from this value by assuming that the ratio of the self-diffusion coefficients for HS⁻ and SO₄²⁻ (1.7) holds for mid-Chesapeake Bay sediments. At the pH of R64E sediments (7.3–7.9; J.C. Cornwell unpubl. data), HS⁻ would account for the major portion (67–89%) of total DS. Thus the correction based on relative HS⁻ and SO₄²⁻ diffusivities is the most appropriate for midbay channel slope sediments.

**Sulfate reduction**—SR rates were measured in 2.5-cm-i.d. subcores (removed from box cores) by the ³⁵S°₄⁻ radiotracer method of Jørgensen (1978a). The subcores had silicone-sealed injection ports through which the tracer solution was line-injected normal to the core axis at 2-cm intervals from 1 to 11 cm. Radioactivity added ranged from 2 to 4 μCi (carrier-free Na₂³⁵S°₄, ICN Corp.; sp act = 40 Ci mmol⁻¹) in 10–30 μl of aqueous solution. After incubation for 6–8 h in a cooler of bottom water at in situ temperature, activity was terminated by freezing the cores.

SR cores sampled on dates when DS flux was measured were analyzed by a reduced Cr distillation procedure (Zhabina and Volkov 1978) to recover all forms of reduced ³⁵S. In a separate experiment, cores collected from station R64 were used to separate the end products of ³⁵SO₄⁻ into different
reduced sulfur fractions. After incubation and freezing, duplicate 12-cm cores were sectioned into 2-cm segments and assayed by the following series of distillations performed under strictly anoxic conditions.

DS was driven off with 20 ml of 0.1 M phosphate buffer pH 6.5. Acid-volatile reduced sulfur (AVS) was then released by adding 30 ml of 6 N HCl per 1 M TiCl₄. TiCl₄ retards oxidation of hydrogen sulfide by Fe³⁺ released during acidification. After filtration (GF/C glass-fiber filters) of the acid-sediment slurry and air-drying of the sediment samples to a constant weight, nonacid-volatile reduced sulfur (NAVS) was evolved with 30 ml of 1 M chromous chloride and 15 ml of concentrated HCl (Zhabina and Volkov 1978). During each distillation, the evolved H₂S was carried by an O₂-free nitrogen stream into a trap containing 10–100 ml of 10% (wt/vol) Zn-acetate, where it precipitated as ZnS. The trap contents were well mixed and 2-ml portions added to 7 ml of Instagel scintillation cocktail (Packard). Radioactivity was determined by liquid scintillation counting with a Packard model 4430 liquid scintillation spectrometer operated in the DPM mode. Quench corrections were made by the external standard channels-ratio method.

SR rates were calculated as the product of the fraction of added radioactivity recovered as reduced ³⁵S per unit time and the sulfate concentration at the corresponding depth in the sediment. Sulfate concentrations in appropriately diluted portions of sediment pore water were determined with a Dionex model 2020i ion chromatograph operated at 30 μS output. The precision of replicate sulfate analyses within the concentration range of 0.1–0.5 mM was ~5%. SR rates were corrected for blanks determined for each reduced sulfur distillation procedure used. The single-step reduced Cr distillation procedure exhibited the highest apparent carryover of unreacted ³⁵SO₄²⁻ into the sulfide trap, amounting to 0.145±0.049% (n = 12) of the total radioactivity added. The other distillations (DS, AVS, and NAVS) gave blanks of <0.03%.

DS concentrations determined by slurrying frozen sediment segments with PO₄ buffer ranged from 70 to 100% of those determined in pore waters obtained by centrifugation. Recoveries of reagent-grade FeS (Aldrich) and FeS₂ (Mallincrodt) mixed with anoxic sediment were 97±4% (n = 3) and 100±6% (n = 6), by means of the 6 N HCl per 1 M TiCl₄ and reduced Cr distillations, respectively.

Sediment CH₄ concentration—Sediment CH₄ (and DS) concentrations were measured at station R64E on several occasions in 1989 in conjunction with a separate research program. Whole sediment subsamples were obtained (with a 3-ml cutoff syringe) from 7.6-cm-i.d. cores as they were extruded (1–2-cm intervals) for collection of material for pore fluid separation. The subsamples were immediately extruded into 15-ml serum bottles, which were crimp-sealed with butyl rubber stoppers and stored frozen until analysis in the laboratory. Within a few days of collection, the sediment samples were simultaneously thawed and degassed by autoclaving at 120°C for 20 min. CH₄ in the headspace of the bottles was quantified 1–2 h after autoclaving by gas chromatography with flame ionization detection (Shimadzu model GC-9A). Previous studies (R. Kiene and D. Capone unpubl. data) have shown that autoclaving is a rapid and effective means of degassing CH₄ from sediment samples.

Results

Direct measurements of DS release—Rates of DS release from sediments underlying anoxic bottom water in August ranged from 17 to 38 mmol m⁻² d⁻¹, with an average value of 27±8 (Table 1). Initial DS concentrations under the benthic chambers were usually within a factor of two of bottom-water [DS] concentrations (relative to bottom-water [DS]) and rate of DS release. These observations indicate that conditions approximating those in situ were present at the beginning of the flux measurements and that any sediment disturbance resulting from chamber emplacement did not contribute to measured DS release. We did not compare DS release during stirred and unstirred benthic chamber incubations. However, rates of water ciru-
Table 1. Measurements of DS flux from central channel slope sediments under benthic chambers (volume, 33.5 liters; sediment area, 0.29 m²).

<table>
<thead>
<tr>
<th>Chamber No.</th>
<th>Bottom-water [DS] (µM)</th>
<th>Hours measured</th>
<th>Initial [DS] (µM)</th>
<th>DS flux* (mmol m⁻² d⁻¹)</th>
<th>n</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 Aug 86</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>27.0</td>
<td>2</td>
<td>43.4</td>
<td>35.1 ± 1.5</td>
<td>5</td>
<td>0.99</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>29.0</td>
<td>27.6</td>
<td>16.6 ± 2.0</td>
<td>5</td>
<td>0.95</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>2</td>
<td>6.9</td>
<td>36.3 ± 2.1</td>
<td>5</td>
<td>0.99</td>
</tr>
<tr>
<td>25 Aug 86</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.2</td>
<td>4</td>
<td>6.9</td>
<td>29.4 ± 1.9</td>
<td>5</td>
<td>0.99</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>1.5</td>
<td>0.9</td>
<td>23.9 ± 3.7</td>
<td>5</td>
<td>0.95</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>1.5</td>
<td>0.9</td>
<td>23.9 ± 3.7</td>
<td>5</td>
<td>0.95</td>
</tr>
<tr>
<td>13 Aug 87</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6.1</td>
<td>2</td>
<td>0.5</td>
<td>29.7 ± 1.7</td>
<td>5</td>
<td>0.99</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>5.3</td>
<td>0.9</td>
<td>20.0 ± 2.0</td>
<td>6</td>
<td>0.97</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>7.3</td>
<td>0.9</td>
<td>17.1 ± 2.5</td>
<td>5</td>
<td>0.92</td>
</tr>
</tbody>
</table>

* Determined from linear regression analysis of [DS] (in water underlying the domes) vs. incubation time. Error term—standard error of the slope of the regression line. n—Number of data points included in the regression.

lation during the incubations (10–15 cm s⁻¹) approximated near-bottom current speeds in the midbay channel (Boynton et al. 1981), so that DS exchange across the SWI should not have been unduly enhanced or retarded relative to that which occurred naturally.

Measurements of ³⁵SO₄²⁻ reduction in midbay bottom water, made in parallel with our experiments (C. Divan and J. Tuttle unpubl. data), gave water-column SR rates (integrated over an average subpycnocline depth of 10 m) <10% of areal SR in the upper 12 cm of sediment. Because the water column underlying the benthic chambers was very shallow (<0.15 m), we assumed that all DS accumulation was attributable to release from sediments.

Pore-water DS profiles—DS concentrations in the upper few centimeters of sediment ranged from 0.1 to 2 mmol liter⁻¹ (Fig. 2), 1–2 orders of magnitude higher than near-sediment water concentrations during summer anoxia (Table 1). Diffusive DS fluxes estimated from surface sediment DS concentrations ranged from 20 to 100% of those obtained by chamber emplacement, with an average value of 52±21% (Table 2). It was not possible to accurately characterize the DS gradient at the SWI by core slicing when the gradient was compressed within the upper centimeter of sediment during bottom-water anoxia. Thus our diffusion estimates should be regarded as minimum values. In addition, if transport processes other than one-dimensional (vertical) molecular diffusion are important (see below), surficial pore-water gradients alone cannot be used to calculate total solute exchange rates, regardless of how accurately they are estimated.

Sulfate reduction rates—Depth profiles and areally integrated rates of SR determined in parallel with DS flux measurements are shown in Fig. 3. The fraction of total SR accounted for by DS flux under benthic chambers ranged from 60 to 80%, with an average value of 70%. In a separate experiment an average of 71±5% of reduced ³⁵S formed in duplicate 12-cm cores (n = 12 core segments) was recovered in the DS fraction (data not shown). The agreement between these findings suggested that formation of solid-phase reduced S could have been responsible for the difference between total SR and DS release during late summer anoxia. A similar ratio of net DS liberation to total SR was observed in anoxic (nonradiotracer) incubations of marsh-flat sediments, which had concentrations of DS and rates of SR comparable to those at station R64 (Swider and Mackin 1989). However, our radiotracer results yield a minimum estimate of the ratio of net DS liberation to total SR, because reduced ³⁵S can be transferred from DS to solid reduced S (SRS) compounds via isotope exchange (Fossing and Jørgensen 1990). SRS reached a maximum concentration (120 mmol liter⁻¹, 1.4% dry wt) at ~4-cm depth and was constant below, indicating that long-term SRS accumulation occurred mainly in the upper 4 cm of sediment. Thus, recovery of 30% of reduced ³⁵S as SRS below this horizon may be more attributable to isotope
**Sediment sulfide release**

**Fig. 2.** Measured (symbols) and steady state model-predicted (lines) [DS] profiles at station R64. Heavy lines: model based on DS production and molecular diffusion (Table 3). Light lines: model based on DS production and enhanced molecular diffusion (see text). Dashed lines: model based on DS production, molecular diffusion, and first-order nonlocal removal (Table 3).

exchange among DS, FeS, and $S^0$ than to net SRS formation.

**Discussion**

Rates of DS production and release approached total SR rates in mid-Chesapeake Bay central channel sediments underlying anoxic bottom water during late summer. Analogous results have been reported for organic-rich Cape Lookout Bight (CLB) sediments, in which DS release rates were determined from DS accumulation in benthic chambers following oxygen depletion (Chanton et al. 1987). Because sediments in both environments lack a significant Fe-oxide surface layer during summer, DS flux is focused on the SWI. DS is oxidized by direct reaction with oxygen at the SWI in CLB sediments (Chanton et al. 1987), whereas it emerges from midbay channel sediments during anoxia and is oxidized farther up in the water column.

Table 2. Comparison of mean ($\pm$SD) DS production and flux estimates at station R64. Units are mmol m$^{-2}$ d$^{-1}$. Values in parentheses—number of determinations.

<table>
<thead>
<tr>
<th></th>
<th>Production*</th>
<th>Chamber flux</th>
<th>Diffusive flux†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Core A</td>
</tr>
<tr>
<td>14 Aug 86</td>
<td>34.4 ± 5.1(2)</td>
<td>29.7 ± 11.4(3)</td>
<td>15.3</td>
</tr>
<tr>
<td>25 Aug 86</td>
<td>25.9 ± 1.7(2)</td>
<td>29.9 ± 6.2(3)</td>
<td>15.8</td>
</tr>
<tr>
<td>13 Aug 87</td>
<td>21.5 ± 1.9(2)</td>
<td>22.3 ± 6.6(3)</td>
<td>4.2</td>
</tr>
<tr>
<td>Mean (±SD)</td>
<td>27.7 ± 6.4(6)</td>
<td>27.3 ± 8.2(9)</td>
<td>14.3 ± 5.8(5)</td>
</tr>
</tbody>
</table>

*Calculated as depth-integrated SR (0–12 cm) multiplied by 0.7 (the fraction of reduced $^{35}$S recovered as DS during SR experiments, station R64 on 6 August 1987).

†Estimated from measured surface sediment DS concentrations ($C_s$) with the formula: flux = $\phi_s \times D_s \times (C_s - C_d)/z$, where $\phi_s$ is surface sediment porosity, $D_s$ the sediment diffusion coefficient for DS, $C_s$ the measured bottom-water [DS], and $z$ the mid-sampling interval depth (0.25 or 0.5 cm). The sediment diffusion coefficient for DS was derived from that measured for sulfate in the upper 5 cm of R64E sediments in August 1986 at 25°C (0.43 cm$^{-1}$ d$^{-1}$).
Approximate agreement between rates of SR and DS release to anoxic overlying water has also been reported for relatively coarse-grained Baltic Sea (Bägander 1977) and Danish coastal sediments having lower metabolic rates than CLB or mid-Chesapeake Bay sediments. In the Baltic Sea study, 80% of the sulfate removed from water overlying sediments covered by an opaque chamber during a 240-d interval between May and January was accounted for by DS accumulation in the overlying water, suggesting that the capacity for sediments to accumulate dissolved and solid-phase sulfide was small compared to the capacity for sulfide production. On a much shorter time scale, sulfide release (during periods of darkness) to the atmosphere over Danish coastal sediments covered with a 1–3-cm-thick layer of anoxic water was about equal to the daily depth-integrated SR rate in the upper 10 cm (Hansen et al. 1978).

The above studies demonstrate that in nonbioturbated coastal sediments subject to unusually high rates of SR or oxygen depletion in the overlying water, a large fraction of sulfide production is likely to be consumed by direct reaction with oxygen at the SWI or lost to the overlying water. In bioturbated sediments, sulfide oxidation can occur below the SWI, either by reaction with oxygen inside burrow tubes or by reaction with solid-phase oxidants (e.g. Fe or Mn oxides) mixed downward into and recycled within the sediment by macrofaunal activity (Swider and Mackin 1989). Measurements of SR and [DS] in sediments on the shallow (10 m) flanks of the midbay (Roden and Tuttle in prep.) indicate that such processes are important in midbay sediments underlying well-aerated waters.

Modeling DS diagenesis—The similarity of SR and chamber DS release rates suggested a close coupling of sulfide production and exchange across the SWI, which led us to question whether the sediment sulfur system, including the DS pool, had approached steady state during late summer. To address this question we constructed a steady state, one-dimensional diagenetic model of DS.
production and diffusion (Table 3). Although midbay sediments never attain long-term steady state with respect to inorganic S pool sizes and transformation rates (because of seasonal variations in temperature, organic deposition, and salinity), bottom-water temperatures range only from 20° to 25°C during summer (±90 d), and sediment SR rates in the vicinity of R64 are relatively constant at 40± 11 (n = 9) mmol m⁻² d⁻¹ (Roden and Tuttle in prep.; Marvin et al. unpubl. data). Because summer reaction rates are high, the steady state assumption is suitable as a first approximation. Our working hypothesis was that model-predicted DS distributions would agree with measured profiles if R64 sediments approached steady state with respect to DS production and vertical diffusive flux in the late summer.

We ignored sedimentation in the model, because this transport process is slow relative to diffusion in midbay sediments. A DS concentration of 0.020 mmol liter⁻¹ was chosen as the surface boundary condition (C₀), based on bottom-water DS measurements (Table 1). The [DS] gradient at depth in the sediment (B) was set equal to zero as the lower boundary condition, in agreement with measured DS distributions (Fig. 2). Depth profiles of SR rate measured on the three dates in August were fit by nonlinear least-squares regression to an equation of the form

\[ R(x) = R_0 \exp(-\theta x) + R_1 \]

(Fig. 3, lines). Based on radiotracer results, we assumed that net DS production was equal to 70% of total SR (f = 0.7; see Table 3) at all depths in the upper 12 cm.

As discussed above, the assumption that f = 0.7 probably yields a conservative estimate of net DS liberation at depth in the sediment. Nevertheless, DS concentrations at depth predicted by the steady state models (Fig. 2, heavy lines) are in great excess of those observed during late summer. Because the models are well constrained in terms of DS production and loss from the sediment, this inconsistency raises the possibility that processes other than vertical molecular diffusion were involved in DS release from the sediment. Before considering this possibility further, we evaluate the validity of the steady state assumption by comparing the steady state model results with those of an analogous transient state model.

**Transient state model**—We used a finite difference model (Table 4) to predict the accumulation of DS in sediment pore waters during summer expected on the basis of production and vertical diffusive transport. Boundary conditions were those used in the
Table 4. Formulation of a transient state model of DS production and diffusion (after Aller and Mackin 1989).

Dissolved sulfide = C(x, t) (µmol cm⁻²)

Model equation for x = 0 to L:

\[ \frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial x^2} + f[R_0 \exp(-\theta x) + R_i]. \]

Numerical approximations:

\[ \frac{\partial C}{\partial t} \approx \frac{C(x_j, t_{k+1}) - C(x_i, t_k)}{dt}, \]

\[ \frac{\partial^2 C}{\partial x^2} \approx \frac{C(x_i+1, t_{k+1}) - 2C(x_i, t_{k+1}) + C(x_i-1, t_{k+1})}{dx^2}. \]

where \(dx\) = depth increment (0.2 cm) and \(dt\) = time increment (0.1 d).

Boundary conditions:

\[ x = 0, \quad C(0, t_{k+1}) - C_0 - 0.020, \]

\[ x = L, \quad \frac{C(L, t_{k+1}) - C(L - dx, t_{k+1})}{dx} = 0. \]

Simultaneous equations:

\[ x = 0: \quad C(dx, t_{k+1}) - C(0, t_{k+1}) = 0, \]

\[ x = dx \text{ to } (L - dx): \quad -D_b C(x_{i-1}, t_{k+1}) + (1 + 2D_b)C(x_i, t_{k+1}) - D_b C(x_{i+1}, t_{k+1}) = C(x_i, t_{k+1}) + f[R_0 \exp(-\theta x_i) + R_i]dt, \]

\[ x = L: \quad C(L, t_{k+1}) - C(L - dx, t_{k+1}) = 0. \]

where \(b = dt/dx^2.\)

Matrix expression: \(AC_{t_{k+1}} = C_{t_k} + R\)

where \(C_{t_k+1}\) = vector of \(C(x_i, t_{k+1})\) values
\(C_{t_k}\) = vector of \(C(x_i, t_{k})\) values
\(R\) = vector of \(f[R_0 \exp(-\theta x_i) + R_i]\) values
\(dt\) = scalar
\(A\) = coefficient matrix

with \(A(1,1) = A(n,n) = 1; A(n,n+1) = 0;\) for \(i = 2 \text{ to } n-1, A(i,i-1) = A(i,i+1) = -D_b, A(i,j) = 1 + 2D_b;\) all other elements of \(A = 0.\)

steady state model. The initial \((t = 0)\) DS profile was set equal to a polynomial fit of the DS distribution measured at R64E on 8 June 1989 (see Fig. 5). The SR rate profile used was the areage of the profiles shown in Fig. 3, which yielded a depth-integrated SR rate similar to the average of SR rate measurements made in the vicinity of R64 on nine occasions between June and September 1986–1989. The net DS liberation rate was assumed to be a constant 70% of the total SR rate.

A 90-d time interval was used in the model runs, during which the matrix expression in Table 4 was solved at 0.1-d increments by Crout reduction (Burden et al. 1981). The DS concentrations predicted at depth after 30 d of accumulation (Fig. 4A, dotted line) were at the upper limit of those measured during summer (Figs. 4A, 5). After 60 and 90 d, predicted DS concentrations at depth (8–10 mmol liter⁻¹) were considerably greater than maximum measured concentrations. Even these very high [DS] predictions should be regarded as minimum values, because a conservative estimate of net DS production relative to total SR was used in the model. Testing showed that increasing the value of \(f\) below 4 cm led to a proportionate increase in the predicted DS concentration at depth in the sediment.

The transient state model required 280 d to produce a profile approximating the steady state solution. The concentration of DS at depth in the sediment predicted after 90 d was slightly greater than half the steady state prediction. This result demonstrates that steady state would not be achieved during summer if DS transport were controlled by molecular diffusion. However, because DS production rates are high, the transient state model approaches the steady state solution rapidly during the first 60 d. This phenomenon is reflected by the fact that the predicted ratio of pore-water DS accumulation to total DS production declined from 65% on the first day to <20% after 60 d (data not shown). Because the large increases in sediment DS concentration predicted by the transient state model (Fig. 4A) were not observed in channel sediments during summer (Fig. 5), the results lead to the same suggestion as those of the steady state model, i.e. that processes other than vertical mo-
Sediment sulfide release

**DISSOLVED SULFIDE (mmol liter⁻¹)**

![Graph showing dissolved sulfide profiles](image)

**Fig. 4.** Transient state model (Table 4) predictions of DS profiles (lines) in midbay central channel slope sediments during summer. Symbols are combined data from Fig. 2. A. Model based on DS production and molecular diffusion. B. Model based on DS production and enhanced molecular diffusion. C. Model based on DS production, molecular diffusion, and first-order nonlocal exchange. Different lines correspond to predictions at different time points during a 90-d simulation period.

Molecular diffusion influence DS accumulation during summer.

**DS removal in surface sediments—**Fe oxide availability could influence DS accumulation in surface sediments with the onset of summer conditions. Estimates of temporary SRS storage in the upper 4 cm of R64 sediments during April–August amount to ~1 mol S m⁻², much of which is likely to occur before bottom waters become anoxic (Roden and Tuttle in prep.). We note also that this quantity of DS would be produced in <1 month at an average summer SR rate of 40 mmol m⁻² d⁻¹. These observations suggest that SRS formation in surface sediments does not quantitatively retard DS release during summer.

Comparison of the DS profile of 10 July 1987 under anoxic conditions with that of 8 July 1989 (Fig. 5) when the bottom water was hypoxic (DO = 0.2 mg liter⁻¹) suggested that DS accumulation in the upper few centimeters was related to the presence of anoxic bottom-water conditions. This distinction is supported by the subsequent detection of millimolar DS levels within the upper 2 cm of sediment on 8 August 1989 when the bottom water was anoxic, followed by the absence of DS in the top centimeter of sediment in September when the bottom water again contained oxygen. Although the causal link(s) between bottom-water oxygen and surface sediment DS are not clear, the results indicate that aerobic reoxidation processes influence the fate of DS produced in this interval. However, DS oxidation in the upper few centimeters is not expected to strongly affect DS accumulation at depth in the sediment, i.e. upward flux would be directed to a depth just below the SWI rather than at it precisely.

**Sediment–water DS exchange processes—**Because central channel sediments are not subject to irrigation by macrofauna during summer hypoxia-anoxia, we speculate that gas bubble ebullition, driven by CH₄ production beneath the SR zone, contributes to DS flushing from the sediments. Reeburgh (1969) reported near-saturating CH₄ concentrations below 50 cm depth in midbay channel sediments and suggested that N₂ and Ar are stripped from solution.
Fig. 5. DS profiles measured in the vicinity of station R64. Data for 1986-1987 are results from duplicate cores collected on the same date. Data for 1989 are unpublished data of M. Marvin and D. Capone. Line in 8 June panel is a curve-fit used as the initial DS profile in the transient state diagenetic model.

at depth by diffusion into CH₄ bubbles that are subsequently lost from the sediment. CH₄ concentrations approaching or exceeding saturation were present within the upper 20 cm of R64E sediments during summer (Fig. 6). The CH₄ profiles showed a concave-upward structure, suggesting that some process other than vertical molecular diffusion was involved in CH₄ loss from the sediment.

Martens and Berner (1977) attributed CH₄ removal at >50-cm depth in marine sediments to anoxic oxidation coupled to SR. In our near-surface situation, it seems just as plausible that removal was by bubble ebullition. We have in fact observed bubble ebullition in some central channel gravity cores (50–100 cm long) brought from depth to atmospheric pressure aboard ship, although not in any of the relatively shallow box cores obtained in the present study. In addition, longitudinal sonar scans of mid-bay bottom waters (>10-m depth) during summer anoxia-hypoxia have revealed...
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scattering that, in the absence of fish or other acoustically reflective organisms, has been attributed to the presence of gas bubbles (S. Brandt unpubl. data). In support of this finding, substantial levels (0.5–1 μM) of CH₄ have been detected in midbay bottom-water samples collected in Niskin bottles during summer (M. Marvin unpubl. data). Because of the relatively high sulfate concentration of midbay bottom waters (≥ 10 mM), it is unlikely that CH₄ formation occurs in the water column, implying that dissolved CH₄ and CH₄-containing gas bubbles must originate from the underlying sediments.

Two possible mechanisms of dissolved solid exchange involving gas bubble ebullition in coastal sediments were discussed by Klump and Martens (1981), namely horizontal diffusion into bubble tubes ventilated with bottom water, or buildup of high solute concentrations in stagnant tube waters leading to enhanced diffusive flux across the mouths of the tubes. In the case of DS there is also the possibility that H₂S gas could be stripped in the manner suggested for trace gases such as N₂ and Ar. Measurements of H₂S in gas bubbles released from CLB sediments during summer suggested that this process was insignificant compared to total DS flux (Chanton et al. 1987). This result may be due to the predominance of HS⁻ in the DS pool at pH values typical of sulfidic marine sediments (≥ 7.4, Boudreau and Canfield 1988). The same is probably true for midbay channel sediments in which pH ranges from 7.3 to 7.9 (J. Comwell unpubl. data). Thus the effect of H₂S stripping is likely to be minor compared to dissolved HS⁻ exchange associated with gas bubble ebullition.

Enhanced diffusion coefficients have been used effectively to describe the influence of bubble ebullition on sediment–water chemical exchange in CLB sediments (Klump and Martens 1981, 1989; Martens and Klump 1984; Chanton et al. 1987). In this approach the ratio of diffusive solute flux (estimated from measured concentration gradients) to total measured solute flux is inverted, yielding a diffusion coefficient enhancement factor (EF). Enhancement factors calculated for a tracer solute (e.g. CH₄ in CLB sediments) can then be used to predict transport of other species. Using our estimates of diffusive and total DS flux as the only available tracer for ebullition effects, we calculated an EF of ~2 for each of the three sampling dates, comparable to values estimated for CH₄ in CLB sediments during summer (Klump and Martens 1981). This EF is a maximum value because DS gradients at the SWI could have been steeper than our crude estimates based on surficial DS concentration.

If we assume that vertical diffusion was enhanced throughout the upper 12 cm of sediment, the above EF can be used in diffusion-reaction models. Although our EF is not based on independent tracer data, we can constrain it to values ≤2 based on measured DS fluxes and surface sediment concentrations, assuming that any depth dependency of diffusion enhancement can be ignored (Martens and Klump 1984; Klump and Martens 1989). With an EF of 2, the steady state model predicted DS concentrations considerably higher than measured...
values for two of the three dates (Fig. 2, light lines). We emphasize that total DS flux predicted by the steady state models is the same regardless of the transport process considered, and that these fluxes are equal to measured DS release and production rates. Thus the prediction of DS concentrations in excess of those observed is not indicative of a missing removal term, but of the inability of the steady state enhanced diffusion model to reproduce measured DS distributions. The transient state-enhanced diffusion model also predicted late-summer DS concentrations in excess of those observed (Fig. 4B). These results contrast with those obtained from steady state and transient state models of nutrient and sulfate diagenesis in CLB sediments, which accurately reproduced measured concentration profiles during the summer with EF values based on CH₄ and ²²²Rn data (Martens and Klump 1980; Klump and Martens 1987, 1989).

Emerson et al. (1984) used a first-order, nonlocal exchange term to describe the influence of bioturbation on solute transport in shallow coastal sediments. Boudreau (1984) demonstrated that this model is mathematically analogous to the radial diffusion model of Aller (1980), which accounts for horizontal solute diffusion into well-flushed macrofaunal burrow tubes. This result suggests that the nonlocal model could give a reasonable representation of DS diffusion into and subsequent flushing from gas bubble tubes. We speculate that DS flushing occurs advectively (tube waters exchanged with overlying water) or via eddy diffusion during passage of bubbles through the tubes. A depth-independent, first-order DS exchange term \( k \) was incorporated into the steady state model (Table 3) to see if this approach would give a better fit to measured DS profiles than was obtained with the vertical diffusive transport model. The enhanced diffusion and nonlocal exchange models were mutually constrained by measured DS release rates and by the stipulation that “nonlocal exchange” accounts for the same proportion of total DS flux attributed to “enhanced diffusion” (i.e. 50\%), thereby making their results directly comparable.

A range of \( k \) values of 0.016-0.065 d⁻¹ was estimated for the different profiles. The depth profiles predicted by the nonlocal model (Fig. 2, dashed lines) were closer to measured profiles than those predicted by the enhanced-diffusion model. When we included in the transient state model a nonlocal exchange term calculated as the average of the three \( k \) values used in the steady state models (0.046 d⁻¹), the predicted DS profiles fell in the middle of the observed range (Fig. 4C). The solutions converged to an approximate steady state within 30 d, indicating that steady state modeling is valid on a summer time scale if processes describable by first-order removal occur in concert with molecular diffusion.

The nonlocal exchange models appeared to give a better description of DS diagenesis in central channel sediments than those assuming enhanced vertical diffusivity. This stands to reason if, in fact, horizontal diffusion into and flushing from bubble tubes were involved in DS removal from the upper 10-15 cm of sediment. Unfortunately it remains speculation, because gas bubble ebullition has not been directly documented in midbay channel sediments. Moreover, the lack of detailed DS concentration gradient measurements in surface sediments precludes a direct evaluation of the quantitative contribution of transport processes other than vertical molecular diffusion, regardless of their mechanism, to measured rates of DS release.

Alternatively, we calculated the difference between DS accumulation in sediment pore waters over the summer predicted by the transient state nonlocal exchange model (330 mmol m⁻²) and that predicted by the transient state molecular diffusion model (990 mmol m⁻²) (Fig. 4A,C) to estimate the potential importance of transport processes other than vertical molecular diffusion to DS accumulation and flux during summer. This difference amounts to 27\% of total DS formation over the 90-d interval at an average rate of 28 mmol m⁻² d⁻¹ (40 × 0.7), suggesting that such processes could significantly promote DS flushing during summer. However, the results also illustrate that regardless of the transport process(es) occurring in the sediment, the major portion (65-95\%) of sulfide production in summer will not be stored in the DS pool. Direct
measurements of sediment [DS] (Fig. 5) favor the nonlocal exchange model (DS storage <10% of production).

**DS flux and oxygen balance**—If we assume a 2:1 stoichiometry for oxygen consumption coupled to DS oxidation, the chamber estimates of DS flux correspond to a potential oxygen demand of 1.2-2.5 g O₂ m⁻² d⁻¹. These rates are as high or higher than measured SOC (W. M. Kemp unpubl. data) at a 10-m flank station (DB, Fig. 1) where the bottom water is normally well oxygenated throughout summer and SR rates are of the same magnitude as at station R64 (Roden and Tuttle in prep.), which demonstrates that S cycling can replace direct oxygen uptake as a major oxygen consumption process in the midbay during summer. Summer bottom-water reaeration rates (via eddy diffusion across the pycnocline) estimated from salinity distributions with a two-dimensional box model are on the order of 1.2 g O₂ m⁻² d⁻¹ (Officer et al. 1984). This rate should be regarded as a minimum estimate because advective exchange undoubtedly results in oxygen input to bottom waters under certain conditions, as evidenced by the periodic reappearance of oxygen in the deep water throughout summer (Tuttle et al. 1987). Still, the oxygen consumption potential associated with DS flux may be twice the eddy-diffusive flux estimate, suggesting that this process is more than sufficient to maintain anoxic conditions under typical well-stratified summer conditions.

An important question is whether our results with sediments in the vicinity of station R64 are representative of other midbay channel sediments underlying anoxic waters in summer. Summer SR rates at several additional sites in the midbay central channel are comparable to those at R64 (Roden and Tuttle in prep.). If a similarly large proportion of total SR results in DS flux from these sediments, there is little doubt that sulfur cycling can maintain anoxia in midbay bottom waters in summer.

**References**


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