Benthic sulfate reduction along the Chesapeake Bay central channel. II. Temporal controls

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ABSTRACT: Seasonal and interannual controls of benthic sulfate reduction (SR) were examined at 3 sites (upper [UB], mid- [MB] and lower [LB] bay) along the Chesapeake Bay central channel, from early spring through fall, for 6 yr (1989 to 1994). The combined influences of temperature, sulfate, organic loading and bioturbation affected seasonal SR rates differently in the 3 regions. Consistently low SR rates at UB resulted from low overlying-water sulfate concentrations and the dominance of refractory organic terrestrial material. Combined seasonal variation in temperature and sulfate accounted for 50% of the annual variability in 0 to 2 cm depth interval SR rates, while sediment organic content had no significant seasonal influence. In contrast, MB and LB sites had high rates of SR fostered by high levels of overlying water SO4^2– and organic input dominated by labile phytoplankton detritus. New organic loading (measured as chl a) stimulated 0 to 2 cm SR during spring at both sites. Combined organic quantity (as particulate C and/or N) and temperature accounted for >75% of the variability in 0 to 2 cm SR at MB during spring and fall. Molecular diffusion supplied 25 to 45% of the SO4^2– needed to fuel 0 to 12 cm depth interval SR at MB, with the balance presumably supplied by S-recycling. Interannual differences in summertime SR rates were linked to the extent of freshwater flow during spring, with high-flow years associated with high SR rates at UB and MB, and low rates at LB. The negative trend between benthic SR and river flow at LB may result from the up-estuary transport of senescing organic matter in bottom water, which increases in the lower reach of the estuary with increasing freshwater inflow.

KEY WORDS: Sulfate reduction · Benthic metabolism · Sediment · Estuary · Chesapeake Bay

INTRODUCTION

Microbial sulfate reduction (SR) is a major pathway of organic matter mineralization in coastal marine and estuarine sediments (Jørgensen 1977, Capone & Kiene 1988). Factors that impact SR rates include temperature (Abdollahi & Nedwell 1979), electron donor and acceptor availability (Goldhaber & Kaplan 1975, Boudreau & Westrich 1984), organic matter quality (Westrich & Berner 1984), sedimentation rate (Berner 1978), and bioturbation (Hines & Jones 1985). While single-factor controls on SR have been extensively investigated, few studies have considered the interrelationships and interactions among factors as they mediate SR over various temporal and spatial scales. This is partially due to the limited number of appropriate long-term data sets. While a few notable exceptions exist for coastal marine (Martens & Klump 1984, Crill & Martens 1987, Moeslund et al. 1994), salt-marsh (King 1988), and lake (Sherman et al. 1994) systems, comparable investigations are lacking for estuaries.

The 1989–1994 National Science Foundation Land-Margin Ecosystem Research (LMER) Program for the Chesapeake Bay represents one of the longest continuous multi-site records of estuarine benthic SR to date. In an earlier report (Marvin-DiPasquale & Capone 1998), we considered how the above factors influenced the spatial variation in SR at 3 regionally
distinct sites along the Bay’s central axis. We concluded that SR was limited by organic C in the oligohaline and polyhaline regions of the Bay, and by organic C at the sediment surface and SO$_4^{2-}$ at depth in the mesohaline. The mechanisms of control varied regionally and were based on differences in the quality and quantity of organic matter deposited to the benthos, SO$_4^{2-}$ availability, bioturbation, overlying water O$_2$ conditions, reduced-S reoxidation dynamics, and iron-sulfide mineral formation. We now explore the temporal controls on SR in the LMER study, focusing on the monthly to seasonal timescales. We additionally consider the seasonal dynamics of SO$_4^{2-}$ diffusion versus sulfur recycling in fueling mesohaline SR, and the interannual relationship between summertime SR rates and spring freshwater input in all 3 bay regions.

**MATERIALS AND METHODS**

**Sampling.** The 3 benthic sites (upper [UB], mid- [MB] and lower [LB] bay) lie along the western slope of the central channel of the Chesapeake Bay main-stem (Fig. 1). The oligohaline UB site is strongly influenced by the input of terrestrial organic and inorganic matter from the Susquehanna River (Zimmerman & Canuel 2001). Sediment at UB is bioturbated by a diverse community of bivalves and polychaetes, and is characterized as oxidized silty clay. Mesohaline MB sediment is organic-rich, sulfidic, highly reducing, non-bioturbated for most of the year, and receives deposited organic matter as mostly autochthonous phytoplankton detritus (Zimmerman & Canuel 2001). Polyhaline LB sediment is oxidized silty sand that is heavily bioturbated by the tube-building polychaete Chaetopterus variopedatus (Schaffner 1990) and other organisms, and receives organic matter primarily as phytoplankton detritus (Canuel & Zimmerman 1999). Sites were sampled monthly from March to November (excluding October) during 1989 in order to discern overall monthly and seasonal trends. In subsequent years (1990 to 1994), 3 to 5 cruises were conducted per year, which included at least 1 spring, summer and fall sampling. Measurements in April and July were made every year.

**Sulfate reduction and ancillary biogeochemical analysis.** A detailed description of onboard sediment processing and subsequent laboratory analyses was previously published (Marvin-DiPasquale & Capone 1998). In brief, duplicate subcores (2.5 inner diameter x 20 cm) were taken from a single larger sediment box core. Depth-integrated SR was measured throughout the top 12 cm of sediment (in 2 cm intervals) using the $^{35}$SO$_4^{2-}$ radiotracer method (Jørgensen 1978a, Roden & Tuttle 1993a). Four-hour incubations were conducted at in situ temperature and were initiated onboard within 2 h of sediment collection. Incubations were arrested with 10% zinc-acetate followed by freezing. Subsequently, both radiolabeled and non-radiolabeled reduced-S was collected via chromium-reduction acid distillation, and quantified via liquid scintillation counting and colorimetric spectrophotometry (Cline 1969), respectively.

The top 16 to 20 cm of sediment from a separate box core was sub-sampled at 0.5 to 2 cm intervals for porosity and total organic matter (TOM), the latter calculated as percent loss dry weight after combus-
tion at 475°C. Pore water was collected via centrifugation under anaerobic conditions and subsequently analyzed for SO$_4^{2–}$ and Cl$^–$ via ion chromatography with conductivity detection. Pore water from MB (only) was analyzed for free sulfide (ΣH$_2$S) (Cline 1969). Surface sediment (top 1 cm) was sampled for particulate carbon (PC), particulate nitrogen (PN) and chl $a$. PC and PN were analyzed, after combustion to CO$_2$ and N$_2$ gas, via thermal conductivity detection with a Perkin-Elmer$^\text{TM}$ 240-XA elemental analyzer. Chl $a$ was analyzed fluorometrically (Strickland & Parsons 1972). Sediment redox ($E_h$) was measured via platinum electrode (Cowen & Boynton 1996). Bottom-water dissolved O$_2$, temperature and salinity were measured using a Seabird$^\text{TM}$ CTD or Hydrolab$^\text{TM}$ 4000.

**Temperature coefficient.** An Arrhenius-like model (Marvin-DiPasquale & Capone 1998) was used to investigate the apparent temperature influence on SR for different sites/seasons. The linear form of this model was fit to the SR and temperature data:

$$\ln(SR_i) = (– C_1 / R) \times T^{-1} + \ln(A) \quad (1)$$

where SR$_i$ is the 0 to 2 cm (SR$_2$) or 0 to 12 cm (SR$_{12}$) depth-integrated rate (mmol SO$_4^{2–}$ m$^{-2}$ d$^{-1}$), $T$ is temperature (K), $C_1$ is the temperature coefficient (kJ mol$^{-1}$ K$^{-1}$), $R$ is the gas constant (0.008314 kJ mol$^{-1}$ K$^{-1}$), and $A$ is a constant. Values of $C_1$ and $A$ were calculated from the linear-regression slope and $y$-intercept, respectively. The temperature coefficient ($C_1$) is analogous to the well-known Arrhenius activation energy ($E_h$). However, the latter is typically measured for a set of replicate samples incubated simultaneously at a range of experimentally fixed temperatures (Abdollahi & Nedwell 1979). In contrast, $C_1$ was calculated from SR rates measured throughout this study at various in situ temperatures.

**Sulfate diffusion model for Site MB.** The rate of SO$_4^{2–}$ diffusion into the sediment from the overlying water was calculated for each MB profile using Fick’s 1st Law equation (Berner 1980):

$$J_s = – \phi \times D_{s(T)} \times (\delta C / \delta x) \quad (2)$$

where $J_s$ is the sediment diffusion flux (mmol SO$_4^{2–}$ cm$^{-2}$ d$^{-1}$), $\phi$ is sediment porosity, $D_{s(T)}$ is the whole sediment temperature corrected diffusion coefficient (cm$^2$ d$^{-1}$), $\delta C / \delta x$ is the 1st partial derivative of the SO$_4^{2–}$ concentration with respect to depth, calculated as the linear-regression slope of SO$_4^{2–}$ versus depth data for the upper surface interval (linear portion, n = 3 to 13 data points). An average MB $\phi$ of 0.9 was used in all calculations. Values for $D_{s(T)}$ were calculated using $D_s = 0.43$ cm$^2$ d$^{-1}$ at 25°C, which was previously measured at a nearby (>0.5 km) mesohaline site (R64E) (Roden & Tuttle 1992) using the $^{35}$SO$_4^{2–}$ instantaneous source technique (Jørgensen 1978b), and assuming the relationship:

$$D_{s(T)} = 0.43(D_{s(T)}^o/D_{s(T)}^{25})^{-1} \quad (3)$$

where $D_{s(T)}^o$ and $D_{s(T)}^{25}$ (in cm$^2$ s$^{-1}$) are the infinite dilution diffusion coefficients at temperature $T^\circ$C and 25°C, respectively, and were calculated from data given in Li & Gregory (1974) by Krom & Berner (1980):

$$D_{s(T)}^o = 10.7 + 0.23(T – 25) \quad (4)$$

**Data analysis.** Quantitative seasonal analysis was conducted by grouping data into the following 3 mo intervals: spring = March to May, summer = June to August, and fall = September to November. A grouping designated YEAR was used for the complete sampling period (March to November). Commercial software (S-Plus and Microsoft Excel) was used for all statistical tests, with accepted error set at $p < 0.05$ in all cases, unless otherwise indicated. The response of SR to the combined effect of temperature and a second controlling factor was assessed by a linear multiple-regression model of the generalized form:

$$SR = f(T, X) = (a \times T) + (b \times X) + c \quad (5)$$

where $a$ and $b$ are coefficients, $c$ is a constant, the independent variable $T$ is temperature ($\circ$C), $X$ is one of the following: SO$_4^{2–}$, PC, PN, PC:PN ratio, chl $a$, or TOM. This model assumed that SR was linearly dependent on each independent variable, and that $T$ and $X$ were independent of each other.

The interannual variation in SR was investigated with respect to the 7 yr (1987 to 1994) record of monthly averaged Susquehanna River flow data (USGS 1987–1994). Linear-regression analysis was used, with July SR$_2$ as the dependent variable and time-averaged river flow (prior to July) as the independent variable. The timing and duration of river flow that most affected SR was determined by varying the time-window used for averaging river flow data, both in terms of size (1 to 9 mo averages) and initiation period (October of the preceding year to June of the same year). Months from the preceding year (October to December) were included to determine whether a ‘memory effect’ of autotrophic production from the previous fall was carried over to the following year. Previously published July 1987 SR$_2$ data (Roden & Tuttle 1993a) from Sites R64 and LB3 (located <1 km from Sites MB and LB, respectively) were included to increase the number of observations in these Bay regions. The interannual-comparison data set included an exceptionally high SR$_2$ value measured at UB during July 1993 (at least 12× greater than all other values measured at UB), although this datum was excluded from all other calculations and monthly–seasonal comparisons.
RESULTS

Monthly and seasonal trends

SR rates

The complete 1989 to 1994 Chesapeake Bay LMER database of depth-integrated SR_{12} has been previously published (Marvin-DiPasquale & Capone 1998). Presented here as monthly averaged depth profiles, the rise and fall of SR rates at MB and LB, throughout the composite year, is clearly illustrated (Fig. 2). UB rates were low throughout the year (<100 nmol SO_{4}^{2–} cm⁻³ d⁻¹ at all depths), essentially vertical with depth during spring and October/November, and exhibited a slight increase with depth below 2 cm from June through September. In contrast, MB rates decreased sharply with depth from late spring through fall, with peak SR_{2} (>800 nmol SO_{4}^{2–} cm⁻³ d⁻¹) during July. LB exhibited elevated SR_{2} during August and September (480 and 370 nmol SO_{4}^{2–} cm⁻³ d⁻¹, respectively), but were essentially constant with depth (<300 nmol SO_{4}^{2–} cm⁻³ d⁻¹) throughout the remainder of the year. Depth-integrated monthly SR_{12} rates similarly exhibit differences among sites with respect to the magnitude of temporal variation, which was greatest at MB and smallest at UB, as the absolute difference between maximum and minimum monthly SR_{12} rates was 6 (UB), 58 (MB) and 21 mmol m⁻² d⁻¹ (LB) (Fig 3a). Monthly averaged SR_{2}:SR_{12} ratios were also computed, as a measure of how SR in the surface 0 to 2 cm sediment interval varied temporally compared to the overall 0 to 12 cm depth-integrated profile (Fig. 3b).

The resulting ratios were compared to the ratio of 0.17 (e.g. 1:6), which represents the theoretical SR_{2}:SR_{12} ratio calculated for a 6-interval profile with a depth-constant SR rate. This comparison indicated that SR_{2}:SR_{12} ratios were suppressed at UB from April to September and enhanced at MB throughout the sampling period. The ratio approximated 0.17 at LB from April through June, then increased to an August maximum followed by a decrease through October/November. Significant within-site seasonal differences were evident for both SR_{2} and SR_{12} rates (Table 1), including peak SR_{12} rates during summer at MB and during both summer and fall at UB and LB. There were no significant seasonal differences in site-specific SR_{2}:SR_{12} ratios.

Ancillary data

Pore water SO_{4}^{2–} profiles at UB were nearly constant with depth and generally <8 mM SO_{4}^{2–} throughout the sampling period, with minimum concentrations (<3 mM SO_{4}^{2–}) during summer (Fig. 4). At MB, SO_{4}^{2–} shifted from a near-linear decrease with depth during spring to early summer (March to June), to an exponential decrease during mid-summer through fall (July to November), and was often undetectable below 5 and 10 cm during summer and fall. This was coincident with temporal variations in dissolved ΣH_{2}S, which increased linearly with depth from March through June and exhibited mid-depth maximum just above the depth of SO_{4}^{2–} depletion from July to November, with a September maximum (>5 mM). At LB, SO_{4}^{2–} (~20 mM)
exhibited no depletion with depth throughout the sampling period.

Examining the ratio of biogeochemically reactive SO$_4^{2-}$ to the more conservative Cl$^-$ anion provides a means for separating temporal variations in pore water SO$_4^{2-}$ concentration due to changing SR rates versus changes due to diffusion of overlying water SO$_4^{2-}$ into sediment resulting from variable freshwater flow. The molar SO$_4^{2-}$:Cl$^-$ ratio for full-strength seawater (0.05‰) is an order of magnitude lower than that of average river water (0.53‰) (calculated from data given in Turekian 1968). The increase in this ratio, along a conservative mixing gradient going from full-strength seawater (36‰) to river water (assuming 0‰), is negligible above 2‰ salinity (SO$_4^{2-}$:Cl$^-$ ratio = 0.06). Below 2‰, the ratio increases gradually until 0.1‰ (SO$_4^{2-}$:Cl$^-$ ratio = 0.11), at which point the ratio rapidly increases to 0.53 as salinity approaches 0‰. The high SO$_4^{2-}$:Cl$^-$ ratios (>0.05) in UB surface sediment from April through August (Fig. 5) coincided with the period of decreasing salinity (Fig. 6c) and decreasing Susquehanna River flow (Fig. 6a). Because UB often exhibited overlying water salinity <2‰, surface sediment at this site was susceptible to SO$_4^{2-}$:Cl$^-$ ratios >0.05, whereas MB and LB were not. Higher UB salinity in early spring (March) and fall resulted in a SO$_4^{2-}$:Cl$^-$ ratio ~0.05 in the uppermost sediment layer, with this ratio decreasing only at depths below 5 cm. In contrast, a continuous decrease in the SO$_4^{2-}$:Cl$^-$ ratio with depth was evident at UB from April through August. Profiles of SO$_4^{2-}$:Cl$^-$ similarly decreased with depth at MB throughout the sampling period, but were essentially constant at 0.05 for LB.

Table 1. Seasonal averages of 0 to 2 cm surface sediment and 0 to 12 cm depth-integrated sulfate reduction (SR) rates and ancillary parameters for the 1989 to 1994 Chesapeake Bay Land-Margin Ecosystem Research (LMER) program, from 3 sites (upper [UB], mid- [MB] and lower [LB] bay) along the Chesapeake Bay central channel. SD given in parentheses. Significant differences (p < 0.05) among seasons (within-site) are indicated by different letters with ranking determined using Tukey’s multi-comparison method. The number of observations is given as n. E$_h$: sediment redox; PC: particulate carbon; PN: particulate nitrogen

<table>
<thead>
<tr>
<th>Parameter/ Season</th>
<th>UB</th>
<th>MB</th>
<th>LB</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR; 0 to 2 cm (mmol m$^{-2}$ d$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>0.2 (0.2)</td>
<td>B 10</td>
<td>8.2 (8.9)</td>
</tr>
<tr>
<td>Summer</td>
<td>0.5 (0.4)</td>
<td>AB 8</td>
<td>16.2 (10.2)</td>
</tr>
<tr>
<td>Fall</td>
<td>0.7 (0.4)</td>
<td>A 7</td>
<td>8.6 (4.1)</td>
</tr>
<tr>
<td>SR; 0 to 12 cm (mmol m$^{-2}$ d$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>2.0 (1.6)</td>
<td>B 10</td>
<td>21.4 (18.0)</td>
</tr>
<tr>
<td>Summer</td>
<td>5.1 (3.3)</td>
<td>A 8</td>
<td>54.5 (40.4)</td>
</tr>
<tr>
<td>Fall</td>
<td>4.0 (1.7)</td>
<td>AB 7</td>
<td>21.4 (7.9)</td>
</tr>
<tr>
<td>SO$_4^{2-}$ pool; 0 to 2 cm (mmol m$^{-2}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>38 (36)</td>
<td>B 10</td>
<td>217 (42)</td>
</tr>
<tr>
<td>Summer</td>
<td>34 (25)</td>
<td>B 9</td>
<td>141 (43)</td>
</tr>
<tr>
<td>Fall</td>
<td>83 (40)</td>
<td>A 7</td>
<td>209 (37)</td>
</tr>
<tr>
<td>SO$_4^{2-}$ pool; 0 to 12 cm (mmol m$^{-2}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>241 (149)</td>
<td>AB 10</td>
<td>941 (284)</td>
</tr>
<tr>
<td>Summer</td>
<td>170 (121)</td>
<td>B 9</td>
<td>502 (230)</td>
</tr>
<tr>
<td>Fall</td>
<td>369 (132)</td>
<td>A 7</td>
<td>505 (173)</td>
</tr>
<tr>
<td>$\Sigma$H$_2$S; &lt;2 cm (mmol m$^{-2}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>0.4 (1.4)</td>
<td>B 11</td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>17.8 (17.9)</td>
<td>A 12</td>
<td></td>
</tr>
<tr>
<td>Fall</td>
<td>4.0 (5.5)</td>
<td>B 8</td>
<td></td>
</tr>
<tr>
<td>$\Sigma$H$_2$S; 0 to 12 cm (mmol m$^{-2}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>60 (34)</td>
<td>B 11</td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>233 (110)</td>
<td>A 12</td>
<td></td>
</tr>
<tr>
<td>Fall</td>
<td>226 (104)</td>
<td>A 8</td>
<td></td>
</tr>
<tr>
<td>Bottom water temperature (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>13.5 (6.1)</td>
<td>B 10</td>
<td>11.3 (4.5)</td>
</tr>
<tr>
<td>Summer</td>
<td>25.1 (3.4)</td>
<td>A 9</td>
<td>23.5 (2.8)</td>
</tr>
<tr>
<td>Fall</td>
<td>16.3 (4.6)</td>
<td>B 7</td>
<td>18.3 (3.4)</td>
</tr>
<tr>
<td>PC:PN ratio</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>16.4 (4.3)</td>
<td>A 7</td>
<td>7.9 (0.7)</td>
</tr>
<tr>
<td>Summer</td>
<td>17.6 (5.1)</td>
<td>A 8</td>
<td>7.6 (0.7)</td>
</tr>
<tr>
<td>Fall</td>
<td>14.8 (2.9)</td>
<td>A 6</td>
<td>7.5 (0.5)</td>
</tr>
<tr>
<td>Eh; 1 to 1.5 cm depth (mV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>121 (138)</td>
<td>A 9</td>
<td>-3 (63)</td>
</tr>
<tr>
<td>Summer</td>
<td>215 (123)</td>
<td>A 9</td>
<td>-105 (52)</td>
</tr>
<tr>
<td>Fall</td>
<td>203 (108)</td>
<td>A 6</td>
<td>74 (169)</td>
</tr>
</tbody>
</table>
Since temporal changes in SR were most dynamic in
the uppermost sediment layers, we focus much of our
assessment on biogeochemical changes at the sedi-
ment-water interface. Fig. 4 depicts monthly averaged
ancillary data for overlying bottom water (Fig. 6b–d)
and the surface 0–1 to 0–2 cm sediment horizon
(depending on the constituent) (Fig. 6e–m). The pre-
dictable rise in temperature from spring through sum-
er, and subsequent decrease during fall, was evident
(Fig. 6b, Table 1) at all sites. Salinity increased from
UB to LB, but was temporally less variable at MB and
LB than at UB (Fig. 6c). Dissolved oxygen in over-
lying water decreased from April through August at all
sites, with MB being the most depleted during summer
(Fig. 6d). Both MB and LB sediments exhibited highest
chl a concentrations during May (Fig. 6e). There were
no significant (within-site) seasonal differences re-
lected in sediment PC, PN, PC:PN, TOM or
total reduced sulfur data, although consistent
among-site differences were evident throughout the sampling period for all of
these parameters (Fig. 6f,h–j,l). The decrease in MB pore water SO$_4^{2-}$ concentration during
summer was significant, as was the corre-
sponding decrease in sediment redox po-
tential and increase in $\Sigma$H$_2$S (Fig. 6g,k,m,
Table 1). Compared to overlying water concen-
trations, pore water SO$_4^{2-}$ was depleted in
the top 0 to 2 cm at UB from May through July, and at MB from April through Novem-
ber, but was generally at or near water-
column concentrations at LB throughout the
year (data not shown).

SR and temperature

An Arrhenius-type model was applied to
data grouped by season, site and integration
depth to quantify the apparent temperature
influence on SR. Significant seasonal model
results are summarized in Table 2, and in-
clude: UB (0 to 12 cm data, fall only), MB
(both integration depths, spring and fall only),
and LB (all depth/season combinations,
except the 0 to 2 cm data during spring). The
fall data-grouping resulted in the best model
fit ($r^2 > 0.5$) at all sites. No significant seasonal
difference in $C_t$ values was found for any of
the 3 sites. When data were pooled into 2 tem-
perature ranges (< or $\geq$ 20°C), rates were sta-
tistically higher at $\geq$20°C at all 3 sites and
both integration depths (SR$_2$ and SR$_{12}$), except
for UB SR$_2$ (data not shown). When the tem-
perature model (Eq. 1) was applied to these 2
data groupings, a significant positive SR–temperature
relationship was observed at MB for the <20°C group-
ing, but not for the $\geq$20°C grouping (both integration
depths). No significant SR–temperature relationships
were found for either temperature grouping at UB or
LB (at either integration depth). Only when the com-
plete data set (all temperatures) was used for these
latter 2 sites was a temperature relationship evident
(i.e. Table 2, ‘Year’ grouping).

SR and surface sediment parameters

The relationship between SR$_2$ rates and individual
surface-sediment parameters (SO$_4^{2-}$, chl a, PC, PN,
PC:PN, and TOM) were investigated with linear-
regression analysis (Table 3). Data were pooled by
Table 2. Summary of $C_t$ values (the temperature coefficient) calculated from Arrhenius-type model regressions of sulfate reduction (SR) and temperature data grouped by site and season, from 3 sites (upper [UB], mid-[MB] and lower [LB] bay) along the Chesapeake Bay central channel. All regressions were significant at $p < 0.05$, except those with the $r^2$-value designated with an asterisk, where $0.10 > p > 0.05$. Non-significant ($p > 0.1$) regressions are designated (ns). Seasons were omitted when neither integration depth yielded a significant regression. $C_t$ (units: kJ mol$^{-1}$) calculated from the slopes of regressions of ln(SR) versus temperature$^{-1}$; $C_t$ SEs are given in parentheses.

<table>
<thead>
<tr>
<th>Site</th>
<th>Season</th>
<th>n</th>
<th>0 to 2 cm $r^2$</th>
<th>$C_t$</th>
<th>0 to 12 cm $r^2$</th>
<th>$C_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB</td>
<td>Fall</td>
<td>7</td>
<td>ns</td>
<td>0.81</td>
<td>57 (12)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Year</td>
<td>25</td>
<td>0.19</td>
<td>53 (25)</td>
<td>0.39</td>
<td>51 (13)</td>
</tr>
<tr>
<td>MB</td>
<td>Spring</td>
<td>11</td>
<td>0.39</td>
<td>96 (39)</td>
<td>0.34*</td>
<td>73 (34)</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>8</td>
<td>0.67</td>
<td>84 (24)</td>
<td>0.58</td>
<td>60 (21)</td>
</tr>
<tr>
<td></td>
<td>Year</td>
<td>31</td>
<td>0.45</td>
<td>62 (13)</td>
<td>0.48</td>
<td>60 (11)</td>
</tr>
<tr>
<td>LB</td>
<td>Spring</td>
<td>9</td>
<td>ns</td>
<td>0.39*</td>
<td>69 (33)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>9</td>
<td>0.42*</td>
<td>70 (31)</td>
<td>0.49</td>
<td>38 (15)</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>5</td>
<td>0.87</td>
<td>72 (16)</td>
<td>0.89</td>
<td>62 (13)</td>
</tr>
<tr>
<td></td>
<td>Year</td>
<td>23</td>
<td>0.58</td>
<td>90 (17)</td>
<td>0.68</td>
<td>59 (9)</td>
</tr>
</tbody>
</table>

Table 3. Values of $r^2$ from significant ($p < 0.05$) linear regressions of sulfate reduction rate (0 to 2 cm) against individual surficial sediment parameters [$X$], for data grouped by site/season or site/year (all site-specific data, irrespective of season), from 3 sites (upper [UB], mid-[MB] and lower [LB] bay) along the Chesapeake Bay central channel. Non-significant regressions are indicated (ns) and the number of observations is given in parentheses. PN: particulate nitrogen; TOM: total organic matter.

<table>
<thead>
<tr>
<th>Site</th>
<th>X</th>
<th>Spring</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB</td>
<td>SO$_4^{2-}$</td>
<td>ns</td>
<td>0.24 (25)</td>
</tr>
<tr>
<td>MB</td>
<td>PN</td>
<td>ns</td>
<td>0.18 (24)</td>
</tr>
<tr>
<td>MB</td>
<td>TOM</td>
<td>0.64</td>
<td>ns</td>
</tr>
<tr>
<td>MB</td>
<td>Chl a</td>
<td>0.95</td>
<td>ns</td>
</tr>
<tr>
<td>LB</td>
<td>Chl a</td>
<td>0.89</td>
<td>ns</td>
</tr>
</tbody>
</table>

Contribution of sulfate diffusion in supporting mesohaline sulfate reduction

Molecular diffusion of SO$_4^{2-}$ in sediment is controlled by porosity, temperature, and the SO$_4^{2-}$ gradient (Eq. 2). Of these, the latter 2 factors had the greatest temporal influence on diffusion, and subsequently on the supply of new SO$_4^{2-}$ for benthic SR at site MB. While temperature increased through spring (Fig. 6b), SO$_4^{2-}$ gradients varied little (Fig. 4), and the resulting SO$_4^{2-}$ diffusion rate remained nearly constant and low through May (~2 mmol m$^{-2}$ d$^{-1}$), and increased only modestly (to ~4 mmol m$^{-2}$ d$^{-1}$) through July (Fig. 7).
However, as SR\textsubscript{12} increased more than 8-fold from 8 to 67 mmol m\textsuperscript{-2} d\textsuperscript{-1} during the March through July period (Fig. 3a), the fraction of the SO\textsubscript{4}\textsuperscript{2–} demand supplied by diffusion necessarily decreased from 33% in March to <10% in the May through July period. The fraction of SR\textsubscript{12} supported by SO\textsubscript{4}\textsuperscript{2–} diffusion increased sharply to >30% in August due to a decreased SR\textsubscript{12} and to a sharp increase in SO\textsubscript{4}\textsuperscript{2–} diffusion, driven by peak temperatures and a steep SO\textsubscript{4}\textsuperscript{2–} gradient. With decreasing temperatures and SR\textsubscript{12} rates in the fall, the corresponding fraction of SO\textsubscript{4}\textsuperscript{2–} supplied by diffusion rose to a maximum of 50% by November. A similar quantitative assessment of SO\textsubscript{4}\textsuperscript{2–} diffusion at UB and LB was not practical because monthly SO\textsubscript{4}\textsuperscript{2–} gradients were either
minor or zero (Fig. 4), largely due to bioturbation, and thus diffusion calculations were not reliable.

**Interannual variation in summertime sulfate reduction rates**

For the years 1987 to 1994, spring peak flow from the Susquehanna River occurred as early as February and as late as May (Fig. 8). The magnitude of this peak was highest in April 1993, followed by April 1994, and lowest in April 1992. Significant relationships between spring river flow and July SR$_2$ rates were observed at all 3 sites (Fig. 9), although the time window for river flow-averaged data that resulted in the best regression fit varied among sites. The strongest relationship at Site UB was found using April river flow. However, this regression was heavily weighted by the 1993 data, Table 4. Significant (p < 0.05) results for multiple-regression models (Eq. 5), where $T$ is temperature, $X$ is a single surface sediment variable, and $N$ is the number of observations. Data, from 3 sites (upper [UB], mid- [MB] and lower [LB] bay) along the Chesapeake Bay central channel, were pooled by site–season. The site–year grouping indicates all data were used, irrespective of season. The level of significance for individual regression coefficients (a and b) are indicated by *p < 0.1, **p < 0.05, or ***p < 0.005, respectively. PC: particulate carbon; PN: particulate nitrogen

<table>
<thead>
<tr>
<th>Site</th>
<th>Season</th>
<th>Model</th>
<th>$r^2$</th>
<th>N</th>
<th>T</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB</td>
<td>Year</td>
<td>$\text{SR}_2 = a[T] + b[SO}_4^2- + c$</td>
<td>0.49</td>
<td>25</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>MB</td>
<td>Spring</td>
<td>$\text{SR}_2 = a[T] + b[PC] + c$</td>
<td>0.78</td>
<td>7</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>MB</td>
<td>Fall</td>
<td>$\text{SR}_2 = a[T] + b[PC] + c$</td>
<td>0.82</td>
<td>7</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>MB</td>
<td>Year</td>
<td>$\text{SR}_2 = a[T] + b[PC] + c$</td>
<td>0.29</td>
<td>24</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>MB</td>
<td>Spring</td>
<td>$\text{SR}_2 = a[T] + b[PN] + c$</td>
<td>0.80</td>
<td>7</td>
<td>*</td>
<td>**</td>
</tr>
<tr>
<td>MB</td>
<td>Fall</td>
<td>$\text{SR}_2 = a[T] + b[PN] + c$</td>
<td>0.92</td>
<td>7</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>MB</td>
<td>Year</td>
<td>$\text{SR}_2 = a[T] + b[PN] + c$</td>
<td>0.37</td>
<td>24</td>
<td>**</td>
<td>**</td>
</tr>
</tbody>
</table>

Integrating sulfate diffusion rates into the mid-bay Site MB sediment (line with white squares) and the percentage of 0 to 12 cm depth-integrated sulfate reduction rate supported by this amount of sulfate diffusion (bars)

![Fig. 7](image-url)

Fig. 7. Monthly averaged sulfate diffusion rates into the mid-bay Site MB sediment (line with white squares) and the percentage of 0 to 12 cm depth-integrated sulfate reduction rate supported by this amount of sulfate diffusion (bars)

![Fig. 8](image-url)

Fig. 8. Continuous monthly average Susquehanna River flow data (USGS 1987–1994) from January 1987 to July 1994, with the month of highest flow indicated for each year. The annual July 0 to 12 cm integrated sulfate reduction rate for each site is shown as symbols. Previously published 0 to 12 cm monthly average sulfate reduction rate (SR$_{12}$) data (Roden & Tuttle 1993a) is included from July 1987 for sites R64 and LB3, located <1 km from sites MB and LB, respectively

![Fig. 9](image-url)

Fig. 9. Site-specific linear regressions of monthly averaged Susquehanna River flow data versus July 0 to 2 cm sulfate reduction rate for the 3 study sites (upper [UB], mid- [MB] and lower [LB] bay). The time window for river flow was varied in each case until the best fit to the data was obtained
which had a July SR₂ rate (18.0 ± 4.3 mmol m⁻² d⁻¹, n = 2) more than 12× that of any other value measured for this site. This enhanced rate appeared to be due to the rapid input of utilizable carbon during the intense spring 1993 freshet, rather than to increased SO₄²⁻; as July 1993 SO₄²⁻ concentration throughout the top 12 cm of sediment (1.4 to 2.4 mM) was comparable to values observed during July for the other 5 yr of sampling (Fig. 4). None of the UB regressions were significant when the 1993 data was omitted. A significant positive relationship between July SR₂ at MB and river flow was observed only when a wide-averaged time window (February to June) was used. In contrast, a strong negative relationship between April and June time-averaged river flow and SR₂ was evident for LB. Regressing the annual peak river-flow rates (letting the specific month vary) against July SR₂ did not improve regression fits at any site.

**DISCUSSION**

The 6 yr LMER time series allows for examination of the factors controlling microbial SR in estuarine sediments on monthly, seasonal and interannual time-scales. Qualitative trends and interactions are evident at all 3 scales, while statistically significant quantitative trends are most apparent seasonally, and to a lesser extent interannually.

**Temperature**

Temperature exerts an ever-present control on microbial metabolic rates. While individual bacterial strains have discrete temperature optima, a continuous increase in whole-sediment community SR rates throughout the environmental range of temperatures can be reasonably expected. However, seasonal patterns of site-specific SR rates and temperature did not always parallel each other (Table 1). While the SR–temperature relationship was significant for most seasons/site/depth combinations (Table 2), the exceptions point to conditions when SR was substantially influenced by other factors. The lack of a significant SR–temperature relationship during spring and summer at UB (both depths) was primarily linked to the decreasing pool of overlying water SO₄²⁻ (i.e. SO₄²⁻ limitation) associated with increased river flow during this high-flow period.

Sulfate limitation does not explain the lack of a significant SR–temperature relationship during spring at LB (0 to 2 cm interval), as evidenced by the persistently high SO₄²⁻ concentration at this site. Since SR at Site LB is C-limited overall (Marvin-DiPasquale & Capone 1998), it is presumably most limited just prior to deposition of the bulk of the annual spring phytoplankton bloom in late May to early June (Malone et al. 1988). Further, an increase in macrofauna bioturbation rates with increasing spring temperature can stimulate both microbial SR (Hines & Lyons 1982) and other heterotrophic microbes (e.g. aerobes, denitrifiers, Fe- and Mn-reducers) by replenishing suitable electron acceptors (e.g. O₂, NO₃⁻, Fe[III], Mn[IV]) (Aller & Aller 1998). Thus, during the period of peak C-limitation, other bacterial groups may effectively compete with SRB for organic substrates, which would suppress the SR maximum rate in near-surface sediments and mask the spring SR–temperature relationship at LB. This competition for organic substrate may be relieved after the spring-bloom material has been deposited and mixed into the sediment, and the pool size of electron acceptors more favorable than SO₄²⁻ has declined. In contrast to both UB and LB, the spring SR₂–temperature relationship was significant at MB, where neither SO₄²⁻ nor C were limiting, and bioturbation was minimal to absent (Kemp et al. 2000, USACE 2000).

The lack of a significant SR–temperature correlation at MB (both depths) during summer, and for the ≥20°C data grouping, suggests that factors other than temperature limit SR at this site and season (or temperature range). For SR₁₂ this clearly reflects SO₄²⁻ limitation at depth during mid- to late summer (Fig. 4). A similar explanation for SR₂ would seem unlikely because SO₄²⁻ concentration in the 0 to 2 cm surface sediment remained consistently high (>5 mM) throughout the year. Thus, short of temperature or sulfate limitation, it would appear that the availability of specific organic substrates (e.g. acetate, lactate, etc.) limits SR in the 0 to 2 cm interval at MB during summer. Even though there is a supply of recently deposited fresh organic matter in the mesohaline surface sediment, in the form of senescent spring diatoms, the supply of suitable low molecular weight organic substrates for SRB may ultimately be limited by the activity of fermenting bacteria that generate these substrates from high molecular weight organic precursors (Ahmed et al. 1992). The lack of a significant SR–temperature relationship for the ≥20°C data grouping was similar to the lack of correlation between temperatures >20°C and heterotrophic bacterioplankton abundance, production or specific growth rate reported for mesohaline Chesapeake Bay waters (Shiah & Ducklow 1994). In that study it was concluded that organic substrate supply limits bacterioplankton production and abundance during summer only, and that temperature limits these parameters during all non-summer periods.

Temperature may have been the strongest controlling influence on SR rates during fall, as this season consistently exhibited the best model fit (r² ≥ 0.5) at all
sites (Table 2). By fall, much of the diatom bloom that was rapidly deposited during spring has been degraded (Malone et al. 1988, Zimmerman & Canuel 2001). Further, the phytoplankton biomass reaching the sediment during both summer and fall has decreased, relative to spring, due to nutrient limitation and a shift from larger diatom cells to picoplankton (Smith & Kemp 1995, 2001). Thus, the apparent SR–temperature relationship during fall is not subject to as much perturbation due to rapidly changing organic loading conditions, as is the case during the spring–summer transition.

A major assumption underlying the Arrhenius relationship is that $E_a$ is constant over the temperature range of reactions. Previous work with salt marsh sediments demonstrated that neither the $E_a$ nor the temperature optima for in situ SRB varied seasonally (Abdollahi & Nedwell 1979). In that study, true $E_a$ values were calculated each season from simultaneous incubations at multiple temperatures. In contrast, seasonal differences may be observed for apparent $E_a$ (i.e. $C_i$) values calculated from seasonal SR data generated from incubations conducted on different dates at in situ temperatures. Apparent $E_a$ values ranged from 21 kJ mol$^{-1}$ in winter to 117 kJ mol$^{-1}$ in summer for Cape Lookout Bight marine sediments (Crill & Martens 1987). Seasonal differences were attributed to changes in reaction mechanisms, with winter rates being further from steady state. The lack of winter samples in the current study did not allow for the same winter–summer comparisons, and the error associated with the $C_i$ values was sufficiently large to mask any significant seasonal differences within each site (Table 2). However, these studies illustrate the importance of differentiating between true versus apparent $E_a$ calculations. Only by experimentally varying temperature alone can the temperature influence on microbial rates be explicitly ascertained. Apparent $E_a$ ($C_i$) calculations, as conducted in the current study and Cape Lookout Bight study, may be influenced by temporal variations in other factors, such as electron donor and acceptor availability.

**Sulfate concentration**

Sulfate is the electron acceptor for SR, and thus may limit this microbial process at low concentrations (Capone & Kiene 1988). The supply of SO$_4^{2-}$ from the overlying water to the sediment varies with salinity (cf. Fig. 6k and c) on timescales from hours (tidal cycles) to months (seasonal variations in river flow). The diffusive flux of SO$_4^{2-}$ may be either into or out of the sediment, depending on relative concentrations in the overlying water. Diffusion may be particularly important in the oligohaline region of the Bay, which has comparatively low SO$_4^{2-}$ and is the region most strongly impacted by seasonal changes in Susquehanna River freshwater flow. Overlying water and surface sediment (0 to 1 cm) SO$_4^{2-}$ concentrations were generally at or near equilibrium at UB, and ranged from 0.6 to 9 mM. This was both above and below the 1 to 3 mM range considered limiting for SR in marine sediments (Boudreau & Westrich 1984, Skyring 1987). However, half-saturating substrate concentrations ($K_s$) values as low as 0.03 mM SO$_4^{2-}$ have been shown for SR in low-salinity estuarine environments (Roden & Tuttle 1993b). On short timescales, the degree of SO$_4^{2-}$ limitation thus depends on the overall $K_s$ of the particular SR community. On longer timescales (months to seasons), the rate at which the community composition can shift between populations having higher or lower SO$_4^{2-}$ affinities may dictate the degree and duration of SO$_4^{2-}$ limitation. The extent to which apparent (community-integrated) $K_s$ values may vary in response to changing SO$_4^{2-}$ levels has not been adequately addressed in transitional coastal systems.

The positive relationship between SR$_2$ and SO$_4^{2-}$ at UB (Table 3), as well as the fact that SO$_4^{2-}$ and temperature combined could account for approximately 50% of the variability in SR$_2$ (Table 4), demonstrates that SR$_2$ was at least partially controlled by SO$_4^{2-}$ in the UB region. However, since in both cases these SR$_2$-SO$_4^{2-}$ relationships were significant for the Year grouping only, and not for any specific season, the periodicity of these relationships appears to be out of phase with our seasonal delineation. Alternatively, the relationships are sufficiently subtle as to not be detectable with the limited number of seasonally specific observations. Assessing SO$_4^{2-}$ limitation at UB in deeper sediment by considering SO$_4^{2-}$ depth profiles (Fig. 4) is difficult because concentrations are low to begin with, and generally decrease only gradually with depth. It is therefore helpful to consider the molar SO$_4^{2-}$:Cl$^{-}$ ratio (Fig. 5). This allows biologically and chemically mediated changes in pore water SO$_4^{2-}$ concentration to be separated from physical processes of molecular diffusion and advection (Jørgensen 1977). Assuming no significant biological or abiotic chemical removal or production, pore water Cl$^{-}$ concentration is controlled by diffusion and advection, and profile gradients reflect the magnitude and direction of Cl$^{-}$ flux (Matisoff 1980). Both increasing and decreasing linear Cl$^{-}$ gradients were observed for UB and MB, while LB profiles were generally vertically constant (data not shown). The decrease in SO$_4^{2-}$:Cl$^{-}$ ratios with depth at UB and MB thus reflects SO$_4^{2-}$ depletion via SR. In our earlier report (Marvin-DiPasquale & Capone 1998), we argued that SR in the top 12 cm of sediment is primarily controlled by C-
limitation in the oligohaline region of the Bay. However, the SO$_4^{2-}$-Cl$^-$ profiles presented here indicate that SO$_4^{2-}$ is being depleted relative to Cl$^-$ most dramatically from April through August, and at depths below 5 cm during early spring and fall. Thus, SO$_4^{2-}$ limitation also appears to be an important factor at UB and MB, particularly in deeper sediments (>12 cm). The constant SO$_4^{2-}$-Cl$^-$ ratio at LB, at or near the conservative mixing ratio, confirms our earlier findings that this site was C- and not SO$_4^{2-}$-limited.

The observation that SO$_4^{2-}$ diffusion accounted for <10% of the SO$_4^{2-}$ demand at MB during the spring–summer transition (May to July), and a larger proportion (30 to 50%) during early spring and late fall (Fig. 7), was similar to an earlier report in which depth-integrated benthic SR exceeded modeled diffusive influx of SO$_4^{2-}$ (Urban et al. 1994). The balance of the SO$_4^{2-}$ needed to fuel SR can only be supplied by advective transport and/or by S-recycling. Bioturbation may facilitate the transport of both SO$_4^{2-}$ and O$_2$ into sediment, the latter of which may further reoxidize reduced-S compounds back to SO$_4^{2-}$ (Berner & Westrich 1985). However, the absence of benthic macrofauna at Site MB during the warm months suggests that bioturbation is not significant in this case, and that any S-recycling must occur by other pathways. Potential microbial pathways include the disproportionation of thiosulfate to SO$_4^{2-}$ and sulfide (Jørgensen 1990a,b) and anaerobic elemental S$^0$ oxidation via Fe(III) and/or Mn(IV) reduction (Thamdrup et al. 1993, Lovley & Phillips 1994). By difference, such reoxidation processes accounted for roughly 50 (late fall) to 90% (April to July) of the SO$_4^{2-}$ demand. A direct analysis of the temporal dynamics of the above constituents would be necessary to validate this conclusion. However, the possibility that SR$_{12}$ rates are overestimated due to inadvertent SO$_4^{2-}$ stimulation of SRB is not likely, as carrier-free $^{35}$SO$_4^{2-}$ amendments (i.e. no non-radioactive SO$_4^{2-}$) were used in all ‘true tracer’ whole-core SR rate assays (final pore water $^{35}$SO$_4^{2-}$-amendment concentration per interval = 0.1 nM).

Another possibility is that the calculated SO$_4^{2-}$ diffusion rates are underestimated, which could result if the sediment porosity ($\phi$), the whole sediment temperature-dependent diffusion coefficient ($D_{a(T)}$), or change in SO$_4^{2-}$ concentration with depth measurement ($\Delta\Sigma/\Delta x$) were underestimated in Eq. (2). Values of both $\phi$ and $\Delta\Sigma/\Delta x$ were measured directly and thus well established. Therefore, if any of the parameters in Eq. (2) were underestimated it is most likely $D_{a(T)}$, which was calculated from Eq. (3) based on 1 previous assessment of $D_{a(T)}$ at a nearby mesohaline site (Roden & Tuttle 1992). However, even if the actual diffusion coefficient value at Site MB (at 25°C) is 50% greater than the measurement by Roden & Tuttle (1992; i.e. assume 0.65 cm$^2$ d$^{-1}$), then the estimate of how much total SR is directly supported by SO$_4^{2-}$-diffusion for the May to July low period would only increase from an average of 8.6 to 13.0%. Thus, our conclusion would remain unchanged regarding this period, as being a particularly important time for S-recycling supporting SR. While a similar assessment of SO$_4^{2-}$ diffusion and S-recycling at UB and LB was not practical, advective transport of SO$_4^{2-}$ was likely more important than diffusion in these heavily bioturbated surface sediments.

**Bioturbation**

Sediment mixing by benthic macrofauna may vary seasonally in temperate marine sediments due to temporal variations in both temperature and organic C supply and the abundance and type of macrofauna (Kemp & Boynton 1981, Martin & Sayles 1987, Aller & Aller 1992). Increased bioturbation facilitates increased aerobic and anaerobic microbial activity (Aller & Yingst 1985, Berner & Westrich 1985, Kristensen & Blackburn 1987), nutrient regeneration (Cowen & Boynton 1996, Cowan et al. 1996, Kemp et al. 1997), and reduced-S oxidation (Berner & Westrich 1985, Aller & Rude 1988). The generally vertical SR depth profiles at UB and LB through the year (Fig. 2) in part reflect bioturbation, as this process homogenizes the active SR zone and partially mitigates SO$_4^{2-}$ limitation. This is in contrast to the essentially non-bioturbated MB site, where SR profiles exhibit much larger monthly changes. While not examined quantitatively in the current study, we believe bioturbation was most intense during summer at Sites UB and LB, based on high temperature, adequate C deposition, and macrofauna abundance. In Great Bay Estuary (NH), a significant increase in bioturbation activity was noted in May to June when bottom water temperatures exceeded 15°C (Hines et al. 1982). This increased macrofauna activity was followed by a tripling in the SR rate. Since maximum SR rates in the current study were observed during summer and fall at UB and LB (Table 1), we conclude that bioturbation was a factor in stimulating microbial rates at these sites. At MB, it appears that seasonal variation in SR has a stronger impact on macrobenthic community metabolism than the reverse. Bivalve spat typically colonize MB sediments during early spring, when SR rates are at their annual minimum and H$_2$S tends not to penetrate the sediment-water interface (Fig. 6m). With increasing temperature and sulfide flux across the sediment–water interface, these organisms are generally killed by early summer (Kemp et al. 2000, USACE 2000).
Organic carbon

Both the quantity and quality of deposited organic matter can influence benthic anaerobic metabolism (Goldhaber & Kaplan 1975, Kelly & S.W. 1984, Westrich & Berner 1984, Sampou & Oviatt 1991, Marvin-DiPasquale & Capone 1998). The chl a and PC:PN data (Fig. 6e,j) support earlier findings that indicate organic deposition to upper Bay sediments is refractory terrestrial material, while MB and LB sediments receive more labile phytoplankton detritus (Marvin-DiPasquale & Capone 1998, Canuel & Zimmerman 1999). Spring bloom deposition at MB and LB was indicated by peak chl a concentration in surface sediment during May, and spring was the only season during which organic parameters (chl a and TOM) alone exhibited significant correlations with SR2 (Table 3), suggesting the linkage between phytoplankton deposition and the rapid response of SR at the sediment surface. However, the fact that >75% of the variability in spring and fall MB SR2 rates (or ≥30% for the Year grouping) could be explained by temperature and PC (or PN) combined (Table 4) indicates that SR in the mesohaline region of the Bay is generally very responsive to variations in organic input. While seasonal relationships between SR2 and organic quality (as PC:PN) were not detected, the general influence of organic quality on the SR-temperature relationship was evident, as the sites that receive primarily autochthonous C (i.e. MB and LB) had higher rates of SR overall compared to UB (Figs. 2 & 3). We conclude that the influence of organic loading on surface sediment SR rates was most important during spring at MB and LB, and resulted from fresh phytoplankton deposition.

Interannual variation in summertime sulfate reduction rates

Interannual variation in the fluvial input of nutrients to the Chesapeake Bay directly affects the magnitude of annual primary production and benthic nutrient recycling (Malone et al. 1986, 1988, Kemp et al. 1999). We initially hypothesized that inter-annual variations in peak SR rates are similarly linked to inter-annual variations in the timing, duration, and magnitude of freshwater flow to the estuary. During high-flow years, increased primary production should lead to increased deposition of labile phytoplankton detritus, and subsequently to increased benthic SR rates, relative to low-flow years. A second hypothesis was that the magnitude of peak SR rates reflects the magnitude of the previous year’s deposition. This type of temporal sediment ‘memory’ response has been suggested with respect to nutrient regeneration dynamics in the Chesapeake Bay (Boynton et al. 1982).

The positive relationship between SR2 and river flow at both UB and MB (Fig. 9) support the original hypothesis. However, the fact that the UB relationship was heavily weighted by a single year indicates that for the oligohaline portion of the estuary the effect of river flow on benthic SR is most pronounced in high-flow years (e.g. 1993) and less of a factor during low- to moderate-flow years. The positive response of SR2 to increasing river flow was more continuously distributed at MB, reflecting the fact that the mesohaline deep channel is a major focal point of deposition for phytoplankton produced bay-wide, including from the (1) oligohaline via down-estuary surface water transport (Biggs & Flemer 1972), (2) overlying water column, (3) shallow mesohaline flanks via lateral transport (Malone et al. 1986), and (4) polyhaline via up-estuary bottom water transport (Tyler & Seliger 1978, Malone et al. 1988). Hence, the mesohaline portion of the Bay is a better integrator of the effect of interannual fluctuations in river flow on net primary production than is the oligohaline region. Interannual variation in July SR2 rates at MB appears to be most responsive to the cumulative input of organic matter throughout the late-winter to early summer period, as the best relationship was found only when a very wide time averaged river flow window was used (February to June). While the highest average monthly flow occurred in April 1993, the second highest was of longer duration and occurred 1 mo earlier (March to April 1994) (Fig. 8). Of these 2 years, July MB SR2 was highest in 1994. However, water column data collected as part of the LMER study suggests that the exceptionally large 1993 freshet may have pushed the majority of the phytoplankton bloom biomass south of Site MB, which may explain the lower SR2 rates in 1993 compared with 1994 (Fig. 9).

The negative relationship between SR2 and river flow at LB was not predicted by our original hypothesis. We subsequently propose that this trend resulted from up-estuary transport of spring algal bloom biomass. Due to the Bay’s 2-layer circulation pattern, as freshwater flows seaward at the surface, return-flow high-salinity bottom water moves up the estuary (Schubel & Pritchard 1987). This hydrology is responsible for the up-estuary transport of phytoplankton in bottom waters, produced in the lower Chesapeake Bay surface waters during spring. The volume of bottom-water return flow at the Bay mouth is roughly 10× the Susquehanna River outflow (Day et al. 1989). Hence, the larger the spring freshet, the greater the up-estuary flow velocity, and the larger the fraction of sinking biomass transported away from the lower Bay region of production. As the effect of up-estuary transport decreases with distance from the Bay mouth, an increased fraction of sus-
pended particulate matter is deposited to the benthos. Zimmerman & Canuel (2001) recently reported that a high spring flow year for the Susquehanna River resulted in increased fresh algal-derived organic matter in mesohaline surface sediments that same year, but not in lower Bay sediments. These findings are in agreement with our current conclusions. When the average river-flow time window included data from the previous fall (October to December), no regressions were significant at any site. A SR response to some sediment ‘memory’ of stored labile C from the previous year’s deposition was therefore not implied.

Implications with respect to bottom-water anoxia

As a dominant microbial process in estuaries, sulfate reduction impacts a number of related ecosystem processes, including the net remineralization of fixed carbon, the biogeochemical cycling of sulfur, the cycling of iron and manganese via the formation of metal-sulfide minerals, and the consumption of dissolved oxygen linked to the reoxidation of reduced-S end-products. The latter process is largely responsible for bottom water hypoxia/anoxia in Chesapeake Bay (Roden & Tuttle 1992), which is ultimately driven by system eutrophication leading to enhanced autochthonous production and enhanced microbial respiration. Hypoxia/anoxia has long been recognized as a problem in this and other estuaries (Seliger et al. 1985, Summers et al. 1997), as low dissolved oxygen conditions have negative repercussions, both aesthetically and with respect to the survival of estuarine biota (Holland 1985, Breitburg et al. 1997). The current study illustrates how the interaction of multiple biogeochemical and physical factors ultimately control the response of estuarine SR on multiple temporal scales (months, seasons and years), and how these temporal responses vary for different regions of the system. Of particular significance are the findings that the magnitude of the spring river flow influenced that year’s summertime SR rates, and that there was a correlation between the quantity of phytoplankton detritus (as chl a) and SR rates in surface sediments during spring in the meso- and polyhaline portions of the estuary. Both observations support the hypothesis that there is a tight coupling between benthic SR rates and the amount of phytoplankton biomass deposited to the benthos. Hence, the ecosystem benefits from management practices that limit the input of inorganic nutrients, and subsequently limit the low oxygen conditions driven by enhanced SR, which may be realized on timescales as short as years, as opposed to decades.

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