The sedimentary Mn cycle in Long Island Sound: Its role as intermediate oxidant and the influence of bioturbation, O₂, and Corg flux on diagenetic reaction balances

by Robert C. Aller

ABSTRACT

The potential importance of sedimentary Mn as a secondary oxidant and redox intermediate between O₂ and Corg is often discounted in nearshore sediments. Study of the Mn cycle at 19 stations in Long Island Sound (LIS) demonstrates that sedimentary Mn can be a significant redox intermediate, accounting in many cases for 30-50% of the benthic O₂ flux (annual mean = 40 ± 35%). At some sites and times, the import of solid oxidant as Mn in suspended matter is also apparently greater than the dissolved O₂ flux to the bottom. The relative importance of the Mn cycle as redox intermediate varies substantially both seasonally (summer > fall > spring > winter) and spatially as a function of biogenic reworking, Corg flux, and O₂ concentration in the overlying water. During warmer seasons, the net flux of Mn⁺⁺ from the bottom decreases (~5-10×) generally from west to east, correlating directly with the benthic flux of planktonic debris and storage of residual Corg. Average fluxes are ~0.003, 0.43–0.94, 2.2, and 0.43 mmol Mn/m²/d during winter, spring, summer, and fall respectively. Mn⁺⁺ fluxes are relatively elevated during the spring bloom despite low temperatures. At most sites and times, surface sediments are enriched in excess Mn (4–17 μmol/g) above lithogenic background, with exponentially decreasing concentrations to 2–3 cm depth. A regular seasonal and spatial cycle of excess Mn occurs. Excess Mn inventories are often ~5–10 μmol/cm² but range from ~0–25 μmol/cm². The highest inventories are found in mid LIS, in the transition area between high Corg flux and seasonally low O₂ regions of the western Sound and the lower Corg flux, better oxygenated regions of central LIS. Excess Mn decreases at most sites following the spring plankton bloom and is lost entirely from westernmost sediments of highest Corg flux, several months before noticeable O₂ depletion in overlying water. The bloom is a major factor in mobilization of metals into suspended matter and promotes lateral redistribution of Mn. Destratification and oxygenation of the water column in the fall results in the capture and reestablishment of excess sedimentary Mn in all regions of the Sound. Bioturbation transports Mn and Corg into anoxic sediment zones. When overlying water is well-oxygenated, the resulting Mn⁺⁺ is efficiently irreversibly adsorbed or reoxidized (~80–90%, during summer–fall), closing the sedimentary Mn cycle and inhibiting net Mn⁺⁺ fluxes. The internal Mn cycle is therefore most important as an intermediate oxidant during warm periods of high bioturbation, well-oxygenated overlying water, and moderate Corg flux. S species apparently dominate the direct reduction of Mn.
1. Introduction

Mn is characterized by one of the most dynamic and geochemically important metal cycles at the earth's surface. Insoluble Mn(III,IV)-oxides, stable under oxic conditions, are readily reduced under suboxic conditions by a range of commonly occurring biogenic or abiogenic reductants (Stone, 1987). The resulting mobilized, relatively soluble Mn(II) can be locally reprecipitated as an insoluble reduced solid such as a Mn-carbonate, be adsorbed by particles, or be transported into adjacent environmental regions and precipitated distal to the Mn(II) source as either oxidized or reduced authigenic minerals. The interaction of this simple basic phenomenological behavior with natural transport processes, complex geometries and scales of environmental redox conditions, and varied rates of reprecipitation reactions results in dramatic and continuous redistribution of Mn in surficial regions (e.g., Bender et al., 1977; Campbell et al., 1988; Froelich et al., 1979; Sundby et al., 1981). Because Mn-oxides act as carrier/scavenger phases for a variety of trace metals and organic compounds, the reductive dissolution-reprecipitation cycle of Mn has a critical role in controlling the composition of natural waters and sediments (Jenne, 1968; Turekian, 1977). The oxidation and reduction of Mn are also typically directly or indirectly mediated by chemoautotrophic and heterotrophic biological activity (Lovely, 1991; Nealson and Myers, 1992), coupling the surficial Mn cycle strongly to those of O2 and C (Fig. 1). In C-rich marine sediments underlying oxygenated waters, the overall reactions associated with this coupling (Table 1) often express themselves in characteristic distribution patterns for Mn in the dissolved and particulate sedimentary phases with depth (Fig. 2).

Although in some hemipelagic sediments Mn cycling is apparently the major redox intermediate between O2 and Corg during organic matter remineralization (Aller, 1990), an important role for Mn in nearshore or continental margin benthic remineralization processes is usually discounted (e.g., Reimers et al., 1992 but also see Canfield et al., 1993). In the present study, the spatial and seasonal sedimentary Mn cycle in surficial deposits from Long Island Sound, an estuarine environment along the NE coast of N. America is quantitatively examined. It is demonstrated that sedimentary Mn distributions are not only remarkably sensitive to O2/Corg dynamics within the estuary, as found in other C-rich environments, but that Mn can be a significant benthic redox intermediate. The relative significance of the Mn cycle in this regard varies strongly seasonally and spatially as a function of bioturbation intensity, benthic organic C flux, and O2 concentration in overlying water.

2. Study area

Long Island Sound is a shallow estuarine basin approximately 150 km long from west to east with variable north-south widths of 5–40 km (Fig. 3). The Sound is commonly divided into several distinct regions: the western narrows, and the
Figure 1. The Mn cycle is intercalated with the O₂ and C₉ₑ₉ cycles as an intermediate oxidant/reductant in a variety of possible ways. (A) Closed aerobic respiration/photosynthesis. (B) Direct coupling of Mn intermediate redox cycle with O₂ and C₉ₑ₉ cycles. (C) Indirect coupling of Mn in series through S reduction/oxidation with O₂ and C₉ₑ₉. Additional intermediate cycles in series or parallel are also possible (e.g. N, Fe).

Table 1. Idealized diagentic reactions affecting Mn.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide reduction/dissolution (heterotrophic)</td>
<td>2MnO₂ + C₉ₑ₉ + 3CO₂ + 2H₂O → 2Mn⁺⁺ + 4HCO₃⁻</td>
</tr>
<tr>
<td>Oxic Mn⁺⁺ oxidation/precipitation (chemoautotrophic)</td>
<td>2Mn⁺⁺ + O₂ + 2H₂O → 2MnO₂ + 4H⁺</td>
</tr>
<tr>
<td>Anoxic Mn⁺⁺ precipitation</td>
<td>xMn⁺⁺ + (1 - x)Ca⁺⁺ + 2HCO₃⁻ → MnₓCa₁₋ₓCO₃ + CO₂ + H₂O</td>
</tr>
<tr>
<td>Anaerobic nitrification/lithothrophic Mn reduction</td>
<td>7H⁺ + 4MnO₂ + NH₃ → 4Mn⁺⁺ + NO₃⁻ + 5H₂O</td>
</tr>
<tr>
<td>Anaerobic Fe⁺⁺ oxidation/lithothrophic Mn reduction</td>
<td>MnO₂ + 2Fe⁺⁺ + H₂O → Mn⁺⁺ + 2FeOOH + 2H⁺</td>
</tr>
<tr>
<td>Anaerobic sulfide oxidation/lithothrophic Mn reduction</td>
<td>8H⁺ + 4MnO₂ + FeS → 4Mn⁺⁺ + SO₄²⁻ + Fe⁺⁺ + 4H₂O</td>
</tr>
</tbody>
</table>
Figure 2. Typical expression of the Mn redox cycle as solid and pore water sedimentary distributions in C_{org} rich deposits underlying oxygenated waters. (A) Solid phase Mn illustrating characteristic enrichment at sediment-water interface. Reactive Mn indicates Mn involved in diagenetic reactions, background (Bkg) indicates structurally stable lithogenic Mn, recycled Mn indicates Mn in essentially closed diagenetic cycle within surface sediment (e.g. Fig. 1B). Difference between reactive and recycled Mn represents burial of reduced authigenic minerals. (B) Characteristic dissolved Mn distribution. L_{O_2} represents O_2 penetration depth, L_{Mn} represents boundary between upward and downward diffusing Mn. Mn in this case is shown as almost completely reprecipitating in the surface oxidized zone.

Figure 3. Map of Long Island Sound indicating positions of sampled stations. The more completely sampled reference stations are marked by a 'star' symbol.
western, central, and eastern regions. Water depths average \( \sim 20 \) m overall, deepening to a southern trough in the central region \( \sim 40 \) m and in the easternmost passages to a maximum depth of \( \sim 100 \) m. Significant freshwater inputs, largely from the Connecticut River at the east end \( \sim 0.03 \) km\(^3\) d\(^{-1}\), result in a general circulation eastward of less saline surface water and inflow westward of relatively saline bottom waters. Several, large counterclockwise gyres are present in the central and western regions (Wilson and Vieira, in prep.). Surface salinity throughout the Sound is usually only \( 1-2 \) ppt less that bottom waters. Average annual salinities vary from \( \sim 18 \) (west) to \( 32 \) ppt (east). Annual temperature variation is approximately sinusoidal between \( \sim 2^\circ \)C (February) and \( \sim 22^\circ \)C (August–September) (Riley, 1956).

Circulation patterns and current strength result in sandy sediments in the eastern \( \sim 1/3 \) of the basin (east of 72\(^{\circ} 40'\)W), with silt-clay sediments accumulating in the central and western Sound, generally fining westward. Net sedimentation rates are variable (up to \( \sim 1.8 \) mm yr\(^{-1}\)) are found in the deep trough of the southern central basin (Kim and Bokuniewicz, 1991). Surfacedeemost (\( < 0.1 \) mm) sediments are resuspended frequently by tidal currents. The upper \( \sim 1-2 \) cm in shallow regions (\( < \sim 15 \) m) can be eroded and redeposited during major storms (McCall, 1978).

The net annual phytoplankton production is \( \sim 209 \) gC m\(^{-2}\) yr\(^{-1}\) (Riley, 1956). Annual production is characterized by a regular major late winter–early spring bloom, a lesser fall bloom, and small irregular pulses (Conover, 1956; Peterson, 1986). Because of high turbidity, bottom water and benthic primary production are minimal over much of the Sound (Welsh and Eller, 1991). Highest nutrient inputs are in the narrows and western Sound, resulting in relatively increased production and, along with circulation patterns, periods of low oxygen \( (< 100 \ \mu M) \) in the western regions during late summer (Parker and O'Reilly, 1991).

Western narrows regions having periodic low oxygen bottom waters are characterized by poorly developed soft-bottom macrofaunal and meiofaunal benthic communities with low abundances \( (< 7-500 \) m\(^{-2}\), \( > 0.5 \) mm mesh size) and diversities relative to the central and eastern Sound (Aller et al., 1991). Faunal abundances and diversities are typically maxima in western to central Sound transitional regions, reaching \( > 8,000 \) m\(^{-2}\). Central LIS has regular spatial distributions of macrobenthos reflecting patterns of decreasing physical disturbance with depth (McCall, 1977, 1978; Yingst and Rhoads, 1978). Shallow muddy areas \( (< 20 \) m) are intensively bioturbated, particularly in the upper few centimeters, by deposit-feeding protobranch and tellinacean bivalves as well as deeper-burrowing polychaetes such as \( Nephys incisa \). Deeper regions \( (> 20 \) m) of the central and eastern Sound commonly contain relatively large infauna such as maldanid polychaetes \( (Clymenella, Asychis) \) and have somewhat slower surficial but more rapid deeper bioturbation than shallower areas. Mantis shrimp \( (Squilla) \) are present throughout LIS and can burrow 1–2 m (Myers, 1979). Except in very shallow regions subject to active scour by
currents and waves (<10 m) or western narrows areas with methanogenic bubble ebulition, LIS sediments are highly bioturbated and sedimentary structures dominated by biogenic structures (Aller et al., 1980; Benninger et al., 1979; McCall, 1978).

3. Measurements and sampling

Several kinds of measurements were used to characterize the sedimentary Mn cycle and sedimentary processes at the study sites. These included vertical distribution profiles of pore water and reactive particulate Mn, direct measurements of dissolved Mn fluxes across the sediment-water interface, and anoxic time series incubations of sediment for estimating net Mn reduction rates. Associated measurements of sediment oxygen uptake, pore water oxygen microelectrode profiles, excess $^{234}$Th, chlorophyll-a, nutrient fluxes, pore water nutrients, macrofauna, and sediment X-radiographs were made at the same time to characterize particle mixing rates, C flux, remineralization rates, and redox conditions at the study sites (Mackin et al., 1991; Cochran and Hirschberg, 1991; Aller, 1991; Sun et al., 1994).

A total of 19 stations were sampled seasonally throughout Long Island Sound (LIS) during the EPA (U.S. Environmental Protection Agency) sponsored Long Island Sound Study (Fig. 3). Six of these stations (A, C, G, P, R, S) referred to as reference stations and indicated by a star symbol in Figure 3, were studied relatively intensely with, in most cases, a full spectrum of measurement types at five times from May 1988 through May 1989. The remaining stations were sampled less-intensely and at three times from May 1988 through Oct 1988. In these latter cases, pore water solute and microelectrode profiles were not measured.

4. Methods

All measurements were made on various kinds of subcores 10–20 cm in length obtained from a larger Soutar—style box corer ($\sim 0.062$ m$^2$). Two or more box cores were taken at each station. Following box core retrieval, bottom temperature was first estimated using a glass thermometer, the sediment—water interface was checked for integrity (e.g., open burrows, fecal piles, obvious disturbance) and subcores were then gently inserted, capped, and removed along with overlying water. Cores were placed into a dark, temperature-controlled incubator held at $\pm 2$°C of the in situ value until further processing. The water overlying cores was continuously aerated using aquarium aerator pumps except in the case of cores used to estimate oxygen flux. Cylindrical subcores of $\sim 7.5$ and 10 cm diameter were taken for a variety of chemical analyses and incubations. Rectangular acrylic subcores (2.5 cm D x 10–15 cm W) were taken for X-radiography and solid phase analyses, including chloropigments.
a. **Flux core incubations.** At least two cylindrical cores (butyrate acetate tubing, 10 cm O.D./9.5 cm I.D.) containing ~ 1 liter overlying water were used for sediment-water solute flux incubations. One was left open to the atmosphere and continuously aerated. A second was capped without obvious air space by using acrylic plates having O-ring seals and the overlying water was stirred continuously with a centrally-located stir bar magnetically coupled to a motor (Mackin and Swider, 1989). These core and overlying water incubations are referred to as aerated and nonaerated flux cores respectively. A time series of four or more overlying water samples were removed into syringes at 3–6 hr intervals through luer-lock penetrators with three-way valves. Samples were analyzed to estimate net solute fluxes. A replacement volume of bottom water equivalent to the sample volume extracted was injected simultaneously during sampling of sealed nonaerated cores. In some cases bottom water was incubated in corer tubes without sediment and used as a comparative control. Duplicate core incubations were also done at several sites. The initial sample for a flux incubation series was taken within ~ 0.5 hr after box core retrieval. Except for oxygen and pH samples, water was filtered using Poretics polycarbonate membranes (0.4 μm pore size) and inline syringe holders. After flux incubations were complete, typically ~ 24 hrs, cores were sectioned for radiochemical analyses.

b. **Pore water solutes.** Cylindrical cores (7.5 cm O.D.) for pore water analyses were sectioned at 0.25–1 cm intervals in a N₂-filled glove bag, in order to minimize exposure to atmospheric O₂ (e.g., Troup et al., 1974). Sediment was placed into either polypropylene centrifuge tubes or bottles, removed from the glove bag, and centrifuged for 15 min at ~ 5000 rpm in a temperature controlled centrifuge set to temperature of collection. Samples were returned to a N₂ glove bag, pore water drawn into syringes, and filtered through Poretics polycarbonate membranes (0.4 μm pore size) directly into receiver syringes without air contact. Pore water was then rapidly divided into subsamples for further analysis. Centrifuged sediment plugs were frozen for later solid phase analyses.

Cylindrical cores 7.5 cm O.D. were used for oxygen microelectrode profiling after return to shore. Clark type combination microelectrodes mounted on a micromanipulator were standardized in N₂ and air saturated sea water (Revsbech, 1983). Reduction currents (0.75 V) were read directly on a picoammeter or on a pH meter using a picoamp/mvoltage converter. Stirring effects with the electrodes used were <5% of response.

c. **Reaction rates.** At reference stations, two to three cores (7.5 cm O.D.) were used in some cases to estimate net Mn⁺⁺ production rates by the whole core incubation technique outlined in Aller and Mackin (1989). Cores were capped, incubated anoxically, and in-grown pore water profiles sampled at 2–3 time intervals thereafter. Net production of Mn⁺⁺ was estimated from time dependent concentration changes.
d. Sediment analyses. Solid phase Mn analyses were made in two ways. Samples were ashed at 450°C and the 0.5 g ash leached in 25 ml hot 6N HCl for ~12 hrs. Leachate was taken to dryness, picked-up in 0.2 N HCl, and solution filtered through Whatman #44 paper. This method typically releases >90% of the total Mn and is referred to here as 'total' Mn. A second leaching method was used more extensively to better resolve diagenetically cycled Mn, in particular MnO₂, and lower the background Mn in analyses (e.g., Fig. 2). In this case unashed wet samples were reacted with 1M NH₂OH · HCl-0.175 M NaCitrate at a solution/solid ratio of 100 (vol/wt), centrifuged, and the supernatant analyzed for Mn (Robbins et al., 1984). This leach attacks labile Mn compounds comparable to those reactive with the classic Chester Hughes acetic acid/NH₂OH reagent (Chester and Hughes, 1967). Time series analyses demonstrated that for LIS sediments, Mn release was essentially complete and released concentrations were constant after ~12 hr at room temperature (T ~22°C). A leach time of 14 hrs at 22°C was used in the present study.

Sediment water contents were estimated by drying subsamples at ~70°C. Porosities were calculated from weight fraction water assuming a sediment particle density of 2.6 g cm⁻³.

e. Analytical methods. Samples for dissolved Mn analysis in pore waters and flux core overlying water were acidified promptly with HCl to 0.1 N and stored. Mn was analyzed using the formaldoxime method with Fe correction using EDTA/NH₂OH (Goto et al., 1962). Mn in the various leachates was also analyzed using the formaldoxime method with Fe correction. Precision was typically ±3%. Dissolved oxygen in bottom water and flux cores was measured using a modified Winkler technique (Mackin et al., 1991).

5. Results

a. Direct flux estimates. The directly measured net flux of Mn⁺⁺, JDM, was estimated from the time series Mn⁺⁺ concentrations in both aerated and nonaerated flux incubation cores using the time rate of change of Mn⁺⁺ mass, ΣΔM, in overlying water:

$$\Sigma \Delta M = \Sigma [C(t) - C_c(t - \Delta t)] V(t) / A$$

(1)

Where C(t) = solute concentration at time t, C_c(t - Δt) = solute concentration in previous sample corrected for any volume of water replaced during sampling, V(t) = volume of water overlying the core, A = surface area of core (e.g., Mackin and Swider, 1989). Fluxes were approximated from the slope of the ΣΔM versus t relation. Incubation of bottom water in the absence of sediment, demonstrated that no significant 'blank' correction was necessary. If a dramatic change in slope occurred at some time t, either decrease or increase, the slope from two or more points prior to that sample was used and subsequent samples ignored. During the
Table 2. Directly measured and modeled Mn fluxes at nonreference stations.*

<table>
<thead>
<tr>
<th>Station</th>
<th>May/June 88</th>
<th>Aug 88</th>
<th>Oct/Nov 88</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_{DM}^{**}$</td>
<td>$J_{XS}^{**}$</td>
<td>$J_{DM}$</td>
</tr>
<tr>
<td>B</td>
<td>0.37</td>
<td>2.53</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>5.15</td>
<td>1.8</td>
<td>4.49</td>
</tr>
<tr>
<td>E</td>
<td>0.44</td>
<td>12.70</td>
<td>4.3</td>
</tr>
<tr>
<td>F</td>
<td>1.00</td>
<td>4.3</td>
<td>1.70</td>
</tr>
<tr>
<td>H</td>
<td>-0.52</td>
<td>15.9</td>
<td>3.50</td>
</tr>
<tr>
<td>I</td>
<td>0.58</td>
<td>3.3</td>
<td>0.67</td>
</tr>
<tr>
<td>J</td>
<td>0.63</td>
<td>15</td>
<td>2.20</td>
</tr>
<tr>
<td>K</td>
<td>-0.17</td>
<td></td>
<td>2.70</td>
</tr>
<tr>
<td>M</td>
<td>0.04</td>
<td></td>
<td>0.90</td>
</tr>
<tr>
<td>N</td>
<td>1.18</td>
<td>0.14</td>
<td>0.28</td>
</tr>
<tr>
<td>Q</td>
<td>0.17</td>
<td>15.7</td>
<td>0.02</td>
</tr>
<tr>
<td>U</td>
<td>0.25</td>
<td>3.27</td>
<td>1.10</td>
</tr>
<tr>
<td>W</td>
<td>0.69</td>
<td>48.2</td>
<td>1.20</td>
</tr>
</tbody>
</table>

*mmol/m²/d.

**$J_{DM}$: directly measured flux (flux cores); $J_{XS}$: solid phase profile mixing-model production flux.

summer when oxygen concentrations are typically below saturation, aeration of cores often produced a decrease in Mn$^{++}$ in overlying water at western LIS stations. In these cases the first two time series samples from nonaerated cores were used to estimate Mn$^{++}$ flux before O$_2$ had decreased by more than ~10–20% from initial values. At all other times of year the initial (~6 hr) fluxes from aerated and nonaerated cores were usually indistinguishable. When agreement between aerated and nonaerated cores was good, the mean value was used as the accepted flux, otherwise the aerated estimate was accepted in preference. Based on previous study (Aller and Benninger, 1981) and several replicate cores of each type in the present cases, an overall precision of ~30% for flux estimates is typical.

b. Net benthic Mn$^{++}$ flux. Estimated net Mn$^{++}$ fluxes are listed in Tables 2 and 3. The average fluxes at all stations at a given time are plotted versus temperature of core incubation in Figure 4. Highest and lowest fluxes occur during the warm summer and cold winter periods respectively. Mean fluxes during fall are relatively low and those in the late spring are relatively elevated compared to what might be predicted from a regular pattern of change depending only on temperature. The variation in flux is also substantially higher in late spring than in the fall despite relatively similar temperatures. Spatial patterns of net fluxes demonstrate that westernmost LIS sustains the highest net benthic Mn$^{++}$ fluxes while deeper regions of central LIS remain comparatively low throughout the year (Fig. 5). During the summer, high flux regions expand regularly eastward from western LIS and then decrease in the fall across the entire Sound, with localized exceptions. The region just south of New
Table 3. Reference station Mn reaction rate flux summary.*

<table>
<thead>
<tr>
<th>Station</th>
<th>Date</th>
<th>Porosity (0–3 cm)</th>
<th>$J_{DM}$</th>
<th>$J_{PW}$</th>
<th>$J_{DP}$</th>
<th>$J_{PP}$</th>
<th>$\Delta - XS^{**}$</th>
<th>$J_{XS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5/23/88</td>
<td>13.3</td>
<td>0.908</td>
<td>2.61</td>
<td>2.83</td>
<td>3.54</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8/23/88</td>
<td>21</td>
<td>0.908</td>
<td>1.2</td>
<td>0.75</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11/9/88</td>
<td>12</td>
<td>0.901</td>
<td>0.67</td>
<td>2.74</td>
<td>1.91</td>
<td>1.4</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>2/8/89</td>
<td>2.4</td>
<td>0.883</td>
<td>-0.069</td>
<td>1.41</td>
<td>0.27</td>
<td>1.3</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>4/24/89</td>
<td>7</td>
<td>0.926</td>
<td>1.11</td>
<td>2.63</td>
<td>2.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5/23/88</td>
<td>12</td>
<td>0.875</td>
<td>0.14</td>
<td>4.12</td>
<td>3.27</td>
<td>0.015</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>8/23/88</td>
<td>20.7</td>
<td>0.87</td>
<td>2.8</td>
<td>4.69</td>
<td>2.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11/9/88</td>
<td>12.1</td>
<td>0.853</td>
<td>0.3</td>
<td>2.20</td>
<td>0.89</td>
<td></td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td>2/8/89</td>
<td>2.3</td>
<td>0.862</td>
<td>-0.07</td>
<td>0.17</td>
<td>0.08</td>
<td>0.5</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>4/24/89</td>
<td>6.7</td>
<td>0.92</td>
<td>0.44</td>
<td>1.78</td>
<td>1.28</td>
<td></td>
<td>1.07</td>
</tr>
<tr>
<td>G</td>
<td>5/24/88</td>
<td>10.5</td>
<td>0.764</td>
<td>2</td>
<td>0.80</td>
<td>0.95</td>
<td>2.8</td>
<td>0.59</td>
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<tr>
<td></td>
<td>8/25/88</td>
<td>21</td>
<td>0.622</td>
<td>3.8</td>
<td>0.78</td>
<td>1.38</td>
<td>3.3</td>
<td>0.47</td>
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<tr>
<td></td>
<td>10/28/88</td>
<td>14.3</td>
<td>0.61</td>
<td>0.39</td>
<td>1.67</td>
<td>0.3</td>
<td>6.7</td>
<td>7.65</td>
</tr>
<tr>
<td></td>
<td>2/8/89</td>
<td>2.2</td>
<td>0.608</td>
<td>-0.006</td>
<td>0.17</td>
<td>0.01</td>
<td>3.4</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>4/24/89</td>
<td>6</td>
<td>0.75</td>
<td>0.17</td>
<td>1.37</td>
<td>0.72</td>
<td></td>
<td>16.0</td>
</tr>
<tr>
<td>P</td>
<td>5/17/88</td>
<td>12</td>
<td>0.819</td>
<td>3.14</td>
<td>3.81</td>
<td>4.59</td>
<td>0.94</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>8/22/88</td>
<td>21.2</td>
<td>0.772</td>
<td>0.83</td>
<td>1.17</td>
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*mmol/m²/d.

**Calculated from seasonal changes in excess Mn inventory and time between collection (Fig. 6).

$J_{DM}$: directly measured flux; $J_{PW}$: pore water profile model production flux; $J_{DP}$: concentration gradient predicted flux at $x = 0$; $J_{PP}$: closed-incubation net production rate flux; $\Delta - XS$: seasonal inventory change predicted flux; $J_{XS}$: solid phase profile mixing-model production flux.

Haven, CT, for example, has high net fluxes compared to other areas of the central Sound during spring and fall. The overall spatial pattern and relative magnitudes of Mn$^{++}$ fluxes during summer 1988 agree well with those measured in 1977 by Aller and Benninger (1981). The relative seasonal patterns for winter, summer, and fall...
are also similar to those found previously for three central LIS sites (Aller, 1980a; Aller and Benninger, 1981).

c. Solid phase Mn. At most stations and times, Mn showed regular patterns of surface enrichment with concentrations decreasing to a minimum a few centimeters below the interface. Minimum 'total' Mn concentrations in surface sediment ranged from \( \sim 7.3 \, \mu\text{mol/g-ash} \) (\( \sim 400 \, \text{ppm} \)) at Station S (east) to \( \sim 11.7 \, \mu\text{mol/g-ash} \) (\( \sim 645 \, \text{ppm} \)) at Station A (west). Central LIS stations had average minimum concentrations of \( \sim 10.2 \pm 1 \, \mu\text{mol/g-ash} \) (\( \sim 558 \pm 56 \, \text{ppm} \)). These minimum values presumably represent 'background' Mn concentrations (Fig. 2). They are near the expected platform sedimentary rock average of \( \sim 10.2 \, \mu\text{mol/g} \) (\( \sim 560 \, \text{ppm} \)) (Wedepohl, 1980) and the spatial patterns in background likely track decreasing grain size from east to west. Similar background concentrations have been obtained previously in total Mn profiles from central LIS (Thomson et al., 1975; Aller, 1980a).

Vertical profiles of Mn measured using the milder NH\(_2\)OH leach readily demonstrate the spatial and seasonal dynamics of diagenetically mobile Mn superimposed on the lithogenic background (Fig. 6). Surface profiles often show an exponential decrease in concentration with depth as reported previously for total Mn in central...
Figure 5. Spatial and seasonal patterns of net benthic Mn\(^{++}\) fluxes in LIS. Areas of relatively high fluxes are found in the western Sound during spring, expand eastward during summer, and contract during fall. The deep central Sound has relatively low fluxes throughout the year.
Regular patterns of surface enrichment typically occur with Mn concentrations as high as ~17 μmol/g above background in the upper 0.5 cm interval. Surficial Mn concentrations greater than the minimum concentration first encountered with depth in a vertical profile are defined here as 'excess' Mn (e.g., Bender, 1971) and are illustrated by the shaded region in each individual profile for the reference station examples (Fig. 6). This Mn is assumed to be recycled to the sediment water interface. Part of the redistributed excess Mn at each site can be transported to depths below LIS (Thomson et al., 1975; Aller, 1980a). The analytical background in this case ranges from ~4.7 μmol/g at station A (west) to ~1.1 μmol/g at station S (east).
the first profile minimum, causing small secondary maxima (Fig. 2, 6). This downwardly mobile Mn is ignored in the present considerations.

The most dramatic seasonal changes in excess Mn profiles are found in the western narrows and western LIS. Surficial Mn enrichments are present during fall and winter but disappear entirely during spring and are absent in summer (Stations A, C; Fig. 6). The spatial and temporal patterns in excess Mn at individual stations and in LIS as a whole are best demonstrated by converting concentrations into corresponding excess Mn inventories (i.e., area of shaded regions in Fig. 6) using porosity measurements at each site. This has been done for both the reference stations, where the best seasonal coverage is available, and for all stations sampled (Fig. 7). Aside from the regular seasonal oscillation in excess Mn inventories at the westernmost stations and more subtle seasonality to be discussed, there is a spatial progression of increasing average excess Mn inventories from west to east. The highest excess Mn inventories are found in the mid Sound (western region of the central Sound (Stas. I, J, U)), with slight decreases in the maximum observed seasonal values to the east and west. Despite lower overall Mn concentrations at the easternmost stations (e.g. Fig. 6), the lower porosities also typical of the increased average grain sizes in this region result in diagenetically mobile Mn inventories comparable to or higher than many western or central LIS locations (e.g. Stas. M, S vs. P).

Seasonal changes in excess Mn inventories at reference stations have been converted into corresponding estimates of net excess Mn fluxes by taking the difference between Mn inventories at successive sampling times and dividing by the time elapsed between sampling. These represent minimum average fluxes of Mn with respect to the solid excess pools and also illustrate the direction of net inventory changes. All stations show regular periods of loss and gain. A wavelike pattern of loss and gain moves eastward in time beginning during the winter to spring transition (Fig. 8). All stations show gains in surficial excess Mn inventories during the fall to winter transition and all but Sta. S, show loss during the winter to spring transition (Fig. 8); western stations having the highest amplitude gains and losses. Spring-summer and summer-fall patterns are out of phase at the different sites but clearly represent part of an eastward moving pattern of relative net loss followed by net gain.

d. Pore water Mn$^{++}$. Measured pore water Mn$^{++}$ distributions are restricted to the upper 0–3 cm and show the dramatic increases typical of organic-rich deposits (Fig. 9). A portion of the dissolved Mn may be present as Mn$^{+3}$ (Luther et al., 1991), but this possibility is ignored here. All stations achieve concentrations near the sediment–water interface $\geq 100 \mu$M during at least some time of the year. The highest concentrations are found in subsurface maxima at stations A and G ($\sim 300 \mu$M) during winter and summer respectively. At all stations but A, the lowest overall concentrations occur during winter and profiles at all sites are concave up in shape at that time (Fig. 9), implying substantial precipitation of remobilized Mn$^{++}$ within the
Figure 7. (A) Seasonal and spatial excess Mn inventories at reference stations. (B) Seasonal and spatial excess Mn inventories at all sampled LIS stations. Spatially, the highest inventories are found in the west central Sound. Excess Mn is absent during late spring and summer in westernmost LIS.
Figure 8. Seasonal and spatial patterns of change in excess Mn inventories at reference stations. All stations show relative gain during fall → winter transitions and most show loss during winter → spring, with westernmost stations having the greatest gain or loss. A wave of relative loss/gain progresses eastward during spring → summer and summer → fall.

surface-most sediment. Relatively high concentrations, particularly near the sediment–water interface, are typically found during late spring and summer at most sites, except at A where summer concentrations are depressed. Surficial concentrations (0–0.5 cm) begin to decrease generally during fall and are usually minimal during winter. Seasonal profiles at Stations P and R measured in 1988–1989 are very similar in shape and magnitude to those found during 1975 and 1976 at comparable sites (NWC and DEEP of Aller, 1980a).

e. Supporting measurements. The tabulated O₂, chloropigment, and ²³⁴Th data at each site, used here to evaluate the Mn cycle, are available in Mackin et al., 1991; Sun et al., 1994; and Cochran and Hirschberg, 1991; as well as manuscripts in preparation.

f. Sediment incubations. At some stations, time series pore water Mn⁺⁺ profiles were obtained from anoxic whole core incubations (≈0–15 cm) as described previously for surficial pore water profiles. Because the primary emphasis in this case was the potential Mn⁺⁺ production flux in surface sediment, the details of the ingrown
Figure 9. Seasonal pore water Mn\(^{++}\) profiles in upper 0–3 cm at reference stations. Only one core was analyzed at Sta. S. Overlying water concentrations in retrieved box cores average annually: Sta. A \(\approx 3.0 \pm 1.5\); Sta. C \(\approx 2.7 \pm 1.5\); Sta. G \(\approx 1.5 \pm 1.2\); Sta. P \(\approx 1.37 \pm 0.8\); Sta. R \(\approx 1.0 \pm 0.5\); Sta. S \(\approx 0.4\) (winter only) \(\mu\text{M}\); winter concentrations are everywhere <1 \(\mu\text{M}\).

profiles were not used to obtain depth dependent reaction rates (Aller and Mackin, 1989), rather the changes in the average concentration in the upper \(\sim 10\) cm (mostly the upper 0–5 cm) with time of incubation were simply used to estimate the average production rate in the core. The time dependent average concentration is given by:

\[
(1 + K)dC/dt = \Sigma R
\]  

(2)

where:

- \(C\) = average pore water concentration (mass/volume pore water)
- \(K\) = reversible, linear adsorption coefficient
- \(\Sigma R\) = sum of diagenetic reaction rates

Only 2–3 time series samples are available in each instance so that crude linear approximations to the rates with time were assumed. These rates were converted into
production fluxes, $J_{pp}$, using porosity measurements, length of the sampled core interval, and an assumed value of $K \sim 4$ (e.g. Burdige and Kepkay, 1983; Aller and Rude, 1988; Taylor, 1987). Actual total adsorption of Mn$^{++}$ is not reversible and effective values of $K$ are likely $> 15$ (Canfield et al., 1993). In addition, the incubations were done over relatively long periods (2–3 weeks) so that considerable precipitation of reduced Mn likely occurred. Given the various approximations and assumptions, the calculated rates obtained in this way are minima ($J_{pp}$ in Table 3).

g. Diagenetic models. Additional estimates of net Mn$^{++}$ production can be made independently from the pore water profiles, solid phase Mn profiles, and seasonal excess Mn inventory changes. Sedimentation rates are sufficiently small and biogenic sedimentary structures sufficiently predominant, that physical advection of particles can be ignored relative to diffusive or biogenic transport processes in surface LIS sediments. Under these circumstances and assuming a local steady state, minimum net production rates of Mn$^{++}$ can be calculated from pore water profiles using the relation (e.g. Berner, 1980):

$$\frac{(1 + K)\partial C}{\partial t} = D_s \left(\frac{\partial^2 C}{\partial x^2}\right) + \Sigma R$$

(3)

Where: $C =$ pore water Mn$^{++}$ concentration (mass/volume pore water)

$x =$ space coordinate, positive into sediment, origin at sediment-water interface

$D_s =$ whole sediment diffusion coefficient

Other symbols are as defined previously. Compaction is ignored. In the region of the sediment considered here $\Sigma R$ represents net production and is positive. Biogenic irrigation and eddy diffusive mixing are not accounted for in these calculations.

Only the average value of $C(x)$ over finite depth sampling intervals was actually measured. Several methods were used to derive optimal continuous functions $C(x)$, including fitting integral forms of arbitrary $C(x)$ to the profiles. It was found that given the shapes of the profiles, simply assigning the measured concentrations to the midpoint of respective sampling intervals and deriving a least squares polynomial fit for $C(x)$ (4–6 order), gave estimates of $\Sigma R$ in the midrange of the various methods tried. The least squares fits so obtained are used here to calculate $\Sigma R$ from $C(x)$ and Eq. (2). Diffusion coefficients for Mn$^{++}$ were estimated from the relation: $D_s \sim \varphi^2 D_o$, where $\varphi$ is porosity and $D_o$ represents the temperature and viscosity corrected free solution coefficient (Li and Gregory, 1974; Ullman and Aller, 1982). Ion pairing and coupled diffusion are ignored. Resulting estimates of $R$ have been integrated for the upper 0–3 cm at each reference site and are listed as Mn$^{++}$ production fluxes, $J_{pw}$, in Table 3.

The solid phase excess Mn profiles can be used in a similar way to obtain estimates of Mn dissolution and thus net Mn$^{++}$ production rates (Aller, 1980a; 1990; Sundby and Silverberg, 1985). In this case solid phase transport is assumed to be dominated
1994] Aller: Mn cycle in Long Island Sound

by eddy diffusive, biogenic mixing, so that at local steady state:

$$\frac{\partial \tilde{C}}{\partial t} = 0 = D_B (\frac{\partial^2 \tilde{C}}{\partial x^2}) - \Sigma \tilde{R}$$

(4)

Where: \( \tilde{C} \) = concentration of excess Mn (mass/volume total sediment)

\( D_B \) = particle mixing coefficient

\( \Sigma \tilde{R} \) = solid Mn reaction rate

Other symbols are as for Eq. (3). \( D_B \) is assumed constant over the surface interval considered here (0–3 cm).

In this case \( \tilde{C}(x) \) was evaluated at each site by assuming a functional form \( \tilde{C}(x) = \tilde{C}_1 \exp(-\alpha x) \) for solid phase Mn. The measured concentration data over a depth interval \( x_1 \) to \( x_2 \) are \( \overline{C}(x) \) where:

$$\overline{C}(x) = \int_{x_1}^{x_2} \tilde{C}(x) \, dx / \int_{x_1}^{x_2} dx.$$

Least squares minimization of residuals was used to obtain estimates of \( \tilde{C}(x) \) from excess Mn profile concentration series. A similar technique was used to derive \( D_B \) from the finite interval measurements of excess \(^{234}\)Th (\( \Sigma \tilde{R} = \lambda \tilde{A} \); \( \tilde{A} \) = activity, \( \lambda \) = decay constant) (data from Cochran and Hirshberg, 1991).

The calculated estimates of \( \Sigma \tilde{R} \) from solid phase Mn profiles were integrated over the vertical interval from the depth of \( O_2 \) penetration to the base of the surficial excess Mn zone (\( \sim 3 \) cm) to obtain a steady state production flux, \( J_{xs} \) (Table 3).

6. Discussion

a. Factors controlling Mn distributions. Primary chemical factors controlling sedimentary Mn cycling are overlying water \( O_2 \), \( O_2 \) penetration into sediments, and benthic organic C supply (e.g. Lynn and Bonatti, 1965; Grill, 1978; Hunt and Kelly, 1985). \( O_2 \) concentrations and penetration depths control in part the oxidation/reprecipitation efficiency of \( Mn^{++} \) at the sediment-water interface and thus the extent of solid phase enrichment and internal closure of the sedimentary cycle. Organic C supply and decomposition rates determine sediment penetration patterns of \( O_2 \) and, along with the presence of \( MnO_2 \), the vertical production rates and production patterns of \( Mn^{++} \) within deposits (e.g. Holdren et al., 1975; Aller, 1980a; Reimers et al., 1992). These factors are often but not necessarily correlated and their relative importance is strongly influenced by temperature controlled reaction rates in shallow water environments.

Within this context, the bottom waters of LIS are well oxygenated during much, but not all, of the year (Fig. 10A). There is relatively little spatial variability in bottom water \( O_2 \) during fall and winter, slight west to east increases in late spring, and major west to east gradients in late summer when the western narrows has concentrations <80 \( \mu \text{M} \) (Fig. 10A; Parker and O’Reilly, 1991). Oxygen penetration into sediments shows large seasonal changes at each site and dramatic regular west to east increases
Figure 10. (A) Bottom water oxygen concentrations at reference stations at time of sediment sampling. Water is relatively well-oxygenated throughout the Sound except during late summer when substantial depletion in the westernmost areas occurs. (B) Seasonal pore water $\text{O}_2$ penetration depths at reference stations, as measured by microelectrodes.
in O₂ penetration at any given season (Fig. 10B). O₂ penetration at each site is least during summer and greatest during winter, directly correlating with visually obvious relative thicknesses of the yellow-brown colored oxidized sediment surface layer (e.g. Rhoads et al., 1977). At station A, O₂ penetration is only ≤0.1 mm during summer and ~2.5 mm during winter. Summer and winter O₂ penetration at central LIS stations are typically ~2 mm and 5–8 mm respectively.

Although low overlying water O₂ and shallow O₂ penetration clearly prevent benthic retention of mobilized Mn during summer at the westernmost sites, it is obvious from examination of bottom water oxygen patterns and sedimentary excess Mn inventories that initial loss of the excess Mn inventory from surface deposits (Win/Spr → Sum) occurs seasonally before any substantial lowering of overlying water O₂ (Figs. 6, 7, 8, 10). In addition, as shown by station G, O₂ penetration depths as small as ~1 mm are sufficient to retain both substantial excess Mn and characteristic exponential profiles of solid phase Mn near the sediment-water interface of these deposits. Boundary O₂ concentrations per se therefore do not appear to dominate the winter summer transition dynamics of the excess Mn inventories in LIS sediments.

In contrast to O₂ boundary conditions, the seasonal loss of excess sedimentary Mn in the westernmost Sound, and the general relative spatial patterns of inventory distributions in LIS, correlate closely with seasonal and spatial input patterns to the sediment of fresh planktonic material, as measured by sedimentary chlorophyll-a inventories. There are both regular seasonal patterns of delivery of planktonic debris to the bottom at each site and regular west to east decreases in the total quantity delivered and the resulting residual sedimentary C_{org} (Fig. 11; Sun et al., 1994). Because chlorophyll-a decay is a pseudo-first-order process overall, chlorophyll-a inventories directly reflect C_{org} flux (Sun et al., 1994). Seasonally, the spring bloom results in substantial export of planktonic debris to the bottom and a corresponding relative increase in chloropigments at each site. When the C_{org} flux is sufficiently high, as in westernmost LIS, Mn reduction dominates Mn reoxidation processes and the sedimentary excess Mn inventory is completely lost to the overlying water (Fig. 12). This is a seasonal expression of the recognized inverse correlation between sedimentary Mn content and organic loading rates or residual sedimentary C_{org} (e.g. Lynn and Bonatti, 1965; Wedepohl, 1980; Hunt and Kelly, 1985; Lapp and Balzer, 1993). The overall west to east increase in excess Mn inventories is similarly a spatial reflection of the general inverse correlation between Mn and C_{org} content or flux (Figs. 5, 7, 11).

Spatial patterns in Mn inventory distributions are also influenced by O₂ boundary conditions and circulation patterns. The wave-like progression in the sign of inventory gain/loss (Fig. 8) tracks the easternward seasonal progression of maximum productivity and of low O₂ bottom waters (e.g. Parker and O'Reilly, 1991; Welsh and Eller, 1991). The region of LIS having the generally highest excess Mn inventories
Figure 11. Spatial and seasonal patterns of reactive (excess) Chl-\(a\) inventories and average \(\%\) C\(_{org}\) (±seasonal SD) in LIS sediments (data from Sun et al., 1994). A regular west east decrease in both seasonally averaged Chl-\(a\) and residual C\(_{org}\) occurs in LIS. Chl-\(a\) varies seasonally at each site with highest inventories during late winter/spring and lowest during summer/fall, depending on location.

during the spring and summer (Stations G, H, I, J, U) lie generally along the interface between low O\(_2\) waters of the western narrows and relatively high O\(_2\) waters of the central Sound. This general pattern as well as seasonal patterns at individual sites imply estuarine wide lateral redistribution of excess Mn with a tendency for accumulation in sediments underlying low \(\rightarrow\) high O\(_2\) bottom water transitions (for example: station G gains excess Mn inventory at the same time as stations A and C lose). The regions of highest excess Mn also tend to underlie convergence zones between cyclonic gyres in the basin (e.g. Wilson and Vieira, in prep.).

Figure 12. The changes in excess Mn inventories are closely associated with input of fresh planktonic debris as illustrated at stations A and C by the loss of excess Mn following benthic increases in Chl-\(a\) inventories after the spring bloom. Excess Mn inventories are reestablished in the fall when large scale destratification and reoxygenation of the water column takes place.
Figure 13. Variation of benthic Mn\textsuperscript{2+} and O\textsubscript{2} fluxes at station P with season and temperature. The highest fluxes occur at low to intermediate seasonal temperatures and are dramatically associated with input of planktonic debris following the spring bloom (O\textsubscript{2} fluxes from data of Mackin et al., 1991). The water column is oxygenated at all times at this site (Fig. 10).

The overall increase in net Mn\textsuperscript{2+} flux from bottom sediments in spring throughout the Sound correlates closely with the benthic input of fresh organic material from the water column bloom (Figs. 4, 5). The relatively high variability of net Mn\textsuperscript{2+} flux at this time and the disproportionately high flux compared with the relatively low temperature during early spring, corroborates findings from mesocosm experiments showing strong relationships between water column C\textsubscript{org} production and net benthic Mn\textsuperscript{2+} fluxes (Hunt, 1983). The effect of the spring input is particularly dramatic at some stations as illustrated for both Mn\textsuperscript{2+} and O\textsubscript{2} fluxes to the bottom at station P (Fig. 13). These data demonstrate that the efficiency of Mn trapping in the sediment redox cycle decreases temporally during periods of substantially increased reactive C\textsubscript{org} inputs. Although at site P the excess Mn inventory is never lost entirely, as at the westernmost stations, more or less subtle decreases during spring or early summer are noticeable at this and other stations (Fig. 6, 7, 8). The result is a net export of Mn from the bottom into the suspended matter load or adjacent, less organic-rich regions of the estuary (e.g. Grill, 1978; Sundby et al., 1981; Trefrey and Presley, 1982).

The mobilization into the water column of the benthic excess Mn inventory following the spring bloom implies that trace metals and metalloids associated with Mn-oxides, such as Co, Cd, and As, experience substantial redistribution in the estuary at this time (e.g., Balistrieri and Murray, 1986; Heggie and Lewis, 1984; Peterson and Carpenter, 1983). Many studies have emphasized the oxic-anoxic transition in the water column and sediments as a primary factor in such mobilization processes (Sunby et al., 1986; Shaw et al., 1990; Sholkovitz et al., 1992). The lateral advection of low O\textsubscript{2} waters over adjacent otherwise oxygenated regions must itself promote mobilization distally to low O\textsubscript{2} source areas (Wollast et al., 1979). However,
in LIS, major sedimentary Mn loss associated with the spring bloom input of $C_{org}$ occurs long before lowering of water column $O_2$ anywhere in the estuary. Similar rapid response to the spring bloom of Mn distributions in suspended matter and underlying sediment have been reported for areas of the North Sea although the gain/loss relations were in the opposite sense: suspended matter Mn loss, benthic Mn gains (Dehairs et al., 1989). Blooms may be particularly dramatic vehicles of metal redistribution in shallow water environments and deserve more emphasis in future studies.

Reoxygenation of the water column during the fall and decreased planktonic inputs (Conover, 1956; Peterson, 1986) results in the reestablishment of efficient oxidation of surficial sedimentary Mn throughout LIS, reconstituting excess Mn inventories, and completing the seasonal inventory cycle (Fig. 6, 7, 8, 10). As demonstrated by the general correspondence in the magnitude of the net benthic Mn$^{++}$ flux and the minimum fluxes required by inventory changes (Figs. 4, 8), inventory gains could be accounted for by capture at the oxygenated sediment surface of new Mn$^{++}$ supplied by diffusion from depth in the deposits. Additional calculations based on oxygen flux balances (see later discussion) and analogies with other shallow water environments, suggests that a portion of the reconstituted benthic excess Mn also returns from the suspended matter and slow bleeding-out from adjacent regions. $^{234}$Th inventory patterns demonstrate directly that surficial regions of LIS undergo extensive and constant lateral exchange of particles consistent with both lateral recapture and export of Mn by seasonally depleted regions (Aller et al., 1980; Aller and Benninger, 1981; Cochran and Hirschberg, 1991).

b. Diagenetic reaction balances. The potential role of Mn in benthic $O_2$ and $C_{org}$ cycles can be estimated from relative rates of Mn$^{++}$ production and reprecipitation. Minimum rates of Mn$^{++}$ production are represented by the net benthic Mn$^{++}$ flux at each site. The average annual flux of Mn$^{++}$ from LIS sediments is $\sim 0.9$ mmol/m$^2$/d, compared with the annual flux of $C_{org}$ of $\sim 12-15$ mmol/m$^2$/d (Riley, 1956; Mackin et al., 1991; based on Redfield ratio $O_2/C_{org} \sim 1.3$). Assuming direct reduction of Mn with $C_{org}$ alone and an idealized stoichiometric ratio of $2Mn/1C_{org}$ (Fig. 1B, Table 1), then a minimum of $\sim 3-4\%$ of the $C_{org}$ flux could be involved in the benthic Mn cycle. Indirect coupling through S or other reduced sedimentary components rather than direct reaction with $C_{org}$ is likely. Regardless, this represents a minimum average contribution as an intermediate oxidant because of reoxidation of Mn$^{++}$ at the sediment-water interface and cycling of Mn internally in the deposit.

More accurate estimates of Mn$^{++}$ production rates and details of the Mn cycle are obtained from pore water and solid phase Mn distributions (Eqs. 4, 5; Table 3). The diffusive flux of Mn$^{++}$, $J_{DP}$, across the sediment-water interface can be estimated from Fick’s First Law (Berner, 1980) and simple linear approximation to the concentration gradient at the sediment water interface (overlying water–uppermost
Figure 14. (A) Relations between directly measured net benthic Mn\(^{++}\) fluxes \((J_{DM})\) and concentration gradient diffusion predicted flux \((J_{DP})\) at reference sites. Substantial variation occurs. The geometric mean regression through all data, \(J_{DM} = 0.89J_{DP} - 0.088\), is shown along with ratio envelopes encompassing all values. The central trend line is not a good indicator of relationships in this case (see Fig. 16 and discussion). (B) Considerable variation in the relation between \(J_{PW}\) and \(J_{DP}\) also occurs when all seasons are considered simultaneously. The geometric mean regression (dashed) is: \(J_{DP} = 0.94J_{PW} - 0.51\). There is distinct seasonality and the general relation \(J_{PW} > J_{DP}\) is evident from consideration of individual groups (Fig. 16).

pore water sample):

\[
J_{DP} = -\varphi D_s \frac{\partial C}{\partial x}.
\]  

A geometric mean regression (Model 2; Ricker, 1984) between \(J_{DM}\) and \(J_{DP}\) across all seasons and reference stations results in the central trend relation: \(J_{DM} = 0.89J_{DP} - 0.088\) (Fig. 14A). There is, however, substantial variability in this relationship seasonally and spatially, with a few extreme values strongly influencing weighted trends (i.e., positive skewed distributions of \(J_{DM}/J_{DP}\), large variance). A more detailed comparison of directly measured net fluxes, \(J_{DM}\), from flux cores and the diffusion predicted Mn\(^{++}\) flux, \(J_{DP}\), within seasonal groups suggests that only a fraction of the upwardly directed production flux typically makes it across the sediment-water interface (Fig. 16). If one or two very extreme values are dropped from the seasonal group averages the mean and median values of \(J_{DM}/J_{DP}\) become comparable. Ignoring Stations A(Aug), P(Feb), and S(Feb), the seasonal and station annual mean \(J_{DM}/J_{DP}\) is \(\sim 0.55 \pm 0.90\) with median 0.51 (otherwise average is \(\sim 1.36 \pm 2.5\); median is \(\sim 0.69\)). Individual season averages (±SD) and medians (md) are: \(\sim 0.58 \pm 1.03,\) md \(\sim 0.68\) (May); \(\sim 1.36 \pm 0.95,\) md \(\sim 1.00\) (Aug); \(\sim 0.83 \pm 0.51,\) md \(\sim 0.76\) (Nov); \(\sim 0.56 \pm 0.26,\) md \(\sim -0.50\) (Feb); and \(\sim 0.47 \pm 0.68,\) md \(\sim 0.34\) (Apr) (ignoring Sta. A (Aug), P(Feb), and S(Feb)). The most extreme values of \(J_{DM}/J_{DP}\) tend to occur in summer and winter, and imply that in some cases biogenic transport or reactions at the interface are very important \((J_{DM}/J_{DP} > 1)\) or that a comparatively larger
proportion of upwardly diffusing Mn$^{++}$ is oxidized ($J_{DM}/J_{DP} \ll 1$). There appears to be an overall regular seasonal pattern of relatively high ratios of $J_{DM}/J_{DP}$ during summer and low (negative) values in winter (Fig. 16B, median distributions), consistent with a thicker oxidized zone in winter (precipitation loss) and increased production and biogenic transport during warmer periods as described previously.

A similar comparison of $J_{DP}$ and $J_{PW}$ results in a geometric mean regression (Model 2) between the two variables of: $J_{DP} = 0.94J_{PW} - 0.51$ (Fig. 14B). Again, considerable seasonal variability occurs, compromising the use of such an overall central trend. Examination of individual seasonal groupings suggests that a relatively high proportion of the net pore water production is upwardly mobile during spring when planktonic debris is deposited ($J_{DP}/J_{PW} > 1$). At all other times of year, the ratio $J_{DP}/J_{PW}$ tends to be <1 with an annual mean of $\sim 0.57 \pm 0.46$ and median $\sim 0.52$. Individual seasonal averages ($\pm$SD) and medians are: $\sim 0.90 \pm 0.49$, md $\sim 1.19$ (May); $\sim 0.80 \pm 0.60$, md $\sim 0.67$ (Aug); $\sim 0.47 \pm 0.28$, md $\sim 0.40$ (Nov); $\sim 0.18 \pm 0.15$, md $\sim 0.15$ (Feb); and $\sim 0.55 \pm 0.44$, Md $\sim 0.72$ (Apr). These pore water relationships, together with the calculations of $J_{DM}/J_{DP}$ done previously, indicate that for much of the year only a small fraction of the net Mn$^{++}$ production (average $J_{DM}/J_{PW} < 30\%$, ignoring extremes for $J_{DM}/J_{DP}$) diffuses vertically and escapes the surficial sediment-water interface.

Estimates of Mn$^{++}$ production, $J_{XS}$, from solid excess Mn distributions and $^{234}$Th based particle mixing rates also indicate that in many cases only a very small proportion of produced Mn$^{++}$, 1–10\%, likely escapes the sediment as a net benthic Mn$^{++}$ flux ($J_{DM}$) and also that production rate estimates from diffusive transport models of pore water profiles ($J_{PW}$) themselves often account for only $\sim 10\%$ of total Mn$^{++}$ production (Fig. 15, 16). Only reference stations are plotted in Figure 15 for clarity, nonreference stations essentially mimic the reference station patterns. A large proportion of reoxidation at the sediment-water interface is consistent with rapid microbial control of Mn$^{++}$ oxidation and large populations Mn oxidizing bacteria reported for surface estuarine sediments (Burdige and Kepkay, 1983; Edenborn et al., 1985; Taylor, 1987; Tebo, 1991; Vojak et al., 1985). There is substantial variation in the relation between $J_{XS}$ and other measures of production, with good agreement between $J_{PW}$ and $J_{XS}$ estimates found in some cases (Fig. 15D). Major differences, however, are not randomly distributed about $J_{PW} = J_{XS}$ but are biased strongly to $J_{XS} > J_{PW}$. There are also regular seasonal patterns in the relationships between $J_{PW}/J_{XS}$ and $J_{DM}/J_{XS}$ (Fig. 16). The nonsteady state pulse of bloom material during spring results in rapid release of Mn$^{++}$ not initially reflected in solid phase steady-state model calculations ($J_{PW}/J_{XS}, J_{DM}/J_{XS} > 1$). At other times of year, $J_{PW}/J_{XS}$ and $J_{DM}/J_{XS}$ tend to be $\ll 1$ with an apparent pattern of regular decrease from spring > summer > fall > winter (Fig. 16). For example, seasonal mean ($\pm$SD) and median values of $J_{PW}/J_{XS}$ are: $\sim 3.5 \pm 2.6$, md $\sim 4.6$ (May); $\sim 1.3 \pm$
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Figure 15. (A) Often only 5–10% of the benthic Mn\(^{++}\) production apparently leaves the sediment as shown here by the comparison of directly measured Mn\(^{++}\) fluxes \((J_{DM})\) and production rates calculated from solid phase mixing models \((J_{XS})\). Considerable variation occurs (Sta. G–Aug not plotted, see also Fig. 16). (B) Net Mn\(^{++}\) production rates calculated from pore water profiles apparently underestimate actual production by \(~10–20\times\) in many cases as illustrated by comparison of \(J_{PW}\) and \(J_{XS}\) (Sta. G–Aug not plotted, see also Fig. 16).

2.5, md \(
\sim 0.09\) (Aug); \(~0.47 \pm 0.69\), md \(~0.22\) (Nov); \(~0.32 \pm 0.58\), md \(~0.1\) (Feb); and \(~0.74 \pm 0.97\), md \(~0.09\) (Apr).

Aside from random error, the tendency for \(J_{XS}\) (solid) to greatly exceed \(J_{PW}\) (solute) estimates in many cases is presumably caused in part by not accounting for irrigation

Figure 16. (A) Group seasonal means (±SD) for the production estimate ratios \(J_{DM}/J_{DP}\), \(J_{DP}/J_{PW}\), \(J_{DM}/J_{XS}\), and \(J_{PW}/J_{XS}\) at reference sites. The insert represents \(J_{DM}/J_{XS}\) at nonreference stations. (B) Group seasonal medians for the production estimate ratios as in (A). The skewed distributions of these ratios make the median a more representative indicator of the group properties than the mean. The insert represents nonreference stations. As described in text, distinct regular seasonal patterns are discernible.
and biogenic eddy diffusion transport of solutes in calculations of $J_{pw}$ (likely factor of 2–5×; Aller, 1982; Dicke, 1986; Martin and Banta, 1992). It may also reflect the fact that irreversible adsorption and precipitation of reduced phases occur (Taylor, 1987; Canfield et al., 1993) so that, even at steady state, net rates calculated from models like Eq. (4) could substantially underestimate gross production. The fact that the conservatively estimated production predicted fluxes from closed incubations, $J_{pp}$, are generally higher than $J_{pw}$ (average ~3×) further suggests that the latter estimates are minima (Table 3). Note that irreversible adsorption–precipitation reactions can rapidly affect pore water profiles with little immediate detectable change in solid phase distributions because of the relative mass relations and analytical sensitivity involved.

There are of course large uncertainties in values of $J_{xs}$ calculated from the solid phase distributions. The exponential distribution function assumed may result in overestimates of reaction rates, although excellent reproduction of the measured average concentrations of excess Mn in sample intervals are given by the distribution functions. Bioturbation drives the flux of excess Mn into the anoxic portions of deposits and essentially determines the rate of Mn$^{4+}$ production in sediments underlying oxygenated waters. Estimates of $D_B$ are critical to calculations of Mn$^{4+}$ production from the solid phase patterns. Alternative measures of $D_B$ from chlorophyll-$a$ penetration patterns into the deposit generally agree with those derived from $^{234}$Th but average ~2× greater overall, possibly reflecting differential mixing of particle populations or simply errors in either estimate method (Sun et al., 1994). The values of $D_B$ derived exclusively from $^{234}$Th in estimates of $J_{xs}$ were conservatively chosen.

c. Role of Mn as redox intermediate. The importance of internal cycling of sedimentary Mn as an intermediate in the O$_2$ and C$_{org}$ cycles can now be better evaluated using estimates of both Mn$^{4+}$ production and net fluxes. Assuming that all excess Mn produced in surface sediments has an average oxidation state of Mn(IV) the fraction of the benthic O$_2$ flux used in the oxidation of Mn$^{4+}$, $F_{O_2,Mn}$ is given by:

$$F_{O_2,Mn} = (J_{xs} - J_{nMn})/2J_{O_2}$$

where:

$$J_{O_2} = \text{directly measured benthic O}_2\text{ flux.}$$

Attempts to directly measure solid phase Mn oxidation state in surface LIS sediments by wet chemical measures (e.g. Murray et al., 1984) resulted in very large uncertainties because of large corrections for Fe and S interferences. One particularly well-behaved analysis implied an average excess Mn oxidation state of ~3.8. While not strong evidence for a high oxidation state in surface LIS, it is consistent
with values in $C_{org}$ rich hemipelagic sediments and nearshore suspended particles (Murray et al., 1984; Kahorn and Emerson, 1984).

Calculated values of $F_{O_2,Mn}$ at reference and additionally sampled stations are plotted in Fig. 17 (Jo, from Mackin et al., 1991). These indicate that the Mn cycle may account for a large fraction of the $O_2$ flux to the bottom during summer and fall, with near zero contribution in winter. Values of $F_{O_2,Mn} \sim 0.3-0.5$ are not unusual. The seasonal means (+SD) and medians at all reference and nonreference stations are: $\sim 0.18 \pm 0.33$, md $\sim 0.03$ (May); $\sim 0.94 \pm 1.33$, md $\sim 0.45$ (Aug); $\sim 0.32 \pm 0.30$, md $\sim 0.32$ (Oct-Nov); $\sim 0.22 \pm 0.24$, md $\sim 0.08$ (Feb); and $\sim 0.1 \pm 0.12$, md $\sim 0.09$ (Apr). These indicate an overall pattern for $F_{O_2,Mn}$ of: summer > fall > spring > winter, essentially tracking bioturbation intensity. The annual mean and median are: $\sim 0.40 \pm 0.35$, md $\sim 0.20$ (May, Apr pooled as single season). At some stations extremely high values of $F_{O_2,Mn}$ near or greater than 1 are found (e.g. G, R, H, M, Q, W). This may reflect calculation error, but I interpret $F_{O_2,Mn} > 1$ as indicating nonsteady-state net import of excess MnO$_2$ from suspended matter in the water column. In other words, during some periods input of solid phase oxidant from the water column may exceed diffusive $O_2$ flux. An additional unknown sedimentary oxidant might also account for such discrepancies.

The seasonality in the importance of sedimentary Mn cycling in $O_2$ uptake reflects strong seasonality in bioturbation rates and also $O_2$ concentrations in overlying water. At sites such as station A where low $O_2$ waters prevent reoxidation of Mn$^{++}$ at the interface, Mn cycling is of trivial importance to $C_{org}$ or S oxidation despite relatively high net Mn$^{++}$ fluxes to bottom waters (Fig. 5, 17). In contrast, at highly bioturbated sites underlying oxygenated waters, such as station P or S, excess Mn rapidly penetrates into anoxic sediments resulting in high Mn$^{++}$ production. In these cases, the cycle is effectively closed by efficient reoxidation at the sediment water interface, greatly accentuating the role of Mn as an electron shuttle. Oxic–suboxic and suboxic–oxic water column transitions result in switching between these cycling states with net export or import of suspended matter Mn respectively. The different states of the sedimentary Mn cycle envisioned for LIS are depicted in Figure 18. Generally, during periods other than winter, the Mn cycle is least important as a redox intermediate when net fluxes of Mn$^{++}$ from the bottom are highest ($J_{DM}$).

Although Mn may be reduced by either $C_{org}$ or S (HS-, FeS, FeS$_2$) during movement into anoxic deposits, it seems likely that in LIS sediments most Mn reduction is associated with S rather than direct $C_{org}$ oxidation. This conclusion comes from comparison of direct measures of SO$_4^{--}$ reduction and total $C_{org}$ mineralization estimates. Rates of SO$_4^{--}$-reduction measured in central LIS sediments are of the same order of magnitude as $J_{O_2}$ and the expected $C_{org}$ flux to the bottom (Westrich, 1983; Mackin and Swider, 1989). Relatively little net S storage occurs in much of the central Sound because of reoxidation, implying that a large portion of the $O_2$ flux is utilized in the reoxidation of S, as found in many bioturbated sediments
The fraction of the benthic O$_2$ flux associated with Mn cycling varies substantially both spatially and seasonally. Import of suspended MnO$_2$ probably accounts for fractions > 1. In many cases 30–50% of the O$_2$ flux can apparently be involved in reoxidation of Mn$^{++}$ (annual mean ~40%, progression summer > fall > spring > winter). Much of this flux probably represents indirect oxidation of sedimentary sulfides through the Mn cycle.
(e.g. Goldhaber et al., 1977; Jorgenson, 1977; Aller, 1980b; Chanton et al., 1987). In lieu of a serious mass balance problem, the present study indicates that during warmer periods of intense bioturbation, a large portion of this sulfide oxidation is likely coupled with O$_2$ through the Mn cycle. Much of the anaerobic S oxidation is probably mediated by chemosynthetic bacteria (Aller and Rude, 1988; King, 1989). In the absence of bioturbation, reoxidation processes and the sedimentary Mn cycle in particular would be of little importance to C$_{org}$, O$_2$, and S coupling.

7. Conclusions

Mn$^{++}$ fluxes from bottom sediments of Long Island Sound follow regular spatial and seasonal patterns. Sound-wide fluxes average -0.003, 0.43–0.94, 2.2, and 0.43 mmol/m$^2$/d in winter, spring, summer, and fall periods respectively. Net Mn$^{++}$ fluxes are highest in regions or times of highest sedimentary C$_{org}$ fluxes and residual C$_{org}$. A general west to east decrease in net Mn$^{++}$ flux along the axis of LIS results. Mn$^{++}$ fluxes are lower during the fall than in spring even though temperatures are higher, reflecting the importance of the spring bloom C$_{org}$ flux in promoting remobilization of Mn.
Surficial sediment inventories of excess Mn also show regular spatial and seasonal patterns. Surface sediment is generally enriched 5–20 μmol Mn/g above lithogenic background and decreases approximately exponentially with depth (≈ 2–3 cm length-scale). Excess Mn inventories are typically ≈ 5–10 μmol/cm² but vary between ≈ 0–25 μmol/cm². Inventories increase generally from west to east, varying inversely to Corg. The highest inventories are measured in the mid Sound along the transition between seasonally low O₂ waters to the west and more oxygenated central Sound regions. Inventories decrease in response to the spring bloom and excess Mn is lost entirely from the westernmost areas of highest benthic Corg flux, as measured by Chl a inventories and residual Corg. Overlying water O₂ is depleted during summer in the western regions preventing recapture of lost excess Mn. Reoxygenation of bottom waters during destratification in the fall results in recapture of Mn from the water column or adjacent sediments, oxidative closure of the sedimentary cycle, and reformation of excess Mn profiles in the western region.

The spring bloom and other pulse inputs of organic matter to the bottom are the primary driving forces in the initial seasonal remobilization of Mn and associated trace metals in LIS. Low O₂ in overlying water substantially lags mobilization (months) and is not required for redistribution of Mn.

Pore water and solid phase models of Mn⁺⁺ production rates and reoxidation demonstrate that in many cases large fractions of the produced Mn⁺⁺ are reoxidized (≈ 90%). There are substantial variations in absolute and relative rates of redox reactions and transport mechanisms. The seasonal importance of reoxidation changes regularly with fraction oxidized increasing as: spring < summer < fall < winter. When overlying waters are oxygenated, bioturbation drives a closed sedimentary cycle of reduction–reoxidation which can often account for 30–50% of the benthic O₂ flux (≈ 40% annual mean). The seasonal importance varies as: summer > fall > spring > winter, tracking bioturbation and Mn production rates. Balances between the sulfur cycle and benthic oxygen fluxes in at least some areas of LIS imply that most recycled Mn is reduced by sulfur species rather than directly by Corg. In some cases the Mn cycle accounts for > 100% of the oxygen flux implying that import of solid oxidants in suspended matter from the water may be more a more important source of oxidant than diffusive fluxes of O₂.

The importance of Mn as an intermediate oxidant is determined largely by bioturbation, which transports MnO₂ and reactive Corg into reduced zones, and by the efficiency of Mn⁺⁺ oxidation at the sediment water interface. During warmer seasons, the highest net fluxes of Mn⁺⁺ from bottom sediments often occur where the Mn cycle is not efficiently closed and is therefore least important in the sedimentary redox cycle. The cycle is eventually closed in regions of oxygenated water column or adjacent sediments in such cases.

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