FILE

DEPARTMENT OF COMMERCE ★ UNITED STATES OF AMERICA ★

NOAA Technical Memorandum ERL PMEL-93

A MODELING STUDY OF THE VERTICAL DISTRIBUTION AND TRANSPORT OF MANGANESE IN PUGET SOUND

C. N. Cudaback
A. J. Paulson
J. W. Lavelle

Pacific Marine Environmental Laboratory
Seattle, Washington
September 1991

noaa NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION / Environmental Research Laboratories

NOAA Technical Memorandum ERL PMEL-93

A MODELING STUDY OF THE VERTICAL DISTRIBUTION AND TRANSPORT OF MANGANESE IN PUGET SOUND

C. N. Cudaback
A. J. Paulson
J. W. Lavelle

Pacific Marine Environmental Laboratory
Seattle, Washington
September 1991

UNITED STATES
DEPARTMENT OF COMMERCE

Robert A. Mosbacher
Secretary

NATIONAL OCEANIC AND
ATMOSPHERIC ADMINISTRATION

John A. Knauss
Under Secretary for Oceans
and Atmosphere/Administrator

Environmental Research
Laboratories

Joseph O. Fletcher
Director

NOTICE

Mention of a commercial company or product does not constitute an endorsement by NOAA/ERL. Use of information from this publication concerning proprietary products or the tests of such products for publicity or advertising purposes is not authorized.

Contribution No. 1320 from NOAA/Pacific Marine Environmental Laboratory

---

For sale by the National Technical Information Service, 5285 Port Royal Road
Springfield, VA 22161

CONTENTS

PAGE

A Modeling Study of the Vertical Distribution and Transport of Manganese in Puget Sound

C.N. Cudaback, A.J. Paulson, and J.W. Lavelle

ABSTRACT. A one-dimensional vertical distribution and transport model tracing the fate of Mn in dissolved and fine particulate forms and Mn associated with rapidly settling aggregates is developed and results are compared with measurements. Those measurements take the form of vertical profiles of dissolved and particulate Mn concentrations measured in the water column at one station in central Puget Sound. The model provides a framework relating sources, sinks, distributions and fluxes of Mn in a quantitative manner. The model accurately reproduces the vertical distributions of dissolved and particulate Mn, but shows excessive vertical flux of Mn. The model suggests that particles in each of two size classes should carry nearly the same loading of Mn, but measurements show significantly less Mn loading on macroaggregates than on fine particles. Mn budgets from model results allow comparison of major Mn fluxes in Puget Sound. The flux of Mn into the central main basin in particulate form is about half the diffusive flux of dissolved Mn from the bottom. A significant fraction of the riverine flux of particulate Mn is advected out of Puget Sound in dissolved form.

1. INTRODUCTION

The fate of many toxic trace metals in estuaries is controlled by their adsorption onto manganese enriched particles, although Mn itself is not considered toxic (e.g. Feely *et al.*, 1986, Paulson *et al.*, 1988). The geochemical cycle of estuarine manganese has been studied by a variety of approaches. The variations in dissolved Mn concentrations with salinity and time have been studied by Knox *et al.* (1981) and Morris *et al.* (1982). Many researchers have inferred overall residence times of dissolved Mn from field data (e.g. Grill, 1982; Edenborn *et al.*, 1985; Sunda and Huntsman, 1987). Emerson *et al.* (1982) found time scales of a few days for biologically catalyzed oxidation. Sung and Morgan (1981) found oxidation time scales of 50 days in laboratory experiments with an iron oxide catalyst. Yeats and Strain (1990) combined estuarine field studies of oxidation rates with a vertical advection-diffusion model of dissolved Mn in the water column, finding residence times of 15-25 days. Using a box model for the main basin of Puget Sound, Paulson *et al.* (1988) inferred a 5 day residence for dissolved Mn in the Sound.

In this report we bring together field data from Puget Sound and a model describing the processes controlling Mn cycling and distributions. The model expands on that of Yeats and Strain (1990) by including the effect of particulate fluxes and distributions, and augments the work of Paulson *et al.* (1988) by providing a framework for quantitative studies of Mn cycling. In its exchange features, the model is similar to that used previously for Th by Bacon *et al.* (1985), Nozaki *et al.* (1987), and Lavelle *et al.* (1991a). Unlike Th, Mn has spatially non-uniform sources including fluxes out from the sediment column, features this model addresses.

The model must acknowledge these aspects of Mn cycling and transport in the Sound. First, Mn has both dissolved and particulate forms with continual exchanges between them. In particulate form, Mn is transported vertically by settling. Second, the sediment column is both a sink and a source of Mn. Mn that has reached the sediment in particulate form is subject to remobilization to dissolved form and diffusion back into the water column. Particulates bearing Mn are also subject to resuspension by bottom currents and Mn reenters the water column from the seafloor in that mode (Paulson *et al.*, 1988). Some of Mn eventually finds long-term burial deep in the sediment column. The model must incorporate all exchanges of Mn between the water column and sediments. Third, not all of the Mn entering the Sound on riverine particles finds burial in the sediments (Paulson *et al.*, 1988). Budget studies of Mn indicate that there is a net loss of Mn from Puget Sound through Admiralty Inlet. A model looking at vertical processes must allow for that loss through a sink term in the conservation equations. Lastly, the complex geometry and topography of Puget Sound and the resulting circulation patterns cause surface and bottom water to be stirred together at some locations (Lavelle *et al.*, 1991b). Important for Mn is the landward transport of dissolved Mn in bottom water of East Passage, the upward mixing of bottom water with surface water in Dalco Passage, and the discharge of this mixture in the surface water near Blake Island. This transport by the clockwise residual circulation around Vashon Island (e.g. Ebbesmeyer and Barnes, 1980; Cannon, 1983) is evident in the Mn distributions in Puget Sound (Paulson *et al.*, 1988). This unusual circulation effect on Mn distributions in represented in the one-dimensional model as a vertical transport of Mn which is independent of diffusivity.

2. MEASUREMENTS

Measurements in this paper were taken in central Puget Sound near PS7 (Fig. 1) in the spring of 1985. Vertical profiles of dissolved and particulate manganese (dMn and pMn) were measured, as well as Mn concentrations in settling material collected in sediment traps (sMn). Samples for water column dMn and pMn were collected at MB85-21 (47°42′N, 122°27′W) on April 4 and April 10, 1985. Surface samples of dMn were taken at Station MB85-17, (47°40′N, 122°28′W) on April 3. Settling particles at 30 and 185 meters depth were collected nearby between 1200 April 6 and 0000 April 15 in sequentially sampling sediment traps (Baker and Milburn, 1983). Sediment trap samples at 100 m were collected sequentially over three 4-hour periods starting at 0800 April 10.

2.1 Sampling

Seawater samples for dissolved and particulate Mn determinations were collected in modified 12-l, Teflon-coated Go-Flo™ bottles. Seawater was pressure filtered through an acid-cleaned, pre-tared, 37-mm, 0.4 μm polycarbonate Nuclepore filter held in an acid-cleaned, all-Teflon Savillex filter holder. The filtrate was collected in acid-cleaned, 500-ml high-density polyethylene (HDPE) bottles and acidified to pH 1.6 with concentrated Ultrex™ nitric acid. The

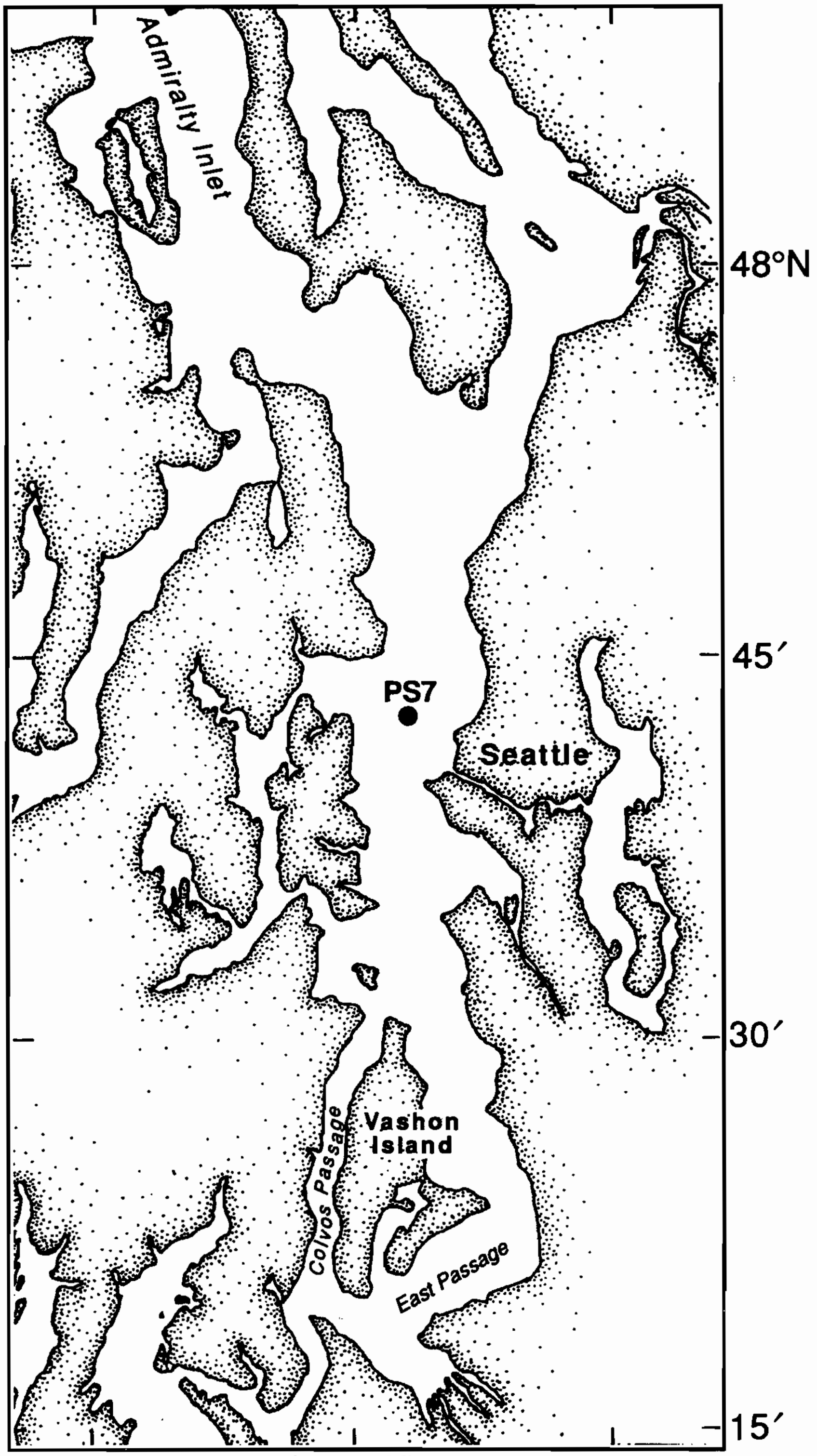

Fig. 1: A map of Puget Sound with the station near which concentration and flux profiles of particles and Mn were measured (PS7, west of Seattle). At PS7, residual estuarine circulation is northward in the surface layer and southward in the bottom layer. Residual circulation around Vashon Island is clockwise, south through East Passage and north through Colvos Passage.

filter was rinsed with Milli-Q™ (MQ™) water adjusted to pH 8 with Ultrex™ NH_4OH. The filter were then vacuum desiccated over NaOH for three days.

Settling matter was collected by sequentially-sampling sediment traps (Baker and Milburn, 1983). The settling material was collected in cylinders (0.2 l) filled with a dense brine (40 ppt) that contained 12 g/l of sodium azide. The traps were deployed so that a single cylinder was opened for 204 hours (30 and 175 m sediment traps) or 4 hours (100 m sediment trap). Upon recovery of the traps, supernate from each cylinder was collected in an acid-cleaned, 30-ml HDPE bottle and acidified to pH 1.6 with concentrated Ultrex™ nitric acid. The slurry containing the settling particles was then sieved through a 63 μm polyethylene screen and the < 63 μm material was collected on an acid-cleaned, pre-tared, 47-mm, 0.4 μm polycarbonate Nuclepore filter. The filter was then rinsed with pH 8 MQ™ water. Material >63 μm diameter was collected on acid cleaned, 47-mm, 0.4 μm polycarbonate Nuclepore filters and rinsed with pH 8 MQ™ water. For the 30 and 175 m traps, large size material from all cylinders was combined on a single filter. The large-size material from each of the cylinders of the 100 m trap was collected on a single filter.

2.2 Analysis

Water column total suspended matter (TSM) concentrations and total particle settling flux rates were determined gravimetrically. Water column samples were analyzed for dMn by graphite furnace atomic absorption spectrometry (GFAAS) after pre-concentration using the Chelex-100™ method of Paulson (1986). The supernates from the sediment trap cylinders were analyzed for dMn in a similar manner using a 1-gm column.

Particulate Mn exists in two forms, reducible Mn (redMn) in surface oxide coatings and residual Mn (resMn) locked into the structure of the particle. Reducible Mn from the suspended matter was selectively extracted using a 0.1 M solution of hydroxylamine hydrochloride in 0.175 M Chelex-100™-extracted sodium citrate according to the method of Robbins *et al.* (1984). The remaining residual material was dissolved in $HCl\text{-}HNO_3\text{-}HF$ according to Eggiman and Betzer (1976). In each case, the resulting Mn in solution was analyzed by GFAAS. The measured amounts of reducible and residual Mn were added together to yield the total amount of Mn on suspended matter. Water column data can be found in tabular form in Paulson *et al.* (1991).

The total particulate Mn concentrations, pMn, in the two size fractions of sediment trap material were measured in a similar fashion. A combined total particulate Mn concentration was then calculated by weight averaging the total particulate concentration of the two size fractions. Total particulate Mn was then corrected for the amount of Mn remobilized into the filling solution:

$$\{pMn\} = f_{<63}\left(\{redMn\}_{<63} + \{resMn\}_{<63}\right) + f_{>63}\left(\{redMn\}_{>63} + \{resMn\}_{>63}\right) + \frac{T_d}{(C_p + C_s)} \qquad (1)$$

where { } is particulate flux-weighted Mn concentration in μg/g; f_i is the fraction of the total particle mass in the ith sized-fraction; here T_d is the dissolved Mn mass concentration (μg/l) in the cylinder supernate; and $(C_p + C_s)$ is here the total particulate mass concentration (g/l) collected in each cylinder.

3. MODEL

3.1 Governing Equations

The one dimensional vertical model used in this study is based on that introduced by Bacon *et al.* (1985) and used by Nozaki *et al.* (1987) and Lavelle *et al.* (1991a) to study the distributions of radioactive Th. In this adaptation of the model, exchanges with bottom sediments have been added. As diagrammed in Fig. 2, the model reservoirs include ones for dissolved and fine particulate tracers, tracers associated with large rapidly settling macroaggregates (marine snow; Alldredge and Silver 1988) and tracers in the sediments. Reversible chemical exchange

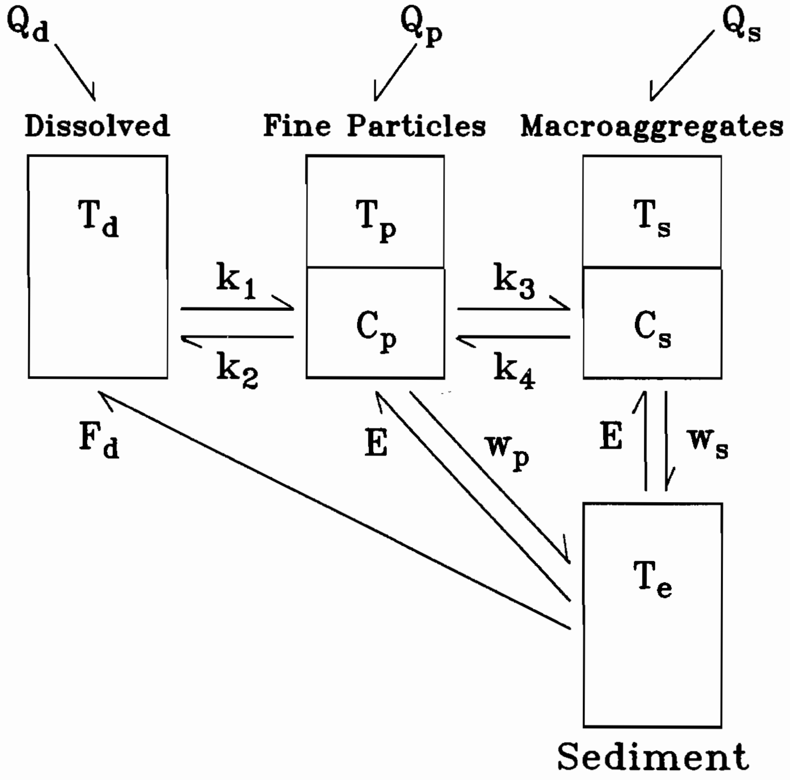

Fig. 2: Schematic of tracer exchange, settling and deposition. T_d, T_p, and T_s represent the mass concentration of tracers in dissolved, particulate and marine snow forms, respectively. Q_d, Q_p and Q_s represent the respective sources of the three forms of tracers. F_d is the diffusion of T_p into the water column from the sediments. C_p and C_s are mass concentration of fine particles and marine snow, and w_p and w_s are their respective settling velocities. E represents the sediment erosion rate.

of Mn between dissolved and fine particle forms is represented, as well as the exchange of mass and tracer between fine particles and macroaggregates. Both solid forms settle at finite velocities and all forms are subject to vertical diffusion. Exchange with the bottom, both by resuspension of particulates and by diffusion of remobilized dissolved Mn, is crucial to this model.

There are several key differences in the use of this model for Th and Mn. Whereas dissolved ^{234}Th is formed radioactively at uniform rates throughout Puget Sound, Mn enters the water column on riverine particles, on particles eroded off the bottom and by diffusion of dissolved Mn from the bottom sediments, so the sources of particulate Mn must be linearly related to sources of particles themselves. So modeled and measured particulate distributions must first be brought into agreement by adjustment of particulate source fluxes. Then the same sources must be multiplied by Mn loading factors to model the vertical distributions of dMn, pMn and sMn.

After Lavelle *et al.* (1991a), the kinetics of a tracer such as manganese are described by:

$$\frac{\partial T_d}{\partial t} = Q_d - k_1 C_p T_d + k_2 T_p + K_z \frac{\partial^2 T_d}{\partial z^2} \tag{2}$$

$$\frac{\partial T_p}{\partial t} = Q_p + k_1 C_p T_d - k_2 T_p - k_3' T_p + k_4 T_s - w_p \frac{\partial T_p}{\partial z} + K_z \frac{\partial^2 T_p}{\partial z^2} \tag{3}$$

$$\frac{\partial T_s}{\partial t} = Q_s + k_3' T_p - k_4 T_s - w_s \frac{\partial T_s}{\partial z} + K_z \frac{\partial^2 T_s}{\partial z^2} \tag{4}$$

T_d, T_p and T_s represent dissolved tracer and tracer associated with fine particles and macroaggregates, and Q_d, Q_p and Q_s are the respective tracer sources. Parameters k_1C_p and k_2 represent the rates of sorption and remobilization of dissolved manganese, respectively. Rate constant k_3' is the scavenging rate of fine particles by marine snow, previously called k_3C_s by Lavelle *et al.* (1991a), and k_4 is the rate at which fine particles are released by macroaggregates. Settling speeds of fine particles and marine snow are w_p and w_s, respectively, and K_z is a constant vertical diffusivity.

The kinetics of the fine particle/aggregate system are described in a similar fashion (Lavelle, 1992) by:

$$\frac{\partial C_p}{\partial t} = Q_{pp} - k_3' C_p + k_4 C_s - w_p \frac{\partial C_p}{\partial z} + K_z \frac{\partial^2 C_p}{\partial z^2} \tag{5}$$

$$\frac{\partial C_s}{\partial t} = Q_{ss} + k_3' C_p - k_4 C_s - w_s \frac{\partial C_s}{\partial z} + K_z \frac{\partial^2 C_s}{\partial z^2} \tag{6}$$

where C_p and C_s represent the mass concentration of fine particles and aggregates, and Q_{pp} and Q_{ss} are their respective sources. In the application here steady state conditions are assumed, so the left hand sides of Equations (2–6) are set to zero.

The model requires values for rates of net sediment deposition, particle settling, particle erosion and upward dMn diffusive flux at the seafloor, and exchange of dMn with fine particles and fine particles with marine snow. All of these quantities have previously been measured or calculated. A coefficient of vertical diffusivity had also to be assigned and distributions for sources of particles and Mn assumed. Existing parameter values, however, were found not to provide the optimal fit to measured Mn distributions. Some parameter adjustments within a reasonable range were needed.

3.2 Boundary Conditions

There is assumed to be no atmospheric source of particles. Thus the boundary conditions for the particle model at the sea surface are:

$$K_z \frac{\partial C_p}{\partial z} - w_p C_p = 0, \qquad \text{at } z = 0 \tag{7}$$

$$K_z \frac{\partial C_s}{\partial z} - w_s C_s = 0, \qquad \text{at } z = 0 \tag{8}$$

There is likewise assumed to be no flux of Mn through the sea surface, and a balance of Mn fluxes at the sediment water interface gives Mn boundary conditions:

$$K_z \frac{\partial T_d}{\partial z} = 0, \qquad \text{at } z = 0 \tag{9}$$

$$K_z \frac{\partial T_p}{\partial z} - w_p T_p = 0, \qquad \text{at } z = 0 \tag{10}$$

$$K_z \frac{\partial T_s}{\partial z} - w_s T_s = 0, \qquad \text{at } z = 0 \tag{11}$$

At the seafloor, vertical particle mass flux equals the sum of the downward settling flux and the upward erosive flux:

$$K_z \frac{\partial C_p}{\partial z} - w_p C_p = \frac{EC_p}{(C_p + C_s)} - w_p C_p, \qquad \text{at } z = -h \tag{12}$$

$$K_z \frac{\partial C_s}{\partial z} - w_s C_s = \frac{EC_s}{(C_p + C_s)} - w_s C_s, \qquad \text{at } z = -h \tag{13}$$

The total erosion flux out of the sediments, E, is assumed to be divided between fine particles and aggregates in proportion to their relative concentrations directly above the sediment water interface.

In the sediment column, Mn is remobilized from particles, raising the dMn concentration in interstitial waters enough to drive a diffusive flux, F_d, of dMn into the bottom of the water column. Measurements of F_d show fluxes between 1000 and 4000 (μgMn/cm^2/yr) in the main basin of Puget Sound (Paulson *et al.*, 1988). The erosive flux of Mn is proportional to the erosion rate of particles, with proportionality constant, R_{pe}, being the mass loading of Mn on particles. The erosive flux is divided between the fine particle and aggregate size classes in proportion to their relative abundance. R_{pe} is 500–1200 ppm by measurement (Paulson *et al.*, 1988). The magnitudes of the bottom fluxes of manganese were adjusted within that range to fit the model to the data. Therefore:

$$K_z\frac{\partial T_d}{\partial z} = F_d, \qquad \text{at } z = -h \qquad (14)$$

$$K_z\frac{\partial T_p}{\partial z} - w_pT_p = R_{pe}\frac{C_p}{(C_p + C_s)}\,E - w_pT_p, \qquad \text{at } z = -h \qquad (15)$$

$$K_z\frac{\partial T_s}{\partial z} - w_sT_s = R_{pe}\frac{C_s}{(C_p + C_s)}\,E - w_sT_s, \qquad \text{at } z = -h \qquad (16)$$

3.3 Mass Balance

Integrating the sum of equations (5–6) in steady state and substituting Eq. (7, 8, 12, 13) produces a particle mass balance:

$$\int_0^{-h} Q_{pp}dz + \int_0^{-h} Q_{ss}dz = w_sC_s(z = -h) + w_pC_p(z = -h) - E = D \qquad (17)$$

The right hand side of equation (17) is the downward settling flux of particles less the upward erosive flux, i.e, total particle flux to the sediments, or net deposition, D.

If tracer equations (2–4) are added together and integrated vertically, and equations (9–11 and 14–16) are substituted, a similar mass balance for Mn in the water column results, where the right hand side of equation is equal to the burial rate of Mn:

$$\int_0^{-h} Q_ddz + \int_0^{-h} Q_pdz = w_pT_p(z = -h) + w_sT_s(z = -h) - F_d - R_{pe}\,E \qquad (18)$$

The mass balance in equation (18) and can be viewed as diagrammed in Fig. 3.

In Fig. 3, the sediment mixed layer represents that part of the sediment column which exchanges with the water column. Older sediments are isolated from exchange with the bottom water. The ultimate burial rate of particle mass under the sediment mixed layer is equivalent to the net deposition onto the sediment layer. The rate of ultimate burial of manganese tracer is proportional to the sediment mass burial, with proportionality constant R_{pb}, the loading of Mn on the particles deep in the sediment column. All the sources of Mn in the water column must sum to the amount ultimately buried.

$$\int_0^{-h} Q_ddz + \int_0^{-h} Q_pdz = R_{pb}\left(\int_0^{-h} Q_{pp}dz + \int_0^{-h} Q_{ss}dz\right) \qquad (19)$$

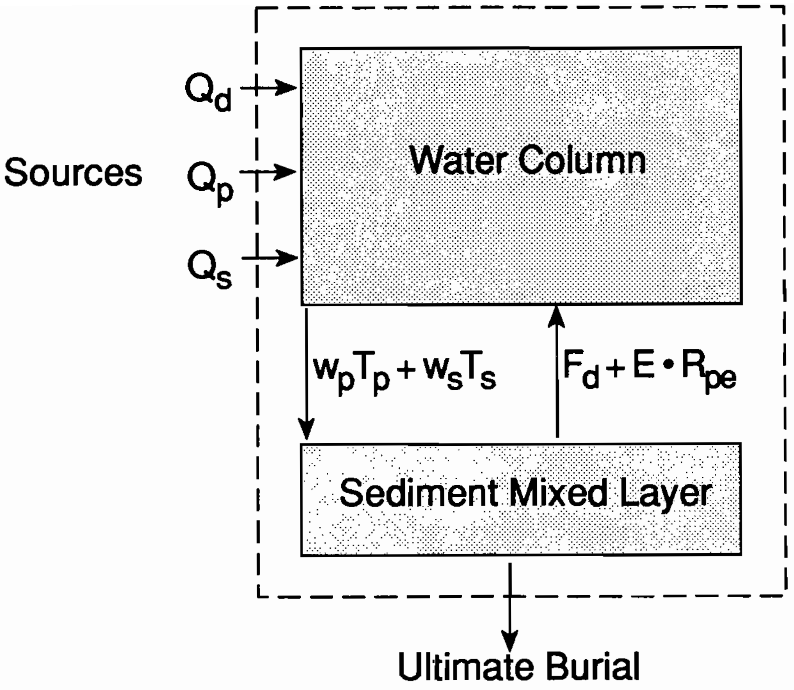

Fig. 3: Mass balance diagram for tracer equations vertically integrated over the water column. Q_d, Q_p and Q_s are manganese sources in the water column. Settling of Mn to the sediment is represented by $w_pT_p + w_sT_s$. Dissolved and particulate fluxes from the sediment into the water are F_d and $E{\cdot}R_{pe}$, respectively. Ultimate burial is the rate at which Mn is buried under the sediment mixed layer so that it no longer exchanges with the water column.

The manganese loading on buried sediments, R_{pb}, is 400–1000 ppm in Puget Sound (Romberg *et al.*, 1984). The loading on sediments entering the water column is 3000 ppm. To account for this difference, the model requires a significant sink of dissolved manganese. As described below, this sink is interpreted as advection of Mn out of the sound through Admiralty Inlet (Fig. 1). This sink is formally represented in the model as a negative contribution to the distribution Q_d.

3.4 Sources

In this one dimensional model, horizontal transports of particulates and Mn are incorporated into source functions. A significant fraction of particles entering the Sound are riverine (Lavelle *et al.*, 1986) and these enter at the surface. For this model application the riverine fraction is assumed to be 40% of the total. The remaining part of the particulate source, Q_{pp} (Fig. 4a), is distributed uniformly through the water column, representing particles eroded off the side walls of the sound (Lavelle *et al.*, 1986).

The source profile of macroaggregates, Q_{ss} (Fig. 4a), was based on other considerations. Water bottle samples (e.g., Feely *et al.*, 1986) indicate that, on average, 20% of the particulate mass in the surface waters is organic. For the purposes of this model, it is assumed that the

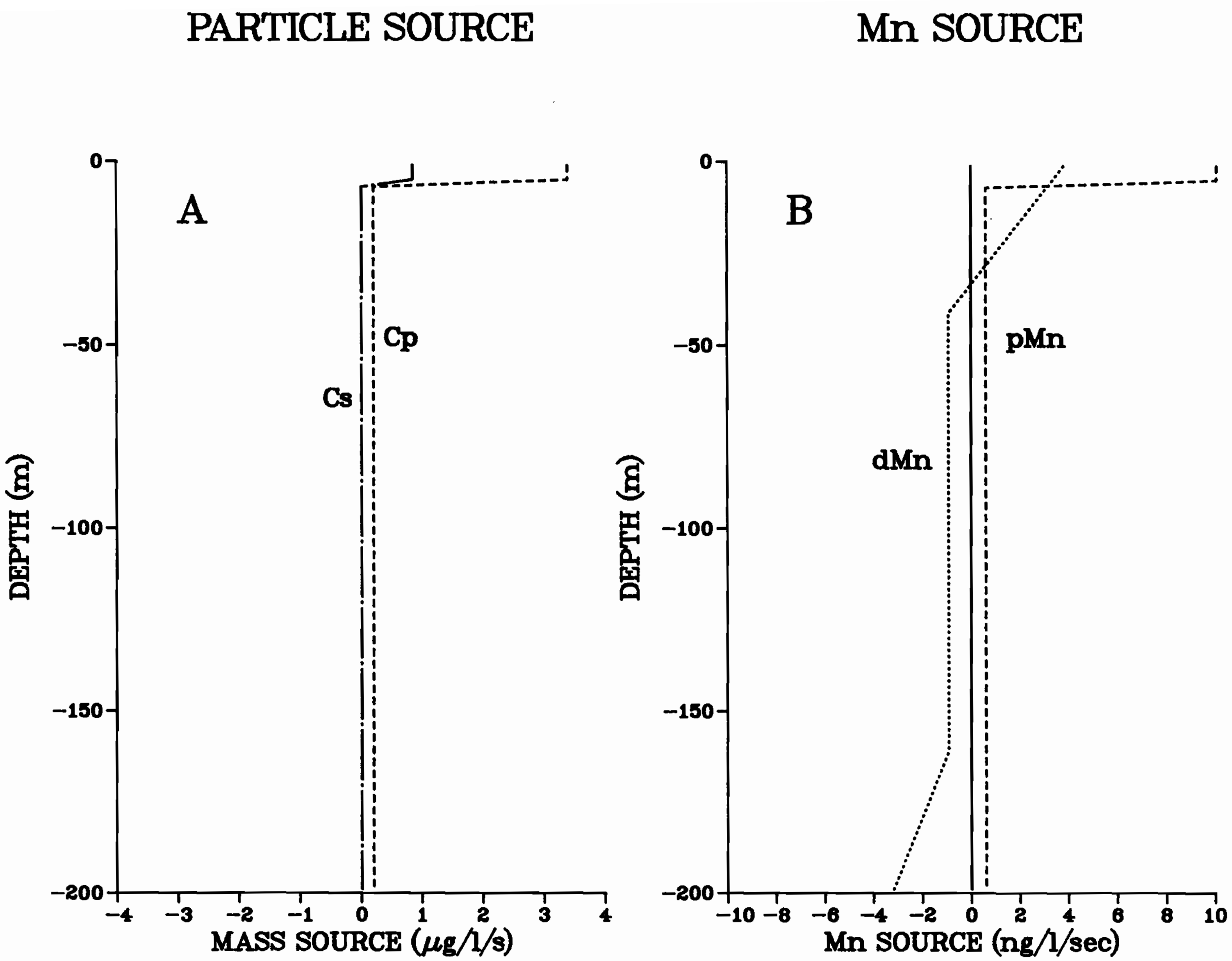

Fig. 4: Sources of fine particle mass (dashed line, 3a) and sources of macroaggregate mass (dot/dash line, 3a). Sources and sinks of dissolved Mn (dotted line, 3b), sources of particulate Mn (dashed line, 3b). There is no source of Mn in macroaggregate form. Negative values correspond to sinks for Mn as described in the text.

organic matter is in the form of large aggregates that are free of Mn. Q_{ss} thus has a concentration spike at the surface and is zero below the surface. Source profiles Q_{pp} and Q_{ss} added together and integrated vertically must equal the net sediment deposition rate, D, of 1000–5000 g/m^2/year as measured in Puget Sound (Lavelle *et al.*, 1986). This constraint sets the overall normalization of the source functions.

Figure 3b shows tracer source/sink functions Q_d, Q_p and Q_s. The Q_d profile represents the sum of sources and sinks of dissolved manganese. It is composed of two parts. First, some dMn is transported from the bottom of the water column, around Vashon Island, and into the surface waters. This recirculation effect is represented by a negative Q_d in the bottom 40 meters and an equal and opposite Q_d in the top 40 meters (sloped dotted lines, Fig. 4b). Second, some dMn must be advected out of Puget Sound, because more particulate Mn enters the system than is ultimately buried (Paulson *et al.*, 1988). This effect is represented by a constant negative value of Q_d over the entire water column (Fig. 4b), the magnitude of which is adjusted to give the correct difference between total Mn input into the system and loss to deep burial in the sediment column. Both components of the Q_d distribution are designed to represent the effects of lateral flow in Puget Sound on the vertical distribution of Mn at PS7.

The source distribution of particulate manganese, Q_p, is the fine particle source distribution multiplied by the loading of Mn on fine particles, R_{po}, assumed to be constant. Measurements of R_{po} in the water column vary between 1000 and 3000 ppm (Paulson *et al.*, 1991). The higher value provided a better fit between model results and measured Mn distributions. The aggregate source is assumed to be organic and carry no manganese. Thus:

$$\begin{aligned} Q_p &= R_{po}\, Q_{pp}, \\ Q_s &= 0 \end{aligned} \tag{20}$$

where R_{po} = 3000 ppm.

4. RESULTS

4.1 Particulates

Most of the parameters used in the particulate model are based on previous work. The aggregate settling velocity, w_s = 100 m/day, is an average from measurements for marine snow (Alldredge and Silver, 1988). The settling velocity of fine particles is, of course, much smaller. A particle of diameter 8 microns and density 1.5 g/cm^3 has a Stokes settling velocity of w_p = 1 m/day, and this is the value adopted for this work. The vertical diffusivity in Puget Sound is assumed to be K_z = 20 cm^2/sec, consistent with the findings of Lavelle *et al.* (1991b). From a model of ^{234}Th distributions, Lavelle *et al.* (1991a) reported a range of k_3' and k_4 values. In this study, values in the middle of the range were used: $k_3' = (4.5\text{ day})^{-1}$ and $k_4 = (1\text{ day})^{-1}$.

The particulate model was run repeatedly for a 200 m deep model space, and results were plotted for comparison with measured suspended matter concentration profiles. Minor adjustments were made within the known range of erosion, E, and net deposition rates, D, to obtain the best visual fit between model results and data. Final values were:

$$\begin{aligned} D &= 6.3 \times 10^{-5}\ \mathrm{g/m^2/s} \\ E &= 2.0 \times 10^{-4}\ \mathrm{g/m^2/s} \end{aligned} \tag{21}$$

The ratio of C_p to C_s was assumed to be 9:1 so that 90% of the eroded particle mass is associated with fine particles and 10% with macroaggregates (Eqs. 12 and 13).

In Fig. 5a, modeled distributions of fine particles and macroaggregates are compared to measurements. Total suspended matter (TSM, small triangles) should equal the sum of fine particle mass (C_p, dashed line) and macroaggregate mass (C_s, dot-dash line), though C_s is much smaller than C_p (Fig. 5). Model C_p compares favorably with TSM.

Figure 5b shows the vertical flux of fine particles (w_pC_p, dashed line) and macroaggregates (w_sC_s, dot-dash line). Mass flux as measured by sediment traps (large triangles) should equal the sum of the two model fluxes. Although the model flux is greater than the measured flux, the difference is within the range of temporal variability in measured mass flux (Baker *et al.*, 1985).

4.2 Manganese

Once the particulate profiles and parameters were established, the Mn tracer model was run repeatedly. Model results were compared visually with measured Mn distributions. F_d, the diffusive flux of dMn out of the sediments, R_{po} and R_{pe}, the Mn loading on source and eroded particles, respectively, and k_1 and k_2 were all adjusted to achieve best visual fit of model profiles to data. The final values of diffusive flux of Mn and mass loadings were:

$$\begin{aligned} F_d &= 3.8 \times 10^{-7}\ \mathrm{g/m^2/s} \\ R_{pe} &= 500\ \mathrm{ppm} \\ R_{po} &= 3000\ \mathrm{ppm} \end{aligned} \tag{22}$$

When the model was run with a scavenging time scale, $1/(k_1C_p)$, of a few days as suggested by Paulson *et al.* (1988), the result showed more pMn and less dMn than the data, suggesting that dMn was being converted to pMn too quickly. The best fit was found using $1/(k_1C_p) = 17$ days with no desorption. This forward rate is typical of either slow biological catalysis or rapid surface catalysis. The data could also be fit separately using a reversible reaction sorption with time scale 21 days and remobilization time scales on the order of months to years. The remobilization of dMn from fine particles is apparently slow enough that k_2 can be set to zero for this estuary setting.

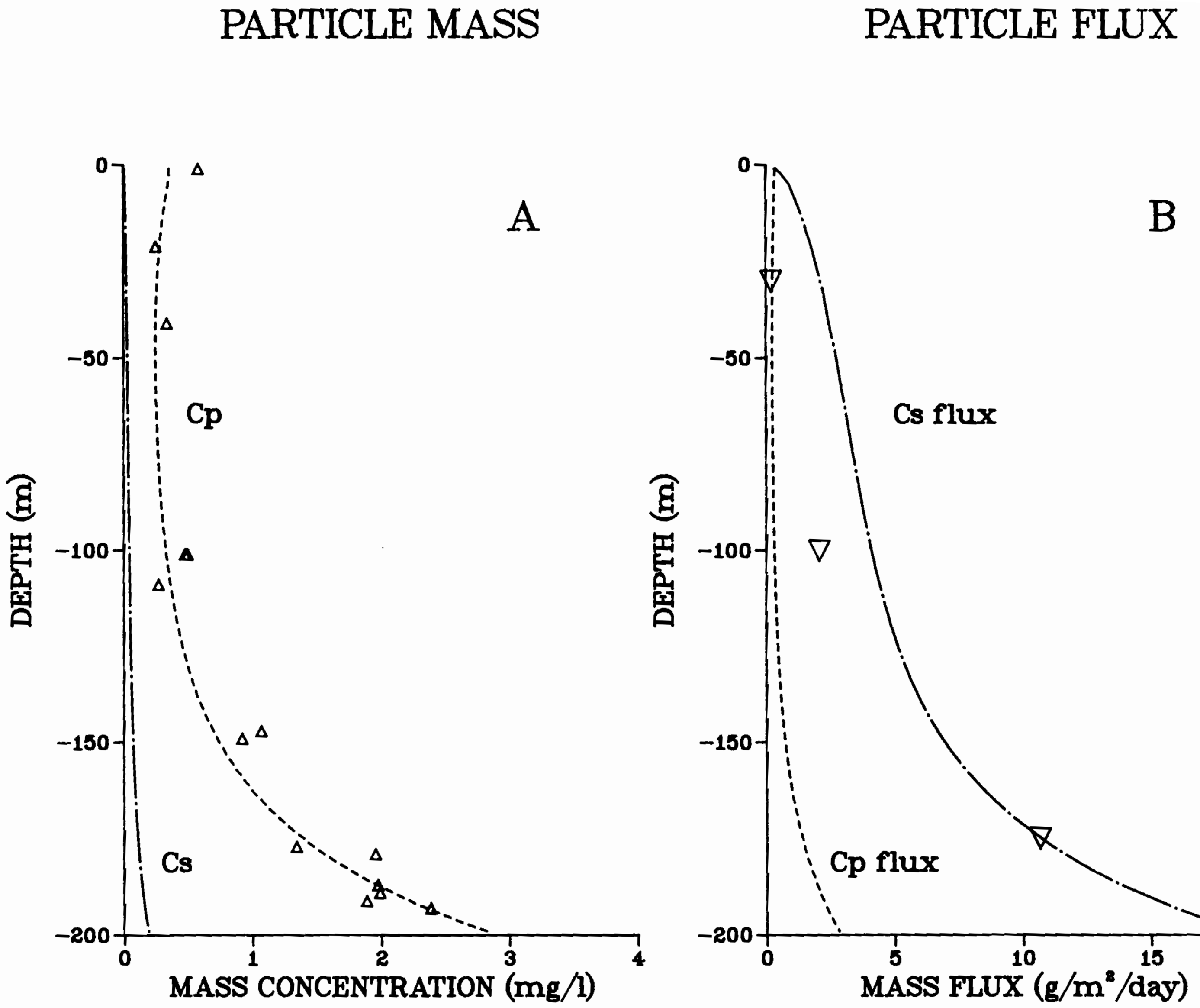

Fig. 5: Particle profiles with line types as in Fig. 3 and a dot/dash line for macroaggregates. Small triangles are measured fine particle mass, and large inverted triangles are measured large particle flux.

The Mn scavenging time scale used here must be compared to those reported by other researchers. There are a very wide range of reported oxidation times for dMn, ranging from hundreds of years for the homogenous reaction to a few days with different catalysts. Some recent work has focused on the surface catalytic effect of oxides of Mn or Fe (e.g., Sung and Morgan, 1981; Yeats and Strain, 1990). These researchers found oxidation time scales between 15 and 50 days. A more common approach is the study of biological catalysis of Mn oxidation in estuaries, as suggested by Emerson *et al.* (1982). Removal time scales for dMn in various estuaries are typically a few days to a week (e.g., Emerson *et al.*, 1982, Sunda and Huntsman, 1987). Paulson *et al.* (1988) reported 2–8 day time scales for Mn oxidation in Puget Sound. All of the above studies assume $k_2 = 0.0$.

Figure 6a shows the comparison between measured and modeled manganese profiles. For dMn (small squares and dotted line) the comparison is quite good. The model shows slightly too much vertical gradient in pMn (dashed line) relative to measurements (small triangles). Flux comparisons tell a somewhat different story. Figure 6b shows the model producing too much vertical flux of manganese. The excess Mn flux is a compound effect of too much particulate mass flux and too much Mn loading on settling material (Fig. 6c).

The quantity measured directly in this data set is the Mn loading (μg/g) on material collected in water bottles (suspended) and in sediment traps (settling). Figure 6c shows significant discrepancies between the model results and the data. Throughout most of the water column, the model suggests Mn loading on suspended and settling material should be similar. As there is an implicit assumption in the model that aggregates are formed of homogenous fine particles, this conclusion is not surprising. The data, however, indicate that Mn loading is significantly less on aggregates than on fine particles.

Figure 7 shows comparisons between Mn on suspended and on settling matter for other available data sets. All the profiles show about 50% less Mn loading on macroaggregates than on fine particles. There are several possible explanations for this phenomenon.

First, the macroaggregates could be half organic material, diluting the relative Mn concentration. However, comparisons of the composition of suspended and settling material (e.g., Feely *et al.*, 1986) indicate that both size classes are 5–10% organic material in most of the water column. Furthermore, other metals such as Zn and Cu do not show the same dilution, implying that there is an unknown geochemical process affecting only the Mn concentrations.

It is possible that the size spectrum of fine particles could lead to preferential adsorption. For example, most of the Mn bound by microbial catalysis is associated with particles greater than 5–8 microns in diameter (e.g., Sunda and Huntsman, 1987). There may be some mechanism by which particles much smaller or much larger than 10 microns are preferentially incorporated into macroaggregates.

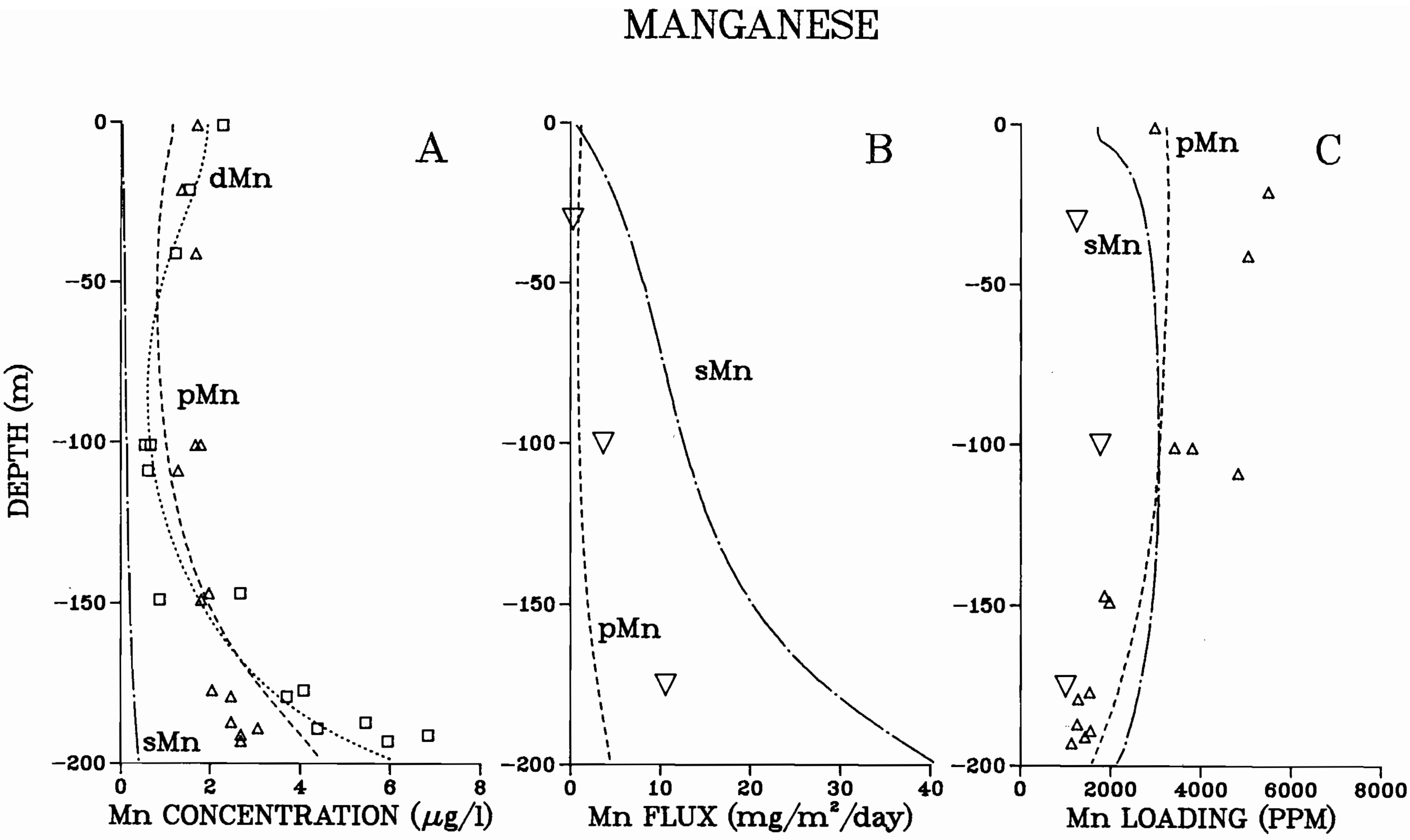

Fig. 6: Manganese profiles with line designations as in Figs. 3 and 5. Small ×'s are dissolved Mn concentrations.

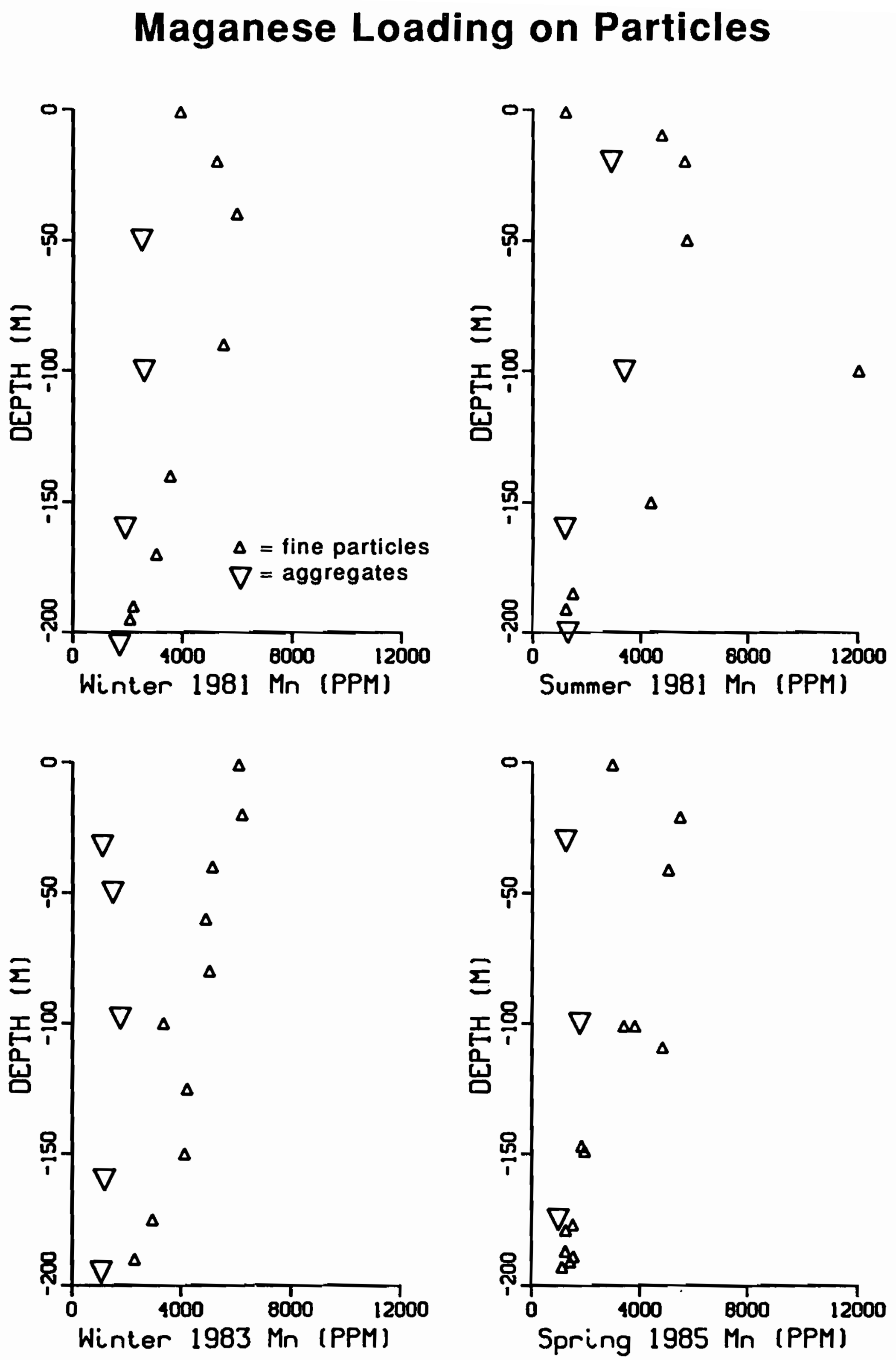

Fig. 7: Comparison of Mn loading on suspended and settling matter (Feely *et al.*, 1986; Paulson *et al.*, 1991; Paulson, unpublished data). Small triangles are Mn on suspended matter, and large triangles are Mn on settling matter.

4.3 Mass Balances and Transports

The individual terms of Eq. 18 have these magnitudes:

$$\begin{array}{rll}
\int_0^{-h} Q_d dz = -1.34 \times 10^{-7} \mathrm{g/m^2/sec}, & \text{(dissolved source of Mn)} & \\
\int_0^{-h} Q_p dz = 1.75 \times 10^{-7} \mathrm{g/m^2/sec}, & \text{(particulate source of Mn)} & (23) \\
w_p T_p(z = -h) = 5.16 \times 10^{-8}\ \mathrm{g/m^2/sec}, & \text{(fine particulate Mn flux to sediments)} & \\
w_s T_s(z = -h) = 4.66 \times 10^{-7} \mathrm{g/m^2/sec}, & \text{(macroaggregate Mn flux to sediments)} & \\
F_d = 3.8 \times 10^{-7}\ \mathrm{g/m^2/sec}, & \text{(dissolved Mn out of sediments)} & \\
R_{pe}E = 1.0 \times 10^{-7}\ \mathrm{g/m^2/sec}. & \text{(resuspended Mn flux)} &
\end{array}$$

Comparison of the magnitude of various terms in equation (18) yields some interesting results. Integrated transports Q_d and Q_p indicate that a significant fraction (77%) of the manganese which enters Puget Sound as particulates is advected out of the Sound in dissolved form. This transport represents the leakage by advection from the Mn diffusive-scavenging mill. Particulate Mn enters the sediment column, where it is reduced. The reduced Mn (Mn^{2+}) diffuses out of sediment. Before the reduced Mn is oxidized and returns to the sediment in the particulate form for another cycle through the mill, a small amount of the reduced Mn is lost from the mill by advection.

Note too that the diffusive flux of dMn out of the sediments, F_d, is more than twice as large as the flux of Mn entering the Sound on particulates, $\int_0^{-h} Q_p dz$, or being lost in dissolved form from the estuary, $\int_0^{-h} Q_d dz$. This large diffusive flux is primarily balanced by an even larger settling flux in macroaggregate form of Mn to the sediments, $w_s T_s$. The Mn flux at the seafloor resulting from particle erosion, $R_{pe}E$, is only about 25% of the upward diffusive flux of dMn there. These flux rates show the significant recycling of Mn in and out of the sediments that transpires in this estuary. This mill can also carry Pb and other metals into the sediments (e.g. Paulson *et al.*, 1988).

Equation (19) can be rewritten to express the loading of Mn on sediments buried under the sediment mixed layer:

$$R_{pb} = \left(\int_0^{-h} Q_d dz + \int_0^{-h} Q_p dz \right) / D \tag{24}$$

giving $R_{pb} = 6.77 \times 10^{-4}$ g/g, or 677 ppm, within the 400–1000 ppm range reported by Romberg *et al.* (1984) for Mn loading on buried sediments in Puget Sound.

5. CONCLUSIONS

A model with water column and sediment reservoirs of Mn and the coupling between them provides a framework to discuss vertical distributions and transport of Mn in Puget Sound. Despite the model's limitation to one dimension, it together with the measured profiles of Mn, suggests that:

1) Remobilized Mn fluxes from the sediments into the bottom waters of Puget Sound at a rate that is several times larger than the distributed rate of supply of new Mn entering the sound from riverine sources. This is a consequence of the manyfold cycling of Mn into sediments by scavenging and settling and into the water column by remobilization of Mn within the sediments;

2) A substantial fraction of bottom water enriched by the diffusive flux of dMn is transported to surface waters by a process other than vertical diffusion, and upwelling in Dalco and recirculation through Colvos Passages must be the suspected pathway;

3) Large aggregated particles, typically sampled by traps, are important to the vertical transport of Mn;

4) The middepth minima in dMn and pMn concentrations are partly the consequence of the rate of settling of macroaggregates and the time scale for their exchange with the fine particle reservoir;

5) The time scale for scavenging of dMn by fine particles is on the order of weeks;

6) Much of the Mn entering the Sound from terrigenous sources must be lost to the ocean in dissolved form through Admiralty Inlet.

The model results further suggest that additional resolution of the particle reservoir for Mn will have to be acquired through field studies and incorporated into models. Differences in fine and macroaggregate Mn mass loadings in field measurements and the near equality of the same in the model seems to make this a necessity. Effects of lateral transport of Mn in Puget Sound were compensated for, to some extent in this one-dimensional approach, by adjustments to source/sink functions. Uncertainties resulting from a such one dimensional treatment will be ameliorated in future work by treatment of Mn cycling in Puget Sound in two-dimensions. High on the list of measurements needed to make that expanded model bear fruit will be source locations around the Sound of both particulates and Mn and their changes in time.

6. REFERENCES

Alldredge, A.L. and M.W. Silver, 1988. Characteristics, dynamics and significance of marine snow. *Prog. Oceanogr., 20,* 41-82.

Bacon, M.P., C.-A. Huh, A.P. Fleer and W.G. Deuser, 1985. Seasonality in the flux of natural radionuclides and plutonium in the deep Sargasso Sea, *Deep Sea Res., 32*(3), 273-286.

Baker, E.T. and H.B. Milburn, 1983. An instrument system for the investigation of particle fluxes, *Cont. Shelf. Res., 1,* 425-435.

Baker, E.T., R.A. Feely, M.R. Landry and M. Lamb, 1985. Temporal variations in the concentration and settling flux of carbon and phytoplankton pigments in a deep fjordlike estuary, *Estuar. Coast. Shelf. Sci., 21,* 859-877.

Cannon, G.A., 1983. An overview of circulation in the Puget Sound estuarine system. NOAA Tech Memo ERL PMEL-48, NOAA, Seattle, WA, 30 pp.

Ebbesmeyer, C.C. and C.A. Barnes, 1980. Control of a fjord basin's dynamics by tidal mixing in embracing sill zones. *Estuar. Coast. Mar. Sci., 11,* 311-330.

Edenborn, H.M., Y. Paquin and G. Chateauneuf, 1985. Bacterial contribution to manganese oxidation in a deep coastal sediment, *Estuar. Coast. Shelf Sci, 21*(6), 801-815.

Eggiman, D.W and P.R Betzer, 1976. Decomposition and analysis of refractory oceanic suspended materials, *Anal. Chem, 48*(6), 886-890.

Emerson, S., S. Kalhorn, L. Jacobs, B.M. Tebo, K.H. Nealson and R.H. Rosson, 1982. Elemental oxidation rate of manganese(II): bacterial catalysis. *Geochim. Cosmochim. Acta, 46*(6), 1073-1079.

Feely, R.A., G.J. Massoth, E.T. Baker, J.F. Gendron, A.J. Paulson and E.A. Crecelius, 1986. Seasonal and vertical variations in the elemental composition of suspended and settling particulate matter in Puget Sound, Washington. *Estuar. Coast. Shelf Sci., 22,* 215-239.

Grill, E.V, 1982. Kinetic and thermodynamic factors controlling manganese concentrations in oceanic waters. *Geochim. Cosmochim. Acta, 46*(12), 2435-2446.

Knox, S., D.R. Turner, A.G. Dickson, M.I. Liddicoat, M. Whitfield and E.I. Butler, 1981. Statistical analysis of estuarine profiles: application to manganese and ammonium in the Tamar Estuary. *Estuar. Coast. Shelf Sci., 13*(4), 357-371.

Lavelle, J.W., 1992. A process model for estuarine sedimentation involving marine snow. Nearshore and Estuarine Cohesive Sediment Transport, submitted, Springer-Verlag.

Lavelle, J.W., E.D. Cokelet and G.A. Cannon, 1991b. A model study of density intrusions into and circulation within a deep, silled estuary: Puget Sound. *J. Geophys. Res.*, in press.

Lavelle, J.W., C.N. Cudaback, A.J. Paulson and J.W. Murray, 1991a. A rate for the scavenging of fine particles by macroaggregates in a deep estuary. *J. Geophys. Res., 96*(C1), 783-790.

Lavelle, J.W., G.J. Massoth and E.A. Crecelius, 1986. Accumulation rates of recent sediments in Puget Sound, Washington. *Mar. Geol., 72,* 59-70.

Morris, A.W., A.J. Bale and R.J.M. Howland, 1982. The dynamics of estuarine manganese cycling. *Estuar. Coast. Shelf Sci., 14*(2), 175-192.

Nozaki, Y., H.-S. Yang and M. Yamada, 1987. Scavenging of thorium in the ocean. *J. Geophys. Res., 92*(C1), 772–778.

Paulson, A.J., 1986. Effects of flow rate and pre-treatment on the analyses of trace metals in estuarine and coastal seawater by Chelex-100. *Anal. Chem, 58*, 183-187.

Paulson, A.J., R.A. Feely, H.C. Curl, Jr., E.A. Crecelius and T. Geiselman, 1988. The impact of scavenging on trace metal budgets in Puget Sound. *Geochim. Cosmochim. Acta, 52*(7), 1765-1779.

Paulson, A.J., H.C. Curl, Jr., R.A. Feely, T. Geiselman, K.A. Krogslund, G.J. Massoth, M.F. Lamb and K. Kelly, 1991. Trace metal and ancillary data in the open waters of Puget Sound, NOAA Data Report ERL PMEL-31.

Robbins, J.M., M. Lyle and G.R. Heath, 1984. A sequential extraction procedure for partitioning elements among co-existing phases in marine sediments. Ref. 84–3. College of Oceanography, Oregon State Univ., Corvallis, OR, 45 pp.

Romberg, G.P., S.P. Pavlou, R.F. Shokes, W. Hom, E.A. Crecelius, P. Hamilton, J.T. Gunn, R.D. Maunch and J. Vinelli, 1984. Presence, distribution and fate of toxicants in Puget Sound and Lake Washington. Toxicant Pretreatment Planning Study Report C1, METRO, Seattle, WA, 231 pp.

Sunda, W.G. and S.A. Huntsman, 1987. Microbial oxidation of manganese in a North Carolina estuary. *Limnol. Oceanogr, 32*(3), 552-564.

Sung, W. and J.J. Morgan, 1981. Oxidative removal of Mn(II) from solution catalyzed by the γ-FeOOH (lepidocrocite) surface. *Geochim. Cosmochim. Acta, 45*(12), 2377-2383.

Yeats, P.A. and P.M. Strain, 1990. The oxidation of manganese in seawater: rate constants based on field data. *Estuar. Coast. Shelf Sci., 31*(1), 11-24.

7. MODEL NOTATION

C_p – mass concentration of fine particles
C_s – mass concentration of macroaggregates
D – net deposition rate of particles
E – rate of erosion of particles at seafloor
F_d – diffusive flux of Mn from sediments
k_1 – sorption rate of Mn onto fine particles
k_2 – remobilization rate of Mn from fine particles
k_3 – large particle aggregation rate
k_4 – release rate of fine from large particles
K_z – vertical eddy diffusivity
Q_d – source rate of dissolved Mn
Q_p – source rate of particulate Mn
Q_{pp} – source rate of fine particulates
Q_s – source rate of macroaggregate Mn
Q_{ss} – source rate of macroaggregates
R_{pb} – mass function of Mn deep in sediments
R_{pe} – mass function of Mn on particles undergoing erosion
R_{po} – mass function of Mn on particles entering via riverine sources
t – time
T_d – mass concentration of tracer (Mn) in dissolved form
T_p – mass concentration of tracer (Mn) in fine particulate form
T_s – mass concentration of tracer (Mn) in macroaggregate form
w_p – fine particle settling velocity
w_s – macroaggregate to settling velocity
z – vertical coordinate

☆U.S. GOVERNMENT PRINTING OFFICE: 1991 - 673-002/41015