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On the formation of the manganese maximum in the oxygen minimum

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Abstract—A simple model that accounts for the formation of the Mn maximum in the oxygen minimum is presented here. In this model, Mn is proposed to cycle in a constant proportion to carbon, as do nitrogen and phosphorous. Superimposed on the Mn-carbon cycle is the removal of Mn(II) via scavenging onto sinking particles and transport by vertical diffusion. Scavenging is assumed to follow the rate law observed in the laboratory for Mn(II) oxidation. Manganese(II) concentrations were calculated with the model at stations in the Pacific and Atlantic Oceans and compared with measurements of dissolved Mn. All parameters in the model were based on laboratory measurements or field observations. The model reproduced Mn(II) maxima of the correct concentration and at the correct depth. This agreement was observed at a range of oxygen concentrations. The calculations demonstrate that the Mn maximum can form because of a reduction in the pseudo-first order scavenging rate constant (k') within the oxygen minimum. The value of k' will decrease in regions of the water column with low oxygen and pH ($k' = k_0 [O_2] \{OH^-\}^2$). These regions will accumulate higher dissolved Mn(II) concentrations before the rate of Mn(II) removal, $k'[Mn(II)]$, equals the input from remineralization of POC and a steady state is reached. An additional source of Mn, such as flux from continental margin sediments or dissolution of Mn oxides, is not necessary to account for formation of the Mn maximum.

1. INTRODUCTION

The vertical distribution of dissolved manganese in the North Pacific Ocean (Fig. 1a) is characterized by concentration maxima near the surface and within the oxygen minimum zone (Klinkhammer and Bender, 1980; Landing and Bruland, 1980, 1987; Martin et al., 1985; Murray et al., 1983). By analogy with nitrite, we refer to the high Mn concentrations near the surface as the primary maximum. The high concentrations within the oxygen minimum are the secondary maximum. These maxima are believed to be produced by changes in oxidation state of Mn. The primary Mn maximum appears to be produced by photoreduction of insoluble Mn(IV) oxides in the photic zone of the ocean to produce soluble Mn(II) (Sunda et al., 1983; Sunda and Huntsman, 1988).

The mechanism responsible for the origin of the secondary Mn(II) maximum is not as clear. Three potential mechanisms were suggested after this feature was first recognized (Klinkhammer and Bender, 1980). Reduction of Mn(IV) oxides in continental margin sediments that intersect the oxygen minimum followed by transport of soluble Mn(II) into the oceans interior, reduction of Mn(IV) oxides within the oxygen minimum as minerals reequilibrate with the water column under low oxygen and pH conditions (Equilibrium Model), and release of soluble Mn(II) from organic matter as it is consumed (Kinetic Model) could all produce the secondary maximum. Martin et al. (1985) suggested that offshore transport of Mn released from continental margin sediments produced the subsurface maximum. However, we recently measured the flux of dissolved Mn(II) across the sediment-water interface in a transect through the oxygen minimum zone (Johnson et al., 1992). These measurements demonstrate that the Mn(II) flux is largest over the continen-

tal shelf. The smallest values of the flux occur in the oxygen minimum layer (Fig. 1b). The flux of Mn from sediments cannot be responsible for formation of the secondary Mn(II) maximum, therefore. Processes acting within the water column must produce the secondary maximum.

Both the equilibrium model and the kinetic model would act within the water column to produce the secondary Mn(II) maximum. The equilibrium model was considered in detail by Klinkhammer and Bender (1980). It overestimates dissolved Mn(II) concentrations by several orders of magnitude in strong oxygen minima and does not reproduce the Mn minimum between the primary and secondary maxima. Measurements of particulate Mn flux also show no reduction in flux through the oxygen minimum (Martin et al., 1985), which would occur if particulate MnO_x was reduced to Mn(II) to restore chemical equilibrium at low oxygen conditions. Here we consider whether the secondary Mn(II) maximum can be produced by Mn(II) release during organic carbon oxidation. Klinkhammer and Bender (1980) did not have sufficient data to test the kinetic mechanism and did not consider it in detail. Landing and Bruland (1980, 1987) considered it a plausible explanation. Neither of these studies were able to make quantitative assessments of the kinetic mechanism. Sufficient knowledge of organic carbon cycling has since accumulated so that it is now possible to assess the role of this mechanism in a quantitative manner.

A kinetic model is used here to examine the processes that might control the concentration of dissolved Mn(II) in the oxygen minimum region. In this model, the dissolved Mn(II) concentration is controlled by a balance between Mn(II) release from particulate organic matter (POM), as suggested by Landing and Bruland (1980), and its subsequent loss from the system after oxidation to particulate
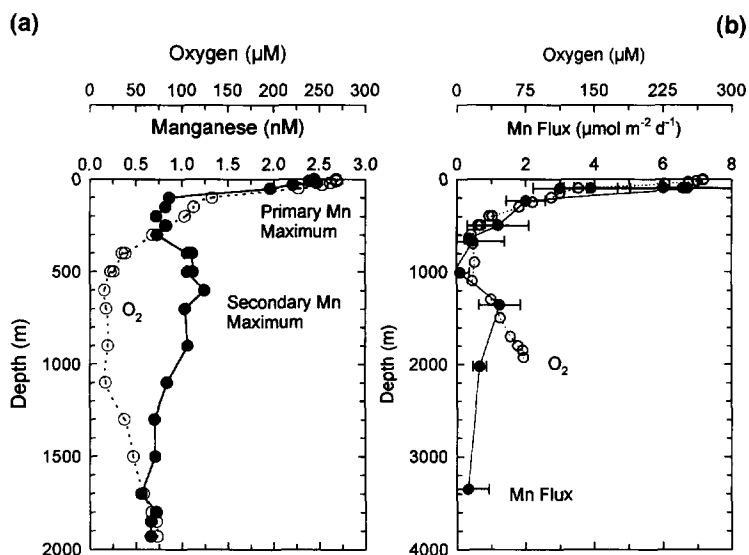
(a)   **(b)**

FIG. 1. (a) Vertical profile of dissolved Mn and oxygen observed off the California coast at 35° 15'N and 121° 52'W (Johnson et al., 1992). (b) Fluxes of Mn(II) across the sediment water interface measured with a free vehicle, benthic flux chamber in a transect down the continental slope in the same vicinity as the profile shown in (a). Measurements from Johnson et al. (1992) and unpublished field work from the central California region.

Mn oxides (MnO_x) that sink from the system. First order scavenging, with respect to Mn(II), sets the dissolved Mn(II) concentration at the point where the removal rate equals the release rate. The predictions of this kinetic model are compared with observations of dissolved Mn(II) at stations from the North Atlantic to the North Pacific.

2. THE MODEL

Consider the processes that might control Mn in the secondary maximum as organic carbon is recycled. Mn(II) is incorporated into organic matter within the euphotic zone by phytoplankton. Export of Mn(II) from the mixed layer occurs as the POM sinks into the deep sea. Remineralization of the POM below the euphotic zone leads to the release of Mn(II) to the dissolved phase. Mn(II) will subsequently be lost by oxidation to Mn oxides, which are then scavenged and removed to the sediments. In order to maintain a steady-state dissolved Mn(II) concentration, the production of dissolved Mn(II) during remineralization of POM must be balanced by the rate of Mn(II) oxidation (ignoring diffusive and advective transport).

The production rate of dissolved manganese from POM remineralization can be estimated from the change in carbon flux vs. depth. Martin et al. (1987) have shown that the vertical flux of particulate organic carbon (POC) at a set of stations throughout the North Pacific could be fit by the equation

$$F_C = F_{100}\left(\frac{Z}{100}\right)^{-b}, \qquad (1)$$

where Z is the depth in meters, F_{100} is the flux (mol C m^{-2} y^{-1}) at 100 m depth, and b was found to have an average value of 0.858. Bishop (1989) reviewed the literature for particulate carbon concentrations and fluxes. He found that Eqn. 1 provided the closest fit to the combined set of data. We have adopted this equation for the work discussed here. If the Mn/C ratio of settling organic particles is Q (μmol Mn/mol C), then the rate of production of dissolved Mn during particle remineralization (P_{Mn}, nmol L^{-1} y^{-1}) is

$$P_{Mn} = Q\frac{\partial F_C}{\partial Z} = \frac{b}{100^{-b}}QF_{100}Z^{-(1+b)} = 45QF_{100}Z^{-1.858}. \qquad (2)$$

The rate of production of dissolved Mn is controlled by the Mn/C ratio of the POM and the export of particulate organic carbon from the euphotic zone (F_{100}).

Production of Mn must be balanced by a scavenging removal term. Whitfield and Turner (1987) developed a scavenging index to characterize trace metal behavior in seawater. This index is expressed as a ratio of the affinity of ions for solution (the inorganic side reaction coefficient) to their affinity for sorption onto particle surfaces (the first hydrolysis constant). Mn(II) and Cd(II) have similar scavenging index values. One might expect that Mn(II) would have a nutrient-like vertical profile similar to that of Cd. However, the Mn concentration profile is nothing at all like that of Cd (Bruland and Franks, 1983). Laboratory experiments demonstrate that adsorption of Mn(II) involves an oxidation step to Mn(III) or Mn(IV) (Nyffeler et al., 1984). This ability to change oxidation states distinguishes Mn chemistry from that of other metals such as Cd.

In this work, we have assumed that scavenging of Mn(II) is controlled by the rate of oxidation of Mn(II). Mn(II) oxidation can proceed via both homogeneous and heterogeneous reactions (Morgan, 1967). The overall rate law for Mn oxidation, which is dependent upon oxygen concentration and hydroxide ion activity (Morgan, 1967), is

$$\frac{\partial[Mn(II)]}{\partial t} = (k_0 + k_1[MnO_2])[O_2]\{OH^-\}^2[Mn(II)]$$

$$= k'[Mn(II)]. \qquad (3)$$

The rate constants k_0 and k_1 for Mn(II) oxidation that were determined by Morgan (1967) in dilute solutions are 4×10^{12} M^{-3} d^{-1} and 10^{18} M^{-4} d^{-1} at 25°C (Diem and Stumm, 1984). The homogeneous rate constant derived from the work of Davies and Morgan (1989) is $k_0 = 1.1 \times 10^{12}$ M^{-3} d^{-1}, if the order of the reaction with respect to OH$^-$ is 2. Murray and Brewer (1977) reported a value for k_1 of 4×10^{18} M^{-4} d^{-1} in seawater. In addition, we have begun a laboratory study of the homogeneous Mn(II) oxidation rates in seawater at initial Mn(II) concentrations near 10 nM. Preliminary results of these measurements in 0.2 μm filtered seawater are consistent with the observations of Morgan (1967). Two experiments yield a mean value of $k_0 = 2.5 \times 10^{12}$ M^{-3} d^{-1} at 25°C and a salinity of 33 (P. von Langen, MLML, pers. commun.). We have used the values derived from Morgan (1967) in this work.

Concentrations of particulate Mn are <0.4 nM at stations in the North Pacific that are not over the continental margin and at depths above the nephloid layer (Landing and Bruland, 1980; Martin et al., 1985). If all of this particulate Mn is Mn oxides, an upper limit on the pseudo third order heterogeneous Mn oxidation rate is k_1 × [MnO_x] < 2 × 10^9 M^{-3} d^{-1}. This is three orders of magnitude less that the homogeneous rate constant k_0. It appears reasonable to assume, therefore, that inorganic Mn oxidation in open ocean seawater occurs primarily by homogeneous reaction, rather than by heterogeneous reaction. We shall ignore heterogeneous reactions in the remainder of this paper. The heterogeneous reaction rate is more important in coastal waters with high particulate Mn (Grill, 1982; Yeats and Strain, 1990) and this assumption is valid only for open ocean waters.

Diem and Stumm (1984) have suggested that the rate constants obtained in laboratory studies are in error due to two potential experimental artifacts: oxidation of Mn(II) by bacteria, or precipitation of rhodochrosite ($MnCO_3$) during the experiment, which might catalyze the oxidation rate. Davies and Morgan (1989) have addressed possible artifacts in k_0 due to rhodochrosite catalysis. They believe that this effect has not biased their results. Rhodochrosite can have no effect on our preliminary measurements in seawater, since seawater at pH 8 with 10 nM Mn(II) is undersaturated with respect to the mineral by many orders of magnitude (Johnson, 1982).

The general agreement of three independent laboratory measurements of k_0 suggests that the influence of bacteria on the Mn(II) oxidation constants measured in these studies was not large. However, Mn encapsulated bacteria are found in the deep sea (Cowen and Bruland, 1985). Sunda and Huntsman (1988) measured the rates of formation of particulate Mn at a station in the Sargasso Sea. In the upper 40 m and at 500 m, they found particulate Mn formation rates of 0.01 nmol L^{-1} d^{-1}. These values correspond to a rate constant k_0 + k_1[MnO_x] that ranges from 2 × 10^{12} to 10 × 10^{12} M^{-3} d^{-1}, at the in situ pH, O_2 and [Mn^{2+}]. This range of values is in reasonable agreement with the value for k_0 determined in the laboratory, which suggests that bacterial catalysis and the heterogeneous mechanism do not overwhelm the inorganic, homogeneous reaction mechanism in the near surface or deeper waters of the Sargasso Sea. Cowen et al. (1990) measured the rates of scavenging of dissolved Mn in the water column over hydrothermal systems. They found that biological scavenging of dissolved Mn was at most 50% of the total Mn scavenging rate. The lowest rate constants for Mn(II) removal in their study were similar to the homogeneous Mn(II) oxidation rate constant.

The particulate Mn formation rates observed by Sunda and Huntsman (1988) at depths from 80 to 120 m were tenfold higher than the inorganic oxidation rate of Mn(II) and the oxidation was inhibited by poisons and heating. The elevated Mn particle formation rate at 80–120 m must have been due to bacterial catalysis. This is the depth range where the bulk of organic matter is remineralized (Martin et al., 1987) and the supply of Mn(II) must be high. We deliberately fixed the upper boundary of the model to coincide with this region and set the dissolved Mn(II) concentration at the boundary to a value similar to that seen at the base of the euphotic zone. This was done to avoid including the much more complex processes that occur in the euphotic zone (photoreduction of MnO_x, photoinhibition of Mn(II) oxidation, biological uptake of Mn(II), dust deposition, etc.).

Estimates of Mn oxidation rates in coastal systems with high Mn concentrations are also many orders of magnitude higher than the rates estimated in the laboratory (Emerson et al., 1982; Yeats and Strain, 1990; Moffett, 1994). Manganese-oxidizing bacteria may play a dominant role in removal of dissolved Mn(II) from seawater where there are high concentrations of Mn(II) or high production rates of Mn(II). The existing observations of Mn oxidation and scavenging in deep-sea environments (Sunda and Huntsman, 1988; Cowen et al., 1990), however, suggest that the rates of removal are comparable to the rates of inorganic oxidation.

We shall assume that the rate of dissolved Mn(II) scavenging (R_{Mn}) is proportional to the homogeneous Mn(II) oxidation rate:

$$R_{Mn} = -\alpha k_0 [O_2] \{ OH^- \}^2 [Mn(II)].   \qquad (4)$$

We have incorporated a term α, as a multiplier of the inorganic Mn

oxidation rate, to investigate the possible role of bacterial Mn(II) oxidation. The bacterial oxidation rate is assumed to be proportional to the inorganic oxidation rate as Cowen and Bruland (1985) found a large decrease in Mn encapsulated bacteria abundance within the oxygen minimum zone where oxidation rates decrease at low oxygen and pH. If scavenging proceeds solely by inorganic oxidation, then $\alpha = 1$ and the scavenging rate equals the oxidation rate. Bacterial oxidation would result in $\alpha > 1$. The impacts of this assumption will be examined in the Discussion. Organic complexation of Mn(II) in seawater is not likely to reduce the oxidation rate ($\alpha < 1$). Mn(II) forms weak organic complexes (Martell and Smith, 1974), and we are unaware of any evidence for strong Mn(II) binding in seawater. The stability constant for Mn(II) with cellular binding sites is twelve orders of magnitude less than that observed for Fe(III) (Sunda and Huntsman, 1985).

Readsorption of Mn(II) back onto POM before it oxidizes appears to be unlikely as another mechanism for loss of Mn(II). Dissolved Cd is present in seawater at a relatively constant ratio to dissolved PO_4^{3-}, which indicates that it is not strongly readsorbed onto the sinking material from which it was released. If it were, then the dissolved Cd/PO_4 ratio would change continuously with depth. As both Mn(II) and Cd(II) have similar scavenging indices (Whitfield and Turner, 1987), Mn(II) should not adsorb either. Chester et al. (1993) also observed no rescavenging of Mn onto aerosol particles, while other metals such as Pb and Zn were.

The dissolved Mn production and removal terms must sum to zero at steady state:

$$0 = P_{Mn} + R_{Mn}$$

$$= 45QF_{100}Z^{-1.858} - \alpha k_0 [O_2] \{ OH^- \}^2 [Mn(II)].   \qquad (5)$$

All diffusive and advective processes are ignored in this very simple model. The effects of transport processes will be considered later in this paper. The dissolved Mn distribution can be obtained by solving Eqn. 5 for [Mn(II)] at each depth if Q, F_{100}, α, [O_2] and {OH$^-$} are known:

$$[Mn(II)] = \frac{45QF_{100}Z^{-1.858}}{\alpha k_0 [O_2] \{ OH^- \}^2}.   \qquad (6)$$

3. RESULTS

3.1. Model without Vertical Mixing

We used Eqn. 6 to calculate the dissolved Mn distribution at the VERTEX V Station 4 (Martin et al., 1985), which is referred to as VERTEX 4. The pseudo-first order rate constant for homogeneous Mn(II) oxidation (k' = k_0[O_2]{OH$^-$}^{2}) at each depth was calculated from the profile of dissolved oxygen measured at the station. The {OH$^-$} profile was calculated from pH values (Fig. 2) that were observed at the nearby GEOSECS Station 204 (Takahashi et al., 1980) and the dissociation constant of water. The calculated rate constant (k') for homogeneous Mn(II) oxidation varies from 1.15 y^{-1} at 100 m ([O_2] = 205 μM, pH = 8.29) to 0.005 y^{-1} at 900 m in the core of the oxygen minimum ([O_2] = 15 μM, pH = 7.68), to 0.05 y^{-1} at 2000 m ([O_2] = 72 μM, pH = 7.84) with $\alpha = 1$.

The ratio of Mn to carbon in sinking organic carbon particles was estimated from sediment trap data collected 90 km off the California coast (Martin and Knauer, 1983; Martin et al., 1985). Manganese that is rapidly released from particles to the brine in sediment traps (trapped exchangeable Mn) is believed to be derived from an organic carbon carrier (Martin and Knauer, 1983). The ratio of the flux of trapped exchangeable Mn to the flux of POC can be used to derive an estimate of the Mn/C in sinking material. The values of the ratio range from 31 ± 10 μmol Mn/mol C (Martin and Knauer, 1983)
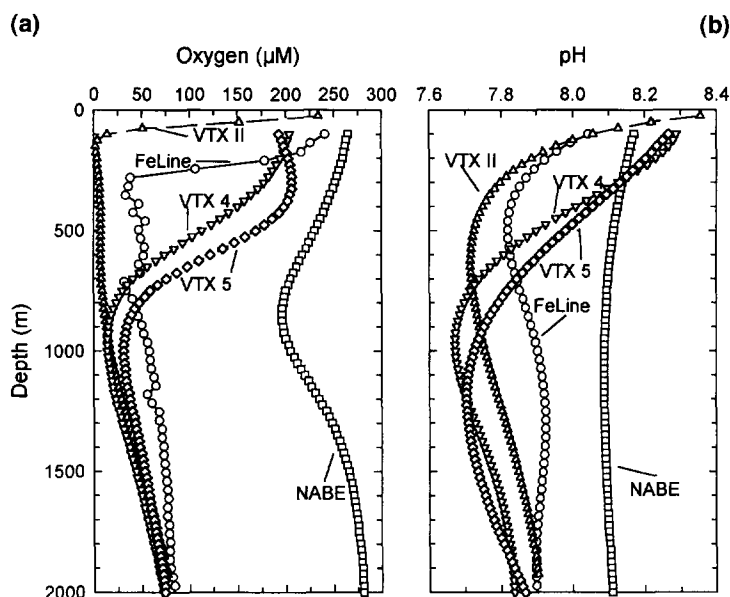
(a) **(b)**

FIG. 2. Profiles of oxygen (a) at VERTEX 4 at 33°N, 139°W and VERTEX 5 at 28°N, 155°W (Martin et al., 1985), VERTEX II at 18°N, 108°W (Martin and Knauer, 1984), FeLine Station 7 at 3°S, 140°W (K. Johnson, unpubl. data), and the NABE station at 47°N, 20°W (Martin et al., 1993). pH profiles (b) for each of these stations were obtained from GEOSECS stations in the Pacific, and from TA and TCO_2 measurements at the NABE station. The smoothed profiles shown here were obtained by fitting continuous functions to the bottle data using the program TableCurve (Jandel), except for the O_2 profile at the Feline station. Oxygen data at that station were measured with an electrode on a CTD and the data are taken directly from the CTD datafile at 25 m intervals.

to 58 ± 36 μmol Mn/mol C (Martin et al., 1985) (all error limits are the 90% confidence interval). We use the mean of these values (44 μmol Mn/mol C) as an estimate of Q. Collier and Edmond (1984) also found that Mn is rapidly released from phytoplankton to solution, which supports the assumption (Martin and Knauer, 1983) that the trapped exchangeable Mn is derived from an organic carrier phase. The effects of this assumption are discussed latter in the paper.

A $Q = 44$ μmol Mn/mol C implies the assumption that all of the manganese released from organic matter is Mn(II). Phytoplankton can accumulate Mn(II) by uptake and storage of Mn(II) or by oxidation of Mn(II) to MnO_x. This latter mechanism is limited to phytoplankton that generate micro-environments with high pH and oxygen (Richardson et al., 1988). It appears reasonable to assume that the bulk of the Mn that is released is in the Mn(II) form.

Martin et al. (1987) have shown that F_{100} varies as a function of primary production in surface waters. In the north Pacific, lowest values (1.2 mol C m^{-2} y^{-1}) were found in the central gyre. The value found at Station 4 was 2 mol C m^{-2} y^{-1}, which we have used in this work.

The dissolved Mn(II) profile for VERTEX 4, which was calculated with Eqn. 6, is shown in Fig. 3. The shape of the calculated profile generally resembles the observed Mn profile. However, the secondary Mn(II) maximum in the modeled profile is much stronger than that observed. This discrepancy becomes even more severe at stations with lower oxygen minimum values.

3.2. Model with Vertical Diffusion

The overestimate of the Mn(II) concentration in the secondary maximum is due to the absence of a vertical mixing term in the model. Manganese that builds up in the secondary maximum of this model can be removed only by scavenging, and not by transport. Vertical eddy diffusion can be included in the model

$$0 = K_Z \frac{\partial^2 [Mn(II)]}{\partial Z^2} + 45QF_{100}Z^{-1.858}$$

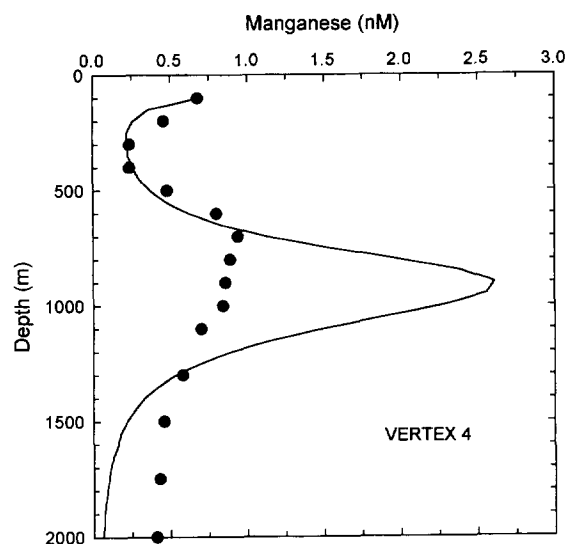$$- \alpha k_0[O_2]\{OH^-\}^2[Mn(II)]. \quad (7)$$

FIG. 3. Mn(II) concentrations at the VERTEX 4 station calculated using Eqn. 6 and the O_2 and pH profiles in Fig. 2. The observed dissolved Mn concentrations are also shown.

This differential equation can be solved numerically, using the oxygen concentration and hydroxide activity determined at each depth, to calculate the dissolved $Mn(II)$ concentration profile. We used a $K_Z = 0.25$ cm^2 s^{-1} in all of our calculations (Ledwell and Watson, 1991). Boundary conditions of 1 nM $Mn(II)$ above 100 m and 0.1 nM $Mn(II)$ at depths below 2000 m, were used to generate the solutions. In the open ocean, Mn concentrations are generally within a factor of three of the values we used at the boundaries. Changing these boundary values did not have a great effect on the shape of the profiles, but merely shifted them up or down in concentration by a corresponding amount near the boundaries. Values in the interior of the model changed very little because the vertical eddy diffusion coefficient is not large enough to transport $Mn(II)$ over great distances before it is removed by scavenging. The root-mean-square vertical distance that eddy diffusion will transport $Mn(II)$ in twenty years, typical of the $Mn(II)$ scavenging residence time at 2000 m, is approximately 125 m.

Dissolved Mn concentrations were calculated using Eqn. 7 at five stations in the Pacific and Atlantic Oceans where there are high quality measurements of $Mn(II)$. These stations are VERTEX 4 at 33°N, 139°W and the VERTEX IV Station 5 (called VERTEX 5) at 28°N, 155°W in the Central North Pacific (Martin et al., 1985), VERTEX II at 18°N, 108°W in the strong oxygen minimum of the eastern Pacific (Martin and Knauer, 1984), FeLine Station 7 at 3°S, 140°W in the equatorial Pacific (Johnson et al., 1994; K. Johnson, unpubl. data), and the JGOFS North Atlantic Bloom Experiment (NABE) station at 47°N, 20°W (M. Gordon, unpublished data). Manganese was measured at each of these stations by preconcentration on Chelex-100 and analysis by furnace atomic absorption spectrophotometry (Martin et al., 1985), except at the FeLine station where shipboard analyses were performed using flow injection analysis with chemiluminescence detection (Chapin et al., 1991). Oxygen concentrations were also measured at each of these stations. The pH values at the Pacific stations were estimated from the values reported at the nearest GEOSECS Stations (202, 204, 343, and 331, respectively) and the in situ temperatures and 1 atmosphere pressure (Takahashi et al., 1980). The pH at the NABE station was estimated from the titration alkalinity and total inorganic carbon measurements listed for that station in the JGOFS database, which is found on the World Wide Web (http://www1.whoi.edu/jgofs.html). All of the pH values were calculated using the carbonic acid dissociation constants of Mehrbach et al. (1973), which are based on the NBS pH scale, to retain consistency with the rate measurements of Morgan (1967). The dissolved oxygen and pH values at each station were fitted to continuous equations (Fig. 2) to facilitate interpolation of the data as the grid size was changed during solutions of Eqn. 7. The parameter α was set equal to 1 in all of the calculations.

These stations represent nearly the complete range of oxygen profiles seen in the open sea (Fig. 2). The NABE station has a weak oxygen minimum (200 μM; Martin et al., 1993). The VERTEX II station is nearly oxygen deficient (1.7 μM; Martin and Knauer, 1984). The other three stations have oxygen minima of intermediate intensity and at different depths. The pH profiles share many similarities with the O_2 profiles (Fig. 2).
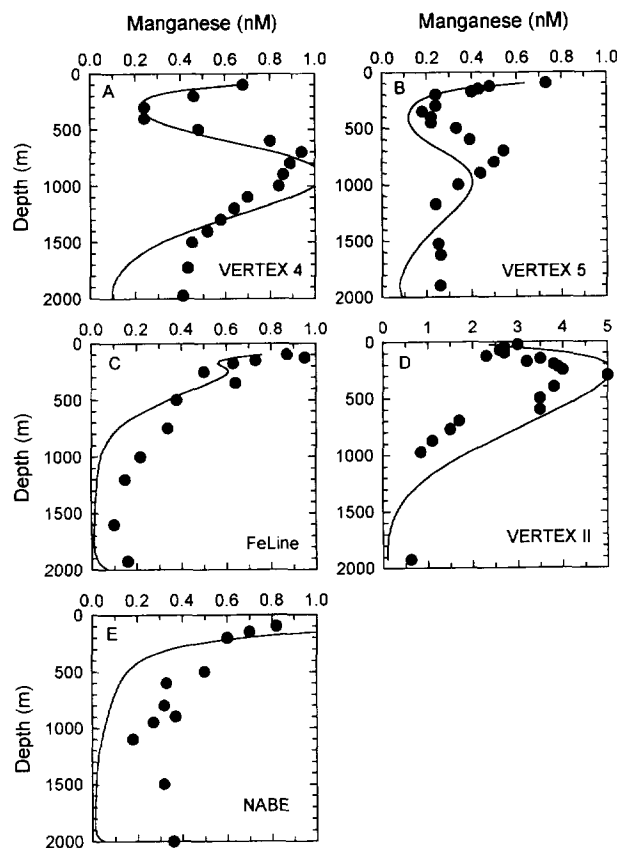

FIG. 4. $Mn(II)$ concentrations at each of the five stations calculated using Eqn. 7 and the O_2 and pH profiles in Fig. 2. The observed dissolved Mn concentrations are also shown. The precision of the dissolved Mn measurements is 0.05 nM.

The export flux of carbon, F_{100}, is needed to calculate the manganese concentration at each station. The value of F_{100} has been measured at each of the VERTEX stations (Martin et al., 1987) and these values were used directly. F_{100} has also been measured at the NABE station during the spring bloom (Martin et al., 1993). The spring bloom carbon flux at 1000 m is 3 times greater than the annual average carbon flux (Honjo and Manganini, 1993) so the measured F_{100} has been reduced threefold. We estimated the value of F_{100} at the FeLine station using the mean of the results reported for 120 m depth at 140°W on the equator (Murray et al., 1994, excluding the single high value of 11 mmol m^{-2} d^{-1}). The 120 m fluxes were adjusted to 100 m using Eqn. 1. The value of F_{100} at 3°S was taken as one half of the average at 0°N because primary production at 3°S is 2 times lower than at the equator (Coale et al., 1996). A constant value of $b = 0.858$ (Martin et al., 1987) was used throughout the calculations.

The estimated $Mn(II)$ concentrations above 1500 m are in excellent agreement with the observed values at each station (Fig. 4). The shape, depth, and magnitude of the secondary $Mn(II)$ maximum are closely reproduced at each station where the maximum is present. In particular, the high concentrations observed in the secondary $Mn(II)$ maximum at the VERTEX II station (note the scale change in Fig. 4) are reproduced quite well. The absence of a secondary maximum at the FeLine

station is also reproduced, despite the presence of a strong oxygen minimum. These model results are good evidence that the secondary Mn(II) maximum can be produced by a reduction in the scavenging rate through the oxygen minimum in combination with an input of Mn(II) from remineralized organic matter that decreases with depth.

The greatest discrepancies in the estimated Mn concentrations are at depths below 1500 m, where the calculated values are all lower than those observed. Concentrations drop below the bottom boundary condition of 0.1 nM within this lower depth range at some of the stations (Fig. 4). This occurs at oligotrophic stations because the Mn(II) input from remineralization of POC is so low that the removal term, which is first order in Mn(II) concentration, can only balance the input with Mn(II) concentrations < 0.1 nM. Either the model removal rate is too high, or there is too low of an Mn(II) input. Overestimates of the scavenging rate in the deep waters may result in part because we have ignored the effects of temperature and pressure on the oxidation rate constant. The rate constant k_0 for Mn(II) oxidation changes twofold from 22 to 11°C (Morgan, 1967). A threefold to fourfold reduction in the oxidation rate, relative to the value used in the model, might be expected at the low temperatures found at 2000 m. A reduction in the oxidation rate of this size would increase the Mn(II) concentrations by a similar factor and eliminate much of the discrepancy between the estimated and observed Mn(II) concentrations in the deep Pacific. However, the Mn(II) concentrations in the oxygen minimum would also increase by a factor of two to three and a correction for temperature effects alone is not satisfactory. A pressure correction could potentially improve the fit, but there is no information available on the effects of pressure on Mn(II) oxidation rates.

The errors in the estimated Mn concentrations at the NABE station in the Atlantic are several times greater than the errors found in the Pacific. The scavenging rate calculated in the deep Atlantic is about 10 times greater than at equivalent depths in the Pacific because the O_2 and pH values are much higher in the Atlantic. These high scavenging rates in the Atlantic lead to modeled Mn(II) concentrations which are tenfold lower than those observed. The high Mn(II) concentrations observed in the Atlantic, relative to the model predicted values, suggest that there are additional sources of Mn. These additional sources may reflect the proximity of the ocean margins in the smaller Atlantic Basin and a higher dust input. Sayles et al. (1994) have also suggested that the vertical flux of organic carbon in the Atlantic is fundamentally different than that observed in the Pacific. If so, this would lead to marked differences in the calculated Mn(II) values, since the model is driven by the flux of POC.

The vertical flux of scavenged Mn $F_{Mn}(Z)$ can be calculated at any depth by integrating the rate of Mn(II) scavenging with respect to depth if particulate Mn is not lost by horizontal transport:

$$F_{Mn}(Z) = \int_0^Z k_0[O_2]\{OH^-\}^2[Mn(II)]dZ$$
$$\approx \sum_i k_0[O_2]_i\{OH^-\}_i^2[Mn(II)]_i\Delta Z_i. \quad (8)$$

The results for the VERTEX 5 station are shown in Fig. 5,

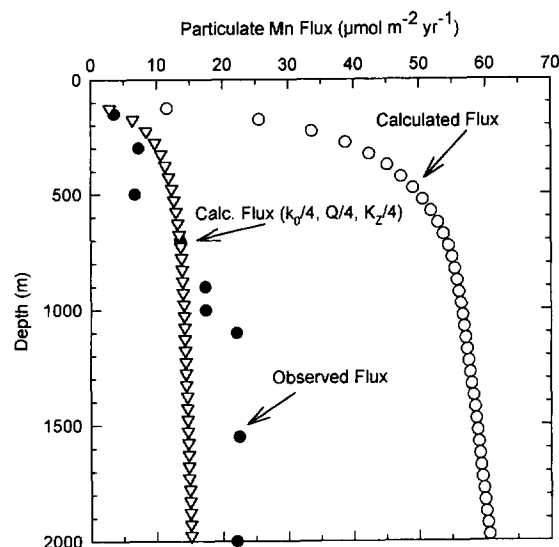Particulate Mn Flux (μmol m^{-2} yr^{-1})

FIG. 5. The flux of scavenged Mn oxide calculated from Eqn. 8 at the VERTEX 5 station is shown along with the flux of weak acetic acid leachable Mn measured at this same station (Martin et al., 1985). The flux calculated after dividing Eqn. 7 by 4 is also shown.

along with the observed measurements of the leachable Mn flux. The weak acetic acid leachable fraction of the flux is assumed to be primarily Mn oxide (Martin et al., 1985). The calculated flux is higher than the observed flux by a factor of 3 to 6. The flux is governed by the rate of scavenging. A reduction in k_0 by a factor of 4 will bring the calculated flux into good agreement with the observed values (Fig. 5). This can be accomplished, without affecting the calculated Mn(II) concentrations, by dividing Eqn. 7 by 4. This is equivalent to reducing k_0, Q and K_Z each by 4 times as the equation is linear in each of these terms.

4. DISCUSSION

The calculations were performed using the rate constant k_0 for Mn(II) oxidation that was measured in the laboratory and by setting α, the factor that might take bacterial catalysis into account, equal to 1. The good agreement between the calculated and observed Mn concentrations with $\alpha = 1$ implies that microbial oxidation of Mn(II) is not required to model Mn concentrations in these systems. The discrepancies in the calculations of Mn(II) concentration indicate that the inorganic oxidation rates used in the calculations are, if anything, too high and adding bacterial oxidation ($\alpha > 1$) would only make the discrepancies worse. The particulate Mn formation rates observed by Sunda and Huntsman (1988) in the Atlantic Ocean and by Cowen et al. (1990) at stations above hydrothermal plumes also suggest that bacterial catalysis of the reaction does not dominate Mn(II) oxidation in the ocean interior.

Bacteria are clearly important agents for oxidation of Mn(II) in regions of the water column where Mn(II) concentrations and supply are high (Sunda and Huntsman, 1988), certain regions of hydrothermal plumes (Cowen et
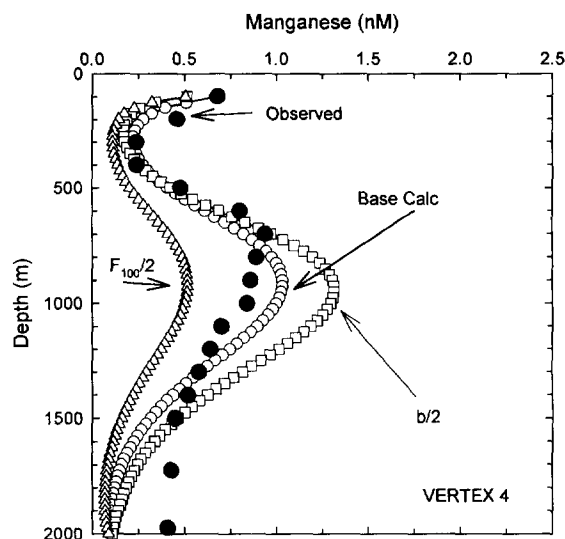
Manganese (nM)

FIG. 6. Mn(II) profiles calculated at the VERTEX 4 station for scenarios with the parameter b reduced 2× to 0.43, and with F_{100} decreased 2 times to 1 mol C m^{-2} y^{-1}. The base model calculation from Fig. 4 is shown ($b = 0.858$, $F_{100} = 2$ mol C m^{-2} y^{-1}) with the observed data.

al., 1990), sediments (Thamdrup et al., 1994), or at the boundaries of suboxic systems such as the Black Sea (Tebo et al., 1991) and Saanich Inlet (Emerson et al., 1982). Bacterial oxidation rates of Mn(II) in these areas have been observed to follow the Michaelis-Menton rate law with half-saturation constants greater than 100 nM (Tebo and Emerson, 1986; Sunda and Huntsman, 1987). It may be that in the deep sea, where dissolved Mn(II) is less than 1 nM, the binding sites are simply not efficient enough to compete for the metal ion.

The calculated Mn(II) concentrations are directly dependent upon the derivative of the vertical flux of sinking POC. The POC flux data was determined with sediment traps. The use of traps has been criticized (Michaels et al., 1990). It is instructive to consider how the calculated Mn(II) profiles would change if there were an error in the POC flux values. Figure 6 shows the effects of changes in F_{100} and b on the calculated Mn profile at the VERTEX 4 station. Manganese concentrations are directly proportional to F_{100} and a smaller export flux from the euphotic zone will decrease Mn(II) concentrations. Reducing b will tend to increase dissolved Mn(II) concentrations at most depths. If there is a swimmer bias, the correct values of b and F_{100} will both be smaller. These effects are offsetting and the model is, therefore, relatively robust with respect to swimmer biases. We should also note that the carbon fluxes used to fit Eqn. 1 were corrected for the presence of swimmers (Martin et al., 1987).

Calculated Mn concentrations are also dependent upon the Mn/C ratio (Q) used in the model. A doubling of Q nearly doubles the predicted Mn(II) concentrations. We have used estimates of Q derived from sediment trap data. Landing and Bruland (1980) have also estimated Q based upon the measurements by Martin and Knauer (1973) of the chemical composition of plankton. Their estimates range from 3 to 14 μmol Mn/mol C, compared to a value of 44 μmol/mol used

here. If the Mn/C ratio is as low as estimated by Landing and Bruland (1980), then there must be a corresponding reduction in the Mn(II) oxidation rate, or the calculated concentrations will be much too small. We have chosen to use the larger value of Q, as it was estimated from measurements on material that had been exported from the euphotic zone. It is clear that better measurements of both Q and k_0 are needed to completely assess the suitability of the model discussed here.

Inclusion of vertical eddy diffusion in the model has a strong effect on the intensity of the secondary Mn(II) maximum (compare Figs. 3, 4). A vertical eddy diffusion coefficient of 0.25 cm^2 s^{-1} was used for all of the model calculations that included vertical mixing. The vertical mixing term has its largest effect on the concentrations calculated in the secondary Mn maximum. Increasing the vertical diffusion coefficient 10 times to 2 cm^2 s^{-1} produces only a twofold reduction in Mn(II) concentrations calculated within the secondary maximum. A tenfold decrease in the vertical eddy diffusion coefficient will increase the calculated maximum Mn(II) concentrations 2 times. Thus, any reasonable changes in the vertical eddy diffusion coefficient will not markedly change the results that we have obtained. The effects of adding an eddy diffusion coefficient are most apparent in the secondary Mn(II) maximum because the second derivative of the Mn(II) profile is so much greater there than anywhere else in the water column.

The calculation of Mn flux is an independent test of the model. The parameters used to calculate the results shown here produce a scavenged Mn flux that is 3 to 6 times higher than that observed (Fig. 5). If the constants k_0, Q and K_Z are all reduced fourfold, then the scavenged Mn flux is in quite good agreement with that observed (Fig. 5), and the dissolved Mn(II) concentration is unaffected. The temperature correction of k_0 discussed above might result in twofold to fourfold decreases throughout the water column, as needed to improve the flux estimate. The values of Q estimated by Landing and Bruland (1980) are also fourfold lower than the value that we used. There are few direct measurements of K_Z in the deep sea. Ledwell et al. (1993) recently determined the K_Z at a depth of 300 m in the main thermocline of the North Atlantic using a deliberate tracer release. They found a mean value of 0.11 cm^2 s^{-1}, which is twofold lower than the value used here (Ledwell and Watson, 1991). We performed the calculations reported here using what appeared to be the best estimates of k_0, Q and K_Z. If the estimates of all three of these quantities are reduced by 4 times, they would still be consistent with our knowledge of oceanographic processes, and the modeled Mn(II) concentrations would not change. The flux results suggest that this might be appropriate.

Model calculations were performed at the VERTEX 4 station to assess the conditions under which a secondary Mn maximum layer will form. The changes in pH and oxygen were found to play nearly equal roles in contributing to the reduction in Mn(II) oxidation rates, which allow the secondary maximum to form. A secondary maximum would be detectable at this station only if the oxygen concentration fell below 100 μM and the pH below 7.85. This is in agreement with the original observation of Klinkhammer and

Bender (1980) that secondary Mn maxima were observed everywhere oxygen concentrations were less than 100 μM.

Oxygen concentrations drop to 32 μM at the equatorial FeLine station, similar to those found at VERTEX 5 (Fig. 2). A secondary Mn maximum is only barely discernable in the observed and calculated data at the FeLine station while it is well developed at VERTEX 5 (Fig. 4). The secondary Mn maximum is not well defined at the FeLine station because a strong Mn minimum does not form between the primary and secondary Mn maxima. The Mn(II) minimum forms due to the decrease in the rate of Mn(II) remineralization as depth increases. The oxygen minimum at the equatorial FeLine station is much shallower than at stations in the North Pacific due to the influence of equatorial upwelling (Fig. 2). The shallow oxygen minimum near the equator does not allow regeneration rates to decrease sufficiently to form a Mn(II) minimum before concentrations begin to increase as scavenging rates drop in the oxygen minimum. As a result, a distinct secondary maximum is not found at the FeLine station in the model or observed data.

The calculations presented here demonstrate that the secondary Mn maximum can form because of a reduction in the scavenging rate within the oxygen minimum. The model used for input of Mn(II) was similar at each of the stations examined here. The main difference from station to station was the pseudo-first order rate constant, k' = $k_0[O_2]\{OH^-\}^2$, for oxidation of dissolved Mn(II). Stations with a low value of k' will accumulate higher dissolved Mn(II) concentrations before the rate of Mn(II) removal, $k'[Mn(II)]$, equals the input from remineralization of sinking organic particles. This reduction in the pseudo-first order rate constant is simply a reflection of the rate law that controls Mn oxidation kinetics. An additional source of manganese, such as flux from continental margin sediments or reduction of Mn oxides is not necessary to account for formation of the secondary Mn maximum.

The model presented here is generally compatible with the conclusions of Martin et al. (1985), who measured Mn concentrations and vertical fluxes along a section from California to Hawaii. They found no evidence that increased scavenging rates were responsible for the Mn minimum between the primary and secondary maxima. The model presented here is consistent with that finding. The Mn minimum results from a decreased rate of release of dissolved Mn(II), due to a decline in the rate of POC and Mn(II) regeneration with depth. The model is also consistent with the conclusion (Martin and Knauer, 1985; Martin et al., 1985) that increased regeneration of Mn(II) in the oxygen minimum, including reduction of Mn oxides, is not responsible for formation of the secondary maximum. They based their conclusions on the observation that Mn oxide fluxes did not decrease within the oxygen minimum. In the model, the vertical flux of MnO_x increases continuously with depth (albeit more slowly in the oxygen minimum) because Mn(II) is oxidized and scavenged at every depth (Fig. 5). However, there is one important difference between our results and those of Martin et al. (1985). They concluded, by process of elimination, that offshore transport from a source at the continental margin must produce the secondary maximum. We believe that our benthic flux measurements rule out a

source at the ocean margin since the oxygen minimum layer is also a region of minimal Mn(II) flux from the sediments (Fig. 1b). The maximum must form within the water column, and we believe that a decrease in the oxidation rate of Mn(II) within the oxygen minimum layer is the most probable mechanism.

Manganese oxide reduction can occur in intense oxygen minimum zones where oxygen and nitrate are depleted (Martin and Knauer, 1984). In such regions, the Mn flux through the oxygen minimum is reduced dramatically. This must augment the intensity of the secondary Mn maximum. However, Martin and Knauer (1984) calculated that only 30% of the dissolved Mn(II) in the secondary maximum was produced by reduction of MnO_x.

The increase in dissolved Mn(II) concentrations within the secondary maximum as the coast is approached (Martin et al., 1985) need not be the result of a sedimentary source. The model demonstrates that it could also be produced by an increase in Mn(II) export from the surface. The concentration of Mn at each station is controlled by the value of F_{100} (Fig. 6). In highly productive coastal waters, F_{100} may be five to ten times greater than in the open ocean (Martin et al., 1987). The increase in F_{100} from VERTEX 5 to VERTEX 4 (Martin et al., 1987) accounts for about half of the difference in Mn(II) concentrations at these stations. The remainder of the change is due to a stronger oxygen and pH minimum layer at VERTEX 4. The increase in manganese concentration that occurs near the coast (Martin et al., 1985) is consistent with the higher export of Mn(II) bound in particulate organic matter in these systems. As a result, Mn is not a strong candidate species for tracing water mass movements through ocean basins.

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