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Manganese cycling in northeast Pacific equatorial waters

by John H. Martin¹ and George A. Knauer¹

ABSTRACT

Sea water samples collected above, within and below a pronounced oxygen minimum (0.5 $\mu\text{mol liter}^{-1}$) were analyzed for their Mn content. Amounts of dissolved Mn slowly decreased with depth and little, if any, relationship with oxygen was found. In contrast, suspended particulate Mn values increased markedly at the top of the oxygen minimum. Concentrations of up to 880 μg weakly leachable Mn per g of dry suspended particulates probably resulted from microbial oxidation.

Labile Mn fluxes, measured with particle interceptor traps at depths of 125, 275, 525 and 900 m slowly increased with depth from 270 at 125 m to 450 $\mu\text{g Mn cm}^{-2} 1000 \text{ yr}^{-1}$ at 900 m. These rates are the same order of magnitude as those estimated for excess Mn accumulating in open-ocean sediments, which implies that biogenic transport is a major factor in the oceanic cycling of Mn.

1. Introduction

In a previous study off central California (Martin and Knauer, 1980), we measured Mn transport in association with passively sinking particles. The fluxes, about 300 $\mu\text{g Mn cm}^{-2} 1000 \text{ yr}^{-1}$, were of the same order of magnitude as those required in explanation of the excess Mn accumulating in open-ocean sediments; i.e., 800 $\mu\text{g cm}^{-2} 1000 \text{ yr}^{-1}$ (Bender *et al.*, 1970, 1977). The Mn we observed appeared to be in association with particulate organic C, implying that the sinking of biological debris could transport Mn in open-ocean as well as nearshore environments. However, it could be argued that open-ocean Mn fluxes would be of limited significance, since production rates of organic C are much lower offshore. The observation of dissolved Mn maxima in association with oxygen minima (Bender *et al.*, 1977; Klinkhammer and Bender, 1980; Landing and Bruland, 1980; Martin and Knauer, 1980) could also suggest that Mn is released back into the water column as passively sinking organic carriers are destroyed.

Obviously, the best way of learning more about this Mn transport mechanism and its possible significance was to actually measure appropriate fluxes in an open-ocean area. We were especially interested in the Clipperton-Clarion fracture zone,

1. Moss Landing Marine Laboratories, P.O. Box 223, Moss Landing, California, 95039, U.S.A.

not only because of the abundance of Mn nodules occurring there (Glasby, 1977), but also because of the recent finding of a major Mn maximum in association with the oxygen minimum (Klinkhammer and Bender, 1980). We initiated research in this general area (exact location cannot be given because of agreement with prime contractor) in April 1980. Organic C and Mn fluxes were measured above, within and below the oxygen minimum and the vertical distributions of dissolved and particulate Mn in the water column were determined. Our findings are presented and discussed below.

2. Methods

In order to measure the vertical fluxes of Mn and C in association with passively sinking particles, free-floating particle interceptor traps were deployed on April 6, 1980 (2150 GMT) ~ 2000 km west of central Mexico at depths of 125, 275, 525 and 900 m. The array was recovered on May 2, 1980 (1510 GMT). The traps traversed a distance of 249 km at an average speed of 11.2 cm sec⁻¹. Tracking and relocation were accomplished via the ARGOS satellite system. Basically, the traps consist of PVC cross frames fitted with eight identical lucite cylinders that were filled with a high-density NaCl solution ($\sigma = 1.05 \text{ g cm}^{-3}$) containing 5% buffered formalin. All internal parts of the traps were thoroughly cleaned with Micro and dilute quartz-distilled HNO₃. Contaminant Mn was removed from the NaCl-formalin solution by passing it through Chelex resin prior to loading. All handling procedures were carried out in shore-based or shipboard filtered-air clean laboratories. Further details about the traps, including a discussion of their accuracy based on ²¹⁰Pb data, have been published elsewhere (Knauer *et al.*, 1979). Sediment traps of different design were recently tested in the Sediment Trap Intercomparison Experiment (STIE). Our traps yielded fluxes comparable to those obtained by Honjo, Gardner, Soutar and Farrington using other trap systems (Spencer, WHOI, pers. comm.).

The particulates from 2-3 of the 8 trap cylinders at each depth were analyzed for Mn using flameless atomic absorption. Both weakly leachable (25% acetic acid; Chester and Hughes, 1967) and refractory (Eggimann and Betzer, 1976) portions were analyzed. Manganese in the high-density NaCl solutions in the trap cylinders was also measured after preconcentration on chelex. Aliquots of trapped particulates were analyzed for organic C using a CHN analyzer after treatment with dilute HCl to remove carbonates (Knauer *et al.*, 1979).

One water sample was collected and processed each day. The two samples from 250 m and the two from 500 m were not true replicates, since they were taken several days apart. Temperature and salinity were measured by XBT and conductivity, respectively. Oxygen was determined using both Winkler and Micro-Winkler techniques. The Micro-Winkler analytical apparatus failed midway through the cruise; hence, oxygen concentrations are uncertain between 400 and 700 m (i.e.,

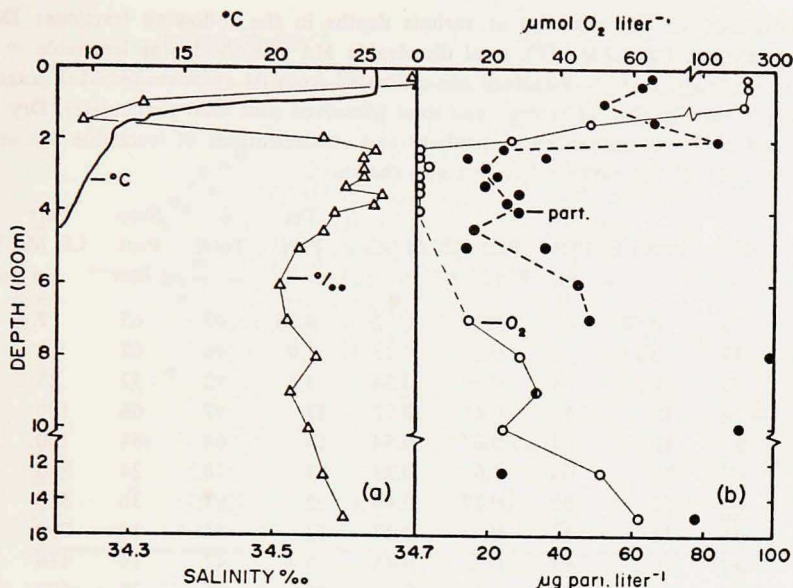


Figure 1. Temperature, salinity (side a), oxygen and sea-salt- CaCO_3 -free-suspended particulate weight (side b) data versus depth.

less than $14 \mu\text{mol liter}^{-1}$, the detection limit for the standard Winkler method).

Teflon coated 30-liter Go-Flo bottles, suspended on nonmetallic Kevlar line, were used for all sea water collections. The samples were filtered through tared acid-washed 142 mm $0.4 \mu\text{m}$ Nuclepore filters mounted in Teflon sandwiches. Manganese in the filtrate was then preconcentrated by passage through Chelex-100 ion exchange resin. After elution with 2 N HNO_3 , the samples were analyzed for their Mn content by flameless atomic absorption. Water column suspended particulates were leached, digested and analyzed using the same methods as those described above for trapped particulates. All of these procedures were carried out using stringent anticontamination techniques that have been described elsewhere (Martin *et al.*, 1976; Bruland *et al.*, 1978, 1979).

3. Results and discussion

The water column in our study area (Fig. 1) can be divided into four distinct zones, largely on the basis of oxygen: (1) the surface layer (0-80 m) with well-mixed, warm (25.6°C), high-salinity (34.7‰) water containing oxygen at, or near, saturation ($220 \mu\text{mol liter}^{-1}$); (2) a near-surface (80-200 m) transition zone characterized by a "tongue" of lower salinity (34.2‰) water in which temperature ($25.6\text{-}11^\circ\text{C}$) and oxygen levels ($210\text{-}26 \mu\text{mol liter}^{-1}$) rapidly fall; (3) the oxygen-minimum ($225\text{-}500 \text{ m}$) with little or no oxygen ($< 5 \mu\text{mol/liter}^{-1}$); and (4) the

Table 1. Amounts of Mn observed at various depths in the following fractions: Dissolved (Diss), particulate leachable (LE), total dissolvable Mn (dissolved plus leachable = TDM), particulate refractory (RE), refractory Mn estimated from Al amounts (Al-Mn), total particulate Mn (leachable plus refractory), and total (dissolved plus total particulate). Dry weights of sea-salt-CaCO₃-free suspended particulates and concentrations of leachable Mn and total Mn associated with these particulates are also shown.

Depth (m)	Diss	Part	LE	TDM	Part	RE	Al-Mn	Tot		Susp	Part	Part
								Part	Total	Part	LE Mn	Tot Mn
				ng	Mn liter ⁻¹					μg liter ⁻¹	μg g dry wt ⁻¹	
25	46	0.48		46	0.27		0.42	0.75	47	65	7.4	12
50	45	0.76		46	0.29		0.25	1.0	46	62	12	16
100	90	1.2		91	0.39		0.54	1.6	92	52	23	31
150	44	12		56	0.61		0.32	13	57	66	180	200
200	51	12		63	0.67		0.54	13	64	84	140	150
225	47	21		68	1.6		0.33	23	70	24	880	960
250-A*	69	21		90	0.77		0.40	22	91	36	580	610
250-B	41	11		52	0.92		0.27	12	53	14	790	860
275	38	9.0		47	0.43		0.41	9.4	47	19	470	490
300	44	11		55	1.0		0.44	12	56	22	500	540
325	33	7.6		41	1.1		0.30	8.7	42	19	400	460
350	36	3.1		39	0.31		0.38	3.4	39	28	110	120
375	47	3.9		51	0.24		0.59	4.1	51	25	160	160
400	30	6.6		37	0.73		1.12	7.3	38	28	240	260
450	41	4.5		46	0.51		0.37	5.0	46	16	280	310
500-A*	38	7.4		45	0.38		0.28	7.8	45	14	530	560
500-B	40	5.9		46	0.39		0.36	6.3	46	36	160	180
600	35	5.9		41	0.55		0.45	6.5	42	45	130	140
700	56	9.5		65	0.38		0.42	9.9	65	48	200	210
800	32	10		42	0.27		0.36	10	42	104	96	96
900	146	5.9		152	0.55		0.33	6.4	153	34	170	190
1000	25	3.9		29	0.35		0.26	4.2	29	90	43	47
1250	22	5.4		27	1.4		0.47	6.8	28	24	220	280
1500	17	5.0		22	0.54		0.53	5.5	23	78	64	70

* These are not true replicates. 250-A was collected on April 15, 250-B on April 25, 500-A on April 19 and 500-B on April 24.

waters beneath the oxygen minimum (depths > 500 m), in which oxygen levels begin to increase. These hydrographic features are very similar to those observed at GEOSECS 343 (see Klinkhammer and Bender, 1980).

Suspended particulate loads generally responded to these hydrographic features (Fig. 1b). Levels, expressed on a sea-salt-CaCO₃-free basis, were relatively high in the layers above the oxygen minimum, with a maximum (84 μg liter⁻¹) occurring at 200 m, corresponding with the bottom of the pycnocline. Much lower and more uniform levels were found in the oxygen minimum; the mean and standard deviation for the 12 samples collected between 225 and 500 m were 23.4 ± 7.6 μg

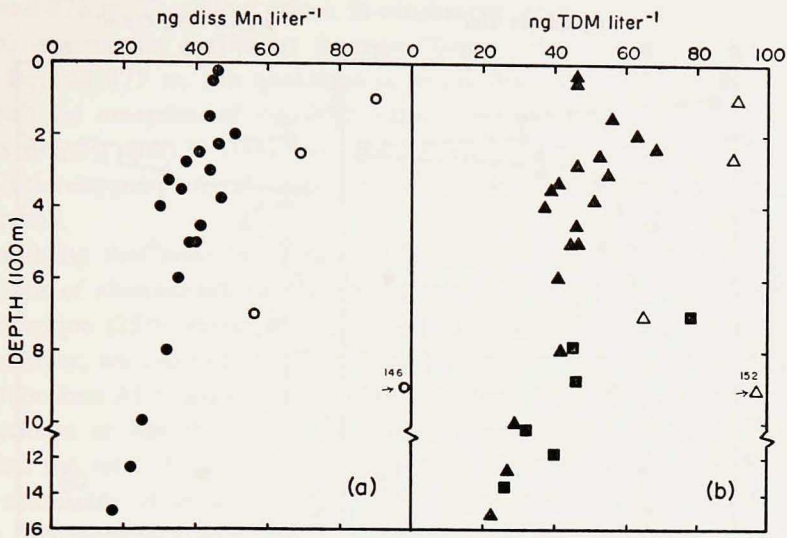


Figure 2. Vertical distributions of dissolved (side a) and total dissolvable Mn (TDM). Boxes in side b represent values reported by Klinkhammer and Bender (1980) at GEOSECS 343.

liter^{-1} . Suspended particulate values increased and became very variable at depths exceeding 500 m.

a. Manganese in the water column. Three fractions of Mn in the water column were measured: dissolved (filterable, preconcentrated on Chelex), particulate leachable (25% acetic acid), and particulate refractory (total digestion of particulates after leaching) (Table 1). Amounts of dissolved Mn were generally low throughout the water column, and most of the values fell within a relatively narrow range (Fig. 2a). For example, all concentrations between 25 and 800 m were from 30 to 51 ng liter^{-1} , with three exceptions; the samples collected at 100 m (90 ng liter^{-1}), 250 m (second collection = 69 ng liter^{-1}), and 700 m (56 ng liter^{-1}). Consistently low values were measured in our deepest samples (25, 22 and 17 ng liter^{-1}) at 1000, 1250 and 1500 m, respectively. The highest dissolved Mn concentration we obtained was 146 ng liter^{-1} at 900 m. There is no reason to suspect contamination, and we have no ready explanation for this value.

With the exception of the few high points mentioned above, the dissolved Mn profile was characterized by a more or less gradual decrease with depth. Pronounced maxima were neither observed in the surface waters nor in the oxygen minimum. These statements also generally apply when amounts of leachable particulate Mn (Table 1) are combined with the dissolved values (Fig. 2b) in order to express the results as total dissolvable Mn (TDM, Bender *et al.*, 1977).

The lack of a maximum in the oxygen minimum is surprising in view of Klink-

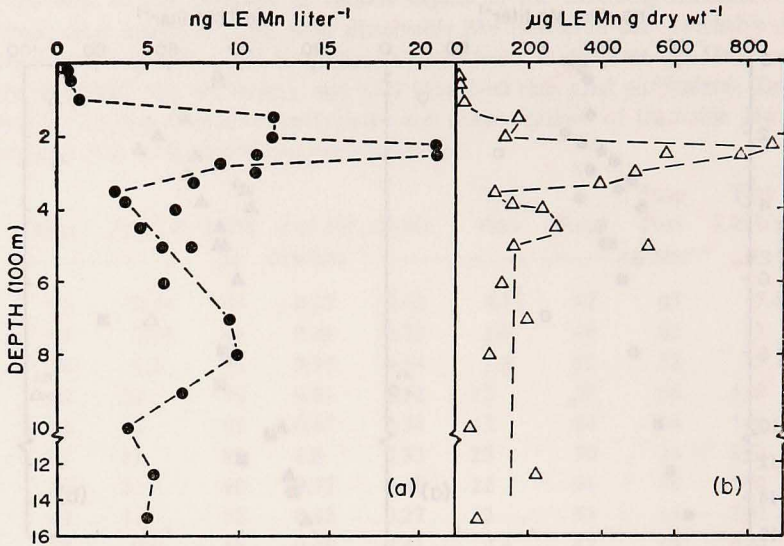


Figure 3. Vertical distribution of weakly leachable (LE) Mn expressed on volume (side a) and per gram dry suspended particulate weight (side b) bases.

hammer and Bender's (1980) finding of a well-developed TDM maximum at GEOSECS 343, a station that was similar to ours hydrographically and in the same general vicinity. We believe these differences to be real and not the result of different sampling/analytical procedures, since close agreement is obtained when our 700-1500 m (excluding 900 m) TDM data are compared with those reported by them at similar depths (Fig. 2b). If analytical differences are eliminated, two possibilities are suggested: Little, if any, dissolved Mn had been regenerated in our water column, in spite of the well-developed oxygen minimum, or dissolved Mn that was originally present in the oxygen minimum had been scavenged onto particulates and removed.

Scavenging and removal would appear to be the case in view of our suspended particulate Mn data shown in Figure 3. In contrast to dissolved Mn, the concentrations of Mn associated with suspended particulates responded markedly to various hydrographic features, especially oxygen (Fig. 1). Particulate leachable (LE) Mn concentrations ($\mu\text{g LE Mn g dry suspended particulates}^{-1}$) increased very slightly with depth in the well-oxygenated surface layer; from 12 at 25 m, to 31 $\mu\text{g g dry wt}^{-1}$ (ppm) at 100 m (Fig. 3). Significant increases (200, 150 ppm at 150, 200 m) observed in the transition zone were over-shadowed by extraordinary concentrations (960, 860 ppm at 225, 250 m) at the very top of the oxygen minimum. Four other samples, collected in the upper 125 m of the minimum, had concentrations between 460 and 610 ppm for an overall average of 650 ppm for the six samples collected between 225 and 325 m. Relatively low Mn amounts (120, 160 ppm) were noted

at 350 and 375 m. These low values, in conjunction with slight increases in salinity (Fig. 1a) suggest that a different layer or "finger" of water was present at these depths. Beyond 375 m, Mn quantities generally fluctuated between 100 and 300 ppm, with the exception of one high value (560 ppm) at 500 m and two low numbers (47, 70 ppm) at 1000 and 1500 m. Thus, all particulate Mn values were higher in the oxygen-poor subsurface waters than in the well-aerated surface waters (12-31 ppm).

A possibility that must be considered is that the particulate Mn we measured leached out of aluminosilicate lattices, in spite of the fact that we used a weak leach technique (25% acetic acid) designed to prevent this occurrence. To check this possibility, we analyzed both leach and refractory portions of the particulate samples for their Al content using standard additions. In order to estimate the maximum amount of Mn that could have been present originally in this form, we multiplied the total Al values by 950/82,300 (Taylor's 1964 estimates for the crustal abundance of these elements). The results of these calculations (Table 1) indicate that maximum possible aluminosilicate Mn amounts are consistently low (< 10%) with the exception of the surface (25-56%) samples and those collected in the 350-400 m "finger" of water mentioned above (11-15%). Where particulate Mn was most abundant (225, 250 m), maximum possible aluminosilicate Mn represents 2% or less of that associated with the particles.

All in all, the particulate Mn maximum we found is very similar to others observed at oxic-anoxic interfaces in the Black Sea (Spencer and Brewer, 1971; Spencer *et al.*, 1972), Saanich Inlet (Emerson *et al.*, 1979), Cariaco Trench (Bacon *et al.*, 1980) and other eastern tropical Pacific Ocean sites (Murray *et al.*, 1982).

b. Mn fluxes. In order to estimate vertical Mn fluxes, we set free-floating particle interceptor traps beneath the mixed layer (125 m) near the top (275 m) and bottom (525 m) of the oxygen minimum, and just beneath the oxygen minimum (900 m) for a period of 26 days. Amounts collected in individual trap cylinders at each depth are shown in Table 2. In general, good replication was observed. Average values in Table 2 were divided by the cylinder diameter (0.0039 m²) and the number of days the traps were set (26) to obtain the fluxes shown in Table 3. Total particulate and organic C fluxes started out relatively high (7.2, 2.3 g cm⁻² 1000 yr⁻¹) at 125 m, decreased sharply at 275 m and then slowly decreased (to 1.6, 0.36 g cm⁻² 1000 yr⁻¹ at 900 m) in the remainder of the water column sampled. In contrast, total Mn fluxes increased steadily with depth from 320 at 125 m to 470 μg Mn cm⁻² 1000 yr⁻¹ at 900 m. The C decreases/Mn increases are reflected in the Mn:C ratios (Table 2) observed at the four depths. Materials trapped at the 125 m depth had Mn:C ratios similar to those reported for living plankton (~ 1 × 10⁻⁵) (Landing and Bruland, 1980), while those at subsequent depths increased by an order of magnitude to levels equal to, or greater than, 1 × 10⁻⁴. Mid-depth (275, 525 m)

Table 2. Amounts of trapped particulate organic C (TPOC) and Mn found in 2-3 replicates at each depth. Amounts of Mn in three fractions are shown: Mn removed from trapped particles using a weak leach (LE); refractory Mn remaining with the particles after leaching (RE) and the Mn found in the trap salt gradient which we call trapped exchangeable (TE) Mn (see Martin and Knauer, 1980). Ratios for Mn:C were calculated using means for TPOC and combined LE and TE Mn. Means and standard deviations for the weights of total trapped sea-salt-CaCO₃-free particles are shown in a footnote at the bottom of the table.

Depth (m)	TPOC mg	RE Mn	LE + TE Mn			Mn Total	Molar Mn:C Ratios × 10 ⁻⁴
			LE Mn	TE Mn	Mn		
Amounts Trapped*							
μg							
125	5.88	0.13	0.14	0.57	0.71	0.84	
	6.78	0.12	0.10	0.69	0.79	0.91	
	6.04	—	—	—	—	—	
\bar{X}	6.23	0.12	0.12	0.63	0.75	0.87	0.26
275	1.72	0.13	0.28	0.59	0.87	1.0	
	1.96	0.14	0.28	0.56	0.84	0.98	
\bar{X}	1.84	0.14	0.28	0.58	0.86	0.99	1.0
525	1.72	0.10	0.42	0.34	0.76	0.86	
	1.55	0.08	0.40	0.54	0.94	1.0	
	1.46	—	—	—	—	—	
\bar{X}	1.58	0.09	0.41	0.44	0.85	0.94	1.2
900	0.66	—	—	0.80	—	—	
	1.05	0.063	0.42	1.6**	—	—	
	0.96	0.055	0.29	0.94	1.2	1.3	
\bar{X}	0.89	0.059	0.36	0.87	1.2	1.3	3.0

* Total sea-salt-CaCO₃-free trapped particle weights (mg) were: 125 m = 19.8 ± 1.68, n = 5; 275 m = 6.74 ± 0.59, n = 4; 525 m = 4.99 ± 1.17, n = 5; 900 m = 4.11 ± 0.85, n = 4.

** Not included in mean.

values are similar to those we observed off central California (Martin and Knauer, 1980).

It is also apparent that the small total Mn flux increases were from added amounts of labile Mn rather than refractory Mn, since total quantities of leachable and trapped exchangeable (TE; see Table 2 legend) Mn increased in a similar fashion, while fluxes of refractory Mn slowly decreased with depth. An important feature of the flux pattern is the fact that fluxes at 125 m were nearly as great as those observed at 900 m, 68% of the total Mn and 60% of the leachable and TE Mn were from the upper 125 m of the water column. These high surface fluxes did not result from greatly elevated amounts of Mn associated with the particles, but rather from the combination of high total particulate fluxes (7.2 g cm⁻² 1000 yr⁻¹), with only moderate amounts of Mn (42 μg g dry weight⁻¹).

Surface Mn uptake can also be illustrated by making simple rate-of-change estimates based on ΔMn/ΔZ calculations; where ΔMn is the change in the labile (LE +

Table 3. Fluxes for total particulates, trapped particulate organic C (TPOC) and various Mn fractions calculated using means from Table 2.

Depth (m)	Tot Part g cm ⁻² 1000 yr ⁻¹	TPOC 1000 yr ⁻¹	RE	LE μg Mn cm ⁻²	TE 1000 yr ⁻¹	LE + TE	Tot Mn
125	7.21	2.3	46	44	230	270	320
275	2.46	0.67	49	100	210	310	360
525	1.82	0.58	33	150	160	310	340
900	1.50	0.32	21	130	320	450	470

TE) Mn flux over an intervening depth interval, ΔZ . Assuming no vertical Mn input in the upper 125 m, the Mn rate of change would be -22 ng liter⁻¹ yr⁻¹, a rate which is an order of magnitude higher than those calculated for the remaining depth intervals ($-2.7, 0, -3.7$ ng liter⁻¹ yr⁻¹).

It is also interesting to note that only a modest increase in the labile Mn flux (from 270 to 310 $\mu\text{g Mn cm}^{-2}$ 1000 yr⁻¹) was observed in the trap set just below the Mn-rich particulate layer located at the top of the oxygen minimum (Fig. 3). An apparent increase in Mn concentrations (from 41 to 140 $\mu\text{g g}^{-1}$) results mainly from the large loss in total particulate weight, rather than gain in Mn amounts. This can be illustrated by dividing the total Mn flux observed at each depth by the total particulate flux measured at the first depth: values of 44, 50, 47, 65 $\mu\text{g g}^{-1}$ are obtained. These observations support the statement of Brewer *et al.* (1980) that: ". . . trapped material is not simply related to . . . membrane-filtered particulate materials." These authors also report marked scavenging of Mn onto sinking particles and their Atlantic Ocean total Mn fluxes are on the same order of magnitude as those we report here ($\sim 100\text{-}800$ $\mu\text{g total Mn cm}^{-2}$ 1000 yr⁻¹).

c. Residence times. The Mn fluxes, together with "standing crop" estimates for dissolved and leachable Mn (from Table 1) enabled us to calculate residence times for Mn in various portions of the water column (Table 4). As expected, Mn resi-

Table 4. Residence time estimates for various portions of the water column using "standing crop" estimates from Table 1 and fluxes from Table 3. See text for explanation of 0-4000 m estimate.

Depth interval (m)	TDM standing crop (mg m ⁻²)	TE + LE Mn flux (mg m ⁻² yr ⁻¹)	Residence times (years)
0- 125	7.2	2.7	2.7
0- 275	17	3.1	5.5
0- 525	28	3.1	9.0
0- 900	52	4.5	12
0-4000	110	4.5	24

dence times were short near the surface (2.7 years for the upper 125 m), then steadily increased with depth until a value of 12 years was reached at 900 m. A residence time of 24 years was also estimated for the 4000 m water column using the flux measured at 900 m and a standing crop estimate based on an average Mn concentration of 20 ng liter⁻¹ for the 900-4000 m portion of the water column. This estimate agrees remarkably well with the 20-year residence time recently reported by Brewer *et al.* (1980) in their Atlantic Ocean sediment trap study. The residence times we report here are also very similar to those we observed off central California and to those made by other investigators using indirect methods (see Discussion in Martin and Knauer, 1980).

d. Mn in the oxygen minimum. As mentioned above, one of the more interesting features of Mn vertical profiles is the association of Mn maxima with oxygen minima. Klinkhammer and Bender (1980) presented three models which might explain this phenomenon: Model A, oxidative processes lower pH and/or pE, causing a shift in equilibrium away from particulate Mn and toward dissolved Mn; Model B, the Mn in oxygen minima originates in nearshore reducing sediments, and is transported laterally along isopycnals out into the open ocean; and Model C, organic matter is oxidized and associated Mn is released. The water column distribution data and vertical transport rates for Mn measured in this study appear to strengthen the case for Model B. Models A and C both call for a release of Mn from particles within the oxygen minimum. No evidence of Mn loss was observed, in spite of the large decrease in the organic C flux; thus, Model C does not appear to pertain. The increase in Mn fluxes and the suspended particulate Mn distribution within the oxygen minimum also appears to eliminate Model A. However, it can be argued that slight changes affecting equilibrium occurred between our station and that of GEOSECS 343, which favored removal onto particles rather than release from them. This might be the case. For example, gross observation of the nitrate profiles at GEOSECS 343 and at our station (unpubl.) suggests a marked denitrification at the former and little, if any, at the latter.

Nevertheless, the probable reason for the particulate Mn maximum we observed is that micro-organisms living in association with suspended particles under low and/or no oxygen conditions are forming Mn oxide. Nealson (1977) points out that Mn oxidation for many strains of marine bacteria is favored by low oxygen levels, and Schweisfurth *et al.* (1977) state that: "Below pH 8 and above an Eh value of +200 mV, Mn is oxidized only by micro-organisms under natural conditions." Although we have no pH or Eh data for our study area, we assume that the pH values are close to those observed at GEOSECS 343 (7.633-7.822 for depths > 140 m), and that the Eh is +400 mV, the median value for sea water. The bacterial Mn oxidation and chemical equilibrium hypotheses can also be combined to suggest that micro-organisms are responsible for the small changes in pE and/or pH that

control dissolved Mn/solid Mn equilibria in the microenvironments created by them on the surface of suspended particles.

Thus, our findings support Klinkhammer and Bender's Model B. Elevated levels of dissolved Mn in oxygen minima originate in nearshore sediments that are reduced when subsurface oxygen is completely depleted by the consumption of large amounts of organic matter falling out of highly productive, nutrient-rich, upwelled surface waters. The dissolved Mn released via this process is then advected laterally along isopycnals out into the open ocean. The dissolved Mn scavenges onto particles which eventually sink, removing it to the bottom. The scavenging process is especially rapid where low oxygen levels ($< 5 \mu\text{mol liter}^{-1}$) favor the microbial oxidation of Mn.

Although the behavior of Mn within oxygen minima is an interesting phenomenon, it would appear to have little importance in relation to the excess Mn found in open-ocean sediments. In the first place, pronounced oxygen minima only occur in subequatorial areas of the eastern Pacific, while excess Mn is observed on almost the entire sea floor. Second, our flux data (Table 3), although limited, indicate that most of the Mn is taken up near the surface rather than within the oxygen minimum.

The fact that Mn remains in association with sinking particles, in spite of large losses in biomass and organic C, is particularly important, since the sinking of biogenic particles can be used to explain the Mn excess, in view of the following: (1) The biogenic transport of Mn is independent of point sources; it occurs throughout the world ocean. (2) Measured fluxes are of the right order of magnitude. (3) A realistic input source necessary to balance output would appear to be surface current advection of dissolved Mn originally introduced into the marine environment either directly or indirectly via continental weathering processes. (4) Arguments against this transport mechanism, based on Mn:C ratios for living plankton are invalid in view of the ratios observed in the detrital remains of these organisms. (5) Continental weathering input/biogenic particulate output can also be used to explain the oceanic surface distribution of dissolved Mn recently reported by Klinkhammer and Bender (1980) and Landing and Bruland (1980). (6) Measured residence times are in agreement with other independent estimates.

In 1874, Mark Twain said, "There is something fascinating about science. One gets such a wholesale return of conjecture out of a trifling investment of fact." This quotation is appropriate in our case. In the above paragraph, we attempt explaining excess Mn found in the sediments of the world ocean based on a few flux estimates. Substantially more fact is needed in support of our conjecture.

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