

Incorporation and deposition of Mn and other trace metals by flocculent organic matter in a controlled marine ecosystem¹

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Abstract

An experiment in large (13 m³) cylinders with and without sediment has shown that dissolved Mn can be rapidly transferred to the particulate phase following a *Skeletonema costatum* bloom. Flocculent organic particulate matter derived from the bloom is implicated in the transfer processes. The kinetics of the phase transition are first order with a rate constant of $5 \times 10^{-6} \text{ s}^{-1}$. Deposition of particulate Mn was slower than the transfer rate to the particulate phase. Particulate Cu and Pb also increased following the bloom. The results suggest that the removal of Mn and certain other metals from the water column of the nearshore and open ocean may be associated with flocculent organic particles derived from phytoplankton. Deposition of Mn was more rapid in the microcosm with sediments than in the one without sediment, indicating that resuspension of sediments acts to increase Mn deposition rates.

Transfer of metals from the water to sediments in nearshore marine environments can occur by several mechanisms. Generally, particles are important carriers in the transfer process (Turekian 1977). Particles in the coastal zone include terrestrial particles added via rivers and the atmosphere, resuspended sediment, and particles produced in situ. In coastal regions, removal rates for those elements strongly associated with particles are linked to the particle flux, which is primarily a function of sediment resuspension rates (Santschi et al. 1979, 1980). Biologically derived particles may also be important in the removal of several metals (Hunt 1979). Evidence for Mn removal in association with such particles has been suggested from field studies (Martin and Knauer 1980; Wangersky and Gordon 1965) and in controlled ecosystems (Hunt and Smith 1980).

A major fraction of the particulate matter in seawater consists of organic aggregates (Riley 1963, 1970). These aggregates (or flocculent organic matter) are ubiquitous (Trent et al. 1978; Shanks and Trent 1979; Riley 1963, 1970). Their gen-

esis is diverse, involving both biological processes and physical processes such as adsorption, agglutination, bubble transport, and turbulence (Riley 1970; Shanks and Trent 1979; Alldredge 1979; Kranck and Milligan 1980). They serve as nutrient-rich particles (Shanks and Trent 1979), can be a major component of the particle flux in nearshore waters (Alldredge 1979), and can settle against vertical currents as high as $0.25 \text{ cm} \cdot \text{s}^{-1}$ (Kranck and Milligan 1980).

The role that these organic aggregates play in the removal of metals from the water has not been determined. Conversion of dissolved Mn to particulate forms during late summer diatom blooms in controlled marine microcosms suggested that Mn was incorporated into particulate organic matter derived from the diatoms (Hunt and Smith 1980). However, the identification and quantification of the phases involved in the conversion were complicated by resuspension of sedimentary particles, rapid removal of Mn in association with these particles, and a large benthic flux of dissolved Mn.

An experiment in a microcosm in which nutrient cycling was studied in the absence of sediments provided an opportunity to examine Mn cycling without

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these complications. The results show that dissolved Mn can be rapidly incorporated into postbloom phytoplankton remains and that deposition of this material may enhance Mn removal from the water. I thank J. Kelly for suggesting that I participate in the experiment and for assisting in sample collection, and G. Vargo and M. Hutchins for providing the phytoplankton and nutrient data.

Methods

Location and sampling methods—The study was done in July 1979 in microcosms of the Marine Ecosystems Research Laboratory (MERL), University of Rhode Island. An individual microcosm consists of a large cylinder (1.8×5.5 m) containing 13,000 liters of seawater exposed to sunlight and natural weather conditions (Pilson and Nixon 1980; Pilson et al. 1980; Oviatt et al. 1980; Hunt and Smith 1982). Microcosms are mixed to simulate normal tidal cycles (Nixon et al. 1980), and their temperature can be regulated.

Previous experience with microcosms operated in late summer without sediments suggested that intense diatom blooms could occur immediately after the cylinders were filled with seawater (G. Vargo pers. comm.). In my study, sediment was excluded from one cylinder, while a second one containing sediments from mid-Narragansett Bay acted as a control. The two were simultaneously filled with seawater over a 24-h period; particles deposited on the bottom of the cylinder without sediment were removed by a diver at the end of this fill. No additional seawater or nutrients were added to the system.

The following were measured daily: dissolved NH_4^+ , SiO_4 , $\text{NO}_2^- + \text{NO}_3^-$, PO_4^{3-} (method of Friederich and Whitledge 1972); dissolved O_2 (Winkler titration); total live plankton cell counts and species composition; chlorophyll and total pigments (Holm-Hansen et al. 1965); dissolved Mn (Mn_d), particulate Mn (Mn_p), total Mn (Mn_T), POC, PON, particulate Fe, Cu, Pb, Cd, Al, and total sus-

pended load (*see below*). Total system productivity was determined by dawn/dusk O_2 changes. The benthic flux of nutrients and Mn_d was evaluated by capping the entire 2.5-m^2 bottom area with a custom-designed benthic respirometer (Hunt 1983; Oviatt 1981) and sampling initial and final concentrations. Depositing particles were collected in containers ($7 \times 76\text{-cm}$ cylinders) located 1 m above the bottom. In addition, the entire mass of deposited particles was removed from the bottom of the microcosm without sediment at the end of the experiment. Flocculent particles from the surface sediment of the microcosm containing sediment were also collected.

Metal analysis—Dissolved Mn was measured by flameless atomic absorption spectrometry (AAS) in $0.4\text{-}\mu\text{m}$ -filtered seawater after acidification with high purity HNO_3 (1% vol/vol). Suspended loads were obtained by filtering duplicate 500-ml volumes of seawater through pre-cleaned, tared $0.4\text{-}\mu\text{m}$ Nuclepore membrane filters. The loaded filters were rinsed with ≈ 5 ml of high purity water (subboiled in an all quartz still), air-dried, and the total mass of particles weighed.

Samples for particulate carbon and nitrogen were collected on glass-fiber filters and the POC and PON determined with a Carla Erba 1106 CHN analyzer. Suspended load samples were also used to determine particulate metal concentrations. Samples were first ashed in quartz boats using an LTA-505 low temperature ashers. Each residue was transferred into a plastic vial with 0.5-ml Merck Suprapure HNO_3 and three 0.5-ml rinses of quartz-distilled water. Merck Suprapure hydrofluoric acid (0.5 ml) was added and the sample stored at room temperature for ≈ 2 weeks. Samples were diluted to 6.0 ml with high purity water and analyzed for Mn, Fe, and Al by flame AAS, and Cu, Pb, and Cd by flameless AAS. Appropriate digestion and filter blanks gave results below the detection limits for both flame and flameless methods.

All metal concentrations were determined from standard curves prepared in

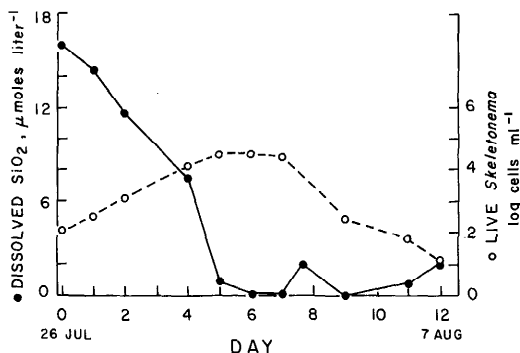


Fig. 1. Growth of *Skeletonema costatum* and depletion of dissolved SiO₂ in a microcosm without sediment.

matrices similar to that of the sample. Procedures outlined by Patterson and Settle (1976) for prevention of metal contamination were used for all laboratory manipulations.

Results

Biological—Isolation of the water column resulted in an immediate bloom of *Skeletonema costatum* in the microcosm without sediment (Fig. 1). No diatom bloom occurred in the one with sediment. Log-phase growth of *S. costatum* continued until day 5 when dissolved silicate was depleted. Total live cell counts on day 6 were similar to those of day 5 but declined from 34,000 to 200 cells·ml⁻¹ by day 12. The bloom increased the water column pH from 7.83 to 7.95 by day 7. Dissolved oxygen increased from 7.1 mg·liter⁻¹ on day 0 to 8.5 on day 7, then decreased to 6.3 on day 12.

Concurrent with the peak in *S. costatum*, large opaque flocculent particles appeared in the water and became visibly more prevalent over the next several days. Particulate organic carbon and nitrogen concentrations did not change with formation of the floc (Table 1). Particulate loads also remained relatively constant throughout the experiment (2.0 ± 0.4 mg·liter⁻¹). Thus, termination of the *S. costatum* bloom resulted in the formation of a flocculent particulate organic phase whose appearance, but not mass and composition, was very different from that

of the original organism. During the experiment the concentration of particulate Al decreased from 2.0 to 0.6 μM (Table 1). Considering that Al contributes ≈10% by weight to clay minerals and assuming that all Al is associated with clays, I estimate the contribution of clay minerals to the total suspended load to have decreased from 28 to 12% by day 4 and to 9% by day 11. Thus, by day 4, Al-bearing phases constituted a minor fraction of the total particulate load.

A small decrease, 0.5 mg·liter⁻¹, in the suspended load between days 7 and 12 suggested some deposition of the floc (Table 1). This was confirmed from diver observations of the bottom of the microcosm. On day 6 very little particulate matter was visible on the bottom. By day 12 the bottom was noticeably covered with flocculent particles. The particle flux determined from sediment traps varied between 0.09 g·m⁻²·h⁻¹ on day 2 and 0.24 on day 11. The low flux coincided with the diatom bloom, whereas the higher flux occurred later, when the floc was present in the cylinder. A total of 25.6 g of particulate matter was collected by diver from the bottom of the cylinder at the end of the experiment. Assuming that this was deposited between days 6 and 12, I calculate a particle flux of 0.071 g·m⁻²·h⁻¹, or 0.035 if deposition continued over the entire experiment. The net reduction in the total particulate load in the water between days 6 and 12 gives an estimated deposition rate of 0.023 g·m⁻²·h⁻¹. The higher particle fluxes calculated from the trap data may reflect trapping of particles resuspended from the bottom. The particle settling velocity estimated from the decrease in particulate matter was 0.2 m·d⁻¹.

Chemical—Dissolved, particulate, and total Mn remained relatively constant during the first 6 days of the experiment (Table 1, Fig. 1). Between days 6 and 11 Mn_d rapidly decreased to undetectable concentrations, with a concurrent increase in Mn_p. Clearly, Mn_d experienced a phase transition after day 6 when the flocculent particulates appeared in the water. Extensive incorporation of Mn into

Table 1. Summary of dissolved Mn, suspended load, POC, PON, and particulate metal concentrations during an experiment evaluating the response of a MERL ecosystem to a diatom bloom in the absence of sediment.

Sample day	Mn _d (nM)	Suspended load (mg·liter ⁻¹)	POC (μM)	PON (μM)	Particulate metal					
					Al (μM)	Mn (nM)	Fe (μM)	Cu (nM)	Pb (nM)	Cd (nM)
Log-phase growth										
0	201±4	1.9±0.6	23.3	2.7	2.0	24	0.59	1.8	1.3	0.03
1	180±5	1.6±0.1	29.3	5.1	1.6	19	0.68	2.1	1.9	0.03
2	175±5	2.8±0.3	39.6	4.3	1.5	29	0.60	2.2	2.5	0.08
4	196±4	1.7±0.1	30.1	5.4	0.96	19	0.35	1.5	1.6	0.01
5	193±10	2.3±0.2	40.5	6.5	1.0	22	0.37	1.2	1.7	0.04
Bloom maximum										
6	174±6	2.2±0.1	49.1	5.2	1.0	24	0.38	1.3	2.7	0.07
7	107±4	2.2	56.8	5.3	1.2	51	0.35	2.6	1.6	0.04
Postbloom										
9	48±2	1.8±0.1	31.2	4.1	0.90	95	0.45	2.9	3.3	0.02
11	ND*	1.8±0.2	24.8	3.7	0.60	140	0.35	3.2	3.1	0.02
12	ND	1.7±0.2	34.0	5.0	1.2	132	0.51	4.3	3.9	0.02

* Not detected, detection limit 10 nM.

particles was not observed during the active growth of *S. costatum*. The conversion of Mn_d to Mn_p was accompanied by a rapid loss of Mn_T from the water between days 5 and 7, followed by a continuous but slower loss until day 12 when the experiment ended.

The rate at which Mn_d was transferred to the particulate phase was examined for first-order and autocatalytic characteristics. If Mn²⁺ oxidation follows first-order reaction kinetics, a plot of log (Mn²⁺) vs. time should be linear, and the concentrations of particulate Mn and Mn_d vs. time should trend concavely downward and upward. If autocatalysis is important, log (Mn²⁺) will not vary linearly with time, and plots of Mn_p and Mn_d vs. time will be sigmoidal (Pankow and Morgan 1981). In the present case, plots of log Mn_d and Mn_d against time were linear and concave upward, suggesting that the transfer of Mn_d to the solid phase was via an oxidation reaction. However, Mn_p vs. *t* was linear, not concave downward. This test of first-order kinetics was complicated by the settling of particulate matter from the water, so that total Mn was not conserved (Fig. 2). If the amount of Mn_T lost from the water is added to the amount of Mn_p remaining in it at each sample period,

then a curve of Mn_p vs. time results which is concave downward. Deposition of particulate Mn was assumed to be the only avenue of Mn loss, since wall cleaning showed no uptake of Mn and the system was in batch mode.

Because no suggestion of autocatalytic reaction was observed, the conversion of Mn_d to Mn_p was treated as a simple first-order reaction to derive a rate constant (*k*) of $5.0 \times 10^{-6} \cdot s^{-1}$ ($0.18 \cdot h^{-1}$) and a half-life ($\ln 2/k$) of 39 h for the transfer process. The rate at which Mn was transferred to the floc was calculated to be $0.5 \mu\text{mole Mn} \cdot \text{g floc}^{-1} \cdot \text{h}^{-1}$. On an areal basis the transfer occurred at $\approx 5.4 \mu\text{moles} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.

I confirmed the rate of Mn uptake by a bottle experiment. Floc which had settled onto the microcosm floor by day 12 was collected, and 4 mg put into each of two plastic bottles containing 0.39 liters of seawater of known Mn_d concentration. Bottles with seawater but without the floc were used as controls. Samples were collected after 2 and 51 h and analyzed for Mn_d. Dissolved Mn decreased by 270 nM in the bottles with the floc, while the control bottles showed no loss. Transfer of Mn to the particulate phase occurred at a rate of $0.5 \mu\text{mole Mn} \cdot \text{g floc}^{-1} \cdot \text{h}^{-1}$.

The rate of Mn uptake by floc depos-

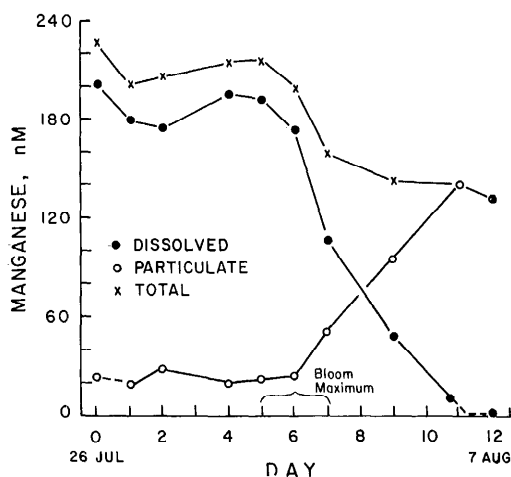


Fig. 2. Response of dissolved, particulate, and total Mn for the *Skeletonema costatum* bloom in the microcosm without sediment.

ited and in place on the bottom of the microcosm was determined using an unstirred benthic respirometer which encapsulates the entire 2.5 m² of the cylinder floor (Hunt 1983). The flux was 0.5 $\mu\text{mole}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ into the sediment on day 7 and 0.4 on day 11. On the basis of the flux on day 11 and the total mass of particles deposited (25.6 g), an uptake rate of 0.04 $\mu\text{mole}\cdot\text{g}\text{floc}^{-1}\cdot\text{h}^{-1}$ was calculated. This rate is a tenth of that observed in the water and bottle experiment. The low uptake rate may have been caused by the lack of turbulence at the boundary layer. The uptake of Mn by the floc in the respirometer contrasts with the benthic Mn flux in the tank with sediment of 11 $\mu\text{moles}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ out of the sediment on day 7.

The rate at which Mn was deposited in association with the floc was 2.5 $\mu\text{moles}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ on the basis of the decrease in total Mn between day 6 and day 12. This is about half the rate of transfer into the particulate phase. The maximum rate of Mn deposition during the active bloom (day 0–5) was $\approx 0.6\ \mu\text{mole}\ \text{Mn}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. Removal rates in the cylinder with sediment can be estimated from budget considerations. Between day 0 and day 5, Mn_T in the water column increased from 283 to 363 nM; it then remained constant

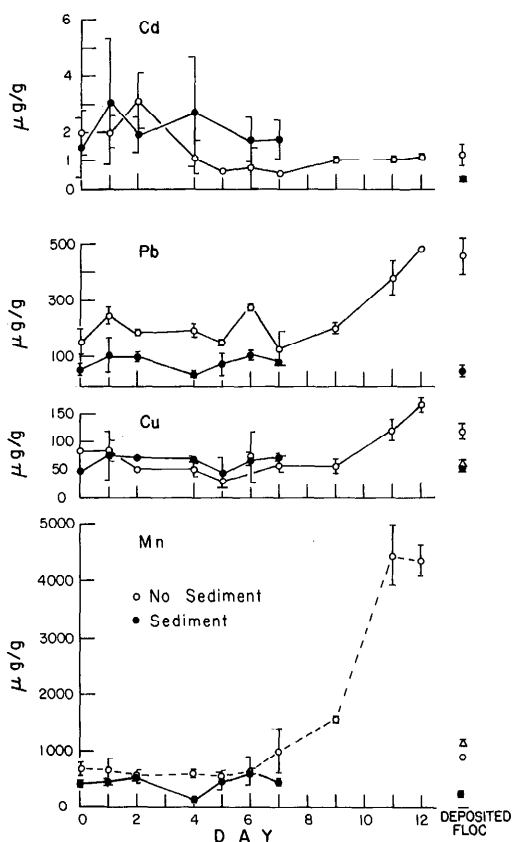


Fig. 3. Comparison of the Pb, Cu, Cd, and Mn content of particles in the water of microcosms with and without sediments in July and August 1979. The metal contents of particles deposited in the microcosm without sediment and the flocculent sediment surface layer are also shown.

until day 7. The total input of Mn to the water from benthic regeneration was 4.6×10^{-3} moles or ≈ 360 nM during the 7 days. Since the system was on batch mode, only 21% of the flux could be accounted for by the increase in the water column. Thus, 79% or 8.7 $\mu\text{moles}\ \text{Mn}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ had to be returned to the sediments (as in the cylinder without sediment, wall uptake did not occur). This rate is 3.5 times higher than that observed in the cylinder without sediment during the postbloom period and occurred in the absence of large organic flocs. This comparison indicates that the presence of sediments, presumably through resuspension and deposition, increases the re-

removal rate of Mn. However, the presence of sediments is not necessarily the only process acting to transfer metals such as Mn from the water column.

During the floc formation there was also a significant increase in the Pb and Cu content of the particulate material (Table 1, Fig. 3). Cd and Fe did not show such large increases. The incorporation of these elements may have resulted from adsorption onto Mn which was rapidly precipitating rather than as a direct uptake by the floc. The exact mechanisms are not evident from this experiment.

Discussion

This experiment shows that particulate organic floc, similar to that described in natural systems (Allredge 1979) and experimentally produced (Kranck and Milligan 1980), may result from diatom growth (in this case *S. costatum*). In this experiment the onset of floc formation in the water resulted in rapid transfer of dissolved Mn (plus Cu and Pb) into the floc. The specific mechanisms (adsorption or oxide formation and precipitation) involved in the transfer are not clear.

Examination of the characteristics of the transfer to the solid phase suggests that first-order kinetics were followed. Evidence for microbial activity and associated oxidation of the Mn_d (Van Veen et al. 1978; Emerson et al. 1982) was not obtained, and thus cannot be eliminated from consideration of the mechanisms causing the transfer. Sediment resuspension appears to increase the Mn removal rate, but transfer into the particles could not be detected in the presence of resuspended sediment (Fig. 3). The two systems studied demonstrate the importance of understanding both the rates involved in transferring metals to the particle phase and the processes acting to remove particles from marine ecosystems.

The ubiquitous occurrence of organic flocs and the rapid incorporation of Mn, Pb, and Cu into them suggest that these particles can be important transfer mechanisms in both the coastal and open ocean. Deposition of Mn in association with particulate organic matter has been suggest-

ed by Martin and Knauer (1980). They found a molar ratio of Mn:particulate carbon collected in sediment traps at <1,500 m in nearshore northeast Pacific waters of 8.5×10^{-5} . This compares with a molar ratio of 3.9×10^{-3} for the particles on day 12 of my study. This high Mn:C ratio results in part from the large reservoir of Mn available in the MERL system (≈ 200 nM Mn) relative to that in Pacific waters (≈ 1 to 4 nM; Martin and Knauer 1980). The results from the MERL experiment suggest that the total uptake of Mn by the organic floc may be limited by the availability of dissolved Mn. The experiment also demonstrates that uptake of Mn by plankton detritus is greater than by living plankton (Fig. 3) (Flegal cited in Knauer and Martin 1980).

Rapid transfer of dissolved Mn to particulate forms was observed in several MERL microcosms in May and June 1978 and 1979, and also in August 1978 during a bloom of *Chaetoceros* sp. (Hunt and Smith 1980). It was not observed at temperatures $<7^\circ\text{C}$ during the course of two long term (≈ 16 month) studies (Hunt and Smith 1982, 1983). Thus, the process may also exhibit some temperature dependence.

These results imply that in the coastal zone, and in other regions, particulate organic floc can incorporate trace metals. Subsequent deposition of this floc acts to remove the metal from the water. In nearshore systems where sedimentary processes (sediment resuspension, filter feeders) strongly influence the processes and particle fluxes in the water column, higher removal rates of metals associated with organic flocs may result from aggregation with the denser sedimentary particles (Kranck and Milligan 1980) or from removal through the activities of filter feeders (Santschi et al. 1982). In either case, organic floc appears to be active in the uptake and removal of metals from marine waters.

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