MANGANESE CYCLING IN THE NEWPORT RIVER ESTUARY, NORTH CAROLINA

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Abstract

Dissolved Mn was measured in the Newport River estuary, North Carolina, in October 1974, February 1975, and April 1975 by extraction on Chelex-100 resin and subsequent analysis by flameless atomic absorption spectrophotometry. Dissolved Mn concentrations at intermediate salinities were in excess of those predicted by conservative mixing of inflowing river and ocean water, with maxima between 4‰ and 14‰ salinity.

Reduction and solubilization of Mn in bottom sediments in the upper estuary probably supplies much of the added dissolved Mn. Fixation of dissolved Mn on particles takes place in the lower estuary with subsequent upstream recycling.

The export of dissolved Mn from the estuary in excess of that input by the river is probably balanced by continuous traction flows of river-derived bed sediment or pulse inputs of suspended sediment in storm runoff followed by partial solubilization.

Introduction

Manganese (Mn) is one of the more biogeochemically active transition metals in aquatic environments. It is readily transferred between solution and solid phases (sediments and suspended matter) in response to changes in environmental conditions such as pH, Eh, and the composition and relative concentrations of dissolved and particulate phases (Hem, 1963).

Estuaries are zones of transition between freshwater and marine environments and as such contain concentration gradients and other variations in geochemical conditions. This has suggested to many (Murata, 1939; Johnson *et al.*, 1967; Kharkar *et al.*, 1968) that estuaries are likely sites of transfer of Mn and other trace metals between solution and sediment phases.

We have sought to detect transfer of Mn between dissolved and particulate phases in the Newport River estuary, North Carolina, and to relate observed concentrations of Mn to possible reaction processes.

If the estuary is a system in steady state with inflowing river water and seawater, the concentration of a conservative dissolved substance is a linear combination of the concentrations in river water and seawater. Deviations from linearity are the result of processes which add or remove the substance from solution. This approach was used by Evans and Cutshall (1973) to observe

nonconservation of radioactive ^{54}Mn in the Columbia River estuary. They concluded that observed positive deviations from linear dilution resulted from desorption from suspended and bottom sediments. More recently, Boyle *et al.* (1974) have developed the mathematics of nonconservative mixing models more rigorously.

Our sampling was carried out in the Newport River estuary, North Carolina (Figure 1). This is a shallow "drowned river" estuary with extensive intertidal areas, often populated by the marsh grass *Spartina alterniflora*. The mean depth at low tide is about one meter, with an intertidal range of 0.7 meters. A more thorough description of the region is given by Wolfe *et al.* (1973). Of particular interest to our study is the region between Cross Rock and 2.2 kilometers (km) upstream where the river proper widens into the estuary. This is the region of maximum salinity gradient where river water mixes with brackish estuarine water. On the flood tide brackish water is swept up the river as much as 8-10 km during periods of low river flow. The Cross Rock region is also important in being a deltaic area where fine sediments are deposited.

Methods and Materials

Sampling for dissolved and particulate Mn was done during three different periods: October 1974, February 1975, and April

1975. Longitudinal sample transects from salinity 0‰ to greater than 30‰ were taken within two hours of high tide on October 30 and 31, February 4, and April 14, and within two hours of low tide on February 5. Water was sampled periodically from the Newport River (0‰ salinity) and from the Atlantic Estuarine Fisheries Center dock (salinities greater than 30‰) during the three weeks preceding both the October 1974 and February 1975 estuary sampling transects. This was done to test the assumption of constant end member input concentrations required by the steady state model. This was not done for the April 1975 period.

During the entire October 1974 period approximately 4.52 cm of rain fell in the river's drainage basin (computed as the average rainfall of Morehead City and New Bern, N.C.). February, on the other hand, was an unusually rainy period. During the three weeks prior to these transects, 15.91 cm of rain fell with 4.45 cm falling during the night of February 4-5. This was sufficient to induce stratification behind Cross Rock at slack low water. Zero salinity was observed at the surface and 14‰ salinity was found at the bottom, only 0.5 meters deeper. During the three weeks prior to the April 1975 transect 8.15 cm of rain fell.

Duplicate water samples were collected from the upstream side of a 5-meter aluminum boat into a cylindrical 400-ml plexiglass

pressure vessel. The samples were immediately pressure filtered with 30 psig N₂ directly through Nuclepore filters (47 mm diam by 0.4 µm pore size) held in acid-washed Nuclepore filter holders. This provided an operational separation of dissolved and suspended particulate fractions. The filters had been previously weighed so that suspended particulate concentrations could be determined later. Salinities were measured in the field with a Beckman RS5-3 inductive salinometer and later on the water samples themselves with an Aminco Cotlove chloride titrator to an accuracy of ±0.3‰.

Filtration was carried out until the filters clogged. This provided samples from about 50 ml in freshwater to 400 ml in seawater. Two filters were often required to provide a minimum 50-ml sample at the low salinity stations. Blanks were run identically using 300 ml of deionized distilled water (DDW). The filtrates were collected directly in acid-washed 500-ml polyethylene bottles and acidified with 0.1 ml redistilled HNO₃.

When returned to the laboratory the filtrates were frozen until time for analysis, and the filters were carefully washed free of sea salts with 15 ml DDW. The filters were then dried in a desiccator for 48 hours before being reweighed.

In preparation for analysis the filtrates were thawed and weighed. Five ml of 5% K₂S₂O₈ solution (previously purified by

passage through a column of Chelex-100 resin) was added to the samples, still in their original polyethylene bottles. The caps were screwed tight and the samples allowed to digest for 16 hours at 90°C in a drying oven. This procedure oxidized dissolved organic matter which might otherwise bind Mn and prevent its subsequent extraction (Noakes and Hood, 1961).

Because sea salts interfere with Mn analysis, Mn was separated by the chelating exchange resin Chelex-100 (BioRad Labs, 50-100 wet mesh). The cooled and digested samples were brought to pH 6-7 with 5 ml of previously purified 8% NaHCO₃ solution. They were then allowed to flow through 0.7 cm diam by 4 cm polypropylene columns (BioRad) containing Chelex-100 resin in the ammonium form. The (uncontrolled) flow rate was about 2.7 ml/min. The columns were subsequently flushed with 30 ml of DDW to remove interstitial sea salts. Elution with 15 ml 2N HNO₃ stripped the collected Mn from the resin. The eluate was collected in 30-ml FEP Teflon beakers, evaporated to dryness at 70°C and then redissolved in DDW to which 0.05 ml HNO₃ was added. The extracts were diluted to 10 ml with DDW in cleaned 15-ml polypropylene test tubes.

The extracts were subsequently analyzed for Mn by flameless atomic absorption spectrophotometry by a Perkin Elmer HGA 2000 Graphite Furnace and Model 403 atomic absorption spectrophotometer. Twenty microliters of the extracts were injected into the

graphite tube with an Eppendorf pipet. The furnace was programmed to dry the sample at 100°C for 30 seconds, ash it at 1100°C for 10 seconds, and atomize it at 2400°C for 12 seconds. Gas interrupt was employed and Deuterium arc background correction was used to correct for non-atomic absorption. Output was in absorbance units to a Perkin Elmer Model 56 strip chart recorder. If necessary, 1:10 dilutions were made to bring concentrations into an analyzable range.

Standards of 0, 1, 2, and 3 µg/l of Mn in DDW and in seawater were extracted by this procedure. Only $83\% \pm 2\%$ (based on the slope and standard error of the resulting least squares calibration lines) of the added Mn in both sets of extracts was detected by the flameless atomic absorption spectrophotometric analysis. Recovery of a ^{54}Mn tracer carried through the same extraction, however, was quantitative. The apparent less than complete recovery probably results from suppression of atomization of Mn in the furnace by salts of Na, Mg, Ca and K which were not completely removed by the extraction procedure. Concentrations of field samples are therefore calculated on the assumption of 83% recovery.

Manganese also was determined on the suspended particulate material. The filters, with associated particulate matter, were digested with 0.1 ml HNO_3 and 0.1 ml HF for 16 hours at 90°C in tightly capped, cleaned polypropylene test tubes. The digests

were brought up to 10 ml volume with DDW and analyzed by flameless atomic absorption spectrophotometry as described above for the filtrates.

Results and Discussion

In Figures 2a, 2b and 2c dissolved Mn concentrations are plotted for the three sampling periods, October 1974, February 1975 and April 1975. Included in Figures 2a and 2b are the concentrations of dissolved Mn flowing into the estuary from the river and ocean during the three weeks prior to the estuary transects. The flushing time of the Newport River estuary varies from 4 to 10 days depending on river flow (Jennings et al., 1970). If the steady state model is to be strictly valid, input concentrations should not vary during the time period of several flushing times prior to estuary sampling. As can be seen from the figures, river input concentrations of dissolved Mn are not constant. They do not vary enough, however, to explain the dissolved Mn variations within the estuary which are discussed below.

It is obvious from Figures 2a, 2b and 2c that dissolved Mn concentrations within the estuary are not merely the result of conservative (linear) mixing of Newport River water and seawater. Dissolved Mn concentrations at intermediate salinities lie well above the line predicted for conservative mixing. (This

line connects the zero salinity river input on the day of the transect, and offshore ocean water, 7 km from the estuary mouth sampled December 3, 1974, which is assumed to represent a constant ocean end member in concentration.) Concentration maxima lie in the range of 4‰ to 14‰ salinity, which is the zone of initial mixing of fresh and salt water. The general similarity of the dissolved Mn/salinity relation during three disparate sampling periods strongly suggests that the nonconservation of dissolved Mn in the Newport River estuary is a general, long-term phenomenon. This, together with near identity of the relationship on consecutive days (Figures 2a and 2b), lends credence to the steady state assumption.

The dissolved Mn concentrations above those predicted by conservative mixing can only result from the addition of dissolved Mn. Because there are no obvious external sources of dissolved Mn (e.g. industrial wastes, atmospheric fallout, or other freshwater runoff) local to this area, the added Mn must result from *in situ* dissolution of particulate Mn.

In such a steady state, the only significant original supply of particulate Mn is that carried in suspension or as traction load by the river and deposited in or transported through the estuary. Kharkar et al. (1968) showed that clay mineral analogs of river suspended matter were capable of adsorbing certain trace

metal radioisotopes in freshwater and partially desorbing them upon contact with seawater. Evans and Cutshall (1973) have shown that Columbia River suspended matter released 30% to 60% of its ^{54}Mn upon contact with seawater. Johnson et al. (1967) and Lentsch et al. (1973) have shown that bottom sediments will release large fractions of their bound ^{54}Mn and stable Mn if exposed to seawater or to salt solutions of the cations Mg, Na, and Ca which are abundant in seawater. All of these results seem explainable in terms of simple ion exchange displacement.

This process cannot, however, explain the magnitude of the dissolved Mn maxima if they represent long-term steady state phenomena. For the October 30 and 31 transects, the difference between the observed dissolved Mn concentration at the maximum at 4‰ salinity and that predicted by conservative mixing is about 13 $\mu\text{g/l}$ or about 14 $\mu\text{g/l}$ of river-derived water. The concentration of suspended particulate Mn flowing into the estuary from the river rarely exceeded 3 $\mu\text{g/l}$ during the three weeks prior (see Figure 3). Thus, even if complete desorption of Mn from suspended particulate matter were to take place, it would supply only a small fraction of the excess dissolved Mn that must have been added. The February and April 1975 samples also show that suspended particulate matter cannot supply the added dissolved Mn. Other mechanisms must be postulated to maintain a steady state dissolved Mn maximum.

As mentioned earlier, Mn associated with bottom sediments can be desorbed by contact with seawater. Other mechanisms exist by which particle-bound Mn can be solubilized. Disruption of living cells due to changes in salinity or decomposition of Mn-containing organic matter could release dissolved Mn. Furthermore, in areas of rapid sediment deposition or slow replacement of dissolved oxygen, sediments are likely to become anoxic, and reducing conditions can develop. Thus in the sediment deposition region near Cross Rock, sediments below the top two or three centimeters are reducing. Under such conditions, oxidized Mn (as MnO_2) on particles is reduced to soluble Mn^{++} or MnS , which is then free to diffuse through the interstitial water to the overlying water. Calvert and Price (1972), among many others, have shown evidence for this process in vertical profiles of sediment Mn which is depleted at depth. Interstitial water Mn was found by them to be higher in concentration than dissolved Mn in overlying water, indicating a flux of dissolved Mn out of the sediments.

To show that bottom sediments from the Newport River estuary can act as a source of dissolved Mn to overlying waters, six sediment cores of 20 cm length and 8 cm diameter were collected with about 30 cm of overlying water on April 17, 1975, from Cross Rock. The salinity was measured at 14.0‰. Three cores were inverted, resuspending the top 5-10 cm of sediment, which was then allowed to settle for one hour. Three other cores were allowed

to remain upright for one hour. The overlying water was sampled in quadruplicate at the same time. Allowed to stand for one hour in coring tubes without sediment, they served as controls. The overlying water in each sample was filtered after the one hour period and analyzed for dissolved Mn as previously described. Table I shows the analytical results. For cores that were not inverted dissolved Mn increased in the overlying water by 7 $\mu\text{g/l}$, from 19 $\mu\text{g/l}$ to 26 $\mu\text{g/l}$. For cores in which the sediment was resuspended dissolved Mn increased in the overlying water by 18 $\mu\text{g/l}$. In a crude way, this shows that bottom sediments can act as sources of dissolved Mn to the overlying water in this region. It is not clear from this experiment whether the mechanism is ion exchange desorption, reduction/solubilization or decomposition of organic matter, and this would require more rigorous experiments to differentiate.

It is therefore possible that bottom sediments in the region of the dissolved Mn maximum can act as a source of the excess dissolved Mn if a mechanism can be found to deposit particulate Mn there in excess of that carried in suspension in the river at the time of sampling. This could be done either by recycling particulate Mn from the lower estuary or by depositing riverborne particulate Mn in large amounts during times when the river suspended particulate Mn was not sampled (i.e. during storm runoff when riverbed sediments are scoured out and carried downstream).

Cutshall (in press) has proposed a model in which the dissolved Mn maximum is maintained by a recycling mechanism, much like the well known estuarine nutrient trap. In his model, dissolved Mn as Mn^{++} is carried downstream from the maximum by the net downstream flow of water in the estuary. In the lower estuary, it is oxidized to insoluble MnO_2 . The new particulate Mn is carried upstream and deposited in the upper estuary where it is reduced and solubilized to complete the cycle. Postma (1967) discussed mechanisms for upstream flow of particulate matter in tidal estuaries which can operate counter to the net downstream flow of water, even in unstratified estuaries such as the Newport River estuary. The coincidence of the dissolved Mn maxima with the region of sediment deposition supports this model. It is entirely analogous to the model used by Spencer and Brewer (1971) to explain the vertical Mn maximum at mid-depth in the Black Sea. It differs conceptually only in being horizontal rather than vertical, with Mn reduction/solubilization occurring in the bottom sediments rather than in the water column.

It also seems possible that Mn could be biologically cycled in the same way as nutrients in the classical nutrient trap. Thus biological uptake of Mn in the lower estuary combined with release in the upper estuary might account for our observations. Our experiments do not differentiate between the chemical and biological alternatives.

If Mn is fixed in the lower estuary as predicted by this model, the concentration of Mn in the suspended matter should be higher in the lower estuary than the upper. Of course, this assumes that non-manganese particulate matter is not created in proportion. Figure 4 shows Mn per gram of suspended particulate matter for the October 1974 period. It increases with the downstream direction in the estuary and drops suddenly near the oceanic end. This is entirely consistent with the recycling model which predicts the creation of high Mn suspended particulate matter in the lower estuary which is recycled upstream.

Complementary to the increase in particulate Mn concentrations at higher salinity in the estuary, dissolved Mn should decrease. If there is a loss of Mn from solution in the lower estuary, the Mn:salinity plot should show a curvature with concavity upward. (See Boyle et al., 1974 for the mathematical derivation of this conclusion.) Figures 2a, 2b, and especially 2c show such a curvature. Loss of Mn from solution does appear to be taking place in the lower Newport River estuary.

A further testable consequence of the model is that, in steady state, no more dissolved Mn should exit the estuary at the ocean end than enters at the river end. In a plot of dissolved Mn against salinity, this implies that Mn concentrations near the ocean end member should asymptotically approach the original

conservative mixing curve. Both October 1974 and April 1975 transects show dissolved Mn concentrations at salinities of greater than 20‰, which do not appear to approach the original conservative mixing line, but rather to lie above it. This means that the system is exporting more dissolved Mn to the ocean than it imports from the river during part of the year.

Since the estuary seems to be exporting more dissolved Mn than it imports in solution or suspended matter from the river under quasi-steady state conditions, it is likely that occasional large inputs of particulate Mn are deposited in the upper estuary during periods of heavy river runoff. Alternatively, bed or traction loads of river borne sediments (which have not been measured) could arrive nearly continuously. Reduction/solubilization of the sedimentary Mn as described above would provide continuous inputs of dissolved Mn to the estuary waters at intermediate salinities. The postulated periodic inputs of particulate Mn have not been measured directly.

Wolfe et al. (1973) have estimated deposition rates of sediment in the Newport River estuary at 1 mm to 4 mm per year, basing their estimate on work by Biggs (1967) in Chesapeake Bay. The upper estimate of 4 mm per year would be representative of the Cross Rock region. If these new sediments have a water free density of 0.5 g/cm^3 and a Mn concentration we have measured by $\text{HNO}_3\text{-HF}$

digestion at 150 $\mu\text{g/g}$, then 30 $\mu\text{g/cm}^2$ of Mn is supplied each year. If all of this Mn is solubilized, the concentration of dissolved Mn in a one-meter column of water above the sediments would be raised by 300 $\mu\text{g/l}$ each year. If the estuary is flushed every six days, or 60 times a year, the water column at steady state could be raised by 5.0 $\mu\text{g/l}$ of dissolved Mn. This is still far less than that observed in this region. Better estimates of sedimentation rate might refine this estimate, but since it was assumed that all deposited Mn was released to solution, it probably represents an upper limit on the estimate.

Conclusions

None of the postulated sources accounts by itself for the observed added dissolved Mn concentrations at steady state. It is probable that they all operate in conjunction. The alternative would require the postulation of a new, as yet unknown, source. The steady state assumption might be a close approximation of average conditions; however, it does not represent temporal variations, especially transient phenomena, such as pulse additions or removals during heavy river runoff. Therefore, this assumption might require modification as well. Nevertheless, there appears to be strong evidence in support of the recycling mechanism in maintaining the dissolved Mn maximum at intermediate salinities.

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Figure 1. The Newport River estuary, North Carolina, USA.

Figure 2. Dissolved manganese ($\mu\text{g/l}$) in the Newport River estuary as a function of salinity: (a) $\bullet$, October 30, 1974; $\circ$, October 31, 1974, (b) $\bullet$, February 4, 1975; $\circ$, February 5, 1975, (c) $\circ$, April 14, 1975. A dashed line connects the mean dissolved Mn concentration in the river on the days of estuarine sampling with the concentration in offshore ocean water sampled December 3, 1974 (presumably representing the oceanic water mixing in the estuary). This line represents the theoretical, conservative mixing concentrations. Also shown in (a) and (b) are the river, $\blacktriangle$, and ocean, $\triangle$, (at AEFC dock) input concentrations during the three weeks prior to estuary sampling.

Figure 3. Suspended particulate manganese ($\mu\text{g/l}$) in the Newport River estuary October 30 ($\bullet$) and 31 ($\circ$), 1974. Also shown are river input concentrations ($\blacktriangle$) and ocean input (at AEFC dock) concentrations ($\triangle$) during the three weeks prior to estuary sampling.

Figure 4. Manganese concentrations on suspended particulate matter ($\mu\text{g/g}$) October 30 ($\bullet$) and 31 ($\circ$), 1974. Also shown are river input concentrations ($\blacktriangle$) and ocean input (at AEFC dock) concentrations ($\triangle$) during the three weeks prior to estuary sampling.

Table I. Dissolved manganese in water overlying sediment cores from Cross Rock April 17, 1975. Control contained no sediment. Inverted had top 5 cm of sediment mixed into the 30-cm water column. Uninverted had the core remain upright without being mixed into the water column. Contact time was one hour.

<u>Sample</u>	<u>Dissolved Mn concentration (µg/l)</u>	
Control	18.8	
	18.8	
	19.0	mean 18.6
	17.9	
Uninverted	28.8	
	21.1	mean 26.2
	28.8	
Inverted	27.4	
	46.9	mean 37.0
	36.7

Figure 1

Figure 2

Figure 3

Figure 4

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