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## Mn, Fe, Cu and Cd distributions and residence times in closed basin Lake Vanda (Wright Valley, Antarctica)

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### Abstract

Mn, Fe, Cu, and Cd concentrations are reported for Lake Vanda, a closed-basin, meromictic, Antarctic lake and for its single major inflow, the Onyx River. Trace metal distributions in the upper lake and annual metal fluxes from the Onyx River were used to estimate chemical residence times in the mixed zone above the chemocline. Residence times, based on *total* metal loads, were 9.4 years for Mn; 1.4 years for iron; 174 years for copper; and 82 years for cadmium. Controls on the steady state concentrations of metals in this system are likely to include: particle settling of Fe and Mn; scavenging of minor elements on metal oxide surfaces; sulfide precipitation from the anoxic brine; and possibly uptake of metals on the surface of benthic algal mats. Model calculations show that metal removal by sinking phytoplankton can account for only a small fraction of the annual loss.

### Introduction

Three glacier-carved valleys cut the Transantarctic mountains to the west of McMurdo Sound. These virtually ice-free oases extend from the high snowfields of the Polar Plateau eastward to the margins of the Ross Sea, and they occupy an area of some 4,000 km<sup>2</sup>. For Antarctica, these valleys are highly atypical landscapes of exposed metamorphic and granitic rock, overlain by sandstones and frequently intruded by dolerite sills. Scattered within this region is a group of cold-desert lakes, most of which occupy closed basins and contain, beneath their permanent ice covers, saline waters of varied and sometimes complex origin.

Lake Vanda is located in Wright Valley and is bordered by the high rock walls of the Asgard and Olympus Ranges. The lake, which is capped by a smooth, permanent, four-meter-thick ice cover, is 5.6 km long, 1.5 km wide, and 68.8 m deep in the western depression. Water is supplied by the Onyx

River during a six-week period from about mid-December to early February. The Onyx, which has its source at the Wright Lower Glacier 28 km to the east, has an annual discharge rate of about 2 billion liters (Chinn, 1982).

Lake Vanda is a meromictic, two-layer system (Angino *et al.*, 1965). The waters above 54 m are fresh, while those below become progressively saline with depth. A convection current having a velocity of 1 cm sec<sup>-1</sup> was detected in the upper layer (Ragotzkie & Likens, 1964) and this is likely to be responsible for the relative homogeneity of the waters in this region. An extremely important feature of the lake's hydrodynamic regime is the remarkably stable diffusion zone which exists below 54 m. Diffusion in this region has presumably been the major mechanism of ionic and molecular transport for the past 1200 years (Wilson, 1964).

This closed-basin lake has been the source of a rich and varied literature over the past two decades. The geochemical work of Angino *et al.* (1965) first

established the major element chemistry of the water column, and since that time numerous hypotheses have been advanced to account for the lake's curious  $\text{CaCl}_2$  composition. Green & Canfield (1984) have recently summarized this literature.

Based on a study of the Onyx River and on a reinvestigation of the lake's major ion geochemistry, Green & Canfield (1984) argued that the salts in the lake are derived from two principal sources: namely, the deep-groundwater reservoir of the Don Juan Basin and the Onyx River itself. The mixing model, using deep groundwater and the Onyx River as end members, shows that the groundwater once contributed most of the  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  found in the lake, while the Onyx River was the dominant source of  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ .  $\text{Na}^+$  appears to have come equally from both sources.

The biology of Lake Vanda has been described by Goldman *et al.* (1967), and most recently by Vincent & Vincent (1982). The lake is recognized as one of the clearest and most oligotrophic in the world, with low algal standing crops as well as low rates of primary productivity observed at all depths, except for a narrow band of more productive water located just above the anoxic zone (60 m). Of additional interest, an extensive population of blue green algae has been discovered on the lake bottom (Love *et al.*, 1983). Little is known at this time about the productivity of these algal mats, or about their ability to ultimately extract nutrients and trace metals from the lake waters.

Boswell *et al.* (1967) carried out the first reported work on trace metals in the lake. They determined six elements at an unspecified depth in the monimolimnion. Their results showed high concentrations of Zn ( $5400 \mu\text{g l}^{-1}$ ) and Fe ( $490 \mu\text{g l}^{-1}$ ). Masuda *et al.* (1982a) presented data on fourteen transition series and rare earth metals in unfiltered lake and (one) river samples and suggested pathways for their entry into the lake. These authors (Masuda *et al.*, 1982b) also presented a qualitative model for the observed iron profile and suggested that redox and diffusion processes in the zone between 55 and 60 m were important in establishing the iron gradient in the brine.

The present study departs from earlier investigations in considering the *dynamics* of metals in the lake and in providing a discussion of possible metal transport and scavenging mechanisms in this closed system.

## Collection and Analytical Methods

Water samples were collected near the major depression toward the western end of the lake on December 19, 1980, using a plastic sampler. For total metal analysis, lake waters were transferred into Nalgene (LPE), 1-liter bottles which had been soaked in 10% nitric acid for one week, in 1% ultrapure (Baker 'Ultrex') nitric acid for 24 hours, and then rinsed with distilled, deionized water and finally with several hundred milliliters of the sample itself. For dissolved metals, water was filtered immediately upon collection through leached  $0.45 \mu\text{m}$  pore size Millipore filters using a plastic, 3-liter, pressurized filtration apparatus. Five milliliters of ultrapure (Baker 'Ultrex') nitric acid were added to each 1-liter sample and bottles were tightly capped. Samples from the Onyx River were obtained weekly from below the spillway of the permanent v-notch weir constructed by the New Zealand Ministry of Works and located approximately 1 km upstream from the lake. These samples were treated in the same manner as those collected from the lake. Analyses were performed at Miami University.

sample were extracted into 10 milliliters of MIBK using APDC and DDDC as chelators, and citric acid and sodium citrate buffer to adjust the pH to about 5 (Kinrade & Van Loon, 1974). Back extraction of the Cu and Cd into 4 N nitric acid was used to insure a stable matrix. Analyses were performed on an IL 951 graphite furnace AAS. Procedural blanks for Cd were  $0.005 \mu\text{g l}^{-1}$  and for Cu  $0.05 \mu\text{g l}^{-1}$ . Detection limits for these elements were 0.002 and  $0.04 \mu\text{g l}^{-1}$ , respectively. Analysis for 'total' iron in the Onyx River could be accomplished without prior concentration. All manganese analyses for waters from the upper lake and from the Onyx River were performed using direct injection. No matrix effects were observed for this element under the conditions of the analysis. Mn in the brine was analyzed after 50 to 100-fold dilutions. Cu and Fe in the lake were determined using the APDC chelate coprecipitation method of Boyle & Edmond (1975). Blanks for the procedure were  $0.04 \mu\text{g l}^{-1}$  for Cu and  $0.1 \mu\text{g l}^{-1}$  for Fe. Extracted and coprecipitated values for Cu (see Table 2) were in reasonably good agreement with one another. Deuterium arc background correction was used for all four elements. Chloride concentrations in Figure 1

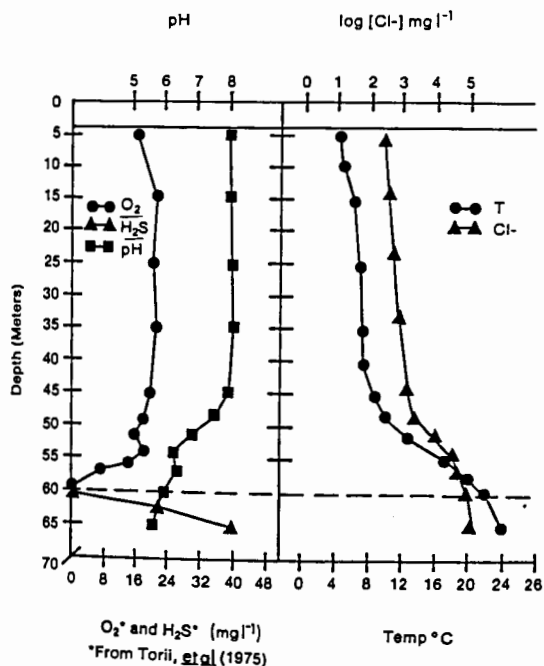


Fig. 1. Vertical profiles of significant chemical and physical parameters.

were measured by mercuric nitrate titration (APHA *et al.*, 1975), and pH values were obtained at the time of sampling with an Orion model 339A analyzer coupled with a 91-05 combination pH electrode.

### Computation of Residence Time

The concept of residence time, or the average time which an element spends in a given waterbody, has been used extensively by chemical oceanographers (e.g., Goldberg & Arrhenius, 1958; Brewer, 1975) for nearly two decades as an index of chemical reactivity in the seas. Vollenweider (1969) applied the concept to the behavior of phosphorus in lakes, and more recently Sonzogni *et al.* (1976) discussed the role of residence time models in lake management. The formalism that follows is based on the discussion by Sonzogni *et al.* (1976).

For a lake, or compartment thereof, which is treated as a mixed reactor, the following equation can be written to express the change in concentration of a chemical species as a function of time:

$$V \frac{dc}{dt} = \phi_i c_i - \phi_o c - kcV. \quad (1)$$

Here,  $V$  is the volume of the waterbody being modeled,  $\phi_i$  is the inflow rate,  $\phi_o$  is the rate of outflow,  $c_i$  is the average concentration of the species in the inflow, and  $c$  is its concentration in the waterbody. The term ' $kcV$ ' represents internal loss and is a measure of removal by biological uptake, sorption onto solid surfaces, flocculation, precipitation, and other biogeochemical processes.  $k$ , which has units of  $t^{-1}$ , is, in effect, a first-order removal rate constant.

Equation (1) can be simplified for a lake which is at steady state ( $dc/dt = 0$ ), and which has no outflow ( $\phi_o c = 0$ ). Under these circumstances the rate of inflow is equal to the rate of removal through internal loss alone; that is,

$$\phi_i c_i = kcV. \quad (2)$$

The residence time,  $t$ , is then defined as:

$$t = \frac{1}{k} = \frac{cV}{\phi_i c_i}. \quad (3)$$

In this study, annual loadings of Mn, Fe, Cu, and Cd were estimated by taking the average metal concentrations obtained during the 1980-81 flow season and then multiplying these by the average annual water input for the Onyx River. This latter value was obtained from the detailed hydrological studies of Chinn (1982) who has been recording Onyx River flows since 1969. The average input over this period was estimated to be  $2 \times 10^9 \text{ l a}^{-1}$  (Chinn, 1982).

The quantity of a metal in the lake between 4 m and 48 m depth was determined by multiplying the volume of successive conic sections, e.g., between 5 and 15 m, by the average of the unfiltered metal concentrations at these depths, and then summing over the entire lake between these depths. Conic section volumes were computed from the bathymetric map of Nelson & Wilson (1972). Conductivity, major ion, and selected trace metal data collected at sites approximately 1, 2, 3, and 4 km from the point of entry of the Onyx River showed that the chemical composition of the water at any particular depth was essentially constant regardless of location on the lake's ice surface.

## Results and Discussion

### Metal Concentrations on the Onyx River

Table 1 presents the mean concentrations of Mn, Fe, Cu, and Cd in the Onyx River during the 1980-81 flow season. For all samples, metal concentrations were in the order:

Fe >> Mn > Cu > Cd.

The average Mn concentration for filtered Onyx River samples ( $0.7 \mu\text{g l}^{-1}$ ) was considerably lower than the  $7 \mu\text{g l}^{-1}$  value reported by Li (1982) as typical of filtered river water worldwide. If particulate Mn is defined as the difference between the filtered and unfiltered concentrations, approxi-

mately 83% of the total influx of this element was associated with river-borne particles.

'Dissolved' iron concentrations ( $7.8 \mu\text{g l}^{-1}$ ) were also markedly lower than the figures given by Martin & Maybeck (1979) as typical ( $40 \mu\text{g l}^{-1}$ ) of world river water. On the average, 97% of the iron in the Onyx River occurred in the particulate form. Boyle (1979) measured Cu and Cd in the Amazon River and obtained dissolved concentrations of  $1.6 \mu\text{g l}^{-1}$  Cu and  $0.01 \mu\text{g l}^{-1}$  Cd. In the Onyx River, unfiltered Cu concentrations averaged only  $0.33 \mu\text{g l}^{-1}$ ; 28% of this element was in particulate form. Average cadmium levels ( $0.04 \mu\text{g l}^{-1}$ ) obtained in this study on the Onyx River were higher than those reported by Boyle (1979) for the Amazon ( $0.01 \mu\text{g l}^{-1}$ ).

Table 1. Mean concentrations for Mn, Fe, Cu and Cd in the Onyx River during the 1980-81 flow season. (All values are in  $\mu\text{g l}^{-1}$ .)

	Mn(U) <sup>b*</sup>	Mn(F) <sup>b**</sup>	Fe(U) <sup>b</sup>	Fe(F) <sup>b</sup>	Cu(U) <sup>a</sup>	Cu(F) <sup>a</sup>	Cd(U) <sup>a</sup>
Standard deviation	(±0.2)	(±0.1)	(±10)	(±0.5)	(±0.1)	(±0.1)	(±0.01)
Mean concentration	4.2	0.7	293	7.8	0.46	0.33	0.04
Number of samples	9	5	10	9	7	6	7
Range	3.0-5.6	0.4-1.0	230-420	1.5-14.5	0.4-0.6	0.2-0.4	0.01-0.07
Particulate fraction		84%		97%		28%	

\* (U) = unfiltered sample.

\*\* (F) = filtered through  $0.45 \mu\text{m}$  pore size filter.

<sup>a</sup> APDC-DDDC MIBK extraction, with  $\text{HNO}_3$  back extraction.

<sup>b</sup> Direct injection into furnace.

Table 2. Mn, Fe, Cu, Cd concentrations in Lake Vanda (67-meter site). December 1980. (All values in  $\mu\text{g l}^{-1}$ .)

Depth (m)	Mn(U) <sup>c</sup> (±0.1) <sup>d</sup>	Mn(F) <sup>c</sup> (±0.1) <sup>d</sup>	Fe(U) <sup>a</sup> (±0.2) <sup>d</sup>	Fe(F) <sup>a</sup> (±0.2) <sup>d</sup>	Cu(U) <sup>a</sup> (±0.1) <sup>d</sup>	Cu(F) <sup>a</sup> (±0.1) <sup>d</sup>	Cd(U) <sup>b</sup> (±0.01) <sup>d</sup>
5	0.6	0.7	3.4	0.9	2.2	0.7	0.06
15	0.2	0.2	8.3	1.3	1.7	0.8	0.05
25	0.5	0.5	6.3	2.3	0.7 (1.0) <sup>b</sup>	0.5	0.04
35	0.5	-	5.9	0.5	0.9	0.4	0.03
45	1.1	0.4	3.7	1.0	1.1 (1.3) <sup>b</sup>	0.8	0.05
48	3.4	3.3	3.5	0.7	1.1	0.9	0.04
51	130	140	<0.1	<0.1	3.1	1.8	0.17
54	350	400	3.7	0.9	3.4 (4.1) <sup>b</sup>	2.6	-
57	220	200	12.4	4.1	5.9	5.6	0.13
60	2000	2000	1040	960	10.2	0.8	0.07
65	3400	-	140	-	7.4	-	0.00
67	3400	3400	420	300	4.1	1.7	0.00

<sup>a</sup> Coprecipitation method.

<sup>b</sup> APDC-DDDC MIBK extraction, with  $\text{HNO}_3$  back extraction.

<sup>c</sup> Direct injection furnace (dilution of brine samples).

<sup>d</sup> Standard deviation based on triplicate injections of sample.

- = not determined.

## Metal Distributions in Lake Vanda

Table 2 lists the concentrations of Mn, Fe, Cu and Cd in filtered and unfiltered samples collected at the 67-meter site on December 19, 1980; the depth distribution of unfiltered metals is presented graphically in Figure 2. At all depths there was virtually no difference between filtered and unfiltered manganese concentrations. In the water column from 4 to 45 m, manganese was generally at the submicrograms per liter level. Below 48 m there was a marked rise in manganese concentrations, and this trend continued down to 65 m. This increase is a response to the falling pH and pe values observed in the lower, reducing waters of the lake. Brewer *et al.* (1975) noted similar behavior for manganese at the oxic/anoxic interface in the Black Sea.

Several aspects of the manganese profile deserve comment. Between 48 and 59 m, there is more than a 100-fold increase in concentration. This abrupt change occurs in a region of rapidly falling pH, where the formation of Mn(II) begins to be favored in the equilibrium with solid oxide phases:

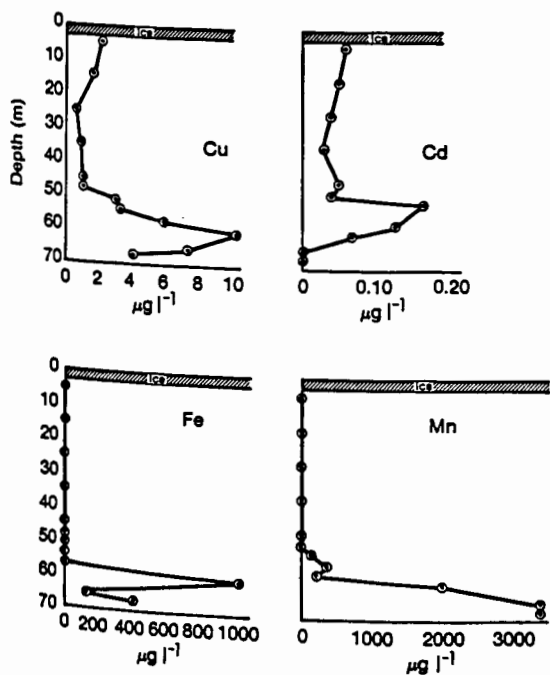
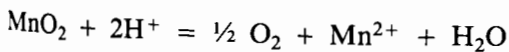


Fig. 2. Concentrations of (a) Cu; (b) Cd; (c) Fe; and (d) Mn with depth. All values are for unfiltered samples, collected December 19, 1980, at 67-meter site.

Between 57 and 60 m there is a further 10-fold increase in concentration, in response to the disappearance of molecular oxygen from the water column.

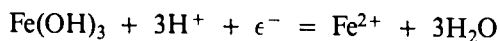
The manganese profile can be explained qualitatively in the following terms: Oxide phases formed in the upper region of the water column slowly settle into the sub-oxic and anoxic zones, where reduction and dissolution occur. Monimolimnetic manganese (II) is transported upward solely by diffusion where it precipitates as  $\text{MnO}_2$  at or above the oxic-anoxic interface. Thus, the observed profile is likely to reflect a complex set of diffusion, particle-settling, and redox processes.

It is possible to calculate whether the present manganese content of the brine below 48 m could have come entirely from recent Onyx River flow. From the concentrations in Table 1 and from the lake's bathymetry (Nelson & Wilson, 1972), the total mass of Mn in the volume between 48 and 67 m is  $1.0 \times 10^4$  kg. The present annual *total* manganese flux to the lake is  $8.2 \text{ kg a}^{-1}$ . Under present flow and loading conditions, it would have taken the Onyx River 2,300 years to deliver this much manganese to the deep depression of the lake, assuming that all of the stream load was transported 4 km from the mouth of the river and deposited within the above volume and not elsewhere in the lake. Since this is a liberal assumption, it must be concluded that there is considerably more manganese in the Vanda brine than could have been delivered by the Onyx River (assuming that present flow conditions are representative of the past) since the last filling event 1200 years ago. Much of the present manganese content of the brine may, therefore, be residual in nature and be left over from earlier concentration events. A similar conclusion was drawn by Canfield and Green (1985) concerning nitrogen, whose abundance in the brine suggests that much of it is a remnant of former lakes.

Iron concentrations in the upper waters of the lake ranged from  $3.4$  to  $8.3 \text{ µg l}^{-1}$ . The bulk of this was associated with suspended particles. The most dramatic feature of the concentration vs. depth profile is the large increase in iron which occurs at the zero oxygen boundary near 60 m. This peak, associated with the conversion of Fe(III) to soluble Fe(II) in this zone, is similar to the peak observed by Brewer *et al.* (1975) at the redox boundary in the Black Sea and by Jacobs and Emerson (1985) in

Framvaren Fjord, Norway. At 60 m in Lake Vanda some 92% of all iron exists in the 'dissolved' form. Below this depth there is a marked reduction in the total iron concentration. This can be attributed to the precipitation of ferrous sulfide phases.

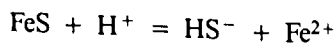
The origin of the iron profile has been discussed by Masuda, *et al.* (1982). Sinking  $\text{Fe}(\text{OH})_3$  particles encounter waters of low pH and  $p_e$ , and are reduced according to the half reaction:



Dissolved Fe(III), in the sub-oxic zone between 57 and 60 m, diffuses upward along a steep Fe-cline, and is oxidized at or above the 57-meter depth. Freshly precipitated hydrous oxide phases then form and resettle toward the anoxic zone.

Our profile shows, in addition, that below 60 m iron removal by sulfide formation is probably controlling the iron concentrations at these depths. At 65 m the ionic strength of the brine is approximately 2.8 M. If, for simplicity, we neglect ionpair formation and complexing and assume that we are dealing with a pure  $\text{CaCl}_2$  solution, and assume further that  $\gamma_{\text{Ca}^{+2}} = \gamma_{\text{Fe}^{2+}}$  and  $\gamma_{\text{Cl}^-} = \gamma_{\text{HS}^-}$ , then from Nesbitt (1984) we estimate that  $\gamma_{\text{HS}^-} = 0.5$  and  $\gamma_{\text{Ca}^{2+}} = 0.6$ .

Total dissolved sulfide at 65 m has been determined by Torii *et al.* (1975) to be  $1.2 \times 10^{-3}$  M.  $\text{Fe}^{2+}$  is  $2.5 \times 10^{-6}$  M and pH is 5.6 at this depth. Using  $\text{p}K_1 = 7.02$  for the dissociation of  $\text{H}_2\text{S}$ , the activity of  $\text{HS}^-$  is calculated to be  $4.5 \times 10^{-5}$  M. The ion activity product for the reaction



is then

$$\text{IAP} = \frac{4.5 \times 10^{-5} \times 2.5 \times 10^{-6} (0.6)}{10^{-5.6}} = 10^{-4.57} \quad (4)$$

While this value is less than the equilibrium constants for amorphous FeS and mackinawite, it is similar in magnitude to the more oxidized iron sulfide phase, greigite,  $\text{Fe}_3\text{S}_4$ . ( $K_{\text{eq}}$  values for these phases are  $10^{-3.05}$ ,  $10^{-3.64}$  and  $10^{-4.39}$ , respectively. These values are from Emerson *et al.*, 1982, recalculated from Berner, 1967).

Iron saturation with greigite has been observed in

other anoxic water bodies (Emerson *et al.*, 1983) and in marine sediment pore waters (Boulegue *et al.*, 1982; Canfield, unpublished data). Greigite, however, is still metastable with respect to pyrite and thus in Lake Vanda, as in sulfidic marine environments, iron is likely removed from solution as some iron sulfide phase and preserved in the sediments as pyrite.

Flux calculations indicate that the mass of iron contained in the monimolimnion below 48 m ( $7.8 \times 10^3$  kg) could have been delivered by the Onyx River (dissolved load) in roughly 400 years. Unlike manganese (and nitrogen), iron shows little evidence of accumulation.

Comparison of the manganese and iron profiles reveals that the Fe-cline develops at about 57 m in the water column, while the Mn-cline has an early onset at 48 m. The difference in the behavior of these two elements is a reflection of their different redox chemistries, and is consistent with the fact that manganese reduction occurs at somewhat higher (more oxidizing) potentials, and at higher pH values, than does the reduction of Fe. Details of the aqueous geochemistry of these elements can be found in Stumm & Morgan (1981).

In the upper waters, total Cu concentrations decreased from a high value of  $2.2 \mu\text{g l}^{-1}$  at 5 m to  $1.1 \mu\text{g l}^{-1}$  at 48 m. Across the major chemocline, there was a steep increase from  $1.1 \mu\text{g l}^{-1}$  to  $10.2 \mu\text{g l}^{-1}$  at 60 m, corresponding to the rapid increase in ionic strength between 48 and 60 m. At lower depths, where anoxic conditions occurred, copper concentrations decreased. For Cu the maximum in the concentration-versus-depth curve occurred near the oxic/anoxic interface, which marks the depth beneath which sulfide phases are being lost to the sediments. Similar Cu vs. depth trends showing Cu maxima followed by a reduction in copper levels below the zero oxygen boundary have been observed in the Baltic Sea (Kremling, 1983) and in Framvaren Fjord, Norway (Jacobs *et al.*, 1985).

It is possible to estimate the state of copper sulfide equilibrium in this system. Following the procedures of Emerson *et al.* (1983), polysulfides are assumed to be in equilibrium with dissolved sulfide in the lake's bottom waters, and copper is assumed to exist in the cuprous state. A filtered water sample was not taken at 65 m, but by comparison with values at 60 and 67 m an interpolated concentration of  $3.1 \times 10^{-8}$  mM is obtained for this depth.

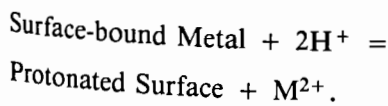
By allowing cuprous copper to exist in equilibrium with polysulfide and chloride complexes (see Emerson *et al.*, 1983, for a listing of stability constants), a concentration of 'free' copper can be obtained. With this value and the values for pH and the activity of HS<sup>-</sup> given earlier, the IAP for copper sulfide, based on the reaction:

$$\text{Cu}^+ + 1/2\text{HS}^- = 1/2\text{Cu}_2\text{S} + 1/2\text{H}^+,$$

$$\text{IAP} = \frac{(2.9 \times 10^{-15}) (0.5) (4.5 \times 10^{-5})^{1/2}}{(10^{-5.6})^{1/2}} = 10^{-14.2} \quad (5)$$

Since the equilibrium constant for chalcocite (Cu<sub>2</sub>S) is 10<sup>-17.35</sup>, it appears that sulfidic Vanda bottom waters are supersaturated with respect to even the most soluble copper sulfide phase, chalcocite. Given this rough calculation and the vertical profile in Figure 2, deposition of sulfide phases is probably an important control on copper in the system.

Cadmium was present at much lower concentrations in Lake Vanda than any of the other metals. Like copper, its concentration with depth decreased initially, and then began to increase in the increasingly saline waters below 50 m. There is a somewhat shallower maximum in the cadmium profile and this suggests that cadmium, bound to the surface of sinking particles (possibly Fe and Mn oxides) may be released earlier than copper to the deep waters of the lake. Both copper and cadmium maxima may be the result of surface reactions of the type:



In this connection, it seems significant that the cadmium maximum occurs in a region characterized

by rapidly declining pH values and increasing chlorinity, coinciding with the rapid increase in dissolved Mn concentrations. Desorption and resulting chloride complexation of the free metal ion or release from dissolving particulate oxide phases could account for the significant metal buildup observed at 51 m. The vertical profile for Cd suggests that, from this level in the water column, cadmium is transported both upward and downward by diffusion. Its encounter with sulfide in the anoxic zone probably results in its ultimate removal to the sediments. Estimates of the state of cadmium saturation will not be attempted due to the uncertainties in the magnitudes and even forms of reduced sulfur complexes with cadmium (see Jacobs *et al.*, 1985, for discussion).

It is interesting, in light of the work of Bruland (1980) on metal-nutrient covariance in the central gyre of the Pacific, to note that copper and cadmium appear to exhibit depth profiles in the upper waters of Lake Vanda which are similar to the upper lake nitrate profile reported by Canfield & Green (1985). This suggests that the distribution of these metals may be linked to carbon and nutrient cycles and that Cu and Cd may undergo similar recycling in the waters of the upper lake. Further work on this question needs to be carried out.

#### Residence Times and Removal Mechanisms

Residence times were computed in two ways: (1) from average values for filtered river samples; and (2) from average values for unfiltered samples. Following Raspor (1980), it was assumed that all available cadmium in the river was present in the dissolved form. Total metal content was determined for the upper waters between 4 and 48 m. The data are summarized in Table 3.

Table 3. Influxes, upper water content, and residence times for Mn, Fe, Cu and Cd in Lake Vanda.

Element	Annual load total metal (kg a <sup>-1</sup> )	Dissolved load (kg a <sup>-1</sup> )	4-48 meters content (kg)	Residence time (a) from dissolved load	Residence from total load	Oceanic residence time*
Mn	8.2	1.4	77	55	9.4	8.9 × 10 <sup>2</sup>
Fe	585	18	830	47	1.4	1.8 × 10 <sup>3</sup>
Cu	1.1	0.81	192	237	174	2.4 × 10 <sup>3</sup>
Cd	0.08	0.08	6.6	82	82	1.8 × 10 <sup>4</sup>

\* Values taken from Martin and Whitfield (1983).

There are few standards against which the residence times reported here can be compared. In one of the few studies on this subject, Imboden *et al.* (1981) examined the dynamics of metals in Greifensee, a Swiss lake having a volume only slightly smaller than Lake Vanda, and they obtained residence times for Cu and Cd (by our calculations from their data) of 0.2 and 0.5 years, respectively. Sonzogni *et al.* (1976) tabulated residence times for the biologically active element phosphorus in 17 lakes in Europe and North America, and found values between 0.3 and 6 years. For nonconservative trace elements, residence times in freshwater lakes appear to range from a fraction of a year to several years at most. In Lake Vanda, by contrast, residence times, as calculated from unfiltered samples, span a range from 174 to 1.4 years, in the order:

Cu >> Cd > Mn > Fe.

There are several possible factors contributing to the longevity of nonconservative elements in this closed-basin waterbody:

1. There is no outflow to physically transport suspended and dissolved materials out of the lake. Ice formation and sublimation, which are the principal mechanisms for achieving hydrologic balance in this system, exclude ion uptake and cannot be significant in the trace metal budget of the lake.

2. The permanent, four-meter ice cover permits virtually no wind-driven mixing of water and sediments, thus reducing metal uptake by sorption onto deposited sediments.

3. The Onyx River flows for only two months. For the remainder of the year no sorbing particles are being delivered to the lake from the watershed.

4. The most important consideration, perhaps, is the low productivity of the lake. In an oligotrophic waterbody (other factors being equal), scavenging of metals by plankton should be lower than in lakes of a higher trophic state. It is useful to estimate the significance of the role which phytoplankton in Lake Vanda might play as scavenging agents for trace metals. To do this the following assumptions are made: The growing season is 135 days long; the depth-average carbon uptake rate of  $0.04 \text{ mg C m}^{-3} \text{ d}^{-1}$  measured by Parker *et al.* (1982) is constant over this period and over the upper lake volume; metals are concentrat-

ed by Lake Vanda phytoplankton to the same degree as reported by Martin & Knauer (1973) for marine phytoplankton; and once a metal atom is fixed in a phytoplankton cell it is removed from the upper lake, without regeneration. Using this model, the annual scavenging rate for manganese is calculated as follows:

$$\text{Rate} = 15.7 \times 10^7 \text{ m}^3 \times \frac{0.04 \times 10^{-3} \text{ g carbon}}{\text{m}^3 \text{d}} \times$$

$$\frac{135 \text{ d}}{a} \times \frac{6.1 \times 10^{-3} \text{ gm}}{\text{Mn}} \times \frac{\text{g phytoplankton}}{\text{g phytoplankton}} \times$$

$$\frac{1 \text{ g phytoplankton}}{0.264 \text{ g C}} \frac{0.5 \mu\text{g l}^{-1} \text{ Vanda Mn}}{0.2 \mu\text{g l}^{-1} \text{ ocean Mn}} \quad (6)$$

Even though the model is somewhat biased in favor of phytoplankton scavenging (a 135-day growing season and zero regeneration are liberal estimates), the calculation shows that only 0.04 kg of Mn could be lost from the upper lake in this way. Since the annual Mn loss (based on the dissolved metal flux) is 1.4 kg, phytoplankton scavenging could account for only 2.8% of the removal. Similar calculations were performed for Fe, Cu and Cd. Marine Mn, Fe, Cu and Cd concentrations were taken from Martin & Whitfield (1983). Since these are average marine values, they are probably somewhat lower than the actual concentrations to which Martin & Knauer's (1973) organisms were exposed in Monterey Bay, California. This fact also tends to bias the calculation toward higher scavenging rates.

Comparison of columns 2 and 3 in Table 4 shows that for all four metals the amount of removal that can be attributed to phytoplanktonic scavenging is only a small fraction of the actual steady state loss. From Table 4 the phytoplankton are likely to play a more significant role in the scavenging of cadmium than they play in the removal of the other metals, but even for Cd maximum removal by this mechanism is only about 26% of the total loss. Given the assumptions of the model, it appears that in this highly oligotrophic lake, metal removal by phytoplankton is not the dominant process controlling residence times and lake concentrations, although in the case of Cd and Cu vertical profiles may be determined by planktonic scavenging and regeneration in the upper lake.



Table 4. Estimated maximum biological removal of metals from upper lake compared with total removal.

Column 1 Metal	Column 2 Maximum biological removal per year (kg)*	Column 3 Steady state loss per year = Onyx River 'dissolved' influx (kg)	Column 4 Maximum percent loss due to biological scavenging
Mn	0.04	1.4	2.8
Fe	1.8	1.8	10
Cu	0.07	0.81	8.6
Cd	0.021	0.08	26

\* Calculated from equation (7) using phytoplankton metal concentrations of  $6.1 \times 10^{-3}$  mg g<sup>-1</sup> for Mn;  $3.2 \times 10^{-3}$  for Cu;  $1.5 \times 10^{-3}$  for Cd; and  $224 \times 10^{-3}$  for Fe; and metal seawater concentrations of  $0.2 \mu\text{g l}^{-1}$  for Mn, 2.0 for Fe, 0.1 for Cu, and 0.01 for Cd. Average upper lake concentrations for Lake Vanda were used in equation (7).

Precisely how the concentrations of these four metals are controlled is a matter for speculation. Since a significant fraction of riverine Fe and Mn exists in particulate form it is likely that much of the annual load of these elements is lost in the shallow 'estuary' where the Onyx River enters the lake, simply by the mechanical process of particle settling. Also in this nearshore area, which is characterized by oxygen supersaturation and by a relatively high pH (approximately 8, one pH unit higher than the river), some conversion of freshly weathered Mn(II) and Fe(II) to hydrous oxide phases must be occurring. This process would contribute further to Mn and Fe loss from the lake.

A significant locus for the removal of Cu may be the anoxic zone. From Table 2 the copper gradient between 57 and 60 m is estimated to be  $2.4 \times 10^{-13}$  moles cm<sup>-4</sup>. Using a diffusion coefficient of  $7 \times 10^{-6}$  cm<sup>2</sup> sec<sup>-1</sup> and the area of the lake's 60 m contour, the flux of Cu into sulfide-bearing waters is calculated by Ficks law to be:

$$2.4 \times 10^{-13} \text{ moles cm}^{-4} \times 1.3 \times 10^{11} \text{ cm}^2 \times 7.6 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1} \times 3.15 \times 10^7 \text{ sec a}^{-1} = 7.5 \text{ moles} = 0.48 \text{ kg a}^{-1}. \quad (7)$$

This loss is roughly one half of the 'dissolved' Cu flux to the lake.

A similar calculation for Cd shows that only an estimated  $0.005 \text{ kg a}^{-1}$  is lost to the anoxic zone by diffusion. Since this represents a small fraction of the annual Cd load ( $0.08 \text{ kg a}^{-1}$ ), another sink for this element must exist. In this connection, Love

*et al.* (1983) have recently reported on the existence of an extensive benthic algal mat in Lake Vanda, consisting largely of the prokaryotic filamentous blue-green algae *Phoridium frigidum* and *Lyngbya martensiana*. While these mats do not exhibit lift-off like the mats of other Antarctic lakes, they could still serve as effective 'traps' for the dissolved metals being circulated across their surfaces. Assuming a mat area of 3 km<sup>2</sup>, steady state concentrations of Cd could be maintained in the water column by an uptake rate of only  $27 \times 10^{-10} \text{ g cm}^2 \text{ a}^{-1}$ . Also, microzones of high oxygen tension and high pH in the vicinity of these mats could promote deposition of iron and manganese hydrous oxide phases and the consequent sequestration of other metals by sorption.

We suspect, then, that several geochemical and biogeochemical processes determine the fates of metals in this closed-basin lake:

1. The bulk of the Fe and Mn flux is lost in the Vanda 'estuary' as a result of particle settling.

2. A significant fraction of Cu is lost by diffusion to the anoxic zone, where it is ultimately sequestered as sulfides.

3. Vertical transport of metals on particle surfaces is likely to be important both in establishing water column profiles and in contributing to metal removal to the sediments.

4. Uptake on the surfaces of benthic algal mats may constitute a major sink for some metals (e.g., Cd).

It is clear that particle trap studies would be useful in further exploring these processes.

Certain useful comparisons can be made between residence time trends in closed-basin lakes

and in the oceans. Residence time data taken from Martin & Whitfield (1983) show that manganese and iron have shorter ocean residence time than cadmium and copper (see Table 3). The iron residence time reported by these authors, however, is considerably larger than that given by Broecker & Peng (1982), who report a value of 54 years. Brewer's (1975) estimate is 200 years for this element. Available data seem to suggest that these two transition elements (Fe and Mn) are rather rapidly scavenged from seawater. Broecker (1982), in fact, has compared their behavior to thorium and lead, whose average lifetimes in the sea are among the shortest known.

In ecosystem studies carried out by Santschi and his colleagues (reported in Broecker & Peng, 1982), sorption and removal of metals were studied under conditions simulating Narragansett Bay. The study showed that Fe, Pb, Po, Th, Pa, and Pu were most rapidly removed (half removal time = 10–20 days); Mn and Co were intermediate (30–50 days); and Cd, Zn, and Se were removed from the tanks most slowly (60–100 days).

The removal trends in these studies are in agreement with our observations in Lake Vanda, where Fe has the shortest residence time; Mn is intermediate; and Cd (of these three elements) has the longest residence time. Once enough systems have been studied in sufficient detail it would not be surprising to learn that in oxic waters near pH = 8, the order of metal residence times is constant from one system to another.

The importance of dissolved oxygen in establishing residence time trends has been underscored by the recent work of Canfield *et al.* (1984). Their study on a seasonally anoxic, open-basin reservoir showed that the residence times of iron and manganese were considerably longer than those of even the conservative elements sodium and chloride—a marked departure from expectations based on metal behavior in the oceans. The long residence times of these metals were attributed to sediment regeneration during summer anoxia and to subsequent recycling with lake overturn.

One further note of comparison between closed-basin lakes and the oceans centers on the degree of solute fractionation which occurs in their waters. Concentrations of major ions (Green & Canfield, 1984), nutrients (Canfield & Green, 1985), and trace elements at 48 m in Lake Vanda range over

nearly eight orders of magnitude ( $1.6 \text{ gl}^{-1} \text{ Cl}$  to  $10^{-2} \mu\text{g l}^{-1} \text{ Cd}$ ), which is comparable to the range of concentrations observed in the ocean. This illustrates again the extraordinary reactivity of trace metals vis-a-vis the major elements in closed systems.

From the foregoing, we suspect that it will be useful in future studies to emphasize the similarities between marine and closed-basin lake systems and to use our understanding of one to illuminate processes in the other. Residence time could conceivably provide an important conceptual link between ocean and lake environments.

## Conclusions

While the residence times of Mn, Fe, Cu, and Cd in Lake Vanda are longer than residence times reported for open-basin systems, it is clear that the concentrations of these elements are being regulated by various biogeochemical processes. Model calculations suggest that in this oligotrophic system, ultimate metal removal by phytoplankton can account for only a small fraction of the annual metal lost from the waters of the upper lake (above 48 m). It is postulated that particle settling of Mn and Fe oxides in the Vanda 'estuary' may be the most important sink for these elements.

Upper lake water column profiles for Cu and Cd indicate that the distribution of these elements may be linked to the distribution of nutrients in this region. Rough equilibrium calculations for Fe, and Cu in the Vanda brine show that the concentrations of these metals are being regulated, in part, by formation of insoluble sulfide phases. Cu, moreover, appears to be lost to the anoxic zone by diffusion and ultimately precipitation of metal sulfides. The large store of manganese in the lake's brine indicates that this element has either been concentrated during past evaporation cycles or has been regenerated from anoxic sediments.

In their processing of riverine metal loads and in their general fractionation of solutes, closed-basin lakes appear to share a number of similarities with the world oceans. It is argued that residence time may provide an important conceptual link between the two types of systems.

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