

## Processes leading to the seasonal variation of the cycling of iron and manganese in a meromictic lake

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The north basin of Lake Lugano (Ticino, Switzerland), with a maximum depth of 288 m, is permanently stratified below 100 m. This stratification separates the basin in an oxygenated layer above 80 m, a suboxic layer between 80 and 100 m and an anoxic layer below 100 m. Anthropogenic eutrophication during the twentieth century resulted in high oxygen consumption in the bottom waters, a progressive build-up of the permanent stratification of the lake, and, concurrently, the build up of an intense cycle of manganese and iron. Reduced species accumulate in the anoxic zone whereas precipitation of oxyhydroxides occurs in the suboxic zone, the water layer between the inflection point of the dissolved oxygen curve and the depth at which  $\text{HS}^-$  is first detected. Precipitation of oxyhydroxides is depth i.e. Eh dependent, the Mn peak develops around 80 m and the Fe peak around 90 m. These depths are subject to some variation in relation with internal waves. Redox processes have been extensively studied in lakes, especially in seasonally anoxic settings (see Davison, 1993, for review). The permanent stratification and the great depth of Lake Lugano north basin make this site particularly interesting for the study of the oxic-anoxic interface zone. We investigated this interface from June 1992 to January 1994 (period I) and again from December 1995 to June 1996 (period II). A major pattern was the precipitation of Fe- and Mn-oxyhydroxides reaching a maximum intensity during spring. This was first observed during period I. Due to its unique character and to its significance for the cycling of certain nutrients ( $\text{PO}_4^{3-}$ : Monnerat *et al.*, 1998), the process was more closely investigated during period II. Possible processes responsible for

this spring peak may range from bio- chemical to hydro-chemical.

### The bio-chemical processes

Trap sediments were deployed during period I at 5 depths covering the whole watercolumn. At the trap levels closest to the redox interface zone (90 m, 130 m) the sedimentation fluxes of oxyhydroxide-Fe and -Mn showed a clear spring peak with a maximum in April. Fluxes were strongly correlated to fluxes of phytoplanktonic detrita (diatomaceous organic matter, biogenic silica from frustules) related to the first planktonic bloom following the winter period of low production (Fig. 1). The strong correlation between these fluxes suggests a link between settling diatoms (Hofmann *et al.*, 1998) and the increase of oxyhydroxide precipitation. Bacteria are known to increase the Mn oxidation rate by more than one order of magnitude (Hastings and Emerson, 1986). Fe-oxyhydroxides have been observed to precipitate massively on polysaccharide fibrils (Lienemann, 1997). The fresh phytoplanktonic material may represent an ideal nucleation site for Fe- and Mn-oxyhydroxides. As the phytoplanktonic material settles at high speeds (estimated at  $8 \text{ m d}^{-1}$ ) due to its association in flocs (Hofmann *et al.*, 1998), the metal oxyhydroxides may be entrained to reducing water layers within 1–2 days, thus bypassing the much slower precipitation-coagulation-sedimentation pathway usually observed (Laxen and Chandler, 1983). The rapid sedimentation may lead to an initial increase of dissolved species in the source layers of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  and result in higher upward-fluxes of the two ions into the suboxic zone, thus

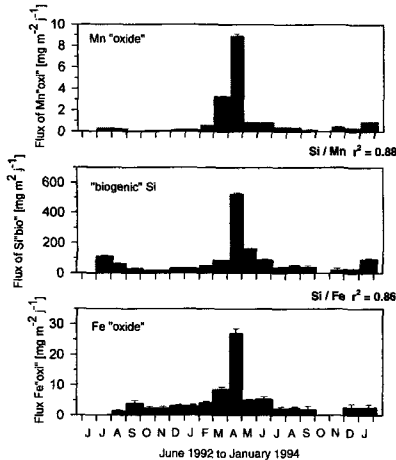


FIG. 1. Fluxes of Fe<sup>3+</sup>oxide, Mn<sup>2+</sup>oxide and "biogenic" Si in sediment traps directly underlying the precipitation peaks (90m, respectively 130 m depth). Adapted from Hofmann (1996).

provoking peak precipitations of Fe- and Mn-oxhydroxides.

### The hydro-chemical dynamics

Although the lake is meromictic, hydrodynamic processes may play a role in the specific evolution of the Fe- and Mn- redox cycles. The winter mixing of the surface layer generally reaches a maximum of 50–60 m depth around end of February-beginning of March. The mixing process increases the oxygen concentration at 60 m from a mean value of 4 mg l<sup>-1</sup> between late spring and early winter to about 6 mg l<sup>-1</sup> between March and May. During the period of maximal mixing, around February/March, the temperature is practically homogeneous throughout the watercolumn and the lake stratification is only maintained by the chemical gradient of dissolved species. As a consequence, the downward diffusion of oxygen is facilitated during this period, resulting in an increase of the inventory of dissolved oxygen below 60 m depth. Field data show that the dissolved oxygen inventory between March and May doubles the annual average. Concentrations of dissolved oxygen in the suboxic layer vary accordingly. Mean values change from 5–30 µg l<sup>-1</sup> in late autumn and early winter to 70–190 µg l<sup>-1</sup> during increased mixing in late winter/early spring. This variation can significantly increase the oxidation rate constant for Mn<sup>2+</sup> (Morgan, 1967) and Fe<sup>2+</sup> (Liang *et al.* 1993). Another oxidative process important for Fe precipitation is the reduction of Mn oxides by Fe<sup>2+</sup>. As higher

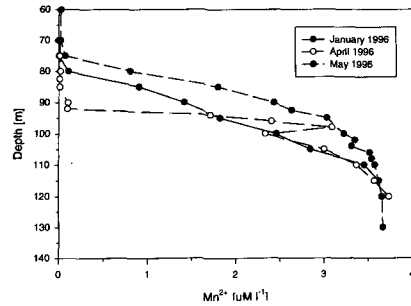


FIG. 2. Concentration profiles for Mn<sup>2+</sup>. Depths are corrected for profile shifts due to the internal wave.

concentrations of MnO<sub>2</sub> sediment towards the depth of Fe-oxidation, this secondary redox process may increase Fe-precipitation as well.

If the downward diffusion of oxygen is more efficient during the late winter/early spring period of low hydrodynamic stability, then this may lead to chemical erosion of the suboxic/anoxic boundary implying a lowering of the base of the suboxic zone. Field data show that 5–10 m can be eroded in this way (Fig. 2). As a consequence, the enlarged suboxic zone will engulf a pulse of oxidizable Mn<sup>2+</sup> and Fe<sup>2+</sup>. Oxidation of this new source could contribute to the observed peaks of Fe- and Mn-oxhydroxides. As precipitation takes place, the concentration gradients of dissolved species are steepened (Fig. 2) leading to higher fluxes of Mn<sup>2+</sup> and Fe<sup>2+</sup> and again feeding the oxidation process.

In conclusion, bio-chemical and hydro-chemical dynamics seem to be both involved in the seasonal variation of the Fe- and Mn-redox cycling in the north basin of Lake Lugano. The dominant process will be determined and quantified with the aid of CHEMSEE, a mathematical model for the simulation of bio-chemical processes in lakes. The coincidence of inputs of oxygen- and organo-mineral particles to the suboxic layer may have a synergetic effect that makes the seasonal variation of the Fe/Mn cycle characteristic for this lake basin.

### References

- Davison, W. (1993) *Earth-Science Rev.* **34**, 119–63.  
 Hastings, D. and Emerson, S. (1986) *Geochim. Cosmochim Acta* **50**, 1819–24.  
 Hofmann, A. Filella M. Lallier-Vergès E. Simona M. Druart and J. C. Dominik J. (1998) *Submitted to Limnol. Oceanogr.*  
 Laxen, D.P., and Chandler, J.M. (1983) *Geochim. Cosmochim. Acta* **47**, 731–41.