

## Scavenging of phosphorous by the 'ferrous wheel' in the northern basin of Lake Lugano (Switzerland/Italy)

M. Monnerat	Institut F.-A. Forel, Université de Genève, 10 rte de Suisse, CH-12900 Versoix, Switzerland
J.-C. Lienemann	Institut de Chimie Minérale at Analytique, Université de Lausanne, BCH, CH-1015 Lausanne, Switzerland
F. Zamboni	Laboratorio di fisica terrestre, ICTS Lugano-Trevano, 6952 Canobbio, Switzerland
D. Perret	Institut de Chimie Minérale at Analytique, Université de Lausanne, BCH, CH-1015 Lausanne, Switzerland
J. Dominik	Institut F.-A. Forel, Université de Genève, 10 rte de Suisse, CH-12900 Versoix, Switzerland

Since the classic works of Einsele (1938) and Mortimer (1941) the coupling of the iron and phosphorous cycles in seasonally anoxic lakes has been recognised. In permanently stratified lakes the existence of a large phosphorus reservoir in anoxic water and the presence of steep concentration gradients lead to a strong upward diffusion fluxes during the whole year. As soon as the dissolved iron(II) reaches the oxic layers, it precipitates as oxihydroxides, scavenging a fraction of dissolved phosphorous. Although the concept of cycling of the iron-phosphorous couple is well understood, only few studies examined quantitatively its transport across the oxycline in meromictic lakes.

Lake Lugano is a large (47.8 km<sup>2</sup>), eutrophic (mean total P content 140 µg/L), hardwater lake located in the southern flanks of the Alps at the Swiss-Italian border. Permanently stratified, deep (max. depth 288 m) northern basin developed an oxycline at about 100 m water depth. The reactive phosphorous content in the anoxic part of the hypolimnion is 220 µg/L and it constitutes a potentially important internal source of bioavailable phosphorous (inventory of about 500 t) for the productive zone. Total (particulate + dissolved) phosphorous input to the basin has been reduced from 144 t/y in 1976 to less than 20 t/y in 1993. (CIPAIS, 1996). We estimate that about 30% of the input is in the form of apatite-P and 70% in the potentially bioavailable forms (soluble + particular organic and non-apatitic P). Thus the total amount of reactive phosphorous in anoxic hypolimnion is about 35 times higher than annual load of potentially available phosphorous from the watershed. It is thus important to quantify the flux of reactive phosphorous across the oxycline, which depends essentially on vertical

diffusion and on phosphorous scavenging by iron oxides precipitating at the oxycline. In this paper we attempt to quantify the fraction of the upward diffusing phosphate which is scavenged by the 'ferrous wheel'. We also discuss the impact of this process on the trophic status of the lake.

### Sampling and analytical methods

Water samples were taken monthly from December 1995 through June 96 from the depth interval 60 to 120 m at a station off-shore from the village Gandria, near the deepest point of the northern basin. Water samples were collected using a PVC tubing lowered to the appropriate depth and a peristaltic pump (Watson-Marlow 701S/R). Raw samples were collected directly from the tube outlet, filtered samples were obtained from an array of filters with nominal porosity of 0.45 µm.

Ferrous iron and orthophosphate were determined in duplicates for each water fraction (raw, filtered) colorimetrically using the ferrozine method and molybdate blue method, respectively. Particulate iron retained on 0.45 µm membranes was determined after digestion in hot HNO<sub>3</sub> 65% with an ICP-OES (TJA POEMS). Inorganic phosphorous on membrane was extracted with 1 M HCl according to Williams *et al.* (1976) and measured by colorimetry.

### Results and discussion

Concentrations of dissolved phosphorous are much larger than those of iron. Particulate Fe and P show distinct maxima at the same depth corresponding to the suboxic zone (fig. 1). Molar PO<sub>4</sub>/Fe ratios in

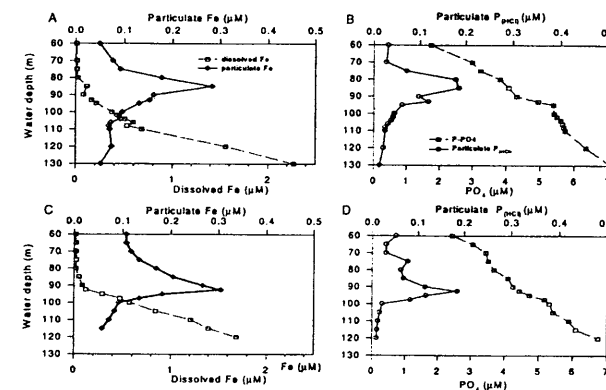


FIG. 1. Typical particulate (filter retained) and dissolved (filtrate) Fe and P concentration profiles from March (C,D) and May (A,B) at the redox interface in the northern basin of Lake Lugano. P<sub>(HCl)</sub> represents inorganic fraction of particulate phosphorous.

particles retained on filters show a large variability with an average value of  $0.54 \pm 0.58$ . The TEM-EDS determination on individual particles or aggregates of iron hydroxides has shown similar but very constant ratio of  $0.50 \pm 0.11$  (Lienemann *et al.*, 1998), suggesting a stoichiometric incorporation of phosphate from solution. Fe(II) and PO<sub>4</sub> concentration gradients in the upper part of the anoxic zone are variable in time but, on average fairly comparable, and thus the fluxes to the suboxic zone should be similar. As Fe(II) concentrations in filtered oxic water above the redox interface fall close to zero we can assume that the totality of upward diffusing iron precipitates in the suboxic zone. Further, we assume the same downward transport dynamics (settling) for the two elements associated in the form of Fe-P hydroxide aggregates with the molecular PO<sub>4</sub>/Fe ratio of 0.5. Thus about 1/2 of the PO<sub>4</sub> flux from the anoxic hypolimnion to the suboxic zone is scavenged by the precipitating iron hydroxides.

Alternatively, we calculate the phosphorous transport from the temporal evolution of PO<sub>4</sub> concentration profiles in anoxic and oxic zones. Although the eddy diffusion coefficients are not precisely known for the depth interval 70–120 m, and probably they vary both in time and space, our rough estimations indicate that in the period of measurements about 50% of PO<sub>4</sub> flux from anoxic hypolimnion is scavenged in the suboxic zone. This percentage varies strongly from 10 to 80% in the period between December and June. These variations depend largely on the intensity of iron cycling which seems to be the highest in spring. The possible reasons for the seasonal variations of iron and

manganese cycling are discussed in a separate paper (Hofmann *et al.*, this volume).

### Conclusions

The present study shows that iron cycling at the redox interface of the deep, meromictic, northern basin of Lake Lugano plays a significant role in phosphorous transport across the interface. Although the Fe(II) concentration in Lake Lugano is relatively low, the high P/Fe ratio in precipitating hydroxides combined with a fast overturn provide an efficient barrier for the phosphorous transport into the surface waters. In the period of decreasing external input of phosphorous, this may be of importance for the total input of bioavailable phosphorous into the epilimnion.

### References

- CIPAIS (1996) *Commissione Internazionale per la Protezione delle acque italo-svizzere*, pp. 109.
- Einsele, W. (1938) *Arch. Hydrobiol.*, **33**, 361–87.
- Hofmann, A., Monnerat, M., Lienemann, C.-H., and Dominik, J. (1998) Process leading to the seasonal variation of the cycling of iron and manganese in a meromictic lake. *this volume*.
- Lienemann, C.-P., Monnerat, M., Dominik, J. and Perret, D. (1998) Stoichiometric phosphorous scavenging by autochthonous iron colloids in a eutrophic lake. *Aquatic Sci.*, in press.
- Mortimer, C.H. (1941) *J. Ecol.*, **29**, 280–329.
- Williams, J.D.H., Jaquet, J.-M. and Thomas, T.L. (1976) *J. Fish. Res. Board. Can.*, **33**, 413–29.