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

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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 oxi-hydroxides, 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^2), 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) phosphorus 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 phosphorus 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_3 65% with an ICP-OES (TJA POEMS). Inorganic phosphorus 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_4/Fe ratios in

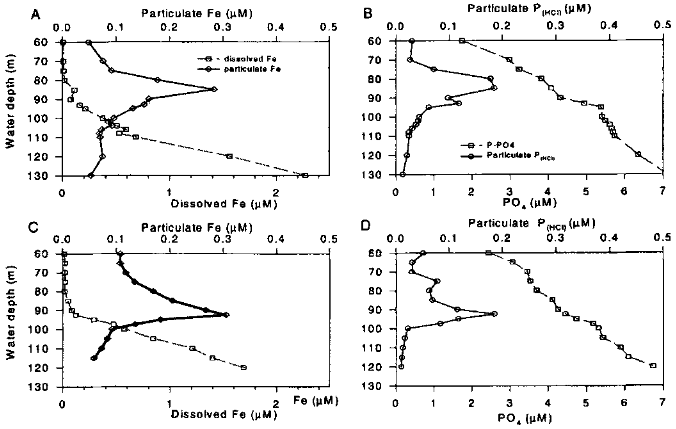

FIG. 1. Typical particulate (filter retained) and dissolved (filtrate) Fe and P concentration profiles from March (C,D) and May (A,B) at the redox interface in the northern basin of Lake Lugano. $P_{(HCl)}$ represents inorganic fraction of particulate phosphorous.

particles retained on filters show a large variability with an average value of 0.54 ± 0.58. The TEM-EDS determination on individual particles or aggregates of iron hydroxides has shown similar but very constant ratio of 0.50 ± 0.11 (Lienemann *et al.*, 1998), suggesting a stoichiometric incorporation of phosphate from solution. Fe(II) and PO_4 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_4/Fe ratio of 0.5. Thus about 1/2 of the PO_4 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_4 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_4 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.

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