

Redox- and mixing-dependent phosphorus fluxes in permanently density stratified anoxic natural water

Ch. Mattenberger
A. Wüest
M. Sturm
G. Goudsmit

Swiss Federal Institute for Environmental Science and Technology (EAWAG) and Swiss Federal Institute of Technology (ETH), CH-8600 Dübendorf, Switzerland

A. Barbieri

Laboratorio di Studi Ambientali, CH-6900 Lugano-Paradiso, Switzerland

Lake Lugano (northern subbasin) is a permanently density stratified perialpine lake in the southern Swiss Alps. Wind protection due to the mountainous environment and the great depth of about 300m are the reasons for reduced mixing, low deep water renewal rates and anoxic conditions below 80 m depth. Consequently, during the last 20 years a slow accumulation of salts and nutrients has occurred in the deep water and in the sediments. Steady-state physical and geochemical conditions allow to study diffusive fluxes and particular phosphorus cycling responding to changes of the external forcing occurring on medium time scales (15 years). Measurements of nutrients in the sediments and the water column have been carried out in order to determine rates of diffusive fluxes. Using a SeaBird CTD profiler, temperature, conductivity and oxygen

were measured to quantify mixing rates.

Mass fluxes and mixing

The external total phosphorus (P_{tot}) balance of the lake (1-box model) including export and net sedimentation (Table 1) allows to determine P input. Phosphorus input has decreased since the wastewater purification plant came under operation in 1979. Only periods of high precipitation and runoff (1992-1995) show increasing input and deposition of particulate P.

The internal balance (Fig. 1), including vertical diffusion (Imboden, D.M. *et al.* 1995, Aeschbach-Hertig, W. *et al.* 1996), reveals the importance of the redox cycle and of the role of convective mixing during winter. Since 1986 the maximal mixing depth has been decreasing and as a result water

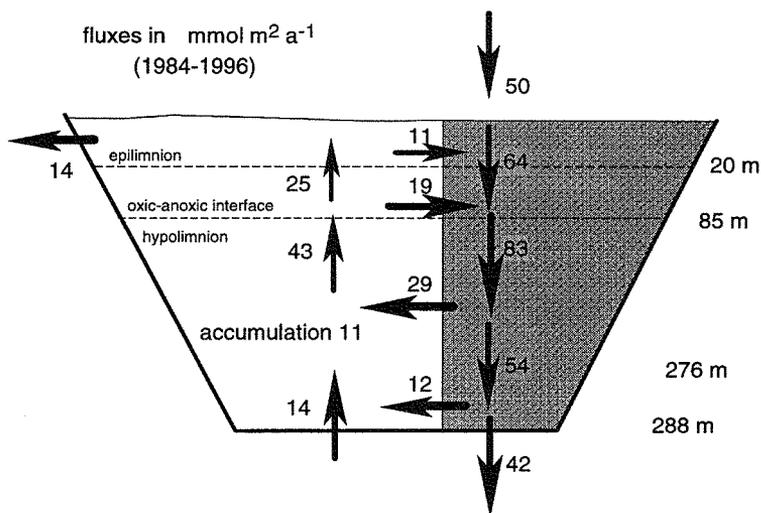
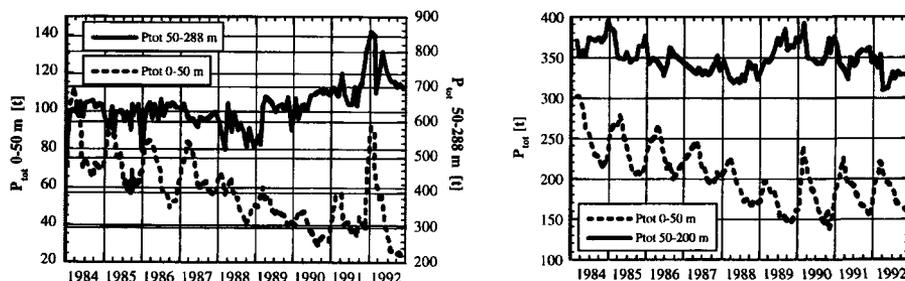


FIG. 1. Internal mass fluxes [$\text{mmol m}^{-2} \text{a}^{-1}$] of particulate (shaded) and dissolved P-species according to a 4-box model (for box limits see the inserted depths).


 FIG. 2. Bulk inventories of P_{tot} in Lake Lugano (left) and Lake Zug (right).

exchange with the hypolimnion due to winter convection has been gradually decreasing as well. Consequently, the contents of both phosphorus and heat is increasing in the permanently stratified layers during this time. P_{tot} is accumulating by 1.5% per year (see Fig. 2). In contrast, the P inventory in the epilimnion decreased since 1986 as a consequence of reduced P input.

Redox cycle

Internal mass balances calculated using a 4-box model (Reichert, 1994) show enhanced inner cycling driven by redox reactions within the water column (Fig. 1). 30% of the upward diffusing P is trapped by adsorption mainly onto iron oxyhydroxides, trans-

porting and eliminating P to deep water and to the sediment surface. Light transmission as well as particle analysis show distinct peaks of manganese and iron oxide formation at the oxic-anoxic interface (Davison, W. 1985; Murray, J.W. 1987). Sorption of nutrients is linked to the process of oxidation. Comparison of fluxes of dissolved P between the boxes reveals a decrease of $19 \text{ mmol m}^{-2} \text{ a}^{-1}$ (equivalent to 12 t per year) for the oxic-anoxic interface. Authigenic oxides are totally recycled within the anoxic hypolimnion and most of NAIP- (nonapatitital inorganic phosphorus) and organic phosphorus is redissolved at the sediment interface. Only 60% of total particulate phosphorus sinks to the bottom and only 50% is permanently incorporated into the sediments.

Comparison with Lake Zug (Fig. 2), which is another deep and anoxic lake in Switzerland, shows a similar reduction in P loading, and a similar sedimentation behaviour as well. But in contrast to Lake Lugano, Lake Zug shows no accumulation of P in the deep water and a different iron-manganese ratio within the oxic-anoxic interface. Due to the different climatic conditions, analysis of oxygen profiles show better mixing efficiency in the hypolimnion of Lake Zug.

TABLE 1. External annual total phosphorus balance

year	P_{tot} [t]	Input [t a ⁻¹]	Export [t a ⁻¹]	Net sedimentation [t a ⁻¹]
1984	731	60	-18	-60
1985	713	30	-14	-8
1986	721	45	-17	-60
1987	689	40	-11	-91
1988	627	39	-9	30
1989	687	31	-5	4
1990	713	21	-4	-25
1991	705	19	-4	-43
1992	677	41	-9	34
1993	743	22	-4	-13
1994	750	21	-9	-5
1995	757	27	-5	0
1996	779	19	-4	1
Average	715	32	-9	-18
		(50 mmol m ⁻² a ⁻¹)	(-14 mmol m ⁻² a ⁻¹)	(-28 mmol m ⁻² a ⁻¹)

References

- Aeschbach-Hertig, W., Kipfer, R., Hofer, M. and Imboden, D.M. (1996) *Limnol. Oceanogr.*, **41**, 707-21.
- Davison, W. (1985) in W. Stumm (edit.). *Chemical processes in lakes*, Wiley Interscience, pp. 31-53.
- Imboden, D.M. and Wüest, A. (1995) in Lerman, A. (edit.), *Physics and Chemistry of Lakes*. Springer New York.
- Murray, J.W. (1987) in R.A. Hites and S.J. Eisenreich (edits.) *Am. Chem. Soc.* 153-84.
- Reichert, P. (1994) *Water Sci. Tech.*, **30**, 21-30.