Aquatic Sciences 54, 3/4, 1992

1015–1621/92/040277–08 $1.50+0.20/0

The role of sediments in the phosphorus cycle in Lake Lugano. I. Geochemical approach

D. Span, J. Dominik, M. A. Lazzaretti[1] and J.-P. Vernet

Institute F.-A. Forel, University of Geneva, 10 route de Suisse, CH-1290 Versoix, Switzerland
[1] Institute of Plant Biology/Microbiology, University of Zürich, Zollikerstr. 107, CH-8008 Zürich, Switzerland

Key words: Sediments, phosphorus cycling, Lake Lugano (Lago di Lugano), forms of phosphorus.

ABSTRACT

The bottom sediment from three coring stations in Lake Lugano (Lago di Lugano) show major differences in their role in the P-cycles related to their geochemistry and characteristics of sedimentation. In the northern basin, the deepest sediment may be considered practically "inactive", due to a permanently reduced condition at the sediment-water interface. In the southern basin, the sediments are "active" with respect to P-recycling with strong seasonal variations. One of the sites (Figino) behaves as a sink for P due to a high iron content and an important rate of detrital sedimentation.

Introduction

Large quantities of phosphorus (P) have accumulated in the sediments of Lake Lugano over many decades. The role of sediments on the P budget of a lake depends on their capacity to retain or to release soluble P. The mobility of P is governed by several chemical factors such as pH, redox potential, adsorption/desorption processes (Bostrom et al., 1988). Most of these factors depend on biological activity. The P cycle is also closely associated with Fe and Mn diagenesis, which in turn are also controlled by variations in the redox potential (Mortimer, 1941). However, the classical chemical model describing P-release under anoxic conditions and P-trapping under oxic conditions is more complex, due to interactions between biological and chemical processes.

This paper (Part I), limited to the geochemical processes, emphasizes the study of the different forms of P in the sediments of Lake Lugano. It provides information on the P origin and the mechanisms regulating its exchange through the sediment-water interface and movement in deeper sediment layers.

Sampling and methods

The three sediment sampling sites are located in the deep parts of Lake Lugano, one at Gandria (−285 m) in the northern basin, one at Melide (−85 m) and the last at Figino (−95 m) in the southeastern basin. These sites correspond to the reference points of the "Commissione Internazionale per la protezione delle acque italo-svizzere" (Fig. 1 in Barbieri and Polli, this issue). The northern basin shows a permanently anoxic hypolimnion (100 to 285 m), with a mean P concentration of 0.30 mg P l^{-1}. The southern basin is monomictic with strong seasonal variations in dissolved oxygen and P content. At the end of summer stratification, the total P concentration at the bottom reaches 0.60 mg P l^{-1} at Melide but only 0.26 mg P l^{-1} at Figino. The dissolved oxygen content in the deepest parts of this lake have progressively decreased over the past 4 years (Barbieri and Mosello, this issue).

Sediment cores were taken by the manned submarine F.-A. Forel using a modified Pfleger corer. To test the variability of sediment samples from the sites, cores from a small area were taken. The local homogeneity of the sample area (example for the site Gandria) was verified using porosity parameter (Fig. 1). Pore water was collected during each sampling, using a dialysis porewater sampler (Brandl and Hanselmann, 1991), developed and built at the Institute of Plant Biology/Microbiology (University of Zürich). The data of the interstitial water study are reported in more detail in the second part of this P-cycle paper (Lazzaretti et al., this issue). In the southern basin, 4 sediment samples were collected between 1989 and 1990, one every 4 months depending on the seasonal condition of the lake. At Gandria, only one sample was taken in March 1990. Immediately upon recovery,

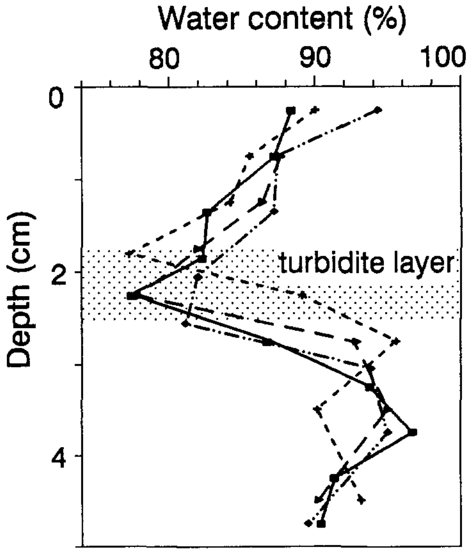

Figure 1. Porosity profiles in sediment cores from the site Gandria (northern basin) indicating the local homogeneity of this sample area. The four cores were taken with about 1 m between each samples. Note an excellent correlation with the turbidite layer

some of the cores were sliced in thin layers (0.5 to 1.0 cm) under a flow of nitrogen in a glove box. Other cores were cut longitudinally and subsampled specifically for some characteristic layers. All sub-samples were freeze-dried, ground and homogenized for chemical analyses. Total Fe and Mn content were analysed by ICP-AE Spectrometry after digestion with $HClO_4$ followed by HF + HCl (Favarger, 1982). Total Organic Carbon (TOC) was measured by an oxydation technique (Gaudette et al., 1974) and Inorganic Carbon (expressed as $CaCO_3$) by CO_2 volumetry following digestion in HCl.

The different forms of phosphorus in the sediments were determined by colorimetry after a sequential leaching procedure (Williams et al., 1976; modified by Burrus et al., 1990). This fractionation distinguishes three operationally-defined forms as follows:

- Organic Phosphorus (OP) associated with allochtonous and autochtonous organic matter (in humic complexes, settling dead organisms, etc.). A part of this OP may be released through bacterial decomposition of the organic matter.
- Apatite Phosphorus (AP) is mainly included in allogenic apatite minerals ($Ca_5(PO_4)_3OH$). Under the existing conditions in the surficial sediment, AP is considered not to be remobilized.
- Non Apatite Inorganic Phosphorus (NAIP) is coprecipitated with amorphous inorganic complexes, such as Fe, Mn or Al hydroxides in oxic environments. Other P minerals such as vivianite ($Fe_3(PO_4)_2 \cdot 8\,H_2O$), formed under reducing conditions, may also be included in this fraction. The NAIP form is known to be the most sensitive to redox variations and its bio-availability has been clearly demonstrated (Williams et al., 1976; Burrus et al., 1990; Santiago et Thomas, 1992).

For further details on sequential chemical extractions the reader is referred to Williams et al. (1976) and Pettersson et al. (1988). The comparison of the different ratios (NAIP + AP/Inorganic P, Inorganic P + OP/Total P and NAIP + AP + OP/Total P) controls the validity of the extraction procedure.

Results

The lithological and geochemical characteristics of the sediments are shown in Fig. 2. The sediments are laminated with a succession of alternating carbonate and clay varves. These deposits consist of a rhythmic sequence of dark (diatoms and organic rich clay material) and light (summer calcite precipitation) laminations. This cyclic sedimentation may be interrupted by detrital layers of varying thickness and grain-size. The complex morphology of Lake Lugano, with steep slopes and high particulate inputs, promotes the development of frequent turbidity currents (Niessen, 1987).

The profiles of the water content in the sediment cores (Fig. 2) reflect the change in sediment type, with the lowest values in the detrital layers. These layers are well developed at Gandria with turbidite series of varying grain-size. The most important turbidite is characterized by a well-sorted sequence of sand at the base and silty clay at

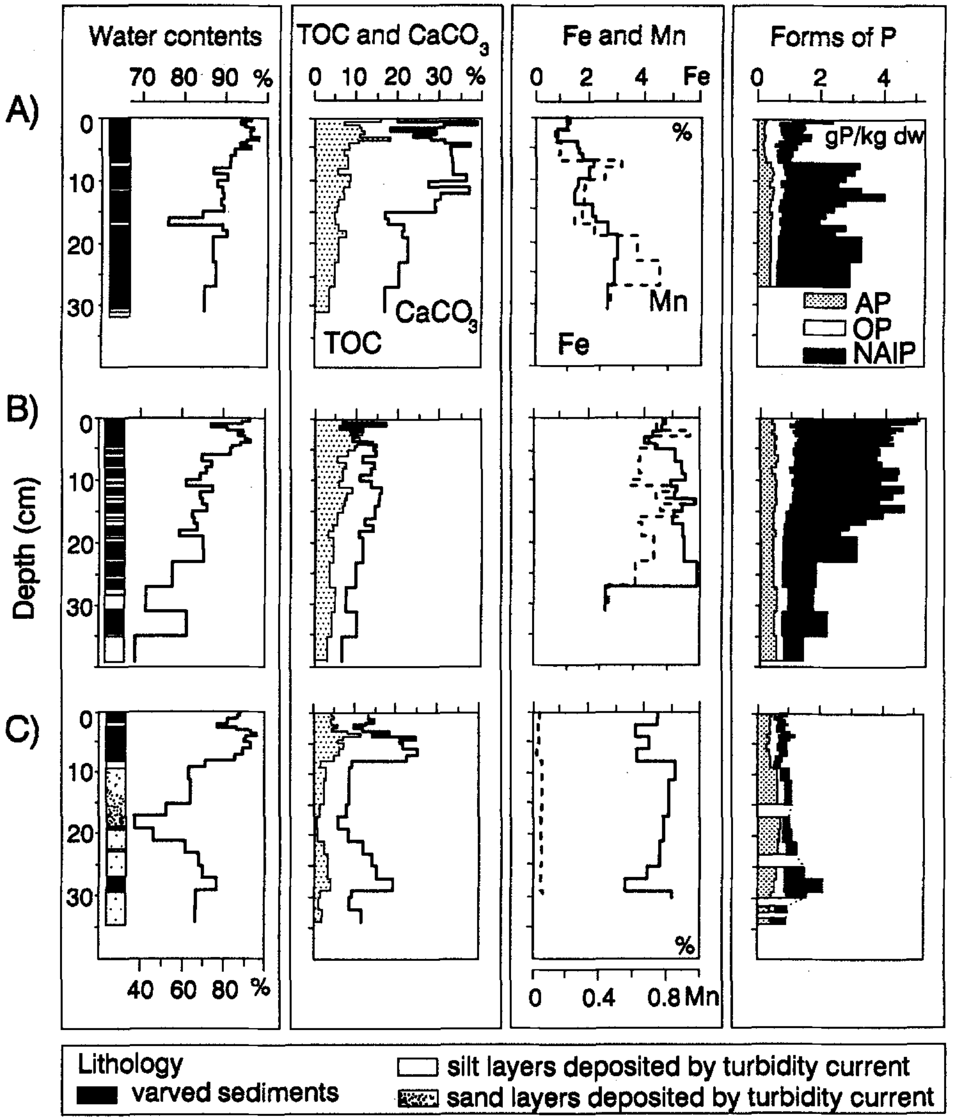

Figure 2. Lithological and geochemical characteristics of sediments from the three sampling sites in Lake Lugano (TOC: Total Organic Carbon; AP: Apatite Phosphorus, OP: Organic Phosphorus and NAIP: Non Apatite Inorganic Phosphorus).
A: Melide, B: Figino and C: Gandria

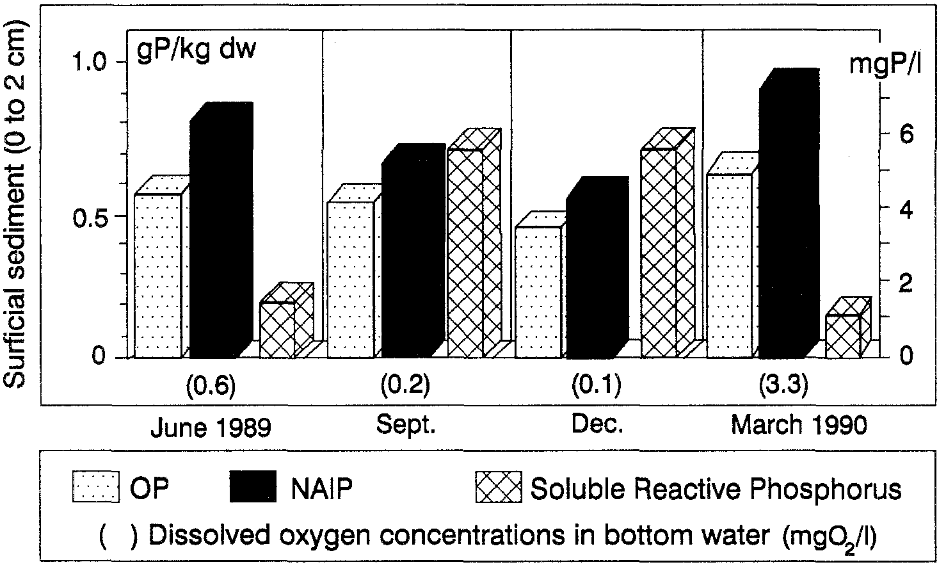

Figure 3. Seasonal evolution of NAIP, OP and SRP in the surficial sediment (0 to 2 cm) of Melide. The mean concentration of SRP were calculated from Lazzaretti et al. (this issue) and the results for dissolved oxygen contents were supplied by the L.S.A. (Laboratorio Studi Ambientali, Lugano)

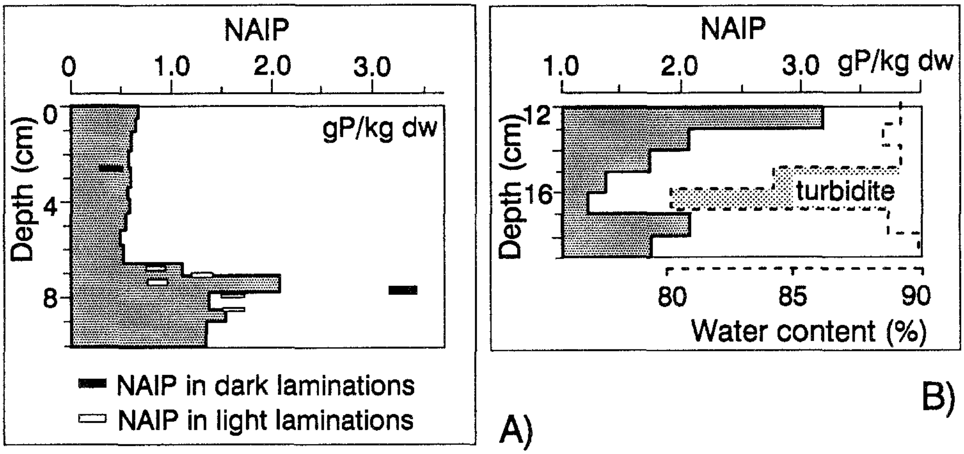

Figure 4. Details of the NAIP profiles in cores from Melide.
A) NAIP contents in normal profile and in some characteristic laminations (Deçember 1989). B) Influence of a turbidite layer on the NAIP profile (June 1989). Low porosity interbedding in varved sediments may preserve mobile NAIP at the ancient sediment water interface

the top. In general, the detrital deposits are silty, poor in carbonates and in organic carbon. At Figino, the deposition of detrital layers seems to be more regular than at Melide. In the context of the observed lithological heterogeneity, P distribution and other parameters are very different at each site. Total Organic Carbon (TOC) contents average 10% in the surficial sediment in the southern basin and 5% in the northern basin. The highest contents in $CaCO_3$ are found at Melide with 30% compared to 15% at Figino. The highest concentrations of Fe and Mn (5 and 0.7% respectively) are found at Figino, which receives the highest solid inputs. The lowest contents of Mn (0.1%) are at Gandria, where reducing conditions remobilize this labile element.

Total P in the upper layers of the cores range from 1 at Gandria to 2 at Melide to 5 $g\,P\,kg^{-1}$ at Figino. Generally, Organic Phosphorus (OP) contents are lower than the inorganic ones, representing only 10 to 20% of the total P. NAIP is the dominant form and averages 70% of total P, except at Gandria where it is only 30% or less. At this site, the most important form is apatite phosphorus AP with about 50% of total P. In comparison to the varved sediment, the detrital layers show higher AP and lower NAIP contents. However, the amount of NAIP just below turbidites are high (Fig. 2a and 4b).

Discussion

The behaviour of P in the sediment at the three sites may be interpreted on the basis of geochemistry. In the first part of the discussion, we will focuse on the P-exchange at the sediment-water interface, particularly in the southern basin. In the second part, the long term cycling of P will be discussed for each site.

P-exchange at the sediment-water interface

One of the goals of this study was to follow the seasonal cycling of P at the interface and to quantify the P-exchange between sediment and bottom waters. In addition the different forms of P in sediment, interstitial water and in bottom water were to investigate. The site at Melide shows an interesting seasonal evolution of different forms of P in sediments (Fig. 3). After the turn-over (situation in March), the upper few centimeters of sediment are oxidized and covered by a thin surface floc of Fe and/or Mn oxyhydroxides with coprecipitated-P. This surficial P-enrichment is the result of the upward diffusion of dissolved P from the lower reduced zone and its precipitation in the top layer. During the short period of oxygenation of the bottom waters, the surficial sediments behave as a sink for the mobile NAIP, and consequently P-fluxes from the sediment to the water column are low (Lazzaretti et al., this issue). During the depletion of dissolved oxygen the surficial sediment becomes reduced, the chemical barrier for P, formed by the Fe oxyhydroxides is gradually dissolved. The NAIP content decreases in the upper centimeters, with 0.90 $g\,P\,kg^{-1}$ in March and 0.53 in December. The pool of dissolved P from NAIP increases in the interstitial water and diffuses to the bottom water. The maximum P-flux occurs in December, when this sediment acts as a significant source of P.

At the site Figino, subjected to the same seasonal variation in dissolved oxygen as the site Melide, the P behavior is different. NAIP content in the surficial sediment is about 5 times greater than at Melide and does not show seasonal variations. The high sink capacity for P at this site can be attributed to the large Fe reservoir in the sediments. Indeed, the Fe^{2+}/PO_4^{3-} ratios in porewater of the reduced zone in the top 5 cm reaches more than 5, as compared to only about 2 for Melide (Lazzaretti et al., this issue). With increase in this ratio, the P adsorption capacity is enhanced and the consequent P-fluxes released to the bottom water are lower (Baccini, 1985). This site receives large particulate inputs from the Vedeggio river and has the highest mean rate of P sedimentation with 15 $mg\,P\,m^{-2}\,d^{-1}$ (Simona, 1988) of which approx. 10 to 20% is released back to the water column. In spite of the increased inputs from a nearby wastewater treatment plant, this sediment does not seem to be "saturated" with P and serves as efficient P-sink.

At Gandria, the permanently anoxic conditions of the bottom waters make the surficial sediment ineffective for P-trapping. The sediments are greatly enriched in AP compared to the other sites, due to a lack of precipitation of NAIP, and may be considered practically "inactive" in the P-cycle. The most active cycling of nutrients is by transfer across the chemocline in permanently anoxic basins (Landing et al., 1991).

Global evolution of P

For all of the sediments, the vertical P distributions are heterogeneous. In general, the correlation coefficients between NAIP and Mn in the sediment are more significant than the relationship of NAIP to Fe ($r = 0.80$ and 0.58 respectively). In the turbidite layers, P correlates negatively with Mn and Fe. If the NAIP/AP, NAIP/Fe or NAIP/Mn ratios are considered, their distribution appears regular, except for Melide where a strong variation in the top 8 to 10 cm sediment layer can be seen. In this zone, NAIP, Fe and Mn contents vary dramatically (Fig. 2 and 4a). The maximum P concentration occurs in a layer with an Fe–Mn enriched zone, just below some thin detrital layers (grey layers) poor in NAIP (Fig. 4a). This zone also corresponds to a change in the water content, where the downward PO_4^{3-} gradient in the interstitial water becomes important (Lazzaretti et al., this issue), in responding to diffusion associated with redox changes. The burial of inorganic Fe–Mn oxyhydroxides into strong reducing sediment zones produces the soluble reduced elemental species (Mn^{2+}, Fe^{2+}, PO_4^{3-}) which diffuse upward in the sediment column. Below this layer, the conditions become suitable for authigenic P mineral formation (such as vivianite or reddingite). Vivianite nodules in recent sediments of Lake Lugano have been observed by microscopic analysis (F. Niessen, personal communication). At site Melide, the deposition of a detrital layer at a depth of 16 cm influences the NAIP profile (Fig. 4b). The deposition of the turbidite instantly isolates the interface from the bottom water and its reoxygenation. The upward migration of P across the turbidite is thus restrained. The change in redox conditions below the turbidite leads to P-trapping in the underlying sediment, where P minerals may precipitate. This process is even more developed in sediment at site Figino where frequent thin turbidites lead to successive P-trapping between the coarse detrital layers (Fig. 2). The details of P trapping mechanism by turbidite in deep lake sediments is given by Span et al. (1992).

At site Gandria, a recent turbidite event (at 2 cm depth) has a minor effect on P-trapping because the anoxic conditions at the sediment-water interface do not allow the retention of P. By contrast, an old interface now located at a depth of 28 cm, just below a series of successive turbidites contains relatively high NAIP amounts, suggesting the presence of oxygen in the hypolimnion at the time of turbidite deposition. Cs-137 data suggest the deposition of these sediments between 1955–1963 (Dominik et al., 1992), in a period preceeding the extensive eutrophication of the northern basin.

REFERENCES

Baccini, P., 1985. Phosphate interactions at the sediment-water interface. In: Stumm (ed.), Chemical Processes in Lakes, 189–205.

Bostrom, B., J. M. Andersen, S. Fleischer and M. Jansson, 1988. Exchange of phosphorus across the sediment-water interface. Hydrobiologia 170:229–244.

Brandl, H. and K. W. Hanselmann, 1991. Evaluation and application of dialysis porewater samplers for microbiological studies at sediment-water interfaces. Aquatic Sciences 53/1:55–73.

Burrus, D., R. L. Thomas, B. Dominik, J.-P. Vernet and J. Dominik, 1990. Characteristics of suspended sediment in the Upper Rhone River, Switzerland, including the particulate forms of phosphorus. Hydrological Processes 4:85–98.

Dominik, J., J.-L. Loizeau and D. Span, 1992. Radioisotopic evidence of pertubations of recent sedimentary record in lakes: a word of caution for climate studies. Climate Dynamics 6:145–152.

Favarger, P.-Y., 1982. Simultaneous determination of 31 elements in lacustrine sediments by ICP. Analytical Techniques in Environmental Chemistry 2, Pergamon Ser. Environ. Sci. 7:371–376.

Gaudette, H. E., W. R. Flight, L. Toner and D. W. Folger, 1974. An inexpensive titration method for the determination of organic carbon in recent sediments. J. Sedimentary Petrology 44:249–253.

Landing, W. M., W. C. Burnett, W. B. Lyons and W. H. Orem, 1991. Nutrient cycling and the biogeochemistry of manganese, iron and zinc in Jellyfish Lake, Palau. Limnol. Oceanogr. 36(3):515–525.

Mortimer, C. H., 1941. The exchange of dissolved substances between mud and water in lakes. I. J. Ecol. 29:280–329.

Niessen, F., 1987. Sedimentologische, geophysikalische und geochemische Untersuchungen zur Entstehung und Ablagerungsgeschichte des Luganersees (Switzerland), Ph. D., ETH, Zürich, 315 p.

Pettersson, K., B. Bostrom and O. S. Jacobsen, 1988. Phosphorus in sediments: speciation and analysis. Hydrobiologia 170:91–101.

Santiago, S. and R. L. Thomas, 1992. Utilization of sediment bound phosphorus from rivers tributary to Lake Geneva to lake phytoplankton. J. Great Lakes Res., in press.

Simona, M., 1988. Sedimentazione. In: Ricerche sull'evoluzione del Lago di Lugano. Ed.: Commissione Internazionale per la protezione delle acque italo-svizzere: 71–78.

Span, D., J. Dominik, J.-L. Loizeau, N. Belzile and J.-P. Vernet, 1992. Phosphorus trapping by turbidites in deep lake sediments. Chemical Geology, in press.

Williams, J. D. H., J.-M. Jaquet and R. L. Thomas, 1976. Forms of phosphorus in the superficial sediments of Lake Erie. J. Fish. Res. Board. Can. 33:413–429.

Received 14 February 1992;
Revised manuscript accepted 21 August 1992.