



Phosphorus fractionation in lake sediments – Lakes Volvi and Koronia, N. Greece

A. Kaiserli, D. Voutsas *, C. Samara

Environmental Pollution Control Laboratory, Chemistry Department, Aristotle University, GR-54006 Thessaloniki, Greece

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Abstract

Sediments from two lakes, the meso-to-eutrophic Volvi and the hypertrophic Koronia, located in N. Greece were examined on the basis of P-fractionation. In both lakes, the rank order of P-fractions was $\text{HCl-P} > \text{NaOH-P} > \text{BD-P} > \text{NH}_4\text{Cl-P}$. The loosely sorbed phosphorus ($\text{NH}_4\text{Cl-P}$) represented $< 1\%$ of the sedimentary inorganic phosphorus, while the reductant phosphorus (BD-P) ranged 5–6%. The calcium bound phosphorus (HCl-P) showed considerable contribution (59–74%) to the sedimentary inorganic P-loads. The metal oxide bound phosphorus (NaOH-P) was higher in the hypertrophic (30–35%) than in the meso-to-eutrophic system (19–28%). Fine-sized sediments exhibited significantly higher concentrations of HCl-P in Volvi and $\text{NH}_4\text{Cl-P}$ in Koronia. Sampling month had significant effect in variance of most P-fractions and other sediment features in both lakes. Use was also made of multivariate statistics to identify the factors which influence the sedimentary phosphorus. NaOH-P was the most reactive fraction in Lake Volvi. Iron compounds and organic matter seem to play a significant role in regulating this labile P-budget. $\text{NH}_4\text{Cl-P}$ was the more reactive fraction in Lake Koronia which was influenced by sedimentation of P-absorbed on clay/silt fine particles. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Phosphorus has been recognized as the most critical nutrient limiting lake productivity. The main sources of phosphorus in lakes are external point and non-point sources such as rainfall, runoff, soil leaching, industrial and municipal effluents. Moreover, there are also internal sources from the system itself such as aquatic plants, algal and sediments.

The trophic status of the lakes is usually dependent on the P-concentration in the water. In addition, the trophic status and the trophic development of the system is also influenced by the phosphorus content in lake

sediments. Usually lake sediments act as a sink of phosphorus. However, under certain environmental conditions, the sediments may become a possible phosphorus source that will support the trophic status of the lake even after a reduction of external loading (Ramm and Scheps, 1997; Zhou et al., 2001). This internal P-loading may delay the recovery of the lakes, once the external P-sources are reduced, and must be evaluated in lake restoration programmes. The phosphorus content in sediments depends on the sediment composition, the sedimentation rate, the physicochemical conditions and the extent of diagenetic processes (Gonsiorczyk et al., 1998). Total concentrations of phosphorus in sediments cannot predict the potential ecological danger. The fraction of available phosphorus is an important parameter for predicting future internal P-loading. The factors governing P release from sediments comprise redox reactions, adsorption, mineral phase solubility

* Corresponding author. Tel.: +30-31-997-858; fax: +30-31-997-747.

E-mail address: dvoutsas@chem.auth.gr (D. Voutsas).

Table 4
Varimax rotated factor matrix^a for sediment data set

Variable	Lake Volvi				Lake Koronia		
	F ₁	F ₂	F ₃	F ₄	F ₁	F ₂	F ₃
NH ₄ Cl-P		0.511	0.765		0.723	-0.581	
BD-P			0.934			-0.635	-0.559
NaOH-P	0.931					0.971	
HCl-P				0.862			0.959
Sand (%)	-0.472			0.703	-0.973		
LOI (%)	0.859				0.928		
CaCO ₃ (%)		0.831			0.817		
Ca _t		0.991			-0.753		
Mg _t			0.725		0.849		
Al _t	0.526			-0.701	0.978		
Fe _t	0.968				0.971		
Mn _t	0.658	0.718			0.923		
Variance (%)	47.2	18.4	13.6	9.7	57.5	17.0	10.2

^a Loadings higher than 0.400 are only given.

important role of iron compounds (more important than aluminum) and organic matter in regulating this mobile P-budget of the lake (Maine et al., 1996). It is also indicated that this P-form can be considered the most reactive one in this system. The *second factor* accounting for 18.4% of the variance was correlated with Ca_{total}, CaCO₃, Mn_{total} and NH₄Cl-P. This factor suggests that carbonates or manganese may control the presence of loosely bound P and probably represents the autochthonous precipitation of P (Sallade and Sims, 1997; Gonsiorczyk et al., 1998). The *third factor* which is strongly correlated with BD-P, NH₄Cl-P and Mg_{total}, shows that redox conditions and the presence of Mg, both depended on algal productivity, could influence the mobile pool of the lake (Gonsiorczyk et al., 1998). Lastly, the *fourth factor* was positively correlated with HCl-P and sand content of the sediment whereas negatively with Al_{total}. This factor could represent the allo-genic origin of the sedimentary phosphorus, probably due to erosion processes.

Three factors accounting for 84.7% of total variance were identified in lake Koronia (Table 4). The *first factor*, accounting for 57.5% of the variance, was positively correlated with NH₄Cl-P, LOI, CaCO₃ and total concentrations of Mg, Al, Fe, Mn while negatively correlated with sand content and Ca_{total}. This factor could be interpreted as representing the processes influencing the loosely bound P that seems to be the most reactive fraction in this system. These processes might include settlement of planktonic diatoms and deposition of fine-sized particles where P is associated with carbonates, organic matter, ferromanganese oxides (Pizarro et al., 1992; Sohrin et al., 1996; Johnson, 1997; Gibson et al., 2001; Pettersson, 2001). The *second factor*, accounting for 17% of the variance, was positively correlated with NaOH-P and negatively with BD-P and NH₄Cl-P thus

representing the interrelationships among the algal available phosphorus fractions. Mineralization of organic matter could be one possible route of mobilized P from NaOH-P to the other P-fractions (Gonsiorczyk et al., 1998). The *third factor*, accounting for 10.2% of the variance, was primarily correlated with HCl-P and negatively with BD-P showing that the terrigenous forms P extracted by strong acids might contain P forms that could be possible source of reductant P, probably due to bacterial activity that could solubilize P-compounds (Maine et al., 1992; Sallade and Sims, 1997).

References

- APHA, AWWA, WPCF, 1985. Standard methods for the examination of water and wastewater, 16th edition.
- Chang, S.C., Jackson, M.L., 1957. Fractionation of soil phosphorus. Soil Sci. 84, 133–144.
- Eckert, W., Nishri, A., Parparova, R., 1997. Factors regulating the flux of phosphate at the sediment–water interface of a subtropical calcareous lake: a simulation study with intact sediment cores. Water, Air, Soil Pollut. 99, 401–409.
- Gibson, C.E., Wang, G., Foy, R.H., Lennox, S.D., 2001. The importance of catchment and lake processes in the phosphorus budget of a large lake. Chemosphere 42, 215–220.
- Gonsiorczyk, T., Casper, P., Koschel, R., 1998. Phosphorus binding forms in the sediment of an oligotrophic and an eutrophic hardwater lake of the Baltic district (Germany). Water Sci. Technol. 37 (3), 51–58.
- Hopke, P.K., 1985. Receptor Modeling in Environmental Chemistry. Wiley, USA.
- House, W.A., Denison, F.H., 2000. Factors in fluencing the measurement of equilibrium phosphate concentrations in river sediments. Water Res. 34 (4), 1187–1200.
- Huanxin, W., Presley, B.J., Armstrong, D., 1994. Distribution of sedimentary phosphorus in gulf of Mexico estuaries. Mar. Environ. Res. 37, 375–392.

- Hupfer, M., Gachter, R., Giovanoli, R., 1995. Transformation of phosphorus species in settling seston and during early sediment diagenesis. *Aquat. Sci.* 57, 305–324.
- Johnson, A., 1997. Fe and Al sedimentation and their importance as carriers for P, N and C in a large humic lake in Northern Sweden. *Water, Air, Soil Pollut.* 99, 283–295.
- Kleeberg, A., Dudel, G.E., 1997. Changes in extent of phosphorus release in a shallow lake (Lake Großer Müggelsee; Germany, Berlin) due to climatic factors and load. *Mar. Geol.* 139, 61–75.
- Kleeberg, A., Kozerski, H.P., 1997. Phosphorus release in lake Großer Müggelsee and its implications for lake restoration. *Hydrobiologia* 342/343, 9–26.
- Kouimtzis, Th., 1999. Annual report. Monitoring of surface water quality in the area of Macedonia, N. Greece. Chemistry Department, University of Thessaloniki (in Greek).
- Koussouris, T.S., Bertakos, T.I., Diapoulis, A.C., 1992. Background trophic state of Greek lakes. *Fresenius Environ. Bull.* 1, 96–101.
- Kozerski, H.P., Kleeberg, A., 1998. The sediments and the benthic pelagic exchange in the shallow lake Müggelsee. *Int. Rev. Hydrobiol.* 83, 77–112.
- Maine, M.A., Hammerly, J.A., Leguizamon, M.S., Pizarro, M.J., 1992. Influence of the pH and redox potential on phosphate activity in the Parana Medio system. *Hydrobiologia* 228, 83–90.
- Maine, M.A., Panigatti, M.C., Sune, N.L., Pizarro, M.J., 1996. Phosphorus forms in lotic and lentic environments of the middle Parana flood valley (Argentina). *Pol. Arch. Hydrobiol.* 43 (4), 391–400.
- Penn, M.R., Auer, M.T., Van Orman, E.L., Korienek, J.J., 1995. Phosphorus diagenesis in lake sediments: investigation using fractionation techniques. *Mar. Freshwater Res.* 46, 89–99.
- Perkins, R.G., Underwood, G.J.C., 2001. The potential for phosphorus release across the sediment–water interface in an eutrophic reservoir dosed with ferric sulphate. *Water Res.* 35 (6), 1399–1406.
- Pettersson, K., 2001. Phosphorus characteristics of settling and suspended particles in Lake Erken. *Sci. Total Environ.* 266, 79–86.
- Pizarro, M.J., Hammerly, J., Maine, M.A., Sune, N., 1992. Phosphate adsorption on bottom sediments of the Rio de la Plata. *Hydrobiologia* 228, 43–54.
- Psenner, R., 1988. Fractionation of phosphorus in suspended matter and sediment. *Ergeb. Limnol.* 30, 98–113.
- Psenner, R., Pucska, R., Sager, M., 1984. Die fractionierung organischer und anorganischer phosphorverbindungen von sedimenten versuch einer Definition ökologisch wichtiger fractionen. *Arch. Hydrobiol. (Suppl. 10)*, 115–155.
- Ramm, K., Scheps, V., 1997. Phosphorus balance of a polytrophic shallow lake with consideration of phosphorus release. *Hydrobiologia* 342/343, 43–53.
- Rydin, E., 2000. Potentially mobile phosphorus in lake Erken sediment. *Water Res.* 34 (7), 2037–2042.
- Sallade, Y.E., Sims, J.T., 1997. Phosphorus transformations in the sediments of Delaware's agricultural drainageways: II. Effect of reducing condition on phosphorus release. *J. Environ. Anal.* 26, 1579–1588.
- Sohrin, Y., Tateishi, T., Mito, S., Matsui, M., Maeda, H., Hattori, A., Kawashima, M., Hasegawa, H., 1996. Nutrients of Lake Biwa in the unusually cool and hot summers of 1993 and 1994. *Lakes Reservoirs: Res. Manage.* 2, 77–87.
- SPSS Base 8.0S for Windows, 1998. SPSS Inc.
- Tan, K.H., 1995. Soil Sampling, Preparation and Analysis. Marcel Dekker, New York.
- Thirunavukkarasu, O.S., Viraraghavan, T., Selvapathy, P., 2000. A comparative account of phosphorus release from sediments of a lake and a reservoir: laboratory experiments. *Fresenius Environ. Bull.* 9, 461–467.
- Ting, D.S., Appan, A., 1996. General characteristics and fractions of phosphorus in aquatic sediments of two tropical reservoirs. *Water Sci. Technol.* 34 (7–8), 53–59.
- Uhlmann, D., Hupfer, M., Appelt, C., 1997. Composition of sediments in drinking water reservoirs as a basis for the assessment of potential changes in water quality. *J. Water SRT-Aqua* 46 (2), 84–94.
- Williams, J.D.H., Jaquet, J.M., Thomas, R.L., 1976. Forms of phosphorus in surficial sediments of Lake Erie. *J. Fish. Res. Board Can.* 33, 413–429.
- Zhou, Q., Gibson, C.E., Zhu, Y., 2001. Evaluation of phosphorus bioavailability in sediments of three contrasting lakes in China and the UK. *Chemosphere* 42, 221–225.