Chemical Fractionation of Phosphorus in Bottom Sediments from the Tietê-Pinheiros-Billings River System, São Paulo.

Ivone S. da Silva
Department of Exact and Earth Sciences
Federal University of São Paulo – UNIFESP –
Campus Diadema – is.silva@unifesp.br

Abstract *An evaluation of the possible forms or phases in which phosphorus could be associated with bottom sediments from the Tietê-Pinheiros-Billings river system in the Metropolitan Area of São Paulo and also Barra Bonita reservoir in the interior of São Paulo State was carried out. Samples were submitted to extraction with 0.1 mol L^{-1} hydrochloric acid and a sequential extraction procedure. Total P contents were considerably higher in sediment samples from the environments most influenced by urban pollution loads, although the residual fraction was significant. Analytical results for HCl extracts showed a similarity in comparison to sequential extraction for the same sample. This means that when the amount of potentially reactive P was increased, a higher content of P extracted with HCl was also observed, indicating that P accumulated in sediments in the studied environments has a considerable potential to be released to overlaying water, especially at Billings and Rasgão reservoirs.*

Keywords *Phosphorus, sediments, chemical and sequential extractions, Billings reservoir, Tietê River.*

Introduction

Phosphorus participates in or controls many of the biogeochemical processes occurring in the biosphere (Jahnke 1992). In aquatic environments, it plays an important role in water fertilization which is accelerated by anthropogenic activities, especially as a result of excessive sewage loads which affect water bodies in urbanized areas.

Phosphorus is the main nutrient that limits primary production in several aquatic environments, so its input control is essential for recovering eutrophicated lakes and rivers (Vollenweider 1985). In addition, the exchange mechanisms between bottom sediments and water column should be understood, since P accumulated in sediments can be potentially released to the aqueous phase (Laseras 1991).

Although bioavailable P is mainly in the dissolved form, it makes up only a small fraction of total P, particulate being a major fraction of total P. The stability and chemical form of particulate in association with environmental conditions regulate its retention and release from the sediment phase

and determine the level of dissolved P in the water column (House 2003).

Since oxi-reduction characteristics of the environment are related to P releasing, many studies have focused on chemical speciation or fractionation of P in sediments, aiming to determine association forms of this element and therefore its availability to the aquatic biota (Maine et al. 1992, Psenner and Pucsko 1988, Sonzogni et al. 1982, Young and De Pinto 1982, Van Eck 1982, Hieltjes and Lijklema 1980).

Analytical procedures proposed for chemical fractionation of P in sediments were derived from soils matrices (Legg and Black 1955, Chang and Jackson 1957, Petersen and Corey 1966, Williams et al. 1967). They are based on the assumption that certain reagents can preferentially extract discrete chemical forms of P associated with a determined geologic material (Van Eck 1982). Similar to heavy metals, functional classification does not necessarily correspond to the chemical species because the extractions do not give a clear distinction between different species (Danen-Louwerse et al. 1993). More recently, phosphorus fractionation procedures were defined as P fractions separated into operationally defined pools using a sequence of increasingly strong reagents to successively remove more recalcitrant forms (Katsaounos et al. 2007).

Fractionation procedures also intend to accomplish the classification of phosphorus according to physical (e.g. size, solubility), biological (e.g. bio-availability) or more frequently chemical (e.g. bonding, reactivity) properties that determine involvement of P in geological, chemical and biological processes (Katsaounos et al. 2007).

Since P accumulation in sediments poses a potential nutrient source for the overlaying water when the eutrophication process develops, it is important to evaluate its availability to the aquatic environment through chemical and reactive forms in relation to its total content in sediments. For this purpose, we applied two extraction procedures in sediment samples from distinct environments of the Tietê-Pinheiros-Billings river system. These environments are exposed to intense pollution loads, as in the Billings, Pirapora, and Rasgão reservoirs in the Metropolitan Area of São Paulo or receive diffuse and diluted pollution loads through the whole system (e.g. Barra Bonita reservoir).

Study Area

The study area is located in the Tietê-Pinheiros-Billings river system, represented by Billings, Pirapora and Rasgão reservoirs in the Metropolitan Area of São Paulo and Barra Bonita reservoir (about 270 km downriver from São Paulo city) as shown in Fig. 1. These environments were chosen for their similarity in terms of accumulation and transfer of pollution loads. In the Metropolitan Area of São Paulo, Pinheiros and Tietê rivers receive a large load of industrial and domestic sewage, resulting in bad water quality. Pollution loads have contributed significantly to increase phosphorus concentrations from anthropogenic sources, since organic pollution loads which stem from domestic and industrial sources correspond to 70 and 30%, respectively (CETESB 2006). The water has become dark and the formation of foam has been observed along the dams located in Tietê and Pinheiros rivers, mostly associated with detergents, as corroborated by surfactant data (CETESB 2006). On the other hand, Billings reservoir has been impacted by algae growth over the last five decades (Branco 1966, Rocha et al. 1986, CETESB 2006). The intensity of this process should be taken into account, since this reservoir has been used as water supply and water treatment depends on its quality (Lamparelli et al 1996, CETESB 1999).

The transfer of pollution loads between the Tietê river in the urbanized area and the countryside (Barra Bonita reservoir) does not occur continually at a similar rate. It varies over time and with water flow levels and the pollution loads that flow through Tietê dams are normally diluted and accumulated into the downriver reservoirs.

The sampling sites were located at Billings (B1 and B2), Pirapora (P1), Rasgão (P2) and Barra Bonita (BB1 and BB2) reservoirs. Sites B1 and B2 were close to Pedreira Dam, located 1 and 2.5 km, respectively, in the direction of the central watercourse. Sites P1 and P2 were located at Tietê river, 3.5 and 2 km, respectively, in the direction of the Pirapora Dam and Rasgão Plant. Sites BB1 and BB2 were in the central area at Barra Bonita reservoir, which faces the main hydraulic structure.

Materials and Methods

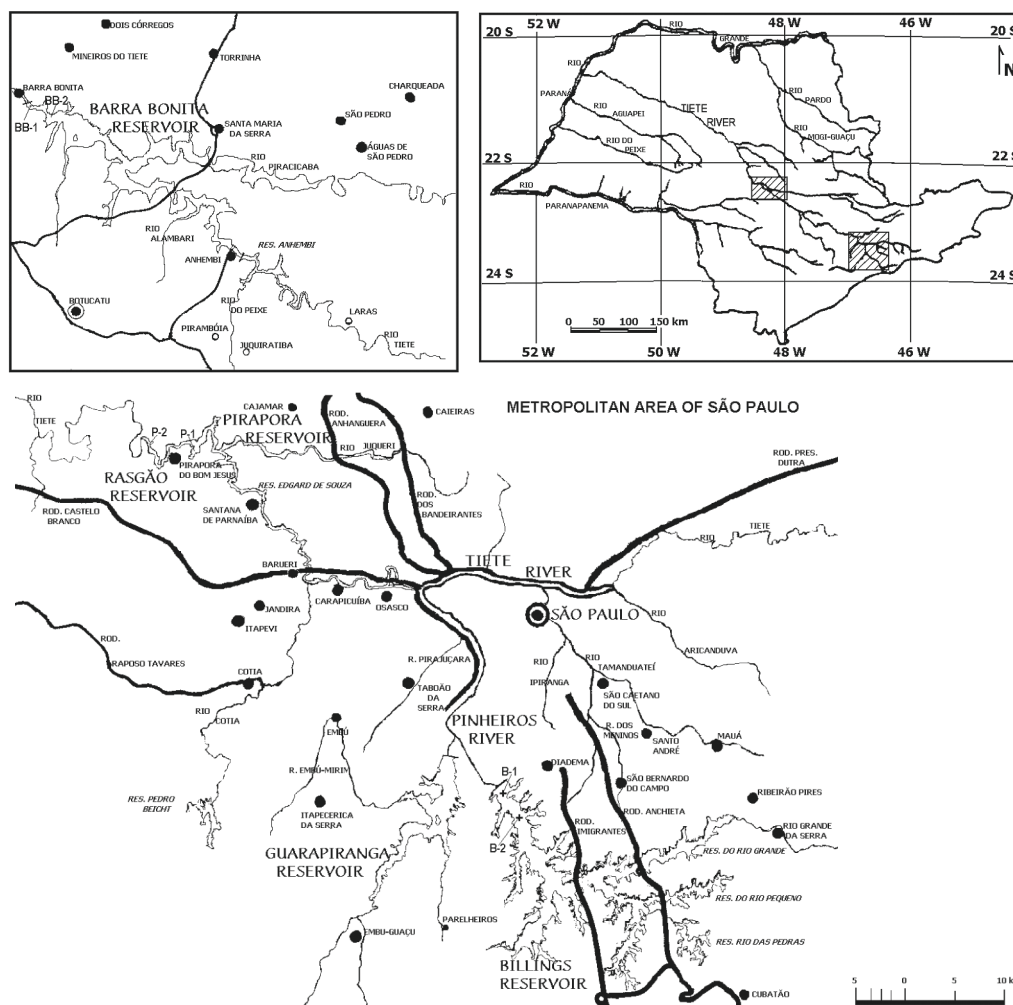Sediment cores (~30 cm depth) were collected

Figure 1 – Location map of the sampling sites.

in the rainy season (February and March 1998) using a gravity sampler. The samples were kept isolated in the acrylic sample tubes to avoid contact with air and possible oxidation. The tubes, containing approximately 30 cm of sediment, were capped and brought to the laboratory. All samples were preserved into Styrofoam boxes containing ice.

Chemical and physical variables such as pH, E_H (redox potential) and dissolved oxygen (DO) of the overlaying water in contact with surface sediment layer were measured during the field work.

Inside a glove box under nitrogen atmosphere, a layer of approximately 10 cm of the sediment closer to the overlaying water was transferred to polyethylene flasks. These flasks were kept in desiccators at approximately 4 °C until the moment of the analysis. To keep the anoxic conditions during

both the 0.1 mol L^{-1} HCl and the sequential extraction experiments, all transfers were performed inside the glove box, using tightly closed 50 mL polypropylene centrifuge tubes from Corning®. These extractions allowed us to evaluate P fractions and their meanings in terms of availability to overlaying water, considering the environmental conditions.

The sequential extraction protocol proposed by Ure et al. (1993) consisted of three steps. The reagents for sequential extractions were: reagent 1: 0.11 mol L^{-1} acetic acid (step 1 of extraction); reagent 2: 0.1 mol L^{-1} hydroxylamine hydrochloride acidified to pH 2 with nitric acid (step 2); reagent 3: 8.8 mol L^{-1} hydrogen peroxide acidified to pH 2-3 with HNO_3; and reagent 4: 1 mol L^{-1} ammonium acetate acidified to pH 2 with HNO_3 (step 3). A

detailed description of the protocol can be found elsewhere (Ure et al. 1993, Fiedler 1995). A fourth step was applied in order to obtain the residual fraction, which was obtained by adding nitric acid to the residue from the last step of the sequential method (Kersten and Förstner 1986).

Samples were also submitted to an extraction with 0.1 mol L hydrochloric acid during two hours in two different conditions: (i) keeping the sample wet and anoxic in a glove box with nitrogen atmosphere and (ii) after drying the sample in the air at room temperature. A ratio of about 1:25 (mass:volume) was adopted for this procedure. In addition, total P contents were determined by an acidic digestion procedure, as described by Silva et al. (2002).

The obtained extracts were centrifuged and immediately filtered using a syringe fitted to a 0.45 μm Millex® membrane. Afterwards, determinations of phosphorus were made by the molbydenum blue method using a Micronal® B382 spectrophotometer with an optical path of 1 cm and standard P solutions with concentration ranging from 0.1 to 1.0 mg L^{-1} (as P). The followed methodology is presented by APHA (1995).

First, we assessed heavy metal contents in the same samples using both 0.1 mol L hydrochloric acid and the sequential extraction procedures and, in parallel, we determined P in the obtained extracts. Results were previously presented by Silva et al. (2002).

The standard reference sediment from NIST SRM-2704 was analyzed as quality control. The accuracy for total P concentration was 91.6%.

Results and Discussion

Tables 1 and 2 present analytical results determined for total contents and P fractions following the adopted procedures.

As shown in Table 1, total P contents were considerably higher in sediment samples from Billings, Pirapora and Rasgão reservoirs (B1, B2, P1 and P2) in comparison to samples from Barra Bonita reservoir (BB1 and BB2).

Total P concentration results obtained by acidic digestion agreed with the ones for the sum of P fractions (r = 0.96, p < 0.01). The majority of P was determined in residual fraction, considering that this element is supposed to be associated with

iron, aluminum and calcium as major sediment constituents (Laseras 1991). In terms of proportion of the residual fraction, it could be noted that samples from Barra Bonita reservoir were enriched in this fraction, which was more than 95% of the total P content (Σ step 1 to 4), while in samples from Billings, Pirapora and Rasgão reservoirs, it corresponded to around 58, 75 and 54%, respectively.

P fraction associated with an oxidized phase was present in all samples, which was not representative of organic P, though total concentrations were relatively higher in B1, B2, P1 and P2 samples compared to BB1 and BB2. To obtain the organic fraction, a procedure has been adopted with calcination of the sample (Pardo et al. 2004). The fraction extracted with hydroxylamine, which could correspond to reducible amorphous oxides and hydroxides of Fe and Mn (Ure et al. 1993), was determined only in samples from sites B1, B2, P1 and P2. From these results, it was suggested that these samples were likely more reactive, besides the higher total contents of P found in samples from Billings, Pirapora and Rasgão reservoirs in relation to Barra Bonita reservoir.

Potentially reactive P could be represented by the contents determined in steps 1, 2 and 3 from the sequential extraction procedure in relation to the total P content. For samples B1 and B2, it varied from 36% to 46%, while for P1 and P2 samples, it represented 25% and 46%, respectively. In BB1 and BB2 samples, the reactive P was very low, representing less than 6% of the total P content. This indicated that phosphorus was weakly bound to sediments, mainly in the environments close to the Metropolitan Area of São Paulo, relating to the pollution loads that constantly reach those environments.

Sediment can act as an internal source of phosphorus for the overlaying water (Zhou et al. 2001) and its release will depend on physical and chemical parameters represented by pH and E_H values, DO, nitrate and sulfate concentrations, and bacterial activity as pointed by Jin et al. (2006). From the data obtained during the field work, the absence of DO and extremely negative E_H values (-568 to -589 mV) was remarkable in overlaying waters for sampling sites B1, B2, P1 and P2, while pH values varied from 6.74 to 6.91. Those values are pointed to as determining conditions for P to release from sediments, characterized by anoxic environments (Esteves 1988).

Table 1 – Concentration values for phosphorus (as P) determined in extracts of sequential procedure. Results are presented in mg kg-1 of dry weight (average ± standard deviation, n = 2).* Not detectable

Sampling site	P- acetic acid (1st step)	P- hydroxy-lamine (2nd step)	P- H_2O_2/ NH_4Ac (3rd step)	P- residual (4th step)	P- Σ step 1 to 4	Total P (digestion procedure)
B1	8 ± 1	417 ± 15	471 ± 39	1.604 ± 35	2.500	2.650 ± 372
B2	16 ± 4	1.246 ± 49	820 ± 120	2.402 ± 291	4.484	3.684 ± 214
P1	15 ± 2	104 ± 3	220 ± 11	1.068 ± 110	1.407	1.356 ± 182
P2	6 ± 0	544 ± 17	448 ± 47	1.214 ± 65	2.212	2.783 ± 203
BB1	n.d.*	n.d.	14 ± 1	254 ± 9	268	373 ± 56
BB2	n.d.	n.d.	5 ± 1	182 ± 8	187	208 ± 5

Table 2 – Concentration values of phosphorus (as P) determined in extracts with HCl treatment. Results are presented in mg kg-1 of dry weight (average ± standard deviation, n = 2)

Sampling site	HCl- P Dry sample	HCl- P Crude sample
B1	637 ± 89	1.220 ± 120
B2	1.344 ± 93	1.624 ± 398
P1	262 ± 78	458 ± 33
P2	1.437 ± 402	1.660 ± 60
BB1	16 ± 4	6 ± 0
BB2	7 ± 1	10 ± 1

In general, the results obtained in this experiment did not agree with the ones determined by Silva and Toledo (1997), comparing samples from Pirapora and Rasgão reservoirs. This is probably due to the differences in analytical methods: the use of specific reactants such as sodium hydroxide, which could be more efficient in attacking dry sediment samples by extracting specific P fractions (Pardo et al. 2004).

HCl extracts are commonly associated with inorganic P (Pardo et al. 2004). Analytical results obtained with HCl treatment (as shown in Table 2) were consistent with the ones determined by the sequential extract (r ≈ 0.88, p < 0.05), as indicated on Table 1, that is, in sediment samples in which the amount of potentially reactive P increased, a higher content of P extracted with HCl in dry and crude samples was also observed, which were significantly correlated (r = 0.97, p < 0.01). This similarity is important, taking into account the levels of accu-

mulation of P and its associated forms in the studied environments. Moreover, other factors should be considered in order to evaluate the potential of P releasing from sediments despite its reactivity such as resuspension of bottom sediments during rainy season and dredging and disposal of bottom sediments from Tietê and Pinheiros river in the Metropolitan Area of São Paulo.

Although the sample from site B2 showed total P content relatively higher when compared to the others (see Table 1), it could be noted that the amount extracted with HCl treatment was close to the ones verified for crude samples from sites B1 and P2. Nevertheless, for sediment sampled at P1 site, results did agree proportionally with B1, B2 and P2 samples when total P content is considered. This behavior seemed to be similar to the data obtained for P by the sequential extraction procedure.

Sediment samples from Barra Bonita reservoir showed relatively low concentration values of P in

the extracts obtained with HCl treatment, despite the fact that its total P contents were much lower than the other samples. It is suggested that these sediments are considerably less reactive in terms of availability of P to the overlaying water in comparison to samples from the other environments.

It is noted that HCl extraction showed relatively higher P contents in crude samples than in dry samples (at sites B1, B2, P1 and P2), which is somehow in agreement with iron behavior for the same sediment samples (Silva et al. 2002). The drying process of samples with high contents of sulfide (B1, B2, P1 and P2) could retain P into Fe oxides through adsorption or even the formation of iron phosphates during sediment oxidation when samples were exposed to room temperature. However, analytical errors determined for samples gave no indication of such behavior, since differences in P concentration values between crude and dry samples were not significant (r = 0.97, p < 0.01).

Conclusion

Total P contents were considerably higher in sediment samples from Billings, Pirapora and Rasgão reservoirs (sites B1, B2, P1 and P2) in comparison to samples from Barra Bonita reservoir (sites BB1 and BB2), reflecting the direct influence of pollution loads from the Metropolitan Area of São Paulo.

Analytical results for HCl extracts showed an important correlation with the sequential extraction for the same sample, which means that when the amount of potentially reactive P was increased, an increase in P concentrations extracted with HCl was also observed, slightly higher in crude samples. This behavior indicates that P accumulated in sediments mainly from Billings, Pirapora and Rasgão reservoirs has a considerable potential to be released to overlaying water and, therefore, sediments may assume an important role in the fertilization process of water, in addition to the pollution loads that reach those environments.

Acknowledgements

References

APHA - American Public Health Association 1995. Standard methods for the examination of water and wastewater, 19th edition, Water Environment Federation, Washington DC, USA.

Branco S.M. 1966. Estudo das condições sanitárias da Represa Billings. *Arq. Fac. Hig. S. Paulo*, **20**:57-86.

CETESB - Cia de Tecnologia de Saneamento Ambiental 2006. Relatório anual da qualidade das águas interiores do Estado de São Paulo. Technical Report.

CETESB - Cia de Tecnologia de Saneamento Ambiental 1999. Monitoramento integrado das Bacias do Alto e Médio Tietê – avaliação da qualidade (água, sedimento e peixes), São Paulo. Convênio CETESB/SABESP contrato 20. Technical Report.

Chang S.C.; Jackson M.L. 1957. Fractionation of soil phosphorus. *Soil Science*, 84:133-144.

Danen-Louwerse H.; Lijklema L.; Coenraats M. 1993. Iron content of sediment and phosphate adsorption properties. *Hydrobiologia*, 253:311-317.

Esteves F.A. 1988. Fundamentos de Limnologia. Ed. Interciência - Finep, Rio de Janeiro, 575p.

Fiedler H.D.L 1995. Método común de extracciones secuenciales de metales en sedimentos: studio sobre la preparación de um material de referencia certificado. PhD Thesis. Barcelona, Spain: Universitat de Barcelona. 283p.

Hieltjes A.H.M.; Lijklema L. 1980. Fractionation of inorganic phosphates in calcareous sediments. *J. Environ. Qual.*, 9:405-407.

House W. 2003. Geochemical cycling of phosphorus in rivers. *Appl. Geochem.*, **18**:739-748.

Jahnke R.A. 1992. The phosphorus cycle. *In*: Butcher, S.S., Charlson, R.J., Orians, G.H., Wolfe, G.V. (eds.). *Global Biogeochemical Cycles*. Academic Press, UK, p. 317–52.

Jin X.; Wang S.; Pang Y.; Chang Wu F. 2006. Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas in Taihu Lake. *China Environ. Pollut.*, **139**:288-295.

Katsaounos C.Z.; Giokas D.L.; Leonardos I.D.; Karayannis M.I. 2007. Speciation of phosphorus fractionation in river sediments by explanatory data analysis. *Wat. Res.*, **41**:406-418.

Kersten M.; Förstner U. 1986. Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. *Wat. Sci. Techol.,* **18:**121-130.

Lamparelli M.C.; Kuhlmann M.L.; Carvalho M.C.; Salvador M.E.P. 1996. Avaliação do Complexo Billings - comunidades aquáticas, água e sedimento (out/92 a out/93), São Paulo. Technical Report.

Laseras P.L. 1991. Sedimentary phosphorus dynamics in epicontinental systems: a literature review. *Oecologia Aquatica*, 10:113-125.

Legg J.O.; Black C.A. 1955. Determination of organic phosphorus in soils: II. Ignition method. *Soil Sci. Soc. Am. Proc.* 19:139-143.

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.

Pardo P.; Rauret G.; López-Sánchez J.F. 2004. Shortened screening method for phosphorus fractionation in sediments: a complementary approach to the standards, measurements and testing harmonised protocol. *Anal. Chim. Acta*, 508:201-206.

Petersen G.W.; Corey R.B. 1966. A modified Chang and Jackson procedure for routine fractionation of inorganic soil phosphates. *Soil Sci. Am. Proc.*, 30:563-565.

Psenner R.; Pucsko R. 1988. Phosphorus fractionation: advantages and limits of the method for the study of sediment P origins and interactions. *Arch. Hydrobiol. Beih. Ergebn. Limnol.*, 30:43-59.

Rocha A.A.; Meiches L.A.M.; Lima Filho R.A. 1986. A qualidade sanitária e a recreação na Represa Billings. *Revista DAE*, **46**: 48-51.

Silva I.S.; Toledo M.C.M. 1997. Distribuição e fracionamento químico de fósforo em sedimentos

do Rio Tietê na região de Pirapora do Bom Jesus, SP. *Geochim. Brasil.*, **11**:243-259.

Silva I.S., Abate G., Lichtig J., Masini J.C. 2002. Heavy metal distribution in recent sediments of the Tietê-Pinheiros river system in São Paulo state, Brazil. *Appl. Geochem*. 17:105-116.

Sonzogni W.C.; Chapra S.C.; Armstrong D.E.; Logan T.J. 1982. Bioavailability of phosphorus inputs to lakes. *J. Environ. Qual.*, 11:555-563.

Ure A.M.; Quevauviller Ph.; Muntau H.; Griepink B. 1993. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International J. Environ. Anal. Chem.*, 51:135-151.

Van Eck G.T.M. 1982. Forms of phosphorus in particulate matter from the Hollands Diep/Haringvliet, The Netherlands. *Hydrobiologia*, 92:665-681.

Vollenweider R.A. 1985. Phosphorus, the key element in eutrophication control. *In*: International Conference Management Strategies for Phosphorus in the Environment. July, 1985. *Proceedings*. Lisbon.

Williams J.D.H.; Syers J.K.; Walker T.W. 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. *Soil Sci. Soc. Amer. Proc.*, 31:736-739.

Young T.C.; De Pinto J.V. 1982. Algal-availability of particulate phosphorus from diffuse and point sources in the lower Great Lakes basin. *Hydrobiologia*, 91:111-119.

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.