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Phosphorous control in a eutrophied reservoir

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Abstract Water in lakes and reservoirs accumulate phosphorous (P) from both internal and external loads. The external P load (EPL) coming from the watershed is considered to be the main cause of eutrophication of water bodies, and control strategies therefore focus on its reduction. However, algae blooms and anoxic conditions often continue even after EPL have been controlled, being the internal P load (IPL) originating from the sediment the main sources of P. To assess the efficiency of the adsorbent Phoslock (a modified bentonite) in controlling P concentrations in water and immobilize releasable P in sediments, mesocosm trials were carried out in a eutrophied reservoir and a model was described and applied that determines the amount of adsorbent and the application frequency necessary to control P concentrations in a eutrophied reservoir. The mesocosm trials confirm that Phoslock reduced P concentrations to or below the limits that define water in mesotrophic state, in approximately 2 weeks. The modeling results suggest that periodic reapplications of the adsorbent are required, unless EPL is reduced by 36 %, which allows the P concentrations in the water column to be constant. Such reduction in EPL would allow future applications of the adsorbent to be required only for control of IPL. The developed model allows planning remediation actions by determining quantities and frequencies for application of adsorbents for P control in eutrophied lakes and reservoirs.

Keywords External phosphorus load · Internal phosphorus load · Mesotrophic state · Adsorbent · Phoslock · Mesocosm trials · Model that describes the duration of P control

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Introduction

The enrichment of nutrients, mainly nitrogen (N) and phosphorus (P), or eutrophication, may cause excessive growths of algae and bacteria in water bodies. Although both nutrients may limit algal and bacterial growth, P is in most cases the limiting nutrient and therefore responsible for the appearance of algal blooms which may cause toxic effects in aquatic systems (CEPIS 2001; Golterman 1984).

Reservoirs receive P loads from external and internal sources. External phosphorous loads (EPL) include wastewater point sources and diffuse sources as urban runoff, agricultural, livestock, and other land uses in the watershed, as well as direct rainfall. The internal phosphorus load (IPL) occurs when P associated with redox-sensitive mineral phases in the sediment is released under conditions of negative redox potential (Eh) and becomes available for the growth of algae and bacteria (Søndergaard 2007).

Sediment P concentrations and IPL are consequences of various physical, chemical, and biological processes in water bodies, causing P to be partially deposited in sediments where it may be released once again to the water column as the sediment acts as a secondary P source (Søndergaard 2007). IPL is determined by the chemical forms of P, the redox potential of the sediment, and the depth of sediment from which P release occurs.

There are several methods to control concentrations of P in water bodies (Cooke et al. 2005). These methods include the control of EPL by eliminating wastewater discharges, installation of wastewater treatment plants with P removal technologies, implementation of different uses of soil, improvements of irrigation methods, control of uses of fertilizers, reforestation to prevent soil erosion, and control of livestock nutrition and discharges (FAO 1997). The IPL control technologies include P coagulation and sedimentation with aluminum (Al), iron (Fe), or calcium salts and removal of P in water and P immobilization in sediment with restoration strategy. Control of P by coagulation and sedimentation presents short duration since the Al and calcium ions dissolve when pH increase in water or decrease in the sediment (Cooke et al. 2005), while Fe dissolve due to decrease in Eh in stratified water columns and sediment (Ozkundakci and Hamilton 2006). In contrast, adsorbents are used to decrease orthophosphate concentrations in the water column and immobilize P in sediment by forming compounds that are stable even under reduced conditions (negative Eh) and during naturally changing pH. Therefore, the use of adsorbents is highly recommended for control of IPL (Liu et al. 2012; Afsar and Groves 2009; Spears and May 2009).

Schauser et al. (2003) developed a tool to describe the results of P control by regulating EPL and IPL (Fig. 1). It is observed that without control of EPL, it is necessary to perform continuous applications of IPL. On the contrary, when EPL is controlled, it may be necessary to apply the IPL control only once.

In this paper, the results of the decrease in P concentrations are presented as a result of application of the adsorbent Phoslock in mesocosm experiments in a eutrophied reservoir, and a model is described that determines the amount of adsorbent and the duration of the P control in water and sediment of lakes and reservoirs. Phoslock is a commercial product based on bentonite that has been modified by ion exchange, containing lanthanum as the active ingredient (Afsar and Groves 2009). This model was applied to a case study in a eutrophic reservoir, considering the EPL as well as a reduction in EPL that allows maintaining at steady state the P concentration in the water column, such as illustrated in Fig. 1d.

The present study was carried out in a eutrophied reservoir that is a multiple-purpose water body used for tourism, fishery, and water supply; it has a surface area of 1,680 ha, an average volume of 328 Mm^3, an average depth of 19.5 m, and presents thermal stratification from March to September. The reservoir is located in an area with temperate climate with an annual rainfall of 928 mm and average temperature of 18.75 °C (CCVBA 2013). The hydrological basin has an extension of 615 km^2, a human population of close to 81,832 habitants (Villanueva-Beltrán 2011), and the land uses include forestry, agriculture, grassland, livestock, fish culture, and urban areas. Based on the P concentrations measured in the reservoir and the OECD (1982) limits for this nutrient, the reservoir is classified as eutrophic throughout the year (Olvera et al. 1998; Merino-Ibarra et al. 2007; Hansen and Márquez-Pacheco 2012a). The

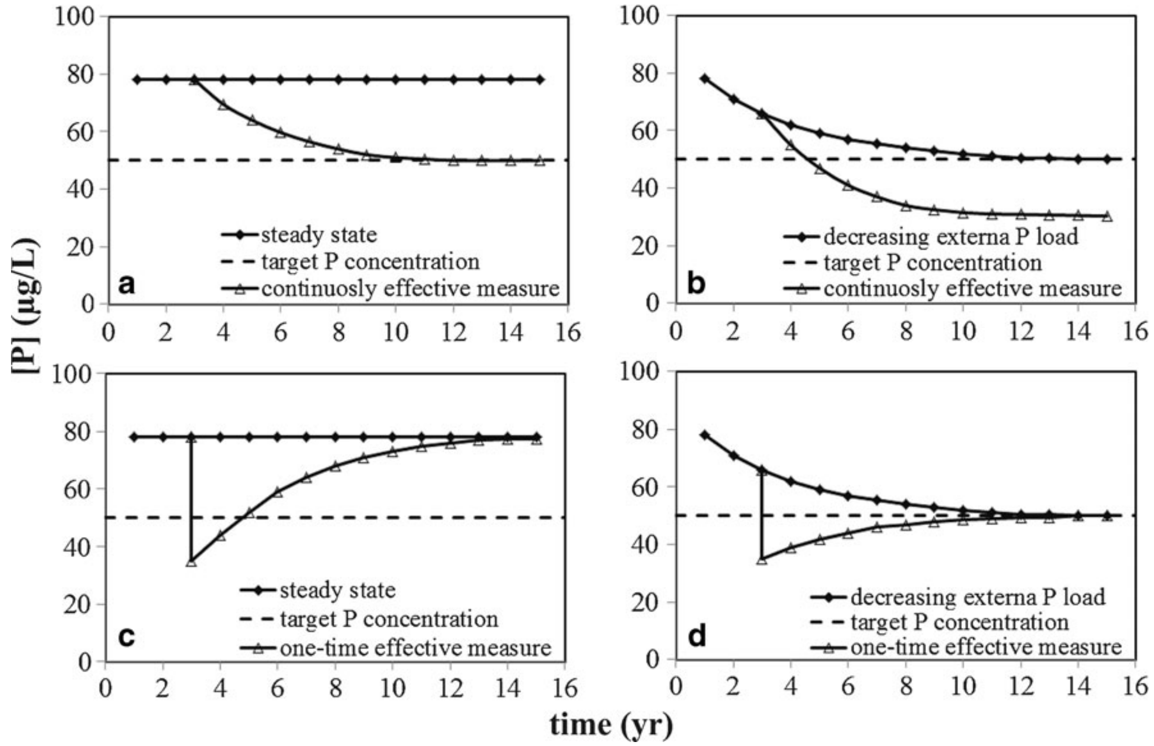


Fig. 1 Effects of control of EPL and IPL on the P concentrations in a lake. Considering continuous IPL control events: **a** unchanged EPL; **b** decreased EPL. Considering a single IPL control event: **c** unchanged EPL; **d** decreased EPL. Modified from Schauser et al. (2003)

sediment texture is clayey silt with high content of organic matter.

Mesocosm experiments with Phoslock

To evaluate the efficiency of Phoslock to reduce P concentrations in the eutrophied reservoir, we installed eight mesocosms (d=0.9 m; h=6.0 m high-density polyethylene pipes with stainless steel cylinders hermetically attached to the bottom of the pipes). The steel cylinders were introduced in the sediment, and each mesocosm was secured at 3-m height with three cables and concrete loads on the bottom of the reservoir, and introduced in steel rings fastened to an anchored floating platform, allowing movement of the mesocosms due to fluctuations in the water level. To achieve reductive dissolution of Fe in the sediment, Eh in the mesocosms were reduced by covering with hermetical high-density polyethylene lids, avoiding thereby contact with atmospheric oxygen. The water depths inside the mesocosms were 5.3±0.2 m.

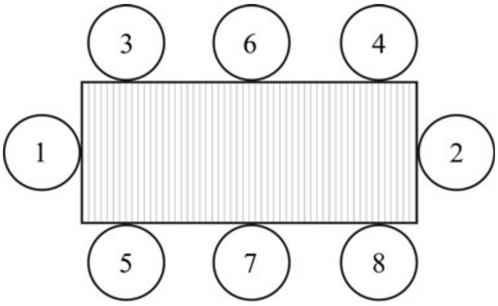
Before adding Phoslock to the mesocosms, the water columns were sampled at 2.5 and 5.0 m depths for determination of initial, Eh, pH, nitrogen as ammonium (N-NH_4), and nitrogen as nitrate (N-NO_3) with Hydrolab DS5 (Hach, Loveland, USA), and water samples were obtained with an acrylic 1-L horizontal water sampler (Wildco Wildlife Supply Co., New York) for determination of orthophosphate (P-PO_4) and total P (TP) by colorimetric methods (Merck Pharo spectrophotometer 300, Darmstadt, Germany) (Merck 2012). Sediments were obtained with a stainless steel 15.2 cm Ekman dredge (Wildco Wildlife Supply Co., New York) and characterized for organic matter content (OM) by ignition at 450 °C (ASTM 2000); TKN (EPA 1993); total P by spectrophotometry (Kou 1996); Al, Fe, and manganese (Mn) by atomic emission spectrometry (EPA 1996); and texture by sedimentation (ASTM 2007). The Hydrolab DS5 was introduced approximately 15 cm in the sediment by free fall, and pH and Eh were determined. Through the sequential extraction method (Psenner et al. 1984), the chemical forms of P were determined in the sediment samples and the amount of potentially releasable P was calculated as the sum of the concentrations of P in interstitial water, P bound to Fe and Mn oxides, P made available by reduction, and organic P. Density was obtained gravimetrically (DOF 2002).

The results of the characterization of water and sediment before adding the adsorbent are presented in Table 1. It is observed that pH in water and sediment was slightly alkaline; the sediment texture was mainly silty with low content of organic matter, according to the limits established in DOF (2002). According to the limits for total P published by OECD (1982), the water may be classified as eutrophic. It is also observed that Eh in both water and sediment were positive representing oxidized conditions.

Table 1 Characterization of water and sediment in the mesocosms before adding the adsorbent

Parameter	Analytical method	Mean± standard deviation
Water (n=16)		
pH	Hydrolab DS5	8.72±0.12
Eh (mV)		43±38
N-NH_4 (mg/L)		0.71±0.12
N-NO_3 (mg/L)		0.06±0.00
P-PO_4 (mg/L)	Spectroquant Merck, 1.14848	0.06±0.01
TP (mg/L)	Spectroquant Merck, 1.14543	0.07±0.01
Sediment (n=8)		
pH	Hydrolab DS5	7.55±0.48
Eh (mV)		45±37
OM (%)	D2974-00; ASTM (2000)	2.11±0.76
TKN (mg/kg dw)	EPA 351.2; EPA (1993)	3,174.8± 430.2
TP (mg/kg dw)	MSA 73–3; Kou (1996)	919.9±58.9
Al (mg/kg dw)	EPA 6010B; EPA (1996)	30,769±4,581
Fe (mg/kg dw)		29,606±899
Mn (mg/kg dw)		443.75±70.33
Sand (%)	D422-63; ASTM (2007)	21.33±23.6
Silt (%)		55.27±12.5
Clay (%)		23.40±11.7
Potentially releasable P from sediment (P_{pr}) (mg/kg dw)	Psenner et al. (1984)	321.7±22.8
Density (kg dw/L)	DOF (2002)	0.17±0.03

Phoslock was added in three different doses to four of the mesocosms (1, 3, 5, and 7), while no adsorbent was added to mesocosms 2, 4, 6, and 8 (Fig. 2). The dose of adsorbent was calculated using Eq. 1. The first dose was the amount of adsorbent necessary to achieve the mesotrophic state (MS) in water and immobilize 10 % of potentially releasable P in sediment, resulting in an overall dose of Phoslock/P 15:1. This dose was determined based on short-term experimental observations of P release in sediment from the water body, reported by Hansen and Marquez-Pacheco (2012a). The second dose was the amount of adsorbent required to achieve the MS in water and immobilize 35 % of the potentially releasable P (P_{pr}), in sediment corresponding to P in interstitial water, P bound to Fe and Mn oxides, and P available by reduction, resulting in an overall dose of Phoslock/P 40:1. This dose was determined based on the chemical forms of P determined by selective extraction of



Mesocosm	Phoslock:P (g/g)
1 ,3, 5, 7	15:1, 40:1, 100:1
2, 4, 6, 8	0:1

Fig. 2 Mesocosms experimental setup

sediment samples from the water body, as reported by Hansen and Marquez-Pacheco (2012a). The third dose of adsorbent was added to achieve MS in water and immobilize 100 % of the potentially releasable available P in sediment, resulting in an overall dose of Phoslock/P 100:1, which is recommended by the manufacturer (Afsar and Groves 2009).

The amounts of Phoslock were calculated according to Eq. 1:

$$\mathrm{Ads} = \pi r^2 \left[([\mathrm{TP}] - \mathrm{MS})L + \left(P_{\mathrm{pr}}\, \rho\, E \right) \right] 10^{-3} \mathrm{dAds} \qquad (1)$$

Where

Ads	Amount of Phoslock (in kilogram)
π	3.1416
r	Radius of the pipe (in meter)
[TP]	Concentration of total P in water (in milligram per liter)
MS	Mesotrophic state P concentration (in milligram per liter)
L	Depth of the water column (in meter)
P_{pr}	Potentially releasable P in sediment (in milligram per kilogram dry weight)
E	Depth of sediment from which P release occurs (in meter)
ρ	Sediment density
dAds	Dose of adsorbent dose per total P
10^{-3}	Factor converting (in cubic meter milligram per liter to kilogram)

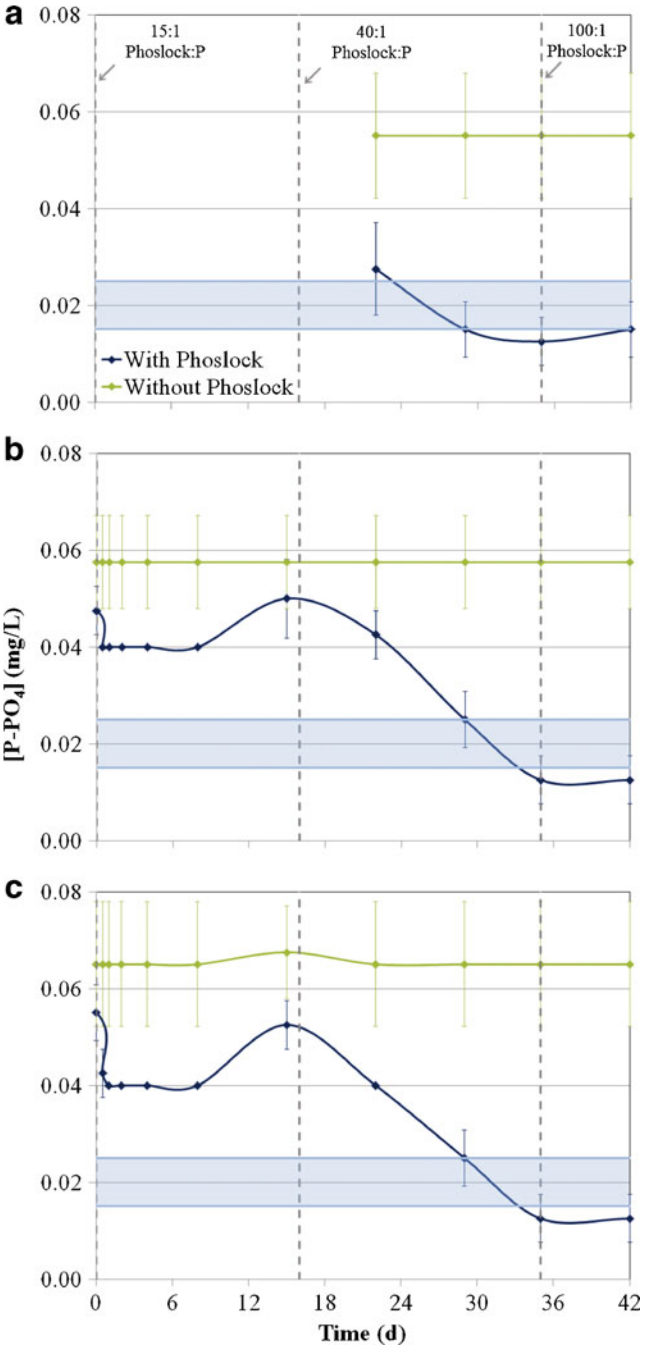


Fig. 3 Mesocosm experiments with Phoslock. Sampling depths: **a** 0.5 m; **b** 2.5 m; and **c** 5.0 m. *Highlighted bands* indicate MS limits according to OECD (1982)

Orthophosphate concentrations were monitored in the mesocosms during 6 weeks after application of the first dose of adsorbent on day 0. The second doses were applied on day 16, and the third dose, on day 34. Results indicate a reduction in P-PO_4 concentrations from 25 to 50 % after application of the dose Phoslock/P 15:1 (Fig. 3). Because there were no inputs to the mesocosms and IPL was observed in the mesocosms without adsorbent during the time period of the experiment, very little variations in phosphate concentrations were observed. In the mesocosms with Phoslock, P-PO_4 concentrations decreased after the application of the first dose. Two weeks later, P-PO_4 concentrations returned to previous values, probably due to IPL caused by molecular diffusion of P-PO_4 from interstitial water in the sediment to the water column where P-PO_4 had been removed by the adsorbent and Eh became increasingly negative. Throughout the experiment, Eh was monitored at the sediment–water interphase. To not disturb the sediment, sediment Eh was determined in the beginning and in the end of the experiment. A reduction of Eh at the sediment–water interphase from 43 to −45 mV was observed, while Eh in the sediment was reduced from 45 to −117 mV.

After application of the dose Phoslock/P 40:1, P-PO_4 concentrations soon became at or below the MS concentrations. This reduction was observed in the entire water column between 12 and 18 days after application. After application of the dose Phoslock/P 100:1, no further change in P-PO_4 was observed, indicating that P released from the sediment was being immobilized by Phoslock.

The results of the mesocosm experiments showed a 75 % reduction in P in 18 days after the second application of Phoslock. High P removal efficiencies by Phoslock were also described elsewhere (Yasseri and Van Goethem 2008; Robb et al. 2003), although the times reported to achieve removal of P were much longer than in these experiments. Our results indicate that Phoslock was effective in removing P from the water column of the eutrophic reservoir within 2 weeks after application. The recommended dose of 100:1 Phoslock/P should be applied to control P in water and P originating from the IPL. To determine the amount of adsorbent to be applied in lakes and reservoirs and the duration of P control, in addition to TP and P_{pr}, it is necessary to consider EPL, the sediment P accumulation rate, and the depth of sediment from which P release occurs.

Model that determines the amount of adsorbent and the duration of the P control

To determine the amount of adsorbent and the duration of the control of P, Hansen and Márquez-Pacheco (2012b) developed the mathematical model MOCONPAI that determines the duration of P control in water and sediment by use of insoluble adsorbents. This model considers TP, IPL, EPL, sediment P accumulation rate, sediment mixing depth, and depth of sediment from which P release occurs, and that once applied, the adsorbent is distributed evenly by physical and biological processes in "x" centimeter of sediment and it reacts with P_{pr}, in this layer. Each year, the thickness of sediment increases by a new annual layer caused by the sedimentation of "y" centimeter, and since a layer of the same thickness is buried, x remains constant. The model equations are described to define the amount of adsorbent and the duration of the P control in sediment and in water for annual and multiannual applications, considering the EPL and a reduction in EPL necessary to obtain stationary state P concentrations.

Phosphorus control in sediment

The amount of adsorbent necessary to immobilize P_{pr} in x centimeter is 100 %. If an excess amount of adsorbent is added ($\mathrm{Ads}_{\mathrm{exc}}$), immobilization of P_{pr} will occur in future layers and the distribution of $\mathrm{Ads}_{\mathrm{exc}}$ in each annual y layer ($\mathrm{Ads}_{\mathrm{layer}}$) can be calculated as:

$$\mathrm{Ads}_{\mathrm{layer}} = \left[\mathrm{Ads}_{\mathrm{exc}} - \frac{100\,y}{x}\right]\frac{1}{(x+y)/y} \tag{2}$$

Where "100 y/x" represents the adsorbent that is consumed by y, and "$(x+y)/y$" represents the number of annual layers in "$(x+y)$."

While $\mathrm{Ads}_{\mathrm{layer}}$ is positive, the ability to immobilize P_{pr} continues, so that the duration of the control of P, "t", is equal to the period that fulfills the condition $\mathrm{Ads}_{\mathrm{layer}}>0$:

$$t = t\left(\mathrm{Ads}_{\mathrm{layer}} > 0\right) \tag{3}$$

The amount of adsorbent necessary to control P in the first annual application ($\mathrm{Ads}_{1.\ \mathrm{annual}}$) is calculated as:

$$\mathrm{Ads}_{1.\ \mathrm{annual}} = x\,\rho\,A\left[P_{\mathrm{pr}}\right]\mathrm{dAds}\ 10^{-4} \tag{4}$$

Where $x\ \rho\ A\ [P_{pr}]$ is the mass of P_{pr} in x in the area (A) where the IPL occurs and 10^{-4} is the factor that converts "centimeter gram hectare milligram per cubic centimeter kilogram" to "ton". The amount of adsorbent necessary to apply every year ($\mathrm{Ads}_{\mathrm{annual}}$) after the first annual application is then determined by:

$$\mathrm{Ads}_{\mathrm{annual}} = \mathrm{Ads}_{1.\mathrm{annual}}\,y/(x+y) \tag{5}$$

The amount of adsorbent necessary to control P_{pr} in the first multiannual application ($\mathrm{Ads}_{1.\mathrm{multianual}}$) is calculated by Eq. 6, while Eq. 7 calculates the amount of adsorbent necessary in the following multiannual applications ($\mathrm{Ads}_{\mathrm{multiannual}}$):

$$\mathrm{Ads}_{\ 1.\mathrm{multiannual}} = \mathrm{Ads}_{\ 1.\mathrm{annual}}\left(1+\mathrm{Ads}_{\mathrm{exc}}\right) \tag{6}$$

$$\mathrm{Ads}_{\ \mathrm{multiannual}} = \mathrm{Ads}_{\ 1.\mathrm{annual}}\mathrm{Ads}_{\mathrm{exc}} \tag{7}$$

Phosphorus control in water

The amount of adsorbent necessary to reach the mesotrophic P concentrations in water ($\mathrm{Ads}_{\mathrm{water}}$) is determined as follows:

$$\mathrm{Ads}_{\mathrm{water}} = ([\mathrm{TP}] - \mathrm{MS})V\ \mathrm{dAds} \tag{8}$$

Where V is the water volume in the lake or reservoir, $([\mathrm{TP}]-\mathrm{MS})\ V$, the amount of P to be removed, and dAds, the dose of adsorbent per unit P.

To determine the reduction of total P (ΔTP) in the water, the P mass balance (Eq. 9) was applied, where EPL and IPL are the external and internal loads of P, $\mathrm{TP_{extr}}$ is P removed from the reservoir (by extraction of water and biota), $\mathrm{TP_{sed}}$ is the sediment P accumulation rate, and ([TP]−MS) V, P removed with the adsorbent:

$$\Delta \mathrm{TP} = \mathrm{EPL} + \mathrm{IPL} - \mathrm{TP_{extr}} - \mathrm{TP_{sed}} - ([\mathrm{TP}] - \mathrm{MS})V \qquad (9)$$

Assuming that the IPL is being controlled by immobilization of P_{pr} in the sediment, this is considered to be zero. Under this assumption, Eq. 9 becomes:

$$\Delta \mathrm{TP} = \mathrm{EPL} - \mathrm{TP_{extr}} - \mathrm{TP_{sed}} - ([\mathrm{TP}] - \mathrm{MS})V \qquad (10)$$

To calculate the concentration of TP in water 1 year after the application, $[\mathrm{TP}]_{n+1}$, ΔTP is divided by V and added to the initial concentration of total P, $[\mathrm{TP}]_n$,

$$[\mathrm{TP}]_{n+1} = [\mathrm{TP}]_n + \frac{\Delta \mathrm{TP}}{V} \qquad (11)$$

When $[\mathrm{TP}]_{n+1}$ exceed MS, a new application of adsorbent is required:

$$t = t\left([\mathrm{TP}]_{n+1} > \mathrm{MS}\right) \qquad (12)$$

Application of the model to determine the amount of adsorbent and the duration of P control in a eutrophic reservoir

The model was applied to calculate the duration of the P control in the reservoir described above. Potentially releasable P_{pr}, EPL, $\mathrm{TP_{sed}}$, x, the depth of sediment from which P release occurs, and $\mathrm{TP_{extr}}$ were obtained as follows.

Potentially releasable P

To determine P_{pr}, $\mathrm{TP_{sed}}$, x, and depth of sediment from which P release occurs, eight sediment cores were obtained from three sampling sites within the reservoir of different depths, using a gravity core sampler (Wildco Wildlife Supply Co., New York) equipped with a 4.8-cm diameter, 50.8-cm length cellulose acetate butyrate liner.

The upper 20 cm of one sediment core from each site was divided in 5 cm sections that were dried at room temperature to constant weight, and TP concentrations were determined by spectrophotometry (Kou 1996). TP in the sediment profiles (Fig. 4) showed a decrease of 30 % in TP in from the first (0–5 cm) to the second section (5–10 cm) of the cores from the intermediate and deep sites, followed by smaller decreases in TP in deeper sections. A total decrease of 35 % TP is observed in the upper 20 cm of these sediment profiles. The sediment core from the shallow site shows a different pattern in TP concentration (Fig. 4), probably due to higher influence from the EPL in this site. Since the shallow part of the reservoir has a relatively small area (Table 2), we considered that P_{pr} from intermediate and deep areas is mainly responsible for the IPL in the reservoir.

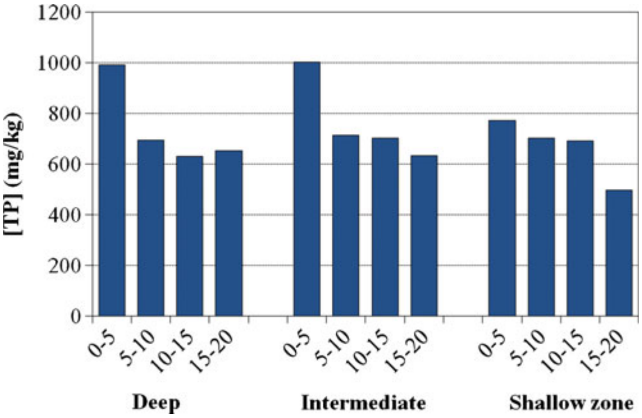


Fig. 4 *TP* in the layers of sediment cores from different depth sites in the reservoir. *Numbers on the x-axis* indicate layer thickness (in centimeter)

External P load

Villanueva-Beltrán (2011) estimated the EPL from the watershed of the study reservoir by determining runoff with a geographical information system (ArcView 9.2). An inventory of livestock and fish farming discharges and runoff from soils with different uses was compiled, and discharge volumes were estimated based on livestock and fish production. The method of rainfall–runoff for the different land uses was applied by analyzing hydrological data for the watershed and obtaining the runoff factors (Aparicio Mijares 2009). Estimated runoffs were verified with existing hydrographical data from the area (Conagua-IMTA 2007). TP concentrations were obtained by Villanueva-Beltrán (2011) from the published literature according to the type of discharge and reported for areas with similar climate and land uses, obtaining EPL of 65.54 t/year. Phosphorous added to the reservoir by 22.5 $\mathrm{Mm^3}$/year direct rainfall was estimated in 0.36 t/year, considering average TP concentrations of 0.017 mg/L (Sawyer et al. 1994). Total EPL is the sum of the P load from the watershed and P entering the reservoir from direct rainfall.

Sediment P accumulation rate

A second core from each sampling site was used for isotope dating. The upper 19 cm of the cores were divided in 1 cm sections and the remaining length of the cores in 2 cm sections. Sections were dried at room temperature to constant weight, and the densities of the core sections were determined. The decays of $^{210}\mathrm{Pb}$ and $^{137}\mathrm{Cs}$ were used for

Table 2 Determination of TP_{sed}

Area	Sediment accumulation rate (g/cm^2 year)	Density (g/cm^3)	Area[a] (km^2)	$[P]_{sed}$[a] (mg/kg)	Sedimentation rate, y (cm/year)	TP_{sed} (t/year)
Shallow ($d<3.5$ m)	0.21	0.61	1.3	597±168	0.34	1.59
Intermediate ($3.5<d<13$ m)	0.38	0.31	8.5	1,083±256	1.23	34.55
Deep ($d>13$ m)	0.21	0.19	7.0	1,145±275	1.11	16.67
Total			16.8		1.17	52.81

[a] Hansen and Márquez-Pacheco (2012a)

dating of the sediment cores and the ^{137}Cs, ^{210}Pb, and ^{226}Ra were determined by gamma spectrometry based on ASTM methods C 1402-98 and E 181-98 similar to the methodology described by Fuller et al. (1999), van Metre and Fuller (2009), and Corbett et al. (2009). Excess ^{210}Pb activities were calculated as the difference between total ^{210}Pb and ^{226}Ra activities. Mass accumulation rates (MAR) were estimated from the linear regression of the natural logarithm of excess ^{210}Pb plotted against accumulated sediment mass per area for each sediment layer. This linear regression is referred to as the constant flux–constant sedimentation rate model and is based on the assumption that (1) the ^{210}Pb flux onto the sediment–water interface is constant, (2) there is a minimum post-deposition ^{210}Pb migration, and (3) the local sedimentation rate is constant. The MAR was converted to linear accumulation rate by dividing with the bulk sediment density. The ^{210}Pb chronologies were compared to the history of nuclear bomb fallout ^{137}Cs in the core profiles. TP concentrations from 23 sampling stations in the reservoir and depth areas of the reservoir were obtained from Hansen and Márquez-Pacheco (2012a).

The sediment accumulation rates showed a difference between the sites of the reservoir, recording the highest values in the intermediate sites (Table 2) and almost half of this value in the cores from the shallow and deep sites. The sediment accumulation rate varied between 0.34 cm/year for the core of the shallow site and 1.23 and 1.11 cm/year for the core from the deep site. The total net sediment P accumulation rate for the reservoir was calculated as 52.81 t/year.

Sediment mixing depth (x)

The sediment mixing depth was determined as the depth where a strong gradient along the ^{210}Pb profile occurred. Mixed layers varied from 3 cm in the core from the deep site, 8.5 cm for the core from the intermediate depth site (Fig. 5), and 11.0 cm for the shallow site. Since areas of intermediate and deep sites are almost the same and represent 92 % of the total area of the reservoir, in this paper we averaged the sediment mixing depths for these areas, resulting in 5.8 cm.

Depth of sediment from which P release occurs

The depth of sediment from which P release occurs was determined by P release experiments. Experimental depths of five sediment cores were adjusted gravimetrically in the sampling tubes, to 5, 10, 15, 20, and 25 cm from the sediment–water interface, and sealed hermetically in the lowest end. A water sample was obtained from the reservoir, TP concentration of 0.08 mg/L was determined and 500 mL split samples were added to each tube. To eliminate air, N_2 (g) (Infra high purity) was supplied to the tubes during 5 min before covering hermetically, and the cores were incubated in the dark at 10.1±0.6 °C. During incubation, the center of the water columns was periodically monitored under low N_2 (g) flow for potentiometric determination (Thermo Orion Dual Star) of pH (Orion ROSS Ultra® electrode), Eh (Orion Redox/ORP Triode electrode), and temperature (Orion electrode ATC Probes). When Eh stabilized at Eh=−391±56 mV, and pH=6.92±0.14, during 2 days, 60 mL water samples was obtained from the center of

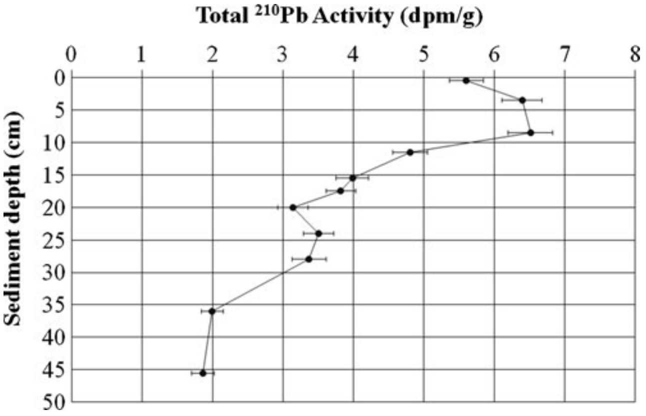


Fig. 5 Lead-210 activity in sediment core vs. sediment depth. Intermediate depth site

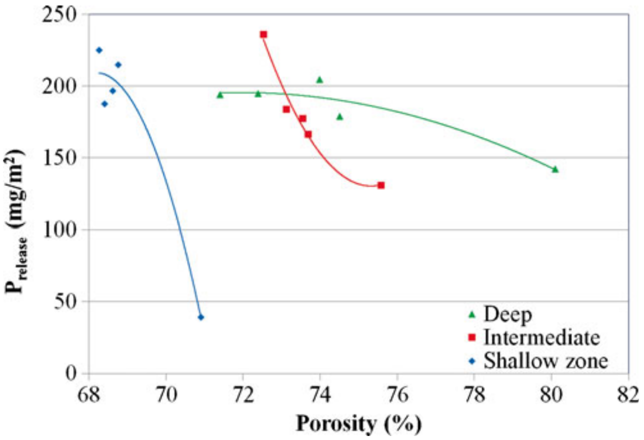


Fig. 6 Phosphorus release and porosity of the sediment cores. Five centimeters increased sediment depth from lowest to highest P release data points. Eh=−391±56 mV

the water columns with a syringe and silicone tube for determination of released P (P release) by colorimetry (Merck Pharo spectrophotometer 300, Darmstadt, Germany) according to Merck (2012).

The porosities of the sediment layers were determined in the remaining cores from each sampling site according to Juárez-Badillo and Rico-Rodriguez (2005). Five centimeter sediment layers were dried to constant weight and the pore volume was determined as the weight difference (water density=1 g/cm^3) in the volume of the section (Eq. 13).

$$\eta = \frac{V_p}{V_s} \times 100 \tag{13}$$

Where

η	Porosity (in percent)
V_p	Volume of voids or pores (in cubic centimeter)
V_s	Volume of the section (in cubic centimeter)

Porosities for each sediment depth were obtained by averaging the porosities for the contained layers. The resulting release of P and porosities are presented in Fig. 6 where it can be observed that for sediments from the deep site, porosity strongly decreased with increasing sediment depth, causing P release to occur up to a 15-cm sediment layer (Fig. 6). For sediments cores from the shallow and intermediate sites, porosities did not vary considerably when sediment depths increased over 5 cm, causing P release to occur in the entire 25-cm depths of the cores.

Determination of extracted P (TP_{extr})

Average extracted water volumes of 6.0 m^3/s and average P concentrations in the water body of 0.062 mg/L (Patricia Flores, Conagua, 2012. Personal communication) were used

Table 3 Parameters and values used to apply the model to determine the amount of adsorbent and the duration of the P control in water and sediment

Parameter	Symbol	Units	Amount
Sediment mixing depth	x	cm	5.8
Average annual sedimentation layer	y	cm	1.2
Concentration of potentially releasable P (determined as 35 % of TP in the sediment, see Fig. 4)	$[P_{pr}]$	mg/kg	SA=271 IA=351 DA=347
Density of x	ρ	g/cm^3	SA=0.61 IA=0.31 DA=0.19
Area[a]	A	ha	SA=130 IA=850 DA=700
Phoslock dose per unit P	dAds	kg/kg	100
Concentration of TP in water	[TP]	mg/L	0.083
MS P concentration interval	0.015<MS<0.025	mg/L	0.015<MS<0.025
Water volume	V	Mm^3	344.9
Total external P load	EPL	t/year	65.90
Extracted P	TP_{extr}	t/year	17.45
Sediment P accumulation rate	TP_{sed}	t/year	52.81
Internal P load	IPL	t/year	17.93

SA shallow area, *IA* intermediate depth area, *DA* deep area

[a] Hansen and Márquez-Pacheco 2012a

Table 4 Distribution of the adsorbent in x ($\text{Ads}_{\text{layer}}$, in percent)

Sediment depth (cm)	Year						
	0	1	2	3	4	5	6
7.2							−0.83
6.0						2.50	−0.83
4.8					5.83	2.50	−0.83
3.6				9.17	5.83	2.50	−0.83
2.4			12.50	9.17	5.83	2.50	−0.83
1.2		15.83	12.50	9.17	5.83	2.50	−0.83
0.0	19.17	15.83	12.50	9.17	5.83	2.50	*−5*
−1.2	19.17	15.83	12.50	9.17	5.83	*15.00*	
−2.4	19.17	15.83	12.50	9.17	*35.00*		
−3.6	19.17	15.83	12.50	*55.00*			
−4.8	19.17	15.83	*75.00*				
−6.0	19.17	*95.00*					
−7.2	*115.02*						
Phoslock buried below x (65.00 %)	**19.17**	**15.83**	**12.50**	**9.17**	**5.83**	**2.50**	**−0.83**

to obtain TP_{extr} in water extractions of 11.65 t/year. Extracted flora, mainly water hyacinth, of 1,217 t DW/year (Patricia Flores, Conagua 2012, personal communication) and considering a P concentration of 0.45 % DW in water hyacinth (Olvera 1988) resulted in a TP_{extr} of 5.5 t/year due to extracted flora. Fishery is estimated in 20 t DW/year. Considering a concentration of 1.5 % P in fish (Sterner and George 2000), a P extraction of 0.3 t/year due to fishery can be estimated. Together, these figures indicated a total TP_{extr} of 17.45 t/year.

Since Phoslock acts as an adsorbent of orthophosphate, remediation is recommended to be carried out when thermal stratification of the water column initiates in the month of February, when concentrations of P-PO_4 are highest and biomass is still low. Application of the model was therefore made with information from February 2010, when the water volume was 344.9 Mm^3 and the average P concentration in 46 sampling points distributed within the reservoir was 0.083 mg/L (Juan Manuel Martínez, Conagua 2012, personal communication, Table 3).

Application of the model

The amount of Phoslock necessary to obtain MS concentrations of TP in water and to immobilize IPL was calculated

Table 5 Amounts of Phoslock and application frequencies for P control in the eutrophied reservoir

Scenarios	Application in water (t)	Application in sediment (t)	Total application (t)
Total EPL 65.90 t/year			
Annual application in sediment			
First year	1,998	9,288	11,286
Future applications	431/year	1,592/year	2,023
Five-yearly application in sediment			
First year	1,998	19,968	21,966
Future applications	431/year	10,681/5 years	11,112
Reduced EPL of 42.18 t/year			
Annual application in sediment			
First year	1,480	5,944	7,424
Future applications	0	1,019/year	1,019
Five-yearly application in sediment			
First year	1,480	12,780	14,260
Future applications	0	6,836/5 years	6,836

applying Eq. 2 to 12. The values of the parameters, obtained as described above, are presented in Table 3.

Application of the model for P control in sediment

The model was applied to calculate the amount of Phoslock necessary for annual and multiannual applications. For the annual application, the amount of Phoslock added was 100 %, while for the multiannual application, 215 % of Phoslock was added; the duration of the restoration was determined, considering that 100 % adsorbent immobilize P_{pr} and the 115 % excess adsorbent (Ads_{exc}) will remove P_{pr} that accumulate during the following years.

The distribution of Phoslock in x and y and Ads_{layer} are presented upright in Table 4. Ads_{exc} is the sum of Ads_{layer} and has been presented in italics. The percentages of adsorbent buried below x are presented in bold. This amount will immobilize IPL generated due to slower kinetic processes in sediment layers of depths up to 20 cm.

It is observed that Ads_{layer} remains positive during 5 years, after which, reapplication of Phoslock is necessary. IPL from the mixed layer represents 85 % of the total IPL and the remaining 15 % is released from below this layer. Since the total amount of adsorbent buried below x, is 65 %, this will immobilize the 15 % IPL that occur below x but the remaining adsorbent would be buried and of no use for the P control in sediment. It is therefore recommended to control the IPL with annual applications of the adsorbent.

Application of the model for P control in water

Applying Eq. 10, we investigated the reduction of the EPL necessary to maintain steady-state P concentration in the water column of the reservoir. By trial and error, we estimated that a 36 % reduction in EPL and one application of adsorbent in water would allow keeping steady-state concentrations of TP in the reservoir. If enough adsorbent is added to obtain TP within MS, future control strategies should include control of IPL only.

Based on this, we determined the amount of adsorbent required to control P in water, considering the following scenarios:

- Total EPL (65.90 t/year)
- Reduced EPL=64 % of total EPL (42.18 t/year)

For the reduced EPL scenario, both TP_{sed} and IPL decrease in the same proportion as EPL. The results are presented in Table 5 together with those for control of IPL.

Considering the actual EPL, constant applications of Phoslock in water and sediment are needed to maintain P concentrations within the MS limits. Reducing the total EPL in 36 % (to 42.18 t/year), one application of the adsorbent in the water column allows limiting the P control strategy to controlling IPL only and applying smaller amounts of Phoslock (Table 5).

Conclusions

The results from mesocosm experiments in a eutrophic reservoir confirm that Phoslock reduces $P\text{-}PO_4$ concentrations to target MS concentrations, in approximately 2 weeks after application and that the adsorbent immobilizes IPL.

We described and applied a model that determines the amount of adsorbent and the application frequency to control P in both water and sediment and we applied this model to determine the P control in the eutrophied reservoir, considering scenarios of actual and reduced EPL. With annual applications, an initial 100 % dose of the adsorbent is required followed by 17.9 % yearly doses. Multiannual applications are nor convenient because the part of the buried adsorbent is in excess compared to P_{pr} in the sediment depth from which P release occurs. Considering the scenario of a 36 % reduction in EPL, and that IPL is being controlled, it was estimated that one application in water would allow P concentrations within the MS limits. Thus, this scenario would allow future applications of the adsorbent to be required only for control of IPL.

This model is a tool that allows planning remediation actions by determining quantities and frequencies for application of adsorbents for P control in eutrophied lakes and reservoirs. Continuous after application measurements of P concentrations in the water column should be carried out to evaluate the effect of the P control in the reservoir.

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References

Afsar A, Groves S (2009) Comparison of P-inactivation efficacy and ecotoxicity of alum and Phoslock. Report Number: IR 015/09. July 2009. Phoslock Water Solutions Limited

Aparicio Mijares FJ (2009) Fundamentals of surface hydrology. Limusa, Mexico City (In Spanish)

ASTM (American Society for Testing and Materials) (2000) D2974-00 standard test method for moisture, ash, and organic matter of peat and other organic soils. IOP publishing astm. http://www.astm.org/DATABASE.CART/HISTORICAL/D2974-00.htm. Accessed 15 Oct 2012

ASTM (American Society for Testing and Materials) (2007) D422-63 standard test method for particle-size analysis of soils. IOP publishing astm. http://www.astm.org/Standards/D422.htm. Accessed 15 Oct 2012

Cooke GD, Welch EB, Peterson SA, Nichols SA (2005) Restoration and management of lakes and reservoirs, 5th edn. Taylor and Francis, New York

Corbett DR, Walsh JP, Marciniak K (2009) Temporal and spatial variability of trace metals in sediments of two adjacent tributaries of the Neuse River Estuary, North Carolina, US. Mar Pollut Bull 58:1739–1765

CCVBA (Comisión de Cuenca Valle de Bravo-Amanalco) (2013) Valle de Bravo dam. State of Mexico. IOP publishing cuencaamanalcovalle. http://www.cuencaamanalcovalle.org/inic.php. Accessed 7 March 2013. (In Spanish)

DOF (Diario Oficial de la Federación) (2002) Norma Oficial Mexicana NOM-021-SEMARNAT-2000. Establishing the specifications of fertility, salinity and sediment classification, survey, sampling and analysis. December 31, p. 85 (In Spanish)

Conagua-IMTA (Comisión Nacional del Agua-Instituto Mexicano de Tecnología del Agua) (2007) National Surface Water Data Bank (BANDAS), (CD-ROM) ver. 2007, Hydrometry and Sediments IMTA, Mexico (In Spanish)

CEPIS (Centro Panamericano de Ingeniería Sanitaria y Ciencias del Ambiente) (2001) Simplified methodology for assessment of the eutrophication in warm tropical lakes. Regional program CEPIS/HPE/OPS, p. 51. (In Spanish)

FAO (Food and Agriculture Organization of the United Nations) (1997) Control of agricultural water resources pollution. FAO Irrigation and drainage—55. FAO, Rome (In Spanish)

Fuller CC, van Geen A, Baskaran M, Anima R (1999) Sediment chronology in San Francisco Bay, California, defined by 210Pb, 234Th, 137Cs, and 239, 240Pu. Mar Chem 64:7–27

Golterman HL (1984) Sediments, modifying and equilibrating factors in the chemistry of freshwater. Verh Int Ver Limnol 22:23–59

Hansen AM, Márquez-Pacheco H (2012a) Method for assessing internal nutrient loads in water bodies. Rev Mex Cienc Geol 29(1):265–275 (In Spanish)

Hansen AM, Márquez-Pacheco H (2012b) MOCONPAI Model that determines the duration of phosphorus control in water bodies by removal and immobilization with insoluble adsorbents. Mathematical model registered by the Mexican Institute of Water Technology. Mexican copyright registration no. 03-2012-092610424400-01, Mexico City (In Spanish)

Juárez-Badillo E, Rico-Rodríguez A (2005) Sediment mechanics I: fundamentals of sediment mechanics. Limusa, Mexico City, p. 644 (In Spanish)

Kou S (1996) Phosphorus. In: Sparks DL (ed) Methods of soil analysis: part 3—chemical methods. Book series 5. American Society of Agronomy, Soil Science Society of America, Madison.

Liu B, Liu X, Yang J, Garman DEJ, Zhang K, Zhang H (2012) Research and application of in-situ control technology for sediment rehabilitation in eutrophic water bodies. Water Sci Technol 65(7):1190–1199

Merck (2012) Merck-chemicals base-parameters-from-a-to-z. IOP publishing merckmillipore. http://www.merckmillipore.com.mx/chemicals/parameters-from-a-to-z/c_nt2b.s1L0LQAAAEWguIfVhTl?back=true&CountryName=Mexico. Accessed 3 Oct 2012

Merino-Ibarra M, Monroy-Ríos E, Vilaclara G, Castillo FS, Gallegos ME, Ramírez-Zierold J (2007) Physical and chemical limnology of a wind-swept tropical highland reservoir. Aquat Ecol 42:335–345

OECD (Organization for Economic Co-operation and Development) (1982) Eutrophication of waters: monitoring, assessment and control. OECD, Paris. OECD 971982031P1. ISBN 9264122982

Olvera VV (1988) Biology and ecology of water hyacinth *Eichhornia crassipes*. Seminar-Workshop: control and use of water hyacinth. Mexican Institute of Water Technology, January 18–20, Cuernavaca, Morelos (In Spanish)

Olvera VV, Bravo L, Sánchez J (1998) Aquatic ecology and management assessment in the Valle de Bravo reservoir and its watershed. Aquat Ecosys Health Manag 1(2–3):277–290

Ozkundakci D, Hamilton D (2006) Recent studies of sediment capping and flocculation for nutrient stabilization. CBER report 53. The University of Waikato, New Zealand

EPA (Environmental Protection Agency) (1993) Method 351.2 Determination of total Kjeldahl nitrogen by semi-automated colorimetry. Chemistry Research Division, Cincinnati, Ohio. IOP publishing caslab: http://www.caslab.com/EPA-Methods/PDF/EPA-Method-3512.pdf. Accessed 5 Dec 2012

EPA (Environmental Protection Agency) (1996) Method EPA 6010 B Inductively coupled plasma atomic emission spectrometry. IOP publishing caslab: http://www.caslab.com/EPA-Methods/PDF/EPA-Method-6010B.pdf. Accessed 5 Dec 2012

Psenner R, Puesko R, Sager M (1984) The fractionation of organic and inorganic phosphorus compounds from sediments attempt to define ecologically important fractions. Arch Hydrobiol 10:115–155 (in German)

Robb M, Greenop B, Goss Z, Douglas G, Adeney J (2003) Application of Phoslock, an innovative phosphorus binding clay, to two Western Australian waterways: preliminary findings. Hydrobiol 494:237–243

Sawyer C, McCarty P, Parklin G (1994) Chemistry for environmental engineering. McGraw-Hill, New York

Schauser I, Lewandowski J, Hupfer M (2003) Decision support for the selection of an appropriate in-lake measure to influence the phosphorus retention in sediments. Water Res 37:801–812

Søndergaard M (2007) Nutrient dynamics in lakes—with emphasis on phosphorus, sediment and lake restoration. University of Aarhus, Denmark, Doctor's dissertation (DSc). p. 74 and 16 associated papers

Spears B, May L (2009) Proposal for the restoration of Loch Flemington using controlled application of a lanthanum-bentonite clay (Phoslock®). Centre for Ecology and Hydrology. Natural Environment Research Council, United Kingdom. IOP publishing ceh. http://www.ceh.ac.uk/sci_programmes/water/documents/RA_30_11_2009.pdf. Accessed 3 Oct 2012

Sterner RW, George NB (2000) Carbon, nitrogen, and phosphorus stoichiometry of Cyprinid fishes. Ecology 81(1):127–140

van Metre PC, Fuller CC (2009) Dual-core mass-balance approach for evaluating mercury and 210Pb atmospheric fallout and focusing to lakes. Environ Sci Technol 43:26–32

Villanueva-Beltrán JT (2011) Evaluation of the external phosphorus and nitrogen loads in the Valle de Bravo reservoir and control scenarios. Master dissertation (MSc), National University of Mexico. p. 118 (In Spanish)

Yasseri S, van Goethem P (2008) Phoslock treatment Het Groene Eiland. IOP publishing phoslock. http://www.phoslock.com.au/IRM/content/pdf/Interim_Report_Het_Groene_Eiland_November_08.pdf. Accessed 8 Nov 2012