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RESEARCH ARTICLE

Internal phosphorus load in a Mexican reservoir through sediment speciation analysis

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Abstract Since the sequential extraction of phosphorus (P) in sediment makes it possible to determine the P potentially available for release, in this paper, we evaluate the fractions of P in sediment profiles from Valle de Bravo reservoir, a eutrophic lake in central Mexico to determine the contributions of each fraction to the internal P load (IPL). The P fractionation scheme employs sequential extractions of sediment with O_2-free water (MilliQ), bicarbonate-dithionite (BD), sodium hydroxide (NaOH), hydrochloric acid (HCl), and potassium persulfate ($K_2S_2O_8$-) to obtain five P fractions. A monitoring of redox potential (Eh), pH, and total phosphorus (TP) in the bottom water of the reservoir indicated variations of these parameters during the year, observing that as Eh decreased, the P concentration increased, it was also observed that when increasing pH, P concentration also increased. Analyzing the behavior of fractions of P in sediment profiles, we found that the dominant fractions are those bound to iron and aluminum oxides, corresponding to approximately 50% of total P since P concentrations of these fractions were twice as high in the top 5 cm of the sediment profiles and decreased with increasing depth. Considering the variations of Eh and pH in the bottom water of the reservoir and that these parameters are factors that control the release of P with the fractions of P bound to Fe/Mn and Al/Fe oxides, we concluded that these fractions contribute most to P potentially available for release in the reservoir, representing a possible IPL of 23.5 ± 1.4 t/year.

Keywords Phosphorus release · Sediment · Redox conditions · Rehabilitation strategies

Introduction

Phosphorus (P) is the nutrient that most often limits primary productivity in water bodies, and excess concentrations of this nutrient can lead to eutrophication of lakes and reservoirs (Cooke et al. 2005). Despite efforts to control P loads through reducing external inputs, it has been observed that eutrophication problems may continue in water bodies due to internal P loads (Steinman and Ogdahl 2008; Schauser et al. 2003). Phosphorus is bound in both organic and inorganic fractions of the sediment and occurs in the water column as particulate inorganic and organic P, as polyphosphates and orthophosphates (Søndergaard 2007). Phosphorus may accumulate in the sediment from where, under anaerobic conditions, it is released to the water column (Heggie et al. 2008; Chowdhury and Bakri 2006; Haggard et al. 2005). In this context, several studies have been conducted to better understand the factors affecting the P release from sediments (Haggard et al. 2005; Solim and Wanganeo 2009; Kim et al. 2003), finding that redox conditions, pH, dissolved oxygen, nitrates, sulfates, and bacterial activities are the main factors that control the release of P from sediments (Kim et al. 2003).

Depending on the composition of the sediment, the sedimentation velocity, and the environmental conditions, P occurs in sediments in different chemical forms (Yalçin et al. 2012). Therefore, information on the different chemical species of P in sediment is useful for understanding if these solids act as sinks or sources of P. The different fractions of P are

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useful to assess the potential of accumulation or release of P in sediment and to determine rehabilitation strategies for eutrophied water bodies. Of special interest is the binding of P to iron, aluminum, and calcium, and the adsorption of P by carbonates and clays are (Jensen et al. 1992). According to Psenner et al. (1984), fractions of P extracted from sediments can be characterized as (1) weakly adsorbed P, (2) P bound to metal oxides (mainly iron and aluminum), and (3) P bound to calcium.

Iron and aluminum have an important role in retaining inorganic P, and P mobility depends on the redox potenti al. Iron sulfide formation coupled to sulfate reduction can reduce the abundance of Fe compounds that can complex phosphate and thereby promote its release into sediment porewater (Perrone et al. 2008; Miao et al. 2006).

Since the sequential extraction of P in sediment makes it possible to determine the P potentially available for release, in this paper, we evaluate the fractions of P in sediment profiles from a eutrophic lake in central Mexico, to determine the contributions of each fraction to the internal P load (IPL).

The present study was carried out in the eutrophied Valle de Bravo reservoir, State of Mexico that is used for tourism, fishery, and water supply in Toluca and Mexico City. This reservoir has a surface area of approximately 1680 ha, an average volume of 328 Mm^3, average depth of 19.5 m, and a maximum depth of 36 m close to the dam northwest of the reservoir (Fig. 1), it is classified as a warm monomictic lake with a thermal stratification period from March to September. With a maximum temperature of 25 °C in the epilimnion and minimum temperatures of 18 °C in the hypolimnion, a relative thermal resistance to mixing of 194 could be calculated, classifying this reservoir as strongly stratified (Wetzel and Likens 2000).

The reservoir is located at approximately 1800 m above sea level in an area with temperate and semicalid and subhumid climate with summer rains, temperatures varying between 12 and 22 °C, and annual precipitations, between 1000 and 1500 mm. The dam receives water from six tributaries: the Amanalco, Molino, and Tizates rivers, and the Santa Mónica, González, and El Carrizal streams. The hydrological basin has an extension of 615 km^2, a human population of close to 80,000 habitants, and the land uses include forestry, agriculture, grassland, livestock, fish culture, and urban areas. In the basin dominate volcanic soils since 74% of the total area of the basin is covered by volcanic rock (INEGI 2010). The sediment textures in the reservoir is clayey silt with high contents of organic matter (Márquez-Pacheco et al. 2013) and, according to Villanueva-Beltrán (2011), the reservoir receives approximately 66 t/year of P, 245 t/year of N, and 14.117 t/year of suspended solids from the watershed.

Materials and methods

Water bottom was monitored from February 2010 to October 2011, with samples taken every 6.1 ± 1.3 week, resulting in a total of 16 sampling events. The monitoring was carried out at 23 sampling stations, located with a mesh design (USEPA

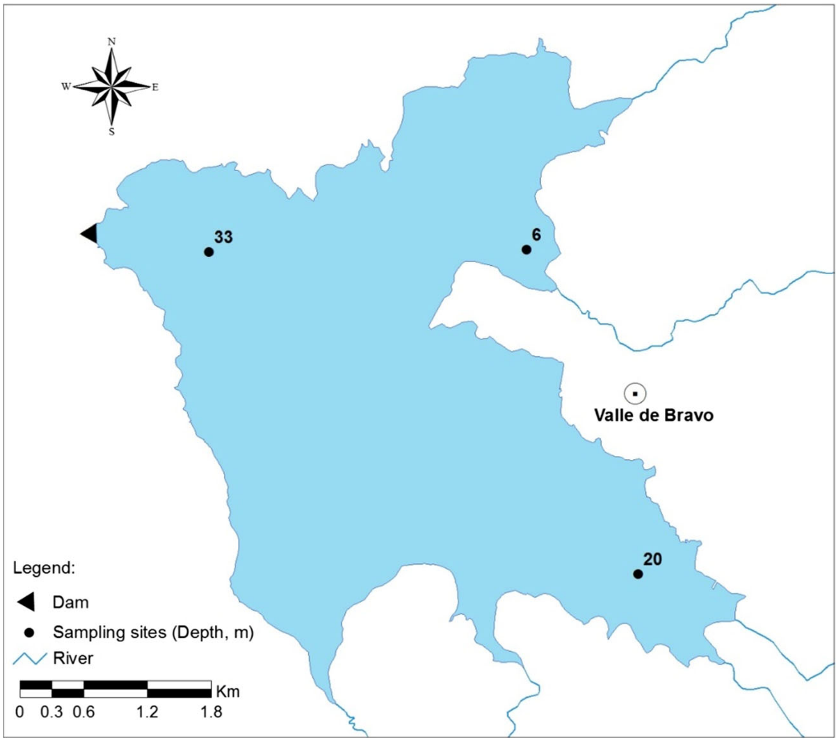

Fig. 1 Location of the sampling stations in the Valle de Bravo reservoir, Mexico

Table 1 Characteristics of the sediment for different depth (d) of the reservoir. Sampling date, July 2009. The sampling was with a 15.2-cm × 15.2-cm stainless steel Ekman dredge (Wildco Instruments) at 23 sampling stations. The data represent the average of a number of sites (*n*)

Characteristics	Shallow (d < 3.5 m)	Intermediate (d = 3.5–13 m)	Deep (d > 13 m)
Area (km^2)	1.3	8.5	7
n	7	10	6
OM (%)	16 ± 6	13 ± 2	13 ± 1
pH	9.0 ± 0.4	7.6 ± 1.1	6.8 ± 0.1
Al (mg/kg)	52,145 ± 17,313	41,009 ± 9438	34,886 ± 6119
Fe (mg/kg)	41,800 ± 2486	37,491 ± 1886	36,437 ± 1456
Mn (mg/kg)	600 ± 286	412 ± 95	503 ± 95
P (mg/kg)	597 ± 64	1071 ± 83	1140 ± 111
Sand (%)	15 ± 9	1 ± 0	0 ± 0
Silt (%)	67 ± 7	66 ± 3	68 ± 8
Clay (%)	16 ± 4	32 ± 7	32 ± 2

2001) with a 1-km grid, plus five monitoring stations located at the inlets of the main tributaries to the reservoir. pH and redox potential (Eh) were monitored using a previously calibrated multiparametric probe (Hach Hydrolab DS5) according to the manufacturer's manual, and water samples were collected at each station at a depth of 0.3 m from the bottom, with a 2-L van Dorn horizontal bottle (Wildco Instruments) for analysis of total P (TP) with a colorimetric method (APHA 2005) (Merck Pharo 300 spectrophotometer, Darmstadt, Germany). During the last five sampling events, surface water samples were collected for colorimetric analysis of chlorophyll *a* (Chla) (APHA 2005).

In March 2011, sediments were sampled with 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. Sediment cores were obtained from three sampling sites (about 6, 20, and 33 m, Fig. 1), which represent areas with different sediment characteristics and depths in the reservoir (Table 1). The upper 25 cm of the cores was divided in 5-cm sections that were dried at room temperature to constant weight.

A selective extraction method was used to determine the amounts of P present in different fractions of each section of the sediment cores. For this, different solvents were used in the sequence illustrated in Table 2. The analysis of soluble reactive P (SRP) and total P (TP) was performed using a colorimetric method (APHA 2005) (Merck Pharo 300 spectrophotometer, Darmstadt, Germany). Non-Reactive P (NRP) was defined as the difference between the TP and SRP.

The following species were separated: labile P (H_2O-TP), P bound to Fe/Mn (bicarbonate-dithionite fraction, BD-SRP), organic P solubilized by reduction (bicarbonate-dithionite fraction, BD-NRP), P bound to Al/Fe oxides (NaOH-SRP), P bound to organic matter (NaOH-NRP), P bound to carbonate and apatite (HCl-SRP), organic P solubilized by acidification (HCl-NRP), and residual P ($K_2S_2O_8$-TP).

To describe how sediments contribute to the internal P load (IPL), P fractions in the sediment profiles were analyzed and determined the amount of P potentially available for release. To do this, first the P content of each fraction was determined in percentage, and then the mass of P per fraction in the surface section of 0–5 cm was calculated, considering this percentage and a constant annual sedimentation of TP in the reservoir of 66.6 ± 4.0 t/year reported by Hansen and Márquez-Pacheco (2015). Once the amount of P per fraction in the surface section

Table 2 Extraction procedures and corresponding P fractions (Psenner et al. 1984)

Solvent	Extraction conditions	P species
O_2-free water (MilliQ)	Stirring 10 min, 25 °C	*H_2O-TP* (labile P)
Bicarbonate-dithionite	Stirring 30 min, 40 °C	*BD-SRP* (P bound to Fe/Mn) *BD-NRP* (Organic P solubilized by reduction)
Sodium hydroxide	Stirring 16 h, 25 °C	*NaOH-SRP* (P bound to Al/Fe oxides) *NaOH-NRP* (P bound to organic matter)
Hydrochloric acid	Stirring 16 h, 25 °C	*HCl-SRP* (P bound to carbonate and apatite) *HCl-NRP* (Organic P solubilized by acidification)
Potassium persulfate	Autoclaving 30 min	*$K_2S_2O_8$-TP* (residual P)
Total Phosphorus (Sum of concentrations of the species above)	*TP-ΣP*	

Italic entries show the procedure and species of phosphorus extraction

TP total P, *SRP* soluble reactive P, *NRP* non-reactive P

(0–5 cm) was known, it was estimated how much the P content in each of the fractions decreases with respect to the deeper sections (5–25 cm), this difference being considered as the amount of P potentially available to release in 1 year.

Results and discussion The results of Eh measured in water from the bottom indicate variations during the year, presenting values below 0 mV during the stratification period of the water column, which coincides with the rainy season (June–September) (Fig. 2a). The pH also showed variations during the year, with slightly more alkaline values at the time of stratification (Fig. 2a). Durante el periodo de estratificación las concentraciones de TP en el agua de fondo se incrementaron, principalmente en los meses de julio a septiembre.

Analyses of linear correlations of the results of water monitoring data, Eh, and pH in bottom water were presented. Negative correlations were found between Eh in bottom water and concentrations of TP, indicating that as Eh decreases, concentrations of P in water increase (Fig. 2b). Also, pH was positively correlated with concentrations of TP (Fig. 2c), showing a direct effect on algae growth in the reservoir, as an increase in *Chl a* concentrations occurred during the same period, that this increase in TP concentrations was observed.

The relative concentrations of the different fractions of P in the sediment profiles (Fig. 3) showed that total phosphorus (TP-ΣP) in the surface sections (0–5 cm) was higher than in deeper sections (5–25 cm). It was observed that concentrations of P decreased from approximately 1000 mg/kg dw in the upper sections of the sediment cores to around 500 mg/kg dw in the lower sections. These results are consistent with the observations in other reservoir (Zhu et al. 2013; Ostrofsky 2012), where the phosphorus concentration decreases with the depth in the sediment profile. The sediment core of the shallow site shows a different pattern in the total P concentration, probably due to a greater influence of the external P load at this site. Since the shallow depth of the reservoir has a relatively small area (Table 1), it is considered that the P released from the sediment of intermediated and deep depth has the greatest contribution on the IPL in the reservoir.

The dominant fraction of P in the sediment profiles was P bound to Al/Fe oxides (NaOH-SRP), representing approximately half of total P (TP-ΣP) in the sediment cores. The concentrations of the Al/Fe oxides (NaOH-SRP) fraction of P in the upper sections were about twice the concentrations observed in lower sections, and concentrations decreased with increasing depth. Some authors have suggested that the extractable P with NaOH-SRP is used to estimate the available short- and long-term P in the sediment and is a measure of the P available for algae (Zhou et al. 2001). NaOH-SRP could be released by changing pH from 8 to 12 (Xiangcan et al. 2006).

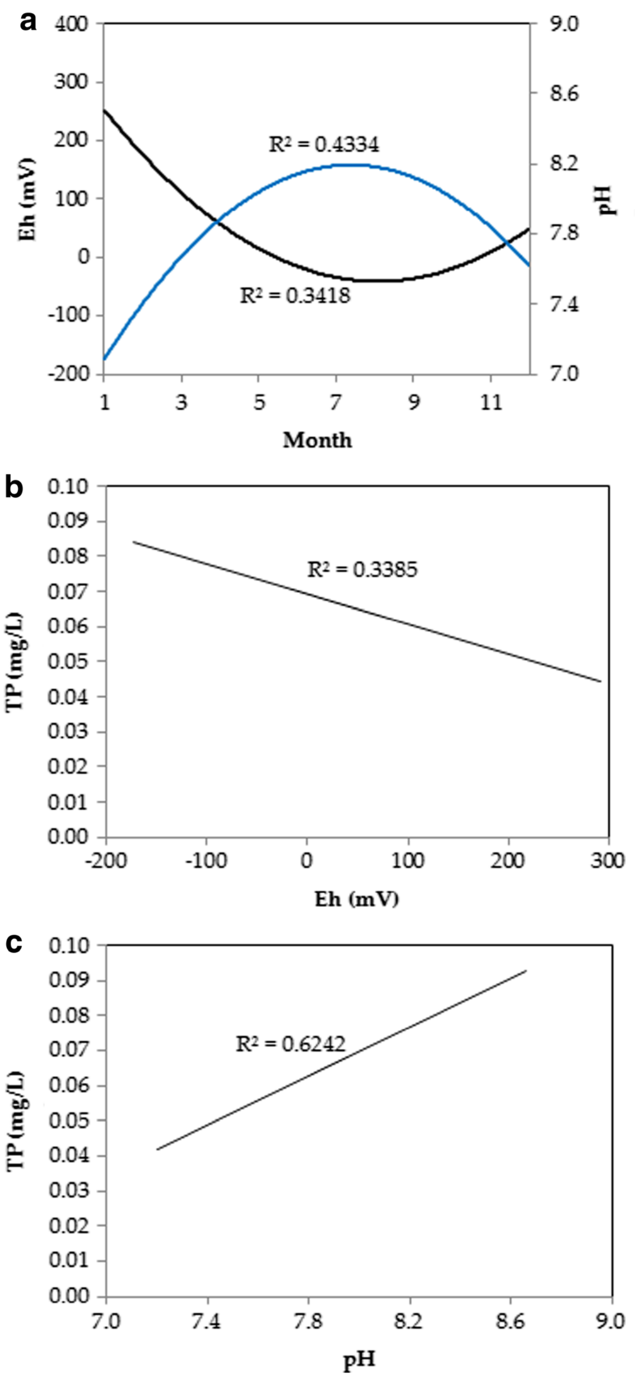

Fig. 2 **a** Trend line of the annual variation of Eh and pH in bottom water. **b** Linear correlation between TP concentration and Eh in bottom water. **c** Linear correlation between TP concentration and pH in bottom water

The concentrations of P bound to Fe/Mn (BD-SRP) were two to three times higher in the upper sections of the sediment cores. The concentrations of this fraction, as well as those of organic P solubilized by reduction (BD-NRP), decreased with increasing depth of the sections in the sediment cores. This release of P can be explained by the generally observed reduced conditions in sediments (Hansen and Márquez-Pacheco 2015), causing the release of P bound to ferric oxides in sediment.

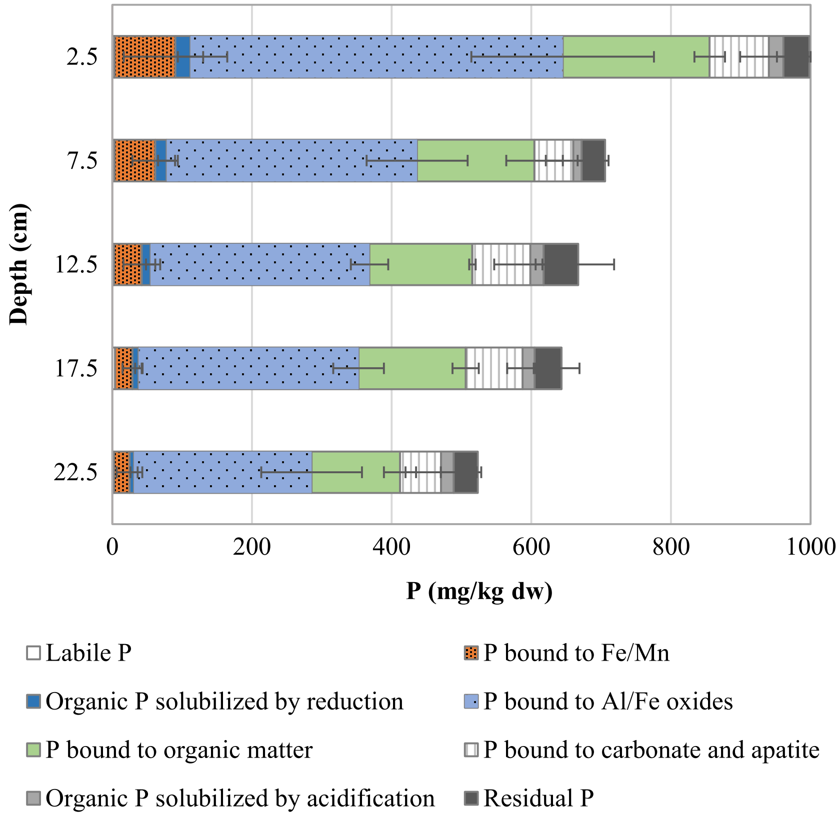

Fig. 3 Speciation of P in sediment profiles from the Valle de Bravo reservoir, Mexico. The results are the average of the analysis of the two cores, intermediate, and deep depth

The P labile (O_2-free water) presents a decrease in the surface; this is consistent with an increasing flux of interstitial P dissolved to the surface layers. In contrast to the observed surficial increases in BD-P and NaOH-P, P bound to carbonate and apatite (HCl-SRP) was consistently immobile. This fraction is assumed to be composed largely of detrital apatite, only sparingly soluble in the normal sedimentary environment, and derived from weathered soils. Similarly, organic P solubilized by acidification (HCl-NRP) showed no evidence for migration in sediment. Residual P ($K_2S_2O_8$-TP) did not vary with depth in the sediment cores.

Given the disappearance of P in the sediment sections and the reported P sedimentation rate of 66.6 ± 4.0 t/year (Hansen and Márquez-Pacheco 2015), an amount of P potently available released of 23.5 ± 1.4 t/year was estimated (Table 3). Phosphorus bound to Al/Fe oxides (NaOH-SRP), P bound to Fe/Mn (BD-SRP), and P bound to organic matter (NaOH-NRP) are all fractions that release P in bioavailable forms to water as orthophosphate (Zhou et al. 2001), being therefore directly available for algae and therefore contributing strongly to primary production (Yalçin et al. 2012). According to Wang

Table 3 Amount of phosphorus released by species at the Valle de Bravo reservoir, State of Mexico. The results are the average of the analysis of the cores of intermediate and deep depth

P specie	Percentage of P section 0–5 cm (%)	P sedimented (t/year)	Decrease of P in the first two sections as a percentage (%)	P released (t/year)	P net sedimented (t/year)
H_2O-TP	0.3	0.20	− 30.8	− 0.06	0.26
BD-SRP	8.8	5.84	71.5	4.18	1.67
BD-NRP	2.2	1.45	59.9	0.87	0.58
NaOH-SRP	53.4	35.54	40.4	14.36	21.01
NaOH-NRP	21.1	14.05	27.1	3.81	10.24
HCl-SRP	8.5	5.68	4.3	0.24	5.43
HCl-NRP	2.1	1.37	15.0	0.21	1.17
$K_2S_2O_8$-TP	3.7	2.47	− 4.3	− 0.11	2.58
Total	100.00	66.60	–	*23.49*	42.94

Italic entry indicates the results obtained (quantities of phosphorus per species in percentage and quantity of phosphorus potentially available for release in the reservoir) et al. (2006) in a study of nine lakes, NaOH-P and BD-P were the major release fractions of P and contributed to more than 80% of total P released in the sediments. In this context, we can say that reservoir sediments have a highly available potential of P for algae, which may contribute to the IPL.

Conclusions

The sequential extraction method contributes to better understanding phosphorus potentially available for release, indicating labile and bioavailable fractions. The main phosphorus fractions in the Valle de Bravo reservoir were P bound to Al/Fe oxides (NaOH-SRP) and P bound to organic matter (NaOH-NRP). Considering the variations of Eh and pH in the bottom water of the reservoir and that these parameters are factors that control the release of P with the fractions of P bound to Fe/Mn and Al/Fe oxides, we concluded that these fractions contribute most to P potentially available for release in the reservoir, representing a possible IPL of 23.5 ± 1.4 t/year.

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