

## EFFECTIVE SEDIMENT DEPTH FOR PHOSPHORUS RELEASE IN A MONOMICTIC EUTROPHIC LAKE

Profundidad efectiva de sedimento para la liberación de fósforo en un lago eutrófico monomíctico

Henri MÁRQUEZ-PACHECO<sup>1</sup> and Anne M. HANSEN<sup>2\*</sup>

<sup>1</sup> Universidad Politécnica del Mar y la Sierra (UPMYS), Carretera a Potrerillos del Norote Km 3, La Cruz, Elota, 82700 Sin. México.

<sup>2</sup> Instituto Mexicano de Tecnología del Agua (IMTA), Paseo Cuauhnáhuac 8532, Jiutepec, 62550 Mor. México.

\*Author for correspondence: [ahansen@tlaloc.imta.mx](mailto:ahansen@tlaloc.imta.mx)

*(Received March 2021, accepted February 2022)*

Key words: sediment cores, sediment profile, sediment porosity, species of phosphorus

### ABSTRACT

Sediments play an important role in phosphorus (P) dynamics in eutrophic lakes. P concentrations are higher in surface sediments compared to deeper layers, representing a pool of P that can be released into the water column. Effective sediment depth for P release is different among lakes and little is known about this depth. Through experimental evaluation of P release in sediment cores, characterization of sediment porosity and distribution of P fractions in the sediment profile from a monomictic eutrophic lake, we determined which sediment layers produce release of P. The release of P in sediment layers of different depths varied between 0.89 and 2.07 mg P/m<sup>2</sup>×d with the highest P flow found in the sediment layer of 0-15 cm. The porosity of the sediment strata varied between 68 and 80%, with higher porosity in the surface sediment and decreasing porosity with depth of the sediment profile. We found that P bound to Fe/Mn (BD-P), Al/Fe oxides (NaOH-SRP), and organic matter (NaOH-NRP) were higher in the layer of 0-15 cm than in deeper layers. Sediment porosity, P release, total P and concentrations of the different P species in the sediment profile declined with sediment depth, stabilizing at the depth of 15 cm in the sediment profile. Therefore, we conclude that the effective sediment depth for release of P in this monomictic eutrophic lake is found up to 15 cm.

Palabras clave: núcleos de sedimento, perfil de sedimento, porosidad de sedimento, especies de fósforo

### RESUMEN

Los sedimentos juegan un papel importante en la dinámica de fósforo (P) en lagos eutróficos. Las concentraciones de P son mayores en sedimentos superficiales comparado con capas más profundas; representando esta diferencia el P, que puede liberarse al agua. La profundidad efectiva del sedimento donde se libera P es diferente entre lagos y se conoce poco acerca de esta profundidad. Mediante evaluación experimental de la liberación de P en núcleos de sedimento, caracterización de la porosidad y la distribución de fracciones de P en perfiles de sedimento de un lago eutrófico monomíctico,

determinamos de qué capas de sedimento se libera P. La liberación de P en capas de sedimentos de diferentes profundidades varió entre 0.89 y 2.07 mg P/m<sup>2</sup>×d con mayor flujo en el estrato sedimentario de 0-15 cm. La porosidad de los estratos sedimentarios varió entre 68 y 80%, con mayor porosidad en los estratos superiores y disminuyendo con la profundidad del perfil de sedimento. Encontramos que P unido a Fe/Mn (BD-P), óxidos de Al/Fe (NaOH-SRP) y materia orgánica (NaOH-NRP) son más elevados en la capa de 0-15 cm que en capas inferiores. Se encontró que la porosidad, la liberación de P y las concentraciones de P total y las diferentes especies de P en el perfil de sedimento disminuyeron con la profundidad, estabilizándose a los 15 cm de profundidad. Por tanto, se concluye que la profundidad efectiva de sedimento para la liberación de P en este lago eutrófico monomictico es hasta 15 cm.

## INTRODUCTION

Internal and external loads of phosphorus (P) in lakes and reservoirs affect water quality, biological productivity, and health of aquatic ecosystems. In addition to external loads, water bodies may receive important internal P loads, since P accumulated in sediments may be released due to biogeochemical processes (Cooke et al. 2016). In sediments of eutrophic lakes and reservoirs, P concentrations are usually higher in surface sediments compared to deeper layers, representing a pool of P that can be released; this pattern diverge from P sediment profiles in oligotrophic lakes, which exhibit increasing concentrations of permanently buried P with depth (Carey and Rydin 2011). The exponential decrease of P with depth in sediments from eutrophic lakes and reservoirs may be due to the degradation of organic matter and subsequent release of P given the limited capacity of the sediment to retain mineralized P (Ahlgren et al. 2005). Also, in oxidized surface sediments, P is temporarily bound to iron oxides or as polyphosphate, and thereby increasing substantially the content of P on the surface, causing an exponential decrease in P until the depth of stabilization (Hupfer et al. 1995, Rydin 2000, Gächter and Müller 2003). Sedimentary processes that regulate P burial may be an important control of internal P load and consequently of the trophic status of lakes and reservoirs (Wang et al. 2009, Carey and Rydin 2011). The release of P can be very persistent and take place over a decade, even after external loads have been sufficiently reduced (Welch and Cooke 1999). In some lakes, the release of P may remain during several decades (Søndergaard et al. 1999). Such delayed responses of lakes to eutrophication control measures are attributed to the slow P release. However, there are many difficulties in evaluating internal P loads, most of these are due to the difficulty of distinguishing P release

mechanisms and sediment depths in which P is released (Søndergaard et al. 2003, Orihel et al. 2017, Le Moal et al. 2019). The P release mechanisms may vary with time and among different water bodies and the sediment layers that interact with P release are probably specific to each lake and depends largely on lake morphology as well as sediment and water characteristics (Søndergaard et al. 2003, Wu et al. 2014, Kamiya et al. 2017, Orihel et al. 2017).

Parameters such as redox conditions, pH, dissolved oxygen, nitrates, sulfates, and bacterial activities are factors that control P release from sediments (Kim et al. 2003, Wu et al. 2014, Anschutz et al. 2019). On the other hand, particle size, porosity, and P concentration in sediments are the factors that affect diffusion of P from sediments to the water column (Zhu et al. 2015). To understand the mechanisms of P release from sediments, it is necessary to understand how P speciation in sediment changes over depth. P release can occur in a variety of ways depending on the P species present in sediment and many examples of P release in the literature, are dominated by degradation of organic matter as well as reduction of iron-oxy-hydroxides (Zeng et al. 2018, Anschutz et al. 2019, Barik et al. 2019, Chen et al. 2019), with P entering the water column from sediments by diffusion or advection through pore water. In most cases, it is considered that P found in sediment depths up to 10 cm participates in the metabolic processes of all lakes (Bostrom et al. 1982), but the mobility of this nutrient has been observed from depths up to 20-25 cm (Søndergaard et al. 1999). Thus, the effective depth for P release may vary between different lakes and reservoirs and little is known about this depth. To better understand P release mechanisms and to create information and tools that allow more efficient P control decision making, in this study we determined the sediment depth from which P release take place through experimental evaluation of P release from

sediment cores, characterization of sediment porosity, and distribution of P fractions in the sediment profile from a monomictic eutrophic lake.

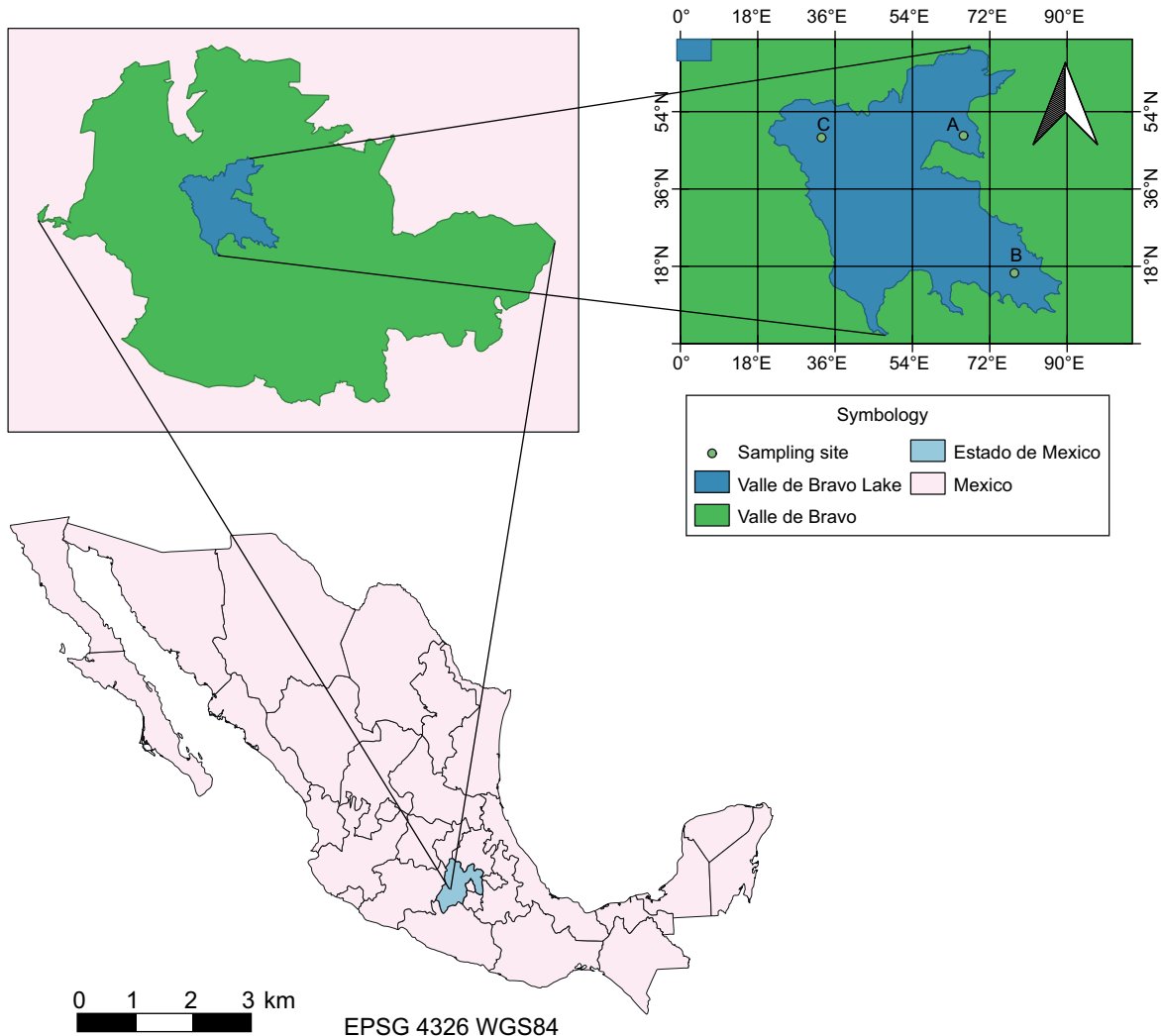
## MATERIAL AND METHODS

### Study area

The present study was carried out in the Valle de Bravo lake, located in the Estado de Mexico at 19°21'30" N and 100°11'00" W (**Fig. 1**) at 1,830 masl. This lake is classified as a warm monomictic lake with a thermal stratification, having a warm layer of water overlying cooler bottom layer for most of the year, except in winter when surface water cools

and windy conditions keep the water column fully mixed. This lake has a maximum temperature of 27 °C in the epilimnion and minimum temperatures of 17 °C in the hypolimnion and, according to Wetzel and Likens (2000), a relative thermal resistance to mixing of 194 can be calculated, classifying this lake as strongly stratified. The sediment texture in the lake is clayey silt with high content of organic matter (Márquez-Pacheco et al. 2013) and, according to Villanueva-Beltrán (2011) approximately 66 t/year of P and 14,120 t/year of suspended solids are emitted in the watershed and could potentially reach the lake as external loads.

Water in the Valle de Bravo lake is being used for water supply in the Valle de México megalopolis as



**Fig. 1.** Location of the Valle de Bravo lake, Mexico. Sampling sites that represent different sediment characteristics and water depths in the Valle de Bravo lake. Water depth: A: shallow (6m), B: intermediate (20m), C: deep (33m).

part of the Cutzamala system, that is a water source for tens of millions of inhabitants. Water quality studies have been conducted for several decades in the Valle de Bravo lake, showing a serious eutrophication problem associated with important accumulation of nutrients and organic matter. This condition generates excessive growth of algae that after die-off, cause further accumulation of organic matter that demand oxygen in the hypolimnion and release of nutrients accumulated in the sediment (Hansen and Márquez-Pacheco 2015).

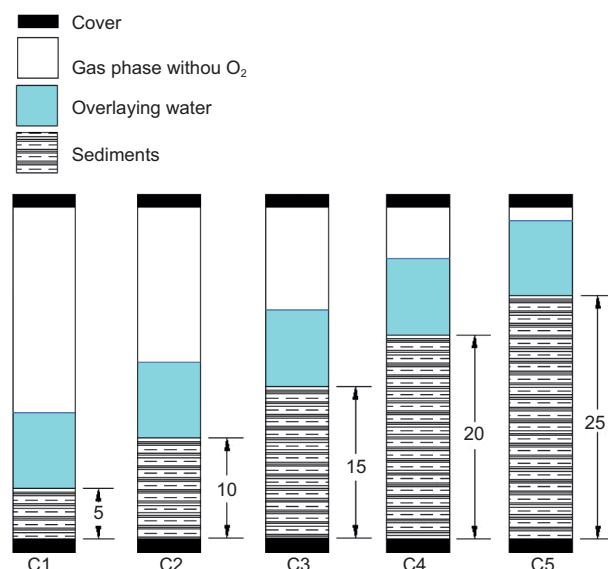
### Sediment sampling

Sediment samples were obtained 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. Seven sediment cores were obtained at each of three sampling sites (**Fig. 1**), which represent areas with different sediment characteristic and water depths (**Table I**). These sampling sites correspond to shallow, intermediate and deep zones, which represent specific ranges of Eh and P concentration (Hansen and Márquez-Pacheco 2012). Lake water samples were obtained close to the sediment-water interface at each sampling station using a 2L horizontal van Dorn bottle (Wildco Instruments, Buffalo, NY). In the laboratory these samples were combined in equal amounts.

### Phosphorus release experiment in sediment cores under anoxic conditions

To assess the P release by different sediment layers, the length of five of the sediment cores collected at each site were adjusted to 5, 10, 15, 20, and 25 cm from the sediment–water interface (C1 to C5, **Fig. 2**) by removing the lower parts of the cores by gravity. Liners were sealed hermetically at both ends

and stored in up-right position during transport to the laboratory, where overlying water was removed and 500 mL combined water sample was added by syphoning. To eliminate air in water and head-space, N<sub>2</sub> (g) (Infra high purity) was added slowly at the sediment-water interface during 5 min before covering the liners hermetically, and keeping them in the dark at 20° C.



**Fig. 2.** Experimental setup of P release experiments. The thicknesses of sediment were adjusted to 5, 10, 15, 20 and 25 cm (C1 to C5, respectively) by removing the lower part of the sediment cores by gravity.

The experimental period was 28 days. On days 1, 2, 4, 8, 15, 21, and 28, pH was measured with an Orion ROSS Ultra® electrode and 50-ml overlying

**TABLE I.** PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE SEDIMENTS AT DIFFERENT WATER DEPTHS IN THE VALLE DE BRAVO LAKE (MÁRQUEZ-PACHECO AND HANSEN 2017).

Sampling sites	Shallow	Intermediate	Deep
Depth (m)	<3.5	3.5-13.0	>13.0
n	7	10	6
Organic Matter (%)	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 ± 9 438	34,886 ± 6 119
Fe (mg/kg)	41,800 ± 2 486	37,491 ± 1 886	36,437 ± 1 456
Mn (mg/kg)	600 ± 286	412 ± 95	503 ± 95
P (mg/kg)	597 ± 64	1,071 ± 83	1,140 ± 111
Sand (%)	15 ± 9	1 ± 0	0 ± 0
Silt (%)	67 ± 7	66 ± 3	68 ± 8
Clay (%)	16 ± 4	32 ± 7	32 ± 2

water samples were obtained with syringe and silicone tube from the center of the water columns in the liners. Subsequently, flows of  $N_2$  (g) were added to maintain anoxic conditions as observed in the lake during thermal stratification (Marquez-Pacheco and Hansen 2017). Phosphorus was determined by colorimetry (Merck Pharo spectrophotometer 300, Darmstadt, Germany) (APHA 2005) and results were analyzed using Equation 1, to calculate P release rates per unit area (Steinman et al. 2004).

$$P_{rr} = \frac{(C_t - C_0)V}{A \times t} \quad (1)$$

Where:

$P_{rr}$  P release rate (mg/cm<sup>2</sup> d)

$C_t$  P concentration at time t (mg P/L)

$C_0$  P concentration at time 0 (mg P/L)

$V$  volume of water in the core (L)

$A$  area of the sediment surface (cm<sup>2</sup>)

$t$  time (d)

### Porosity analysis of sediment

The porosity of a sediment sample is the relation between the volume of interstitial spaces and the total volume of the sample. The porosity of the sediment layers was determined in cores from each sampling site according to the method described by Juárez-Badillo and Rico-Rodríguez (2005). The sediment cores were divided in 5-cm sections dried to constant weight and pore volumes were determined as the weight difference for each subsample (water density=1 g/cm<sup>3</sup>) (Eq. 2).

$$\eta = \frac{V_p}{V_s} \times 100 \quad (2)$$

Where:

$\eta$  Porosity (%)

$V_p$  Volume of voids or pores (cm<sup>3</sup>)

$V_s$  Volume of the subsample (cm<sup>3</sup>)

### P fraction distributions in the sediment profiles

A selective extraction method was used to determine the P fractions in the sediment profile of each sampling station (Psenner et al. 1984). The upper 25 cm of the cores were divided in 5-cm sections and extractions were performed using the sequence illustrated in **Table II**. The analysis of soluble reactive P (SRP) and total P (TP) were 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 results of P of these fraction distributions were reported by Márquez-Pacheco and Hansen (2017).

### Statistical analysis

Statistical analysis of the experimental results and their relation to sediment porosity and P fraction distributions were performed using IBM SPSS software (ver. 25.0; SPSS). The differences between released P, sediment porosity and P forms in sediment with respect to the three sampling sites were determined using a Krustal-Wallis test. If the model was significant at  $p < 0.05$ , the Post hoc test (Games-Howell) was applied. Pearson correlation analysis was used

**TABLE II.** EXTRACTION PROCEDURES AND CORRESPONDING P-FRACTIONS (PSENNER ET AL. 1984).

Solvent	Extraction conditions	P species
O <sub>2</sub> -free water (MilliQ)	Stirring 10 min, 25 °C	<i>H<sub>2</sub>O-TP</i> (labile P)
Bicarbonate-dithionite	Stirring 30 min, 40 °C	<i>BD-P</i> (P bound to Fe/Mn)
Sodium hydroxide	Stirring 16 h, 25 °C	<i>NaOH-SRP</i> (P bound to Al/Fe oxides) <i>NaOH-NRP</i> (P bound to organic matter)
Hydrochloric acid	Stirring 16 h, 25 °C	<i>HCl-P</i> (P bound to carbonate and apatite, solubilized by acidification)
Potassium persulfate	Autoclaving 30 min	<i>K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-TP</i> (Residual P)
Total phosphorus (Sum of concentrations of the species above)		<i>TP-SP</i>

Italic entries show the procedure and species of phosphorus extraction.

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



to identify the relationships between variables, correlations were considered significant at  $p < 0.05$ .

## RESULTS AND DISCUSSION

### Phosphorus release experiment from sediment cores under anoxic conditions

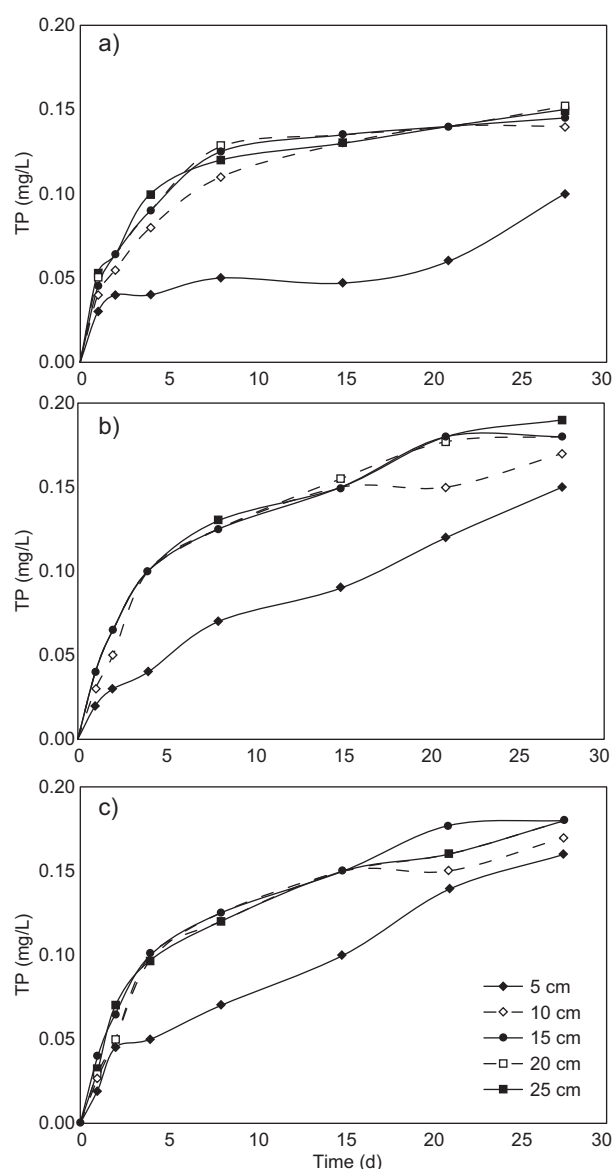
During the incubation period, pH in the overlying water of the P release experiments was  $7.24 \pm 0.74$ , values that were consistent with field observations, specifically for areas with depths of 20 m or more (sites B and C, **Table I**). Total P concentrations in the water overlying the sediment cores increased with time (**Fig. 3**), showing an increase of  $0.12 \pm 0.01$  mg/L in the first 10 days for core depths between 10 and 25 cm, while in the 5-cm cores, concentrations increased  $0.06 \pm 0.01$  mg/L in 10 d. Release of P at the shallowest site (A) with lowest concentration of P in sediment was lower than at the deeper sites (B and C) with higher concentrations of P in sediment (**Table I**). However, there were no statistically significant differences ( $H = 0.307$ ,  $p > 0.858$ ) between the three sampling sites. It is observed that the cores with depths between 10 and 25 cm from the three sampling sites present a similar behavior, reaching concentrations of  $0.17 \pm 0.02$  mg/L after 28 days of incubation.

Due to the contact of the surface sediment and the overlying water, P release from the sediment result from the direct desorption at the water-sediment interface and from diffusion of P through the porous structure of the deeper sediment layers.

The release rate of P per unit of sediment surface from the three sampling sites varied between 0.89 and 2.07 mg P/m<sup>2</sup>×d. These release rates are generally of the same order of magnitude as reported by Beutel et al. (2018). The shallowest cores (C1) from the three sampling sites showed P release rates between 0.8 and 1.4 mg/cm<sup>2</sup>×d while the deeper cores show P release rates between 1.7 and 2.0 mg/cm<sup>2</sup>×d and very little increase for sediment cores deeper than 15 cm (**Fig. 4**). The reasons why P was released from the surface sediment would be the high concentration of potentially mobile P in the surface sediment despite the high capacity of iron to bind P under oxic conditions, and the presence of organic P (Rydin 2000, Søndergaard et al. 2003).

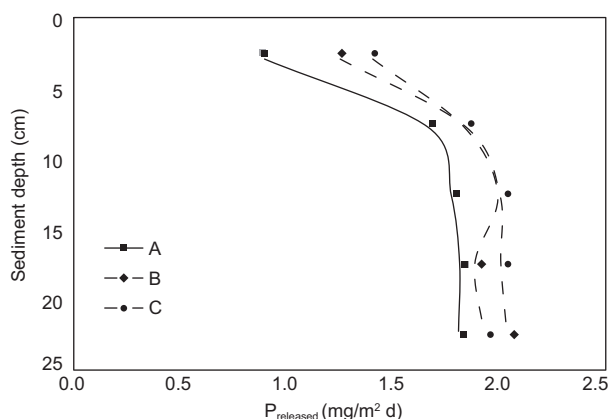
### Porosity of sediment

As P is released from the sediment it is expected to diffuse in upward direction due to the hydrostatic pressure and molecular diffusion. Since this flow

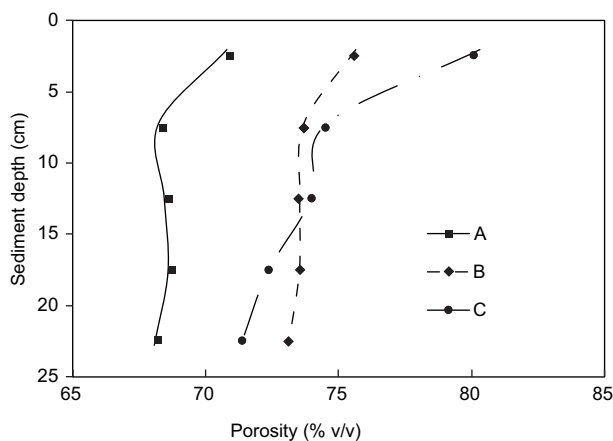


**Fig. 3.** Time-dependent release of TP from the experimental sediment columns A, B, and C.

depends in part on the porous structure of the sediment, the porosity of the sediment profile layers was analyzed. This porosity varied between 68 and 80% v/v, with higher porosity closer to the sediment-water interface and decreasing down to 10 cm depth and then continued constant for sediment profiles from the shallow (6 m) and intermediate (20 m) water depths at sampling sites A and B, respectively, while the sediment profile from the deeper site (C, 33 m) showed a tendency of decreasing porosity in the deeper sediment layers (**Fig. 5**). The porosity presented a statistically significant difference between the three



**Fig. 4.** Release rates of P in the sediment profiles from the three sampling sites (A, B and C).



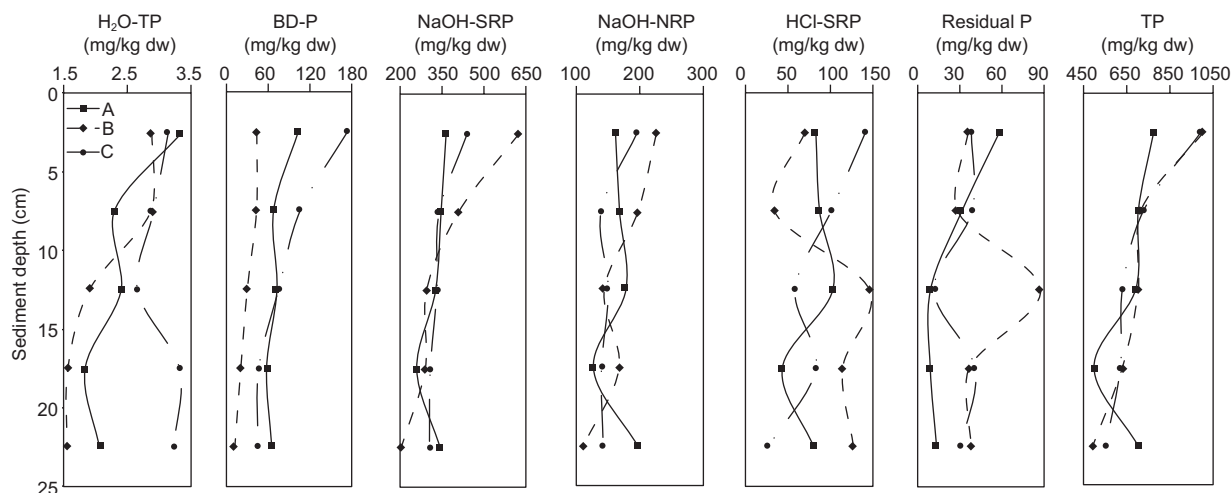
**Fig. 5.** Porosity of the sediment profiles.

sampling sites ( $H = 9.250$ ,  $p > 0.010$ ), mainly for site A compared to sites B and C.

### Phosphorus fractions in the sediment profiles

The concentrations of TP and the different fractions of P in the sediment profiles (**Fig. 6**) show that concentrations of TP decrease with increasing depth of the sediment, from  $\sim 1000 \text{ mg/kg}$  in the sediment surface to  $\sim 500 \text{ mg/kg}$  for sediments at a depth of 25 cm at sites B and C, presenting a decrease of  $\sim 300 \text{ mg/kg}$  from the surface to the 7.5 cm depth layer. The sediment profile from site A had lower TP concentration in the surface layer, this can be understood given that in coarse sediments the P adsorption capacity tends to decrease (Zhu et al. 2015), indicating less accumulation in this courser sediment and consequent lower release of P. In addition, at this site, the forms of P that show a decrease with sediment depth are  $\text{H}_2\text{O-P}$  and BD-P, reaching stabilization at 15 and 5 cm depth, respectively, in the sediment profile (**Fig. 6**).

There were no statistically significant differences in the forms of P with sampling sites, except BD-P ( $H = 9.420$ ,  $p < 0.05$ ), which presents a difference between sites A and B. The concentrations of the different P fractions in the sediment profiles B and C showed that BD-P, NaOH-SRP and NaOH-NRP (Bound to Fe/Mn hydroxides, Al/Fe oxides and P-Organic) were the dominant forms in the sediment. These P fractions are consistent with the changes in TP concentration in the sediment profile at a depth 12.5 cm. Most of the BD-P and NaOH-SRP was found in these layers. The highest concentration of



**Fig. 6.** Speciation of P in the sediment profiles from the Valle de Bravo lake.

BD-P in the sediments was found at site C, while that of NaOH-SRP was found at site B. Some authors suggest that the extractable P with BD-P and NaOH-SRP can be used to estimate the available short- and long-term P in sediment and are measures of P available for algae growth (Zhou et al. 2001).

The fractions BD-P, NaOH-SRP and NaOH-NRP are strongly influenced by the decomposition of organic matter, the reduction of iron oxides and microbial activity in sediments (Chao et al. 2008). The decrease in the fraction of P extractable with NaOH-SRP (Al/Fe oxides) with depth could be explained by increased pH, which improves desorption of P (Márquez-Pacheco and Hansen 2017). Under alkaline conditions the release of P increases due to the exchange between phosphate that is linked to Fe and Al oxides with  $\text{OH}^-$  ions (Xiangcan et al. 2006, Solim and Wanganeo 2009, Wu et al. 2014, Wan-Qiu et al. 2018). In the same way, P in BD-P can be released by reduction reactions in sediment (Holmes 2004, Miao et al. 2006, Perrone et al. 2008). These fractions represent the weakly adsorbed P in the sediment and are the species that release P in bioavailable form to water as orthophosphate (Zhou et al. 2001, Zhu et al. 2013), making it directly assimilable by algae and therefore, strongly contributing to eutrophication (Yalcin et al. 2012). Previous studies of P release in the lake suggest that the release of P is mainly related to the reducing solution of Fe oxides followed by

degradation of organic matter (Hansen and Márquez-Pacheco 2015). P that is not released remains accumulated in the sediment and appears to consist mainly of HCl-P and residual P. In this case, the HCl-P content was higher at site C mainly in the sediment layer of 0-10 cm and subsequently decreasing with depth in the sediment profile. At sites A and B, the contents of HCl-P increased with depth, indicating an accumulation in the sediment profile. Residual P did not show considerable changes in the sediment profile at sites B and C, while site A did show a decrease with the depth in the sediment profile.

### Correlation between P release, P forms, and sediment porosity

The release of P is influenced by the distribution of the P forms in the sediment profile, the diffusion of P in sediment and environmental conditions (Kamiya et al. 2017). Therefore, the relationships between experimental P release results under anoxic conditions, sediment porosity, P fractions potentially available for release and sediment depth were investigated by statistical correlation analysis. Previously for this analysis, P released by 5 cm sediment layers was calculated as the difference between P released from a layer and P released from an upper layer (**Table III**).

From this analysis it is observed that P release occurs from the first three sediment layers (0-5,

**TABLE III.** RELEASE FLUXES OF P FROM SEDIMENTS LAYERS FROM THE THREE SAMPLING SITES. P RELEASE FROM SEDIMENT LAYER REPRESENT THE DIFFERENCE BETWEEN P RELEASE OF A THICKNESS AND P RELEASE OF A THICKNESS 5 cm SMALLER. EXAMPLE: SEDIMENT THICKNESS (10) MINUS SEDIMENT THICKNESS (5).

Sampling site	Sediment thickness (cm)	P release from sediment thickness ( $\text{mg}/\text{m}^2 \times \text{d}$ )	Sediment layer (cm)	P release from sediment layer ( $\text{mg}/\text{m}^2 \times \text{d}$ )
A	5	0.89	0-5	0.89
	10	1.68	5-10	0.79
	15	1.80	10-15	0.12
	20	1.83	15-20	0.03
	25	1.84	20-25	-0.01
B	5	1.26	0-5	1.26
	10	1.87	5-10	0.61
	15	2.04	10-15	0.17
	20	2.04	15-20	0.00
	25	2.07	20-25	0.03
C	5	1.41	0-5	1.41
	10	1.86	5-10	0.45
	15	2.02	10-15	0.16
	20	1.91	15-20	-0.11
	25	1.96	20-25	0.05



**TABLE IV.** RELATIONS BETWEEN P RELEASE, P FORMS, SEDIMENT POROSITIES, AND SEDIMENT DEPTH LAYERS (n = 15).

	Sediment depth	Porosity	P release	H <sub>2</sub> O-P	DB-P	NaOH-SRP	NaOH-NRP	HCl-P	Residual P	TP
Sediment Depth	1	-0.471	<b>-0.885</b>	-0.494	<b>-0.591</b>	<b>-0.710</b>	<b>-0.524</b>	-0.134	-0.270	<b>-0.807</b>
Porosity		1	<b>0.530</b>	0.270	0.347	0.437	0.225	0.372	0.359	<b>0.569</b>
P release			1	<b>0.514</b>	<b>0.612</b>	<b>0.800</b>	<b>0.615</b>	0.127	0.216	<b>0.881</b>
H <sub>2</sub> O-P				1	<b>0.534</b>	0.493	0.264	-0.339	0.075	0.453
DB-P					1	0.315	0.267	0.186	-0.073	<b>0.574</b>
NaOH-SRP						1	<b>0.852</b>	-0.143	0.014	<b>0.885</b>
NaOH-NRP							1	-0.081	-0.146	<b>0.799</b>
HCl-P								1	<b>0.529</b>	0.260
Residual P									1	0.228
TP										1

Bold values are at a significance level of  $p < 0.05$ .

5-10 and 10-15 cm). Once P is liberated due to the reduction of Fe oxides and degradation of organic matter, it diffused upwards through the porewater in overlying sediment.

The analysis of Pearson correlations between P release data, P forms and sediment porosity are presented in **Table IV**. Sediment depth presents a strongly significant inverse correlation with P release, DB-P, NaOH-SRP, and NaOH-NRP, indicating an inverse association between these forms of P and the release of P with depth in the sediment profile. Additionally, a positive correlation was found between the P release and the P forms that represent potentially available P in sediment: H<sub>2</sub>O-P, DB-P, NaOH-SRP and NaOH-NRP. These results confirm that P release from sediments in the lake can be predicted with changes in Eh, pH and degradation of organic matter in sediment and that the concentration of P tend to stabilize with depth. In this sense, Rydin (2000) reported that, for a moderately eutrophic lake, the exponential decrease of P in sediment is linked to Fe/Mn hydroxides that stabilize at a depth of approximately 15 cm. On the other hand, Carey and Rydin (2011) reported an exponential decrease in P due to degradation of organic matter and then stabilization at an average depth of 16 cm.

Additionally, the release of P is associated with the porosity of the sediment, where the sediments with the highest porosity have the highest flux of P (Porosity = 73-80 % v/v, P release 1.7-2.0 mg/m<sup>2</sup>×d). These results can be explained due to the higher diffusion of P in pore water, mainly due to the larger size of the particles and correspondingly higher porosity of the sediment (Jing-Yu et al. 2013, Zhu et al. 2015).

## CONCLUSIONS

The effective sediment depth for P release in the studied monomictic eutrophic lake was determined by analyzing the amount of released P, the sediment porosity and the distribution of the P forms in sediment profiles. It was found that the highest release of P occurred in a 15-cm sediment layer and, as sediment depth increased, the release rate stabilized. In addition, it was found that sediment porosity, P release velocity, and some of the different forms of P in sediment, declined with depth of the sediment profile, being higher in the surface than in the deeper layers. In the same manner, it was found that P release is strongly related to the forms DB-P, NaOH-SRP and NaOH-NRP, which represent potentially available P for release. In this context, we can say that effective sediment depth for P release in this monomictic eutrophic lake occurs in a layer of approximately 15 cm, and the dominant processes are reduction of Fe oxides, degradation of organic matter and the upward diffusion of dissolved P through pore water.

## ACKNOWLEDGMENTS

The authors wish to thank the Organismo de Cuenca Aguas del Valle de México from the Mexican National Water Commission (CONAGUA) for financial support (contract no. OAVMDT-MEX-11-479-RF-CC), Phoslock Environmental Technologies (PET) for the training of HMP in the Psenner extraction technique, and the Mexican National Council of Science and Technology (CONACYT) HMP. Also, thanks to Arturo Hernández Antonio, Luis Carlos

González Márquez, Carlos Corzo Juárez, and Axel Falcón Rojas for their support in the field and in the laboratory.

## REFERENCES

- Ahlgren J., Tranvik L., Gogoll A., Waldeback M., Markides K. and Rydin E. (2005). Sediment depth attenuation of biogenic phosphorus compounds measured by P-31 NMR. *Environmental Science & Technology* 39(3), 867–872. <http://doi.org/10.1021/es049590h>
- APHA (2005). Standard methods for examination of water and wastewater. Methods: 4500-P and 10200 H Chlorophyll. American Public Health Association. Washington DC, USA. 1323 pp. <https://www.standard-methods.org/doi/book/10.2105/SMWW.2882>
- Anschutz P., Bouchet S., Abril G., Bridou R., Tessier E. and Amouroux A. (2019). In vitro simulation of oscillatory redox conditions in intertidal sediments: N, Mn, Fe, and P coupling. *Continental Shelf Research* 177, 33–41. <https://doi.org/10.1016/j.csr.2019.03.007>
- Barik S.K., Bramha S., Bastia T.K., Behera D., Kumar M., Mohanty P.K. and Rath P. (2019). Characteristics of geochemical fractions of phosphorus and its bioavailability in sediments of a largest brackish water lake, South Asia. *Ecohydrology and Hydrobiology* 19(3), 370–382. <https://doi.org/10.1016/j.ecohyd.2019.02.002>
- Beutel M.W., García-Gallardo T., Falcón-Rojas A., Furhmann B. and Hansen A.M. (2018). Use of oxygenation to repress release of redox-sensitive compounds from profundal sediment in the Valle de Bravo reservoir, Mexico. *Proceedings: 6th International Symposium on Sediment Management San Cristóbal de Las Casas, Chiapas, Mexico. Revista Internacional de Contaminación Ambiental* 34(6), 17–20.
- Bostrom B., Jansson M. and Forsberg C. (1982). Phosphorus release from lake sediments. *Archives of Hydrobiology* 18, 5–59.
- Carey C.C. and Rydin E. (2011). Lake trophic status can be determined by the depth distribution of sediment phosphorus. *Limnology and Oceanography* 56(6), 2051–2063. <https://doi.org/10.4319/lo.2011.56.6.2051>
- Chao W., Jin Q., Zhi-Yong G., Li Z. and Xiao-Chen L. (2008). Vertical Distributions of Phosphorus Fractions in Sediments of Three Typical Shallow Urban Lakes in P.R. China. *Polish Journal of Environmental Studies* 17(1), 155–162.
- Chen M., Ding S., Wu Y., Fan X., Jin Z., Daniel C.W. Tsang D.C.W., Wang Y. and Zhang C. (2019). Phosphorus mobilization in lake sediments: Experimental evidence of strong control by iron and negligible influences of manganese redox reactions. *Environmental Pollution* 246, 472–481. <https://doi.org/10.1016/j.envpol.2018.12.031>
- Cooke G.D., Welch E.B., Peterson S.A. and Nichols S.A. (2016). Restoration and management of lakes and reservoirs. CRC Press: Taylor and Francis Group. 612 pp.
- Gächter R. and Müller B. (2003). Why the phosphorus retention of lakes does not necessarily depend on the oxygen supply to their sediment surface. *Limnology and Oceanography* 48, 929–933. <https://doi.org/10.4319/lo.2003.48.2.0929>
- Hansen A.M. and Márquez-Pacheco H. (2012). Procedimiento para evaluar cargas internas de nutrientes en cuerpos de agua. *Revista Mexicana de Ciencias Geológicas* 29(1), 265–275.
- Hansen A.M. and Márquez-Pacheco H. (2015). Internal phosphorus load in a Mexican reservoir: forecast and validation. *Environmental Toxicology and Chemistry* 34(11), 2583–2589. <https://doi.org/10.1002/etc.3102>
- Holmes M. (2004). Relation of phosphorus release and sediment oxygen uptake to sediment characteristics in Big Platte Lake, Benzie Co., MI [D]. Illinois, USA: Central Michigan University.
- Hupfer M., Gächter R. and Ruegger R.R. (1995). Polyphosphate in lake sediments: 31P NMR spectroscopy as a tool for its identification. *Limnology and Oceanography* 49, 1–10. <https://doi.org/10.4319/lo.1995.40.3.0610>
- Jing-Yu F., Xiao-Yan H. and Dao-Zeng W. (2013). Experimental study on the effects of sediment size and porosity on contaminant adsorption/desorption and interfacial diffusion characteristics. *Journal of Hydrodynamics* 25(1), 20–26. [https://doi.org/10.1016/S1001-6058\(13\)60334-0](https://doi.org/10.1016/S1001-6058(13)60334-0)
- Juárez-Badillo E. and Rico-Rodríguez A. (2005). Sediment mechanics I: Fundamentals of sediment mechanics (In Spanish). 2<sup>nd</sup> ed. Limusa. Mexico City, Mexico. 644 pp.
- Kamiya K., Fukushima T., Ouchi T. and Aizaki M. (2017). Phosphorus budgetary analysis of sediment–water interface in a short-term anoxic condition in shallow Lake Kasumigaura, Japan. *Limnology* 18, 131–140. <https://doi.org/10.1007/s10201-016-0496-5>
- Kim L.H., Choi E. and Stenstrom M.K. (2003). Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments. *Chemosphere* 50(1), 53–61. [https://doi.org/10.1016/S0045-6535\(02\)00310-7](https://doi.org/10.1016/S0045-6535(02)00310-7)
- Le Moal M., Gascuel-Oudoux C., Ménesguen A., Souchon Y., Étrillard C., Levain A., Moatar F., Pannard A., Souchu P., Lefebvre A. and Pinay G. (2019). Eutrophication: A new wine in an old bottle? *Science of The Total Environment* 651(1), 1–11. <https://doi.org/10.1016/j.scitotenv.2018.09.139>

- Márquez-Pacheco H. and Hansen A.M. (2017). Internal phosphorus load in a Mexican reservoir through sediment speciation analysis. *Environmental Science and Pollution Research* 24, 24947–24952. <https://doi.org/10.1007/s11356-017-0148-2>
- Márquez-Pacheco H., Hansen A.M. and Falcón-Rojas A. (2013). Phosphorous control in a eutrophied reservoir. *Environmental Science and Pollution Research* 20, 8446–8456. <https://doi.org/10.1007/s11356-013-1701-2>
- Miao S., De Laune R.D. and Jugsujinda A. (2006). Influence of sediment redox conditions on release/solubility of metals and nutrients in a Louisiana Mississippi River deltaic plain freshwater lake. *Science of The Total Environment* 371(1-3), 334–343. <https://doi.org/10.1016/j.scitotenv.2006.07.027>
- Orihel D.M., Baulch H.M., Casson N.J., North R.L., Parsons C.T., Seckar D.C.M. and Venkiteswaran J.J. (2017). Internal phosphorus loading in Canadian fresh waters: a critical review and data analysis. *Canadian Journal of Fisheries and Aquatic Sciences* 74(12), 2005–2029. <https://doi.org/10.1139/cjfas-2016-0500>
- Perrone U., Facchinelli A. and Sacchi E. (2008). Phosphorus Dynamics in a Small Eutrophic Italian Lake. *Water, Air, and Soil Pollution* 189, 335–351. <https://doi.org/10.1007/s11270-007-9551-5>
- Psenner R., Puesko R. and Sager M. (1984). Die Fraktionierung Organischer und Anorganischer Phosphorverbindungen von Sedimenten - Versuch einer Definition Ökologisch Wichtiger Fraktionen. *Archives of Hydrobiology* 10, 111–155.
- Rydin E. (2000). Potentially mobile phosphorus in Lake Erken sediment. *Water Research* 34(7), 2037–2042. [https://doi.org/10.1016/S0043-1354\(99\)00375-9](https://doi.org/10.1016/S0043-1354(99)00375-9)
- Solim S.U. and Wanganeo A. (2009). Factors influencing release of phosphorus from sediments in a high productive polymictic lake system. *Water Science & Technology* 60(4), 1013–1023. <https://doi.org/10.2166/wst.2009.445>
- Søndergaard M., Jensen J.P. and Jeppesen E. (1999). Internal phosphorus loading in shallow Danish lakes. *Hydrobiologia* 408/409, 145–152. [https://doi.org/10.1007/978-94-017-2986-4\\_15](https://doi.org/10.1007/978-94-017-2986-4_15)
- Søndergaard M., Jensen J.P. and Jeppesen E. (2003). Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia* 506(1), 135–145. <https://doi.org/10.1023/B:HYDR.0000008611.12704.dd>
- Steinman A.D., Rediske R. and Reddy K.R. (2004). The reduction of internal phosphorus loading using alum in Spring Lake, Michigan. *Journal of Environmental Quality* 33(6), 2040–2048. <https://doi.org/10.2134/jeq2004.2040>
- Villanueva-Beltrán J.T. (2011). Evaluation of the external load of phosphorus and nitrogen in the Valle de Bravo Dam and proposed solution (In Spanish). Master Thesis. Mexican National Autonomous University (UNAM). Mexico City, Mexico. 134 pp.
- Wang Y., Shen Z., Niu J. and Liu R. (2009). Adsorption of phosphorus on sediments from the Three-Gorges Reservoir (China) and the relation with sediment compositions. *Journal of Hazardous Materials* 162(1), 92–98. <https://doi.org/10.1016/j.jhazmat.2008.05.013>
- Wan-Qiu Y., Xiao H., Li Y. and De-Ren M. (2018). Vertical distribution and release characteristics of phosphorus forms in the sediments from the river inflow area of Dianchi Lake, China. *Chemical Speciation & Bioavailability* 30(1), 14–22. <https://doi.org/10.1080/09542299.2018.1446766>
- Welch E.B. and Cooke G.D. (1999). Effectiveness and longevity of phosphorus inactivation with alum. *Lake and Reservoir Management* 15, 5–27. <https://doi.org/10.1080/07438149909353948>
- Wetzel R.G. and Likens G.E. (2000). *Limnological Analyses*. 3rd ed. Springer-Verlag. New York, USA. XV, 429 pp. <https://doi.org/10.1007/978-1-4757-3250-4>
- Wu Y., Wen Y., Zhou J. and Wu Y. (2014). Phosphorus Release from Lake Sediments: Effects of pH, Temperature and Dissolved Oxygen. *KSCE Journal of Civil Engineering* 18(1), 323–329. <https://doi.org/10.1007/s12205-014-0192-0>
- Xiangcan J., Shengrui W., Yan P. and Feng C.W. (2006). Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas in Taihu Lake, China. *Environmental Pollution* 139(2), 288–295. <https://doi.org/10.1016/j.envpol.2005.05.010>
- Yalcin S., Demirak A. and Keskin F. (2012). Phosphorus fractions and its potential release in the sediments of Koycegiz Lake Turkey. *Lakes Reservoirs and Ponds*. 6(2), 139–153.
- Zeng L., Yang F., Yan C. and Wang X. (2018). High-resolution characterization of labile phosphorus, iron, and manganese in sediments of different trophic waters in Lake Taihu, China. *Water Science & Technology* 77(2), 286–295. <https://doi.org/10.2166/wst.2017.534>
- Zhou Q., Gibson C.E. and Zhu Y. (2001). Evaluation of phosphorus bioavailability in sediments of three contrasting lakes in china and UK. *Chemosphere* 42(2), 221–225. [https://doi.org/10.1016/S0045-6535\(00\)00129-6](https://doi.org/10.1016/S0045-6535(00)00129-6)
- Zhu H.W., Wang D.Z., Cheng P.D., Fan JY. and Zhong B.C. (2015). Effects of sediment physical properties on the phosphorus release in aquatic environment. *Science China Physics, Mechanics & Astronomy* 58, 1–8. <https://doi.org/10.1007/s11433-014-5582-2>

- Zhu M., Zhu G., Li W., Zhang Y., Zhao L. and Gu Z. (2013). Estimation of the algal-available phosphorus pool in sediments of a large, shallow eutrophic lake (Taihu, China) using profiled SMT fractional analysis. *Environmental Pollution* 173, 216–223. <https://doi.org/10.1016/j.envpol.2012.10.016>