

Environmental Toxicology

INTERNAL PHOSPHORUS LOAD IN A MEXICAN RESERVOIR: FORECAST AND VALIDATION

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Abstract: To determine the internal phosphorus load (IPL) as a function of redox potential (Eh) in a Mexican reservoir, the results from a phosphorus (P) release experiment were extrapolated to temporal and spatial variations of Eh in sediments, and an IPL-Eh of 24.2 ± 2.5 t/yr was obtained. This result is compared with the P mass balance (MB) in the reservoir, where the IPL-MB is determined as the difference between P inputs to the reservoir and the outputs. Inputs of P are the sum of the external P load from the hydrological basin, the IPL, and P in atmospheric precipitation; outputs of P are the sum of sedimented P, and the removal of P in water and biomass, and the resulting IPL-MB, is 26.4 ± 4.9 t/yr. In addition, P concentrations in sediment cores (SCs) are analyzed, and the historical release of P from sediments determined, resulting in an IPL-SC of 23.5 ± 1.4 t/yr. The different IPL results are similar, as average values are within the standard deviation of IPL-MB. It is concluded that analysis of the variations in Eh in sediments allows determination of the reservoir's IPL. Six-weekly IPL-Eh and IPL-MB values are analyzed, and it can be seen that IPL occurs mainly during the period from May to August, when the water column is thermally stratified. *Environ Toxicol Chem* 2015;9999:1–7. © 2015 SETAC

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INTRODUCTION

Enrichment of nutrients such as nitrogen (N) and phosphorus (P) is an important water pollution problem, causing increases in primary productivity, algae blooms, decreases in dissolved oxygen, and detrimental biological changes [1]. Nutrients enter water bodies by external and internal nutrient loads. The external nutrient loads include sewage point sources and diffuse sources from urban runoff as well as agricultural, livestock, and other land uses. The internal nutrient loads occur when nutrients associated with minerals or organic matter in sediments are released, becoming available for algae and bacterial growth [2]. Unlike P, N may form gaseous species that may enter from or be released to the atmosphere, involving transfers of atmospheric molecular N through fixation by microorganisms and return to the atmosphere through denitrification processes [3]. In most cases P is the limiting nutrient for growth of phytoplankton [4] and is thus the nutrient that should be controlled to avoid eutrophication of water bodies [5]. Phosphorus bound to organic and inorganic components in sediments may be released to the water column by processes such as desorption, reductive dissolution of inorganic substrates, and degradation of organic matter [6-8].

Degradation of organic matter in sediments depends on the presence of electron acceptors, such as dissolved oxygen in interstitial water. As dissolved oxygen is depleted, organic matter is sequentially oxidized by nitrate (NO₃⁻), manganese oxide (MnO₂), iron oxy-hydroxide (FeOOH), or sulfate (SO₄²⁻) [9], thus generating changes in redox potential (Eh) in the sediment. These changes influence the chemical bonds of P, as described by Hupfer and Lewandowski [7], Miao et al. [10], and Perrone et al. [11]. Under oxidized conditions (Eh > 200 mV), iron (Fe) and manganese (Mn) occur as

oxidized solids (FeOOH and MnO₂), with high affinities for P. At conditions of Eh < 200 mV, Fe and Mn oxides are reduced, forming the soluble Fe^{2+} and Mn^{2+} . This implies that P, which is particle reactive, may also be released to the aqueous phase, generating an internal P load (IPL). The objective of the present study was to demonstrate that the IPL can be estimated based on analysis of spatial and temporal variations of Eh in the sediment. Thus the release of P as a function of Eh was analyzed experimentally in the laboratory with combined sediments from a reservoir, and the experimental results were extrapolated to the spatial and temporal variations of Eh in sediments of the reservoir, obtaining the IPL as a function of Eh (IPL-Eh). This result was compared with the IPL as determined by the P mass balance (IPL-MB) and with the IPL as determined by historical decreases in P concentrations in sediment cores (IPL-SC).

The present study was carried out in a multiple-purpose water body located in central Mexico that is used for tourism, fishery, and water supply. This reservoir has a surface area of approximately 1680 ha, an average volume of 328 Mm³, and an average depth of 19.5 m; 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 [12]. The reservoir is located at approximately 1800 m above sea level in an area with a temperate climate. The average annual rainfall is between 1200 mm and 1400 mm, and the average annual temperature is between 18 °C and 19 °C [13]. The hydrological basin of the reservoir has an extension of 615 km² and a human population of over 80 000 habitants, and the land uses include forestry, agriculture, grassland, livestock, fish culture, and urban areas. The contributions of P from each of these sources as estimated by J.T. Villanueva-Beltrán (2011, Master's thesis, National Autonomous University of Mexico, Mexico City, Mexico) are presented in Table 1.

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Table 1. Contributions of external phosphorus loads (EPL) in the reservoir^a

Source	Amount	EPL (t/yr)
Trout production	485 t/yr	10.2
Pig raising	267 t/yr	12.7
Agriculture	$115.6 \mathrm{km^2}$	13.7
Forest	$332.6 \mathrm{km^2}$	5.4
Wetland	18.3km^2	0.0
Grassland	47.8km^2	1.7
Urban area	10.3km^2	0.9
Wastewater	81 832 inhabitants	21.0
Total		65.6

^aData from J.T. Villanueva-Beltrán, 2011, Master's thesis, National Autonomous University of Mexico, Mexico City, Mexico.

Based on the P concentrations measured in the reservoir and the limits for this nutrient defined by the Organisation for Economic Co-operation and Development [14], the reservoir has been classified as eutrophic throughout the year [15–17].

MATERIALS AND METHODS

Water and sediment were monitored from February 2010 to October 2011 with samples of each taken every 6.1 ± 1.3 wk, resulting in a total of 16 sampling events. The monitoring was carried out at 23 sampling stations, located with a mesh design [18] with a 1-km grid, plus 5 monitoring stations located at the inlets of the main tributaries to the reservoir. Samples were collected at each station at a depth of 0.5 m and 0.3 m from the bottom. In addition, at stations where the water was deeper, samples were collected at a depth of 14 m, representing the depth of the upper hypolimnion; at stations where the water was shallower than 1 m, samples were collected at a depth of 0.5 m only. This distribution of sample stations and depths resulted in the collection of 55 ± 4 water samples during each sampling event. Water samples were collected with a 2-L van Dorn horizontal bottle (Wildco Instruments) for analysis of orthophosphate (P-PO₄) and total P with a colorimetric method [19], as well as spectrophotometry (Merck Pharo 300). During the last 5 sampling events, surface water samples were collected for colorimetric analysis of chlorophyll a (Chla) [20]. Water temperature, pH, dissolved oxygen, NO_3^- , NH_4^+ , and Eh were determined using a previously calibrated multiparametric probe (Hach Hydrolab DS5) according to the manufacturer's manual. The probe was also introduced approximately 15 cm into the sediment by free fall, determining pH and Eh at a sediment depth of approximately 8 cm, when registers had stabilized after approximately 15 min of equilibration time. Correlations between parameters were analyzed statistically using the Pearson correlation and a significance level of p < 0.05%. Areas of the reservoir influenced by specific Eh intervals in the sediments were determined for each sampling event (Surfer Ver 8, Golden Software).

Surface sediment samples of approximately 10 cm to 15 cm depth were obtained with a 15.2-cm × 15.2-cm stainless steel Ekman dredge (Wildco Instruments) and characterized for organic matter by ignition at 450 °C [21], total P by spectrophotometry [22], Al, Fe, and Mn by atomic emission spectrometry [23], and texture by sedimentation [24]. Sediment samples were combined on an equivalent dry weight basis from each depth area in the reservoir (d < 3.5 m, n = 7; 3.5 m < d < 13 m, n = 10; d > 13 m, n = 6), and suspended in Milli-Q

water (Millipore); 1:8 sediment-water slurries were obtained that were kept in suspension by continuous magnetic stirring, with temperatures at 24.9 ± 0.8 °C. Initially, slurries were equilibrated under anaerobic conditions by passing CO₂-free N₂ (Ultra, High Purity) through the suspensions. Using an Eh electrode (Orion Redox/ORP Triode) and a pH electrode (Orion ROSS Ultra), these parameters were monitored potentiometrically (Orion Dual Star). By passing CO₂-free N₂ (Ultra, High Purity) or pumping CO₂-free air through the slurries, Eh was adjusted between -200 and 400 mV with increases of approximately 50 mV. For each increase, Eh was stabilized within \pm 5 mV for at least 2 d, and 40-mL aliquots of the slurries were obtained using a plastic syringe. The aliquots were centrifuged for 20 min at 12 000 rpm (Beckman J2-21), and the supernatant was filtered through 0.45-µm membrane filters (Millipore). Samples were first digested at 119 °C in a Merck TR420 thermo-reactor by adding sulfuric acid for analysis of P, and nitric acid for analysis of Fe, and then analyzed by colorimetric methods [19], and spectrophotometry (Merck Pharo 300). Biodegradation of organic matter in the slurries was determined as continuously emitted CO₂ absorbed in a Ba(OH)₂ solution and precipitated as carbonate, causing a stoichiometric decrease in ionic strength of the solution and its electrical conductivity [25].

Using Equation 1, the P release experiments were extrapolated to calculate P release per unit area of the reservoir.

$$M = \frac{C}{x} \times \rho \times L \times 1000 \tag{1}$$

where M = P released by sediment area (mg/m²); C = P concentration for each increase in Eh (mg/L); x = sediment:water ratio (g/L); $\rho =$ sediment density (kg/m³); L = sediment depth where P release occurs (m); and 1000 = conversion factor (g/kg).

Information on the sediment depth from where the release of P occurs $(20 \pm 5 \text{ cm})$ and the density of the sediment $(0.17 \pm 0.03 \text{ kg} \text{ dry wt/L})$ was obtained from Márquez-Pacheco et al. [26]; the average surface area of the reservoir is 1680 ha. The results of P release per unit area were plotted, and equations were adjusted to describe the P release for sediment areas with specific Eh. The results were extrapolated to areas with specific Eh values, and the P release flow was obtained for each sampling event. The IPL-Eh was obtained for 5 different annual intervals within the monitoring period, and the average IPL-Eh and standard deviation were calculated.

To validate the IPL-Eh, results were compared with the internal P load determined by mass (Equation 2):

$$IPL - MB = \Delta P + P_{extr} + P_{sed} - EPL$$
(2)

where *IPL-MB* = internal P load determined by mass balance (t/sampling period); ΔP = mass variation of P in water of the reservoir (t/sampling period); P_{extr} = P removed by extraction of water and biomass (t/sampling period); P_{sed} = sedimented P (t/sampling period); and EPL = external P load (t/sampling period).

To determine ΔP for each sampling event, the differences in average P concentrations were multiplied by the water volume in the reservoir. The P_{extr} was estimated as the average volume of extracted water and the average concentration of P at the extraction site of water from the reservoir. Extracted biomass was estimated with the water hyacinth extraction and fish catch

data, the water contents and the P concentrations reported for this type of biomass [27,28]. The external P load was determined using a nutrient emissions inventory for the watershed (J.T. Villanueva-Beltrán, 2011, Master's thesis, National Autonomous University of Mexico, Mexico City, Mexico). With this information, external P load was calculated for each sampling period, considering wastewater discharges, livestock, fish culture, and runoffs from different land uses. The amount of P that enters through atmospheric precipitation was estimated as the average precipitation between sampling events [29], and the average concentration of P reported for rain water [30]. The P_{sed} was determined for different depth areas of the reservoir. Using a gravity core sampler (Wildco Wildlife Support) equipped with 4.8-cm-diameter, 50.8-cmlong cellulose acetate butyrate liners, sediment cores were obtained from the 3 sampling sites of different water depths within the reservoir. Sections of the sediment cores were analyzed for ²¹⁰Pb and ²²⁶Ra decays by gamma spectrometry based on ASTM International methods C 1402-98 and E 181-98. Excess ²¹⁰Pb activities were calculated as the difference between ²¹⁰Pb and ²²⁶Ra activities, and mass accumulation rates were estimated from the linear regression of the natural logarithm of excess ²¹⁰Pb plotted against accumulated sediment mass per area for each sediment layer. Phosphorus concentrations from the 23 sampling stations in the reservoir were obtained from Hansen and Márquez-Pacheco [15]. Using Equation 2, the IPL-MB was obtained for periods between sampling events; 5 different annual IPL-MB values were obtained, as well as the average IPL-MB and the standard deviation. Finally, results were compared with the IPL-SC, which was obtained by analysis of P concentrations in the layers of sediment cores; the IPL-SC was determined as the decrease in P concentrations between different depth layers of the cores, multiplied by P_{sed} .

RESULTS AND DISCUSSION

Analyses of Pearson correlations of the results of water monitoring data and Eh in sediments are presented in Table 2. Negative correlations were found between Eh in sediment and concentrations of P (P-PO₄), indicating that as Eh decreases, concentrations of P in water increase. Also, concentrations of Chla were positively correlated with concentrations of P-PO₄,



Figure 1. (A) Average redox potential (Eh) and standard deviation (SD) in sediment (solid lines), and average temperature (T) in bottom water of the reservoir (dashed lines). (B) Average phosphorus concentration (P) in bottom water. (C) Chlorophyll a (Chla) in surface water of the reservoir. Shaded areas represent water stratification periods. Diamonds indicate results from 2010, and squares results from 2011. P-PO₄ = phosphorus as phosphate.

Parameter	Temperature (°C)	Dissolved oxygen (mg/L)	NH4 ⁺ (mg/L)	NO ₃ ⁻ (mg/L)	P-PO ₄ (mg/L)	P _T (mg/L)	pН	Eh _{water} (mV)	Eh _{sed} (mV)	Chla (µg/L)
Temperature (°C)	1	0.468	0.472	-0.155	0.084	-0.023	0.606	-0.168	-0.076	0.645
Dissolved oxygen concentration (mg/L)	0.468	1	0.057	-0.122	-0.075	-0.307	0.508	0.329	0.093	0.688
NH_4^+ (mg/L)	0.472	0.057	1	0.035	0.366	0.093	-0.118	-0.392	-0.150	0.324
NO_3 (mg/L)	-0.155	-0.122	0.035	1	-0.269	-0.032	-0.233	-0.319	-0.217	0.121
$P-PO_4$ (mg/L)	0.084	-0.075	0.366	-0.269	1	0.317	-0.398	-0.190	-0.342	0.637
P_{T} (mg/L)	-0.023	-0.307	0.093	-0.032	0.317	1	-0.232	-0.268	-0.306	-0.160
pH	0.606	0.508	-0.118	-0.233	-0.398	-0.232	1	0.247	0.349	0.783
Eh _{water} (mV)	-0.168	0.329	-0.392	-0.319	-0.190	-0.268	0.247	1	0.789	-0.674
Eh _{sed} (mV)	-0.076	0.093	-0.150	-0.217	-0.342	-0.306	0.349	0.789	1	0
Chla (µg/L)	0.645	0.688	0.324	0.121	0.637	-0.160	0.783	-0.674		1

Table 2. Pearson correlations of the parameters measured in the reservoir (16 sampling events, 55 ± 4 samples per event)^a

^aBold values are at a significance level of p < 0.05.

T = temperature; DO = dissolved oxygen concentration; $NH_4^+ =$ concentration of ammonium ion; $NO_3^- =$ concentration of nitrate; $P-PO_4 =$ concentration of phosphorus as phosphate; PT = concentration of total phosphorus; pH = negative logarithm of the proton activity; $Eh_{water} =$ redox potential in water at the bottom of the reservoir; $Eh_{sed} =$ redox potential in the sediment; Chla = concentration of chlorophyll a.

suggesting an increased algae growth as $P-PO_4$ concentrations increase.

Reduced conditions were observed in sediments throughout the year, reaching values of Eh lower than -150 mV during the period of thermal stratification of the water (Figure 1A), at which point lower redox potentials and higher temperatures in the hypolimnion were observed in the first part of 2011 compared with 2010 (Figure 1A). Increased concentrations of P-PO₄ were also observed in bottom water samples during this time period (Figure 1B). This shows that P-PO₄ is released from the sediment when Eh decreases, having a direct effect on algae growth in the reservoir during early spring, as an increase in Chla concentrations occurred during the same period that this increase in P-PO₄ concentrations was observed (Figure 1C). The changes in P-PO₄ during late summer were probably related to the turnover of the water column rather than to IPL; increased algae growth was not observed during this period.

In addition, the results of the P release experiment revealed that decreased Eh caused higher concentrations of P (Figure 2A) and Fe (Figure 2B) in water, suggesting that FeOOH in the sediment was reductively dissolved, with a consequent release of P. This release of P from the sediment occurred mainly at Eh below +50 mV, whereas the release of Fe had already started at Eh +200 mV.

The production of CO_2 rose as Eh increased from -200 mV to 0 mV (Figure 2C), because of increased mineralization of organic matter and consequent transformation to CO_2 in this range of Eh; at positive values of Eh, no further increase in concentration of CO_2 was observed. The similarity of the P and Fe curves and the difference from the produced CO_2 suggest that the release of P was related to the reductive dissolution of Fe oxides rather than to the degradation of organic matter. Linear regression curves were adapted to the results of P release (Figure 2A). To estimate the IPL in the reservoir, these curves were applied to areas of different Eh in the reservoir as described by Equations 3 and 4 (Figure 3 and Table 3).

$$IPL - Eh = \frac{\sum_{i=1}^{n} (0.2425 \, Eh_i + 9.1015) A_i}{A \times t}$$
(3)

$$IPL - Eh = \frac{\sum_{i=1}^{n} (0.0013 \, Eh_i + 5.555) A_i}{A \times t} \tag{4}$$

where *IPL-Eh* = internal P load estimated by changes in Eh (mg/m² d); Eh_i = redox potential in sediments (mV); A_i = area of sediments influenced by each Eh (m²); A = surface area of the reservoir (m²); t = time between sampling events (d); 0.2425 and 0.0013 = slopes of the linear regression curves (Figure 2A); and 9.1015 and 5.555 = intercepts of the curves on the y-axis (Figure 2A).

Larger IPL-Eh values were observed in the reservoir during the months from May to August, during water stratification (Figure 4). By applying these equations to the sediment Eh changes between sampling events, 5 different annual IPL-Eh values were obtained, with an average of 24.2 ± 2.5 t/yr, corresponding to an average daily P flow of 3.9 ± 0.4 mg/m² d (Table 4).

The results obtained for IPL-Eh values were compared with the IPL-MB values for the reservoir of $26.4 \pm 4.9 \text{ t/yr}$



Figure 2. Internal loads at variable redox potential (Eh). (A) Release of phosphorus (P), (B) release of iron (Fe), and (C) release of carbon dioxide (CO₂). Combined sediments from shallow areas (s < 3.5 m, n=7), intermediate depth (3.5 < i < 13 m, n=10), and deep areas (d > 13 m, n=6), temperature = 24.9 ± 0.8 °C, pH = 5.5 ± 1.5, equilibration time = 2 d.

with an average daily flow of $4.3 \pm 0.8 \text{ mg/m}^2$ d (Table 4). It was found that the IPL-Eh was within the standard deviation of IPL-MB. When results for each sampling period were compared, higher IPL-MB values were observed compared with IPL-Eh values during periods of thermal stratification (from March to September) and lower IPL-MB than IPL-Eh values during the rest of the year (from October to February). To explain these differences, the Pourbaix diagram for Fe was analyzed for experimental and field observations of Eh and pH (Figure 5). For Eh above 300 mV, experimental pH decreased until it was approximately 4, whereas pH measured in the field was approximately 8. At Eh = 300 mVand pH = 8, Fe forms iron hydroxides (Fe(OH)₃), which adsorb P, resulting in lower IPL-MB than IPL-Eh values during initial stratification of the water column. In contrast, when Eh was lower than -200 mV, the pH measured in the field was slightly more alkaline (pH \sim 8) than in the laboratory experiment (pH \sim 7). Under these conditions of Eh below -200 mV and pH approximately 8, Fe probably



Figure 3. Distribution of redox potential (Eh) in sediment of the reservoir during the August 25-26, 2010 sampling event.

Table 3. Areas of the reservoir (km ²) with sp	pecific redox potential (Eh) dur	ring the sampling events,	analyzed as 10-mV	intervals and pres	sented here as
	50-mV	intervals			

		2010 ^a							2011 ^a							
Minimum Eh (mV)	Maximum Eh (mV)	Mar 23	Apr 27	Jun 03	Jul 22	Aug 25	Sep 30	Nov 10	Dec 14	Jan 25	Mar 02	Apr 06	May 17	Jul 06	Aug 25	Oct 10
-300	-250	0.00	0.00	0.00	0.00	2.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
-250	-200	1.53	0.00	0.00	8.26	8.14	0.66	0.00	0.00	0.00	0.00	0.00	0.99	10.28	5.14	0.00
-200	-150	1.96	0.00	0.00	4.85	3.11	6.99	0.03	0.00	0.00	0.49	0.84	11.89	4.17	7.69	0.76
-150	-100	2.50	0.00	0.68	2.21	1.71	4.52	9.48	1.22	1.59	6.49	10.57	2.07	1.85	1.95	11.19
-100	-50	6.61	0.00	3.89	1.13	1.13	2.33	5.63	9.28	5.44	6.35	2.79	1.10	0.57	1.06	3.44
-50	0	4.38	2.43	11.31	0.42	0.39	1.01	1.42	4.13	6.80	2.34	1.21	0.45	0.03	0.68	1.20
0	50	0.07	9.48	0.54	0.00	0.08	1.05	0.35	1.12	2.75	0.85	0.81	0.19	0.00	0.36	0.21
50	100	0.00	4.74	0.17	0.00	0.05	0.19	0.01	0.65	0.24	0.39	0.48	0.11	0.00	0.00	0.06
100	150	0.00	0.18	0.07	0.00	0.00	0.13	0.00	0.37	0.00	0.08	0.28	0.07	0.00	0.00	0.00
150	200	0.00	0.09	0.02	0.00	0.00	0.08	0.00	0.13	0.00	0.00	0.06	0.03	0.00	0.00	0.00
200	250	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
250	300	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total area (km ²)		17.04	16.91	16.69	16.87	16.91	17.02	16.93	17.04	16.82	17.00	17.03	16.91	16.91	16.88	16.86

^aSampling date.



Figure 4. Internal phosphorus loads (IPLs) estimated by variations of redox potential (Eh) in sediment (IPL-Eh) and by mass balance (IPL-MB), from April 2010 to October 2011. Shaded areas represent water stratification periods.

dissolves as reduced iron (Fe^{2+}), releasing adsorbed P. This may explain the higher IPL-MB compared with IPL-Eh values when thermal stratification occurs. Such an increase in the release of P under alkaline conditions has been previously reported, as a result of the exchange with hydroxyl ions of the phosphate adsorbed on $Fe(OH)_3$ [31,32].

The IPL-Eh was also compared with the IPL-SC results obtained by analysis of sediment profiles from different areas of the reservoir (Table 5). Considering that an approximate 35% decrease in P in the top 15 cm to 20 cm of the sediment cores occurred [26], the IPL-SC was estimated as 23.3 ± 1.4 t/yr with an average daily flow of 3.8 ± 0.1 mg/m²d. This value was compared with the IPL-MB and IPL-Eh values (Figure 6), and it could be seen that all estimations were within the standard deviation of the IPL-MB. We conclude that analysis of Eh variations in sediments allows the determination of the reservoir's IPL because this value could be compared with IPL-MB and IPL-SC as independent methods.

Table 4. Comparison of internal phosphorus loads (IPL) determi	ned by analysis of variatior	is in redox potential (IPL	L-Eh) and by mass balance	(IPL-MB)
considering ea	ach sampling event and ann	ual periods		

Sampling event	Sampling date	IPL-Eh (mg/m ² d)	IPL-MB $(mg/m^2 d)$
3	Apr 27, 2010	3.1	9.0
4	Jun 03, 2010	3.7	5.9
5	Jul 22, 2010	5.2	10.5
6	Aug 25, 2010	1.9	-7.2
7	Sep 30, 2010	-7.5	-12.1
8	Nov 10, 2010	-3.1	1.3
9	Dec 14, 2010	-3.2	1.2
10	Jan 25, 2011	-0.3	2.6
11	Mar 02, 2011	2.9	2.7
12	Apr 06, 2011	1.5	-8.7
13	May 17, 2011	7.8	11.2
14	Jul 06, 2011	5.8	-1.9
15	Aug 25, 2011	-1.2	-10.3
16	Oct 10, 2011	-3.7	0.5
Annual period			
3–12	Apr 27, 2010–Apr 06, 2011	3.3	4.7
4–13	Jun 03, 2010–May 17, 2011	3.8	5.0
5-14	Jul 22, 2010–Jul 06, 2011	3.9	4.9
6–15	Aug 25, 2010–Aug 25, 2011	4.0	3.8
7–16	Sep 30, 2010–Oct 10, 2011	4.5	3.2
Daily average $(mg/m^2 d)$	* ·	3.9 ± 0.4	4.3 ± 0.8
Yearly average (t/yr)		24.2 ± 2.5	26.9 ± 4.9



Figure 5. Pourbaix diagram of dissolved iron species (Fe^{2+} and Fe^{3+}) and formation of iron hydroxide, $Fe(OH)_3$, and pyrite, FeS_2 ; pFe = 6 and pS = 3. Modified from from Kehew (2001) as cited in Hansen et al. [33]. $pe = -\log \{e-\}$.



Figure 6. Average and standard deviation of internal phosphorus loads (IPLs) determined by mass balance (IPL-MB), by analysis of redox potential in sediment (IPL-Eh), and by analysis of phosphorus in sediment cores (IPL-SC).

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Depth areas of the reservoir	Area (km ²)	Sediment mass accumulation rate (g/cm ² yr)	[P] _{sed} ±SD (mg/kg d.w.; no. of samples)	$P_{sed} \pm SD (t/yr)$
Shallow $(d < 3.5 \text{ m})$	1.3	0.21	$597 \pm 64 \ (n = 7)$	1.6 ± 0.2
Intermediate depth $(3.5 < d < 13 m)$	8.5	0.38	$1071 \pm 83 \ (n = 10)$	34.6 ± 2.7
Deep (<13 m)	7.0	0.38	1140 ± 111 (n = 6)	30.3 ± 3.0
Total	16.8			66.6 ± 4.0

 $SD = standard deviation; [P]_{sed} = phosphorus concentration in sediment; P_{sed} = sedimented phosphorus.$

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Data availability—Data sources have been cited in the paper and references, more information can be obtained from the author (ahansen@tlaloc.imta.mx).

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