



Phosphorus release from a tropical estuary sediment: a laboratory study of Lake Maracaibo (Venezuela)

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Received: 05 Jul 2023; Received in revised form: 03 Aug 2023; Accepted: 11 Aug 2023; Available online: 19 Aug 2023

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Abstract— The release of phosphorus (P) from bottom sediments is an important source of nutrient enrichment in many lakes. Reductive dissolution of P and iron (Fe) has been regarded as a mechanism responsible for the P mobilization in sediments. In this work, sedimentary P fluxes in the central portion of Lake Maracaibo were studied, considering the influences of dissolved oxygen, redox potential, pH, and Fe in the overlying water. Experiments were performed to laboratory scale in a batch system under anaerobic conditions in 1976, 1983, 1998 and 2009. For 2023, predictive models were applied. The estimated contribution of sediment to the P content in Lake Maracaibo ranged from 4.84 to 8.14×10^6 kgP/year, and the P release rate ranged from 1.66 to 10.30 mgP/m².d. On the last day of the experiment, the P concentration of the sediment was 0.251 mgP/g and of the sediments from the lake (hypolimnetic cone) was 0.253 mgP/g. Fe and the redox potential account for approximately 57% of the variability in total P in overlying water. The annual contribution of sedimentary P to the P content of the lake ranged from 11.13% in 1976 to 27.25% in 2023 (52.72% in 2009).

Keywords— anaerobic conditions, eutrophication, inorganic nutrients, P loading, tropical estuary.

I. INTRODUCTION

Sediments play a key role determining the concentrations of nutrients and pollutants in rivers, lakes, estuaries, and other shallow marine areas. The total phosphorus (TP) concentration is often much higher in sediments than in overlying water columns (Ladakis et al., 2006; Hylén et al., 2021). Consequently, changes in chemical species and their concentrations in sediments or disturbances in the fluxes into or out of water can have an enormous impact on the trophic status of water. Efforts to manage water quality in both fresh and marine water should consider sediment processes to be effective (Wetzel, 1981; Den

Besten et al., 2003; Howarth & Martino, 2006; Dunn et al., 2015; Vo et al., 2021).

Quantifying the nutrient flux within a system can aid in determining the importance of controlling internal or external nutrient loading because it increases the concentration count of soluble forms that can be released into the overlying water column in addition to increasing the total nutrient content of the sediment (Reddy et al., 1998). The management of external nutrient inputs to eutrophic systems can be confounded due to a persistent pool of P in lake sediments (Giles et al., 2016). Although reduction of external phosphorus input can be achieved,

the release of internal phosphorus from sediments can be the major contributor for the lake eutrophication processes (Ma et al., 2019; Cavalcante et al., 2021). Nutrient enrichment of estuarine waters can result in accelerated accumulation of organic matter in sediments, thus leading to a nutrient flux from the sediment to the water column (Malecki et al., 2004).

The study of the behavior of phosphorus in the Lake Maracaibo system, particularly the transfer of phosphorus across the water-sediment interface, provides additional valuable data for implementing measures to mitigate the acceleration of the eutrophication process in this natural reservoir (Parra-Pardi, 1979; Rivas, 1983). Knowledge concerning the phosphorus cycles and transformations is essential to the ecological understanding of estuarine systems (González, 1994). The Lake Maracaibo is a tropical hypereutrophic estuary located in the state of Zulia in North-Western Venezuela. The Maracaibo Basin, located on the northern front of South America, is the most important oil reserve in South America and one of the largest oil reserves in the world. Between 1914 and 1995, the total amount of oil extracted from the basin was 33,000 million barrels ($5,238 \times 10^6 \text{ m}^3$). Most of this oil originates from the bottom of the lake, which is the largest lake in South America and the 17th largest lake in the world (Rodríguez, 1999). The cretaceous source rocks in this petroleum system are responsible for the bulk of the hydrocarbon reserves in the Maracaibo Basin (Goddard & Talukdar, 2002). Accelerated urban expansion (due to the presence of a major petrochemical industrial park), sewage waters, and agricultural activities have exacerbated the deterioration of the basin. Moreover, the continuing development of the lakeshores has reduced the water quality over the years (Parra-Pardi, 1979). Some 500 companies, including chemical refineries and coal mining operations, currently dump wastewater into the lake. Redfield (1958) was the first to note that the hydrobiological conditions of the Maracaibo basin are highly favorable to the processes that start the accumulation of oil-producing materials. Pesticide-loaded runoff from farms and oil leakage from pipelines dynamited frequently by guerrilla rebels in Colombia also flow into the basin through its tributaries, particularly the Catatumbo River. Most of the pollution, however, comes from raw sewage from the approximately 5 million inhabitants surrounding the basin.

The DISCA (División de Investigaciones sobre Contaminación Ambiental) conducted a series of survey cruises to monitor the water quality and biological characteristics of the lake between 1974 and 1978; they found a close relationship between the conformation of the saline hypolimnetic cone and the anaerobic zone. It was

shown that the conformation of the cone, due to the presence of a saline gradient, produces a reduction in water movement, resulting in a drastic decrease in dissolved oxygen between 15 and 17 m depth. During the rainy season, when the hypolimnetic cone diminishes, the influx of fresh water, originating mainly from the Catatumbo River, dilutes the anaerobic water containing organic matter and nutrients. This diluted water then rises and subsequently mixes with water from the epilimnion, thus diminishing the dissolved oxygen. Lake Maracaibo was selected from a group of shallow lakes surrounded by highly populated areas that are vulnerable to eutrophication.

Eutrophication of this lake causes massive growth of blue-green algae at certain times of the year (April-June), presenting an environmental problem (Rodríguez, 2001; Troncone et al., 2006b). This process occurs as a result of the elevated content of nutrients in the water caused by agricultural and industrial activities and the unloading of residual waters (Parra-Pardi, 1983). The continuous accumulation of phosphorus at the bottom of the lake throughout the years has created a phosphorus source that will continue to release phosphorus into the lake for a long time (Rivas, 1983). Kiage & Walker (2009) showed that the main causes of the proliferation of floating vegetation were rainfall anomalies in the preceding months (higher local rainfall would produce more runoff into the lake from approximately 30 rivers) and population growth in the major cities surrounding Maracaibo: Cabimas and Ciudad Ojeda. In a complex ecosystem, such as Lake Maracaibo, the use of models allows for the exploration of possible outcomes of various management options (*e.g.*, closing the shipping channel and/or reducing anthropogenic nutrient inputs) without the risk of inadvertently causing an undesirable change in the ecosystem (Medley, 2001). The study of phosphorus transfer across the water-sediment interface in the Lake Maracaibo system, particularly internal phosphorus loading, provides additional valuable data for implementing measures to mitigate the acceleration of the process of eutrophication in tropical reservoirs. There is currently little information regarding the role of sediments in the eutrophication processes in tropical water bodies.

The main objective of this work was to estimate, in a laboratory under anaerobic conditions (for 1976, 1983, 1998 and 2009), and through predictive regressions (for 2023), the phosphorus flow across the water-sediment interface and the rate of P accumulation in sediments. To accomplish this objective, this study determined: i) P flux from sediments, ii) Influence of Fe on P release from sediments, and iii) The annual internal load of P from the sediment to the overlying water column of the lake. The

experiments were designed to simulate conditions similar to those in the hypolimnetic cone (the area with highest nutrient accumulation), where samples of sediments were taken. During the last years it has not been possible to continue studying in the Lake Maracaibo system due to the difficult situation of the country. Thus, the importance of this work lies in documenting the information about the phosphorus mobility in sediments of a tropical hypereutrophic estuary under the influence of dissolved oxygen concentration, serving as background for the future study of water-sediment interactions in coastal ecosystems, coupled with the impossibility of being able to carry out similar studies in the short and medium term considering the current economic situation in Venezuela and the dismantling of the country's research centers.

II. MATERIALS AND METHODS

2.1. Study area

Lake Maracaibo is a large, tropical, warm (30-32°C), hypereutrophic, oil-polluted aquatic system ($z_{max}= 34$ m, $z_{mean}= 28$ m, $V= 245 \times 10^9$ m³, $A= 12,958$ km²). It is the largest lake in South America and the center of oil

shipping activities in western Venezuela. Although Lake Maracaibo is partially a mixed estuary, the system as a whole includes almost all categories of water bodies: marine (Gulf of Venezuela), estuarine (Strait of Maracaibo and Bay of El Tablazo), fresh water lake (Lake Maracaibo), and flowing streams (tributary rivers). This tropical lake is located between 70°30' and 73°24' W longitude and between 9°00' and 10°30' N latitude (Parra-Pardi, 1979) (Fig. 1).

Lake Maracaibo shows variable salinity, ranging from 5.0 to 8.0 pus, depending on the influx of seasonally fluctuating rainwater from land drainage, and seawater. Outflow from the lake to the Bay of El Tablazo and to the Gulf of Venezuela predominates during the wet season and usually reverses during the dry season (Gadner et al., 1998). The predominant physical feature of the lake water is the formation of a very consistent hypolimnetic cone, with its base in the central area of the bottom of the lake and its apex in a variable point near the center of the lake, at 5 to 15 m. The salinity of the hypolimnetic cone is higher than that of the epilimnion due to the intrusion of diluted seawater (generally 6 to 10%, although the upper

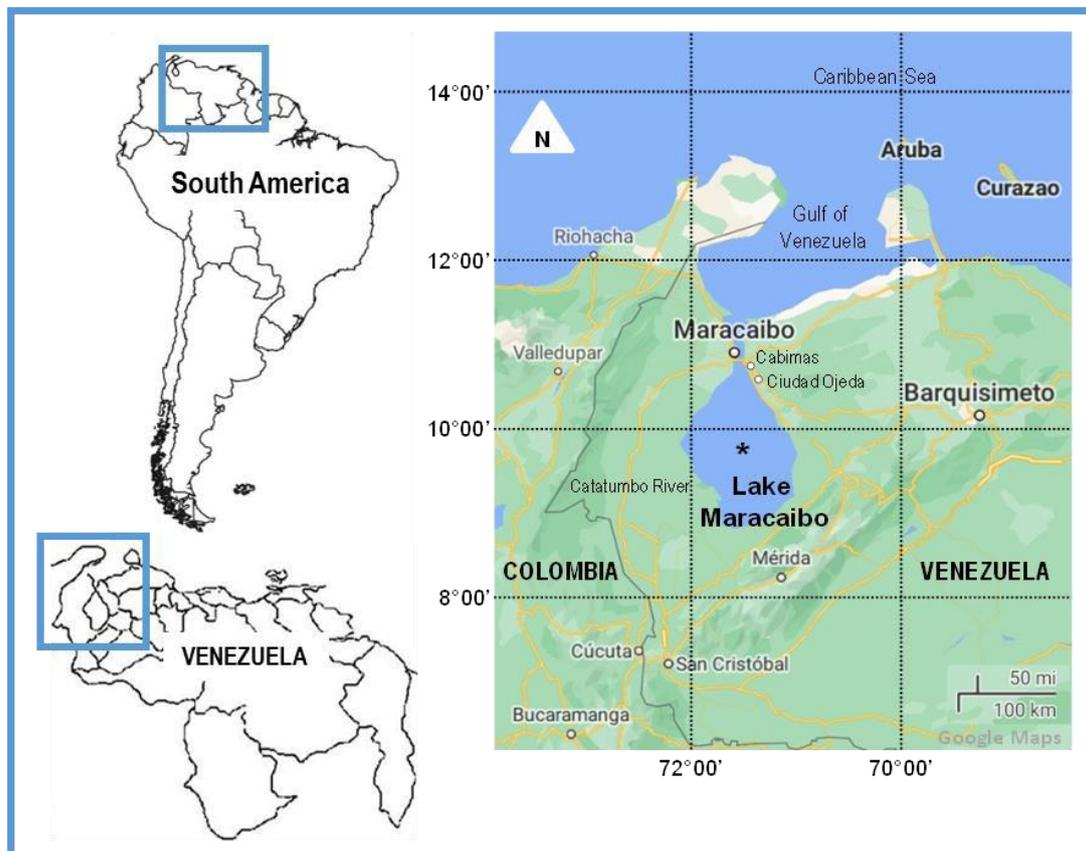


Fig. 1: Location of the Sampling Site (*) from Lake Maracaibo (Venezuela)

limit can be exceeded), which upon arrival at the deeper areas of the lake, is incorporated into the hypolimnion and slowly dispersed toward the epilimnion through the process of erosion (Parra-Pardi, 1983). Seawater enters Lake Maracaibo through an augmented natural connection to the Gulf of Venezuela, which allows an influx of seawater and results in an almost perennial salt stratification within the lake (Laval et al., 2005). The dynamics of this enclosed system are rather unique, with water bodies interacting among themselves and responding to external forces (Antoranz et al., 2001).

2.2. Sampling

Sediment samples from the hypolimnetic cone described above, taken from the central area of the lake (71°31'41" W-09°51'17" N), were used (Fig. 1). Sediment sampling took place during research cruises in 1976, 1983, 1998, and 2009. Bottom sediment and overlying water samples were collected using an Ekman dredge and a water sampling system coupled with a peristaltic pump, respectively. The samples obtained were kept frozen until retrieval at onshore laboratories. Physical and chemical characteristics, including temperature, dissolved oxygen concentrations, electric conductivity, salinity, and pH, were measured using a Hydrolab Surveyor II.

2.3. Experimental system and chemical analysis

To prepare the batch system, sediments were placed into two bottles that were used as reactors. Additional samples of water and sediment were tested for physical and chemical characteristics. Water and sediments were analyzed before and after the experiment. Water from Lake Maracaibo was carefully siphoned on top, avoiding disturbance of the sediment. In each bottle, a bubbler was installed above the sediment. Bottles were aerated by purging argon gas to create anaerobic conditions.

All incubations were performed in darkness at 25°C. Every two days over the course of three months, overlying water samples were analyzed for dissolved oxygen, pH, redox potential (electrometrically), orthophosphate (ion chromatography using Dionex 200i-sp equipment), and total phosphorus (APHA et al., 2017). Dissolved oxygen was measured using a YSI model 58 O₂ meter (Yellow Springs Instruments Company) equipped with a YSI model 5730 stirring electrode by means of the USEPA Method 360.19 (USEPA, 1979). pH values were attained using a Fisher Scientific (Pittsburgh, PA) 640A pH meter, and the redox potential was measured using a Metrohm 678 EP/Kf Processor with a 6.0402.100 platinum Metrohm electrode. Total iron concentrations were analyzed in 5 ml overlying water samples treated with 2 ml of concentrated nitric acid and digested for 4 hours at 130°C in a Parr-type bomb. The final dissolution was analyzed with a flame

atomic absorption spectrometer Perkin Elmer 3100 instrument. Three replicates were performed for each analysis.

For the sampling performed in 2009, iron concentrations were analyzed using 3 ml of overlying water and 2 ml of concentrated nitric acid that were heated for 4 hours at 101±2°C. The samples were diluted to a final volume of 40 ml and centrifuged and analyzed using an inductively coupled plasma emission spectrometry (ICP-AES) Thermo Scientific series 6000. ICP-AES and UV-Vis techniques were compared and present a satisfactory linearity of 0.0085 (Torres, 2012). TP was analyzed using a Shimadzu UV-1800 Spectrophotometer. Sediment samples were analyzed before and after the experiment as follows: i) Total phosphorus: 2.5 g of sediment were ignited for 2 hours in a furnace at 550°C, allowed to cool for 1 hour, diluted with 10 ml of 1 N HCl, and boiled for 1 hour. The sample was then filtered and completed to 10 ml with distilled water to be analyzed as orthophosphate using the standard ascorbic acid method (APHA et al., 2017); ii) Orthophosphate: 2.5 g of sediment were extracted with 100 ml of the acid mixture H₂SO₄-HCl 1 N, stirred for 2 hours, filtered, and analyzed by the standard ascorbic acid method (APHA et al., 2017). The sediment water content (porosity) was determined based on the weight loss upon drying at 105°C; and iii) Iron determination: 0.1 g of sediment sample was digested with 5 ml of concentrated nitric acid and 5 ml of deionized water in a Parr-type bomb at 110°C for 4 hours. The final solution was analyzed by flame atomic absorption spectrometry using the same instrument as above. Three replicates were performed for each analysis.

For the sampling performed in 2009, 2.5 g of lyophilized sediments was heated at 550°C for 2 hours. Samples were cooled, added to 10 ml of 1 M HNO₃, and heated to the boiling point for 1 hour. The samples were diluted to a final volume of 50 ml with deionized water. Phosphorus was determined using a Shimadzu UV-1800 Spectrophotometer. Iron was analyzed using the ICP-AES Thermo Scientific series 6000. The results are expressed in dry weight (DW).

2.4. Statistical analysis

Phosphorus flux rates were determined by measuring changes in the water column concentrations of sediments over time. Using least-square linear fits to the data, fluxes (mgP/m².d) were estimated by multiplying the slope of a plot of concentrations versus time (dC/dt) by the ratio of the overlying water volume (V) to the reactor area (S). Statistical analysis was performed using SPSS 22.0 analysis software. The means and standard deviations of each parameter used for sediment characterization and the

nutrient fluxes were calculated using Microsoft Excel 7.0. One-way ANOVAs were used to determine the significant differences ($P < 0.05$) in phosphorus fluxes under both aerobic and anaerobic conditions. Multiple linear regression analyses were performed using TP as the dependent variable. The independent variables used were pH, total iron (TFe) and redox potential.

In 2023 it was not possible to carry out the laboratory experiments due to the economic crisis that Venezuela is going through; however, predictive estimates were made through regression models according to Zamyadi et al. (2007) and Lathrop et al. (2019), in order to know the TP contribution from sediments at the present time.

III. RESULTS AND DISCUSSION

3.1. Phosphorus concentrations in Lake Maracaibo

The characteristics of the sediments and water overlying the sediment from Lake Maracaibo before the experiments are shown in Tables 1 and 2, respectively. The TP values of the sediment samples ranged from 1.0 to 2.6 mg/g. According to Carignan (1985), when the TP levels of sediment range from 0.325 to 0.771 mg/g, a lake is considered eutrophic. Therefore, Lake Maracaibo can be considered eutrophic. It is particularly noteworthy that the concentrations of TP and TFe in the sediments are higher in samples collected in 2009 than in samples collected

earlier, which is most likely due to sediment saturation (Table 1) and clearly indicates the progressive eutrophication of the lake over the course of these years. This trend is also shown in the overlying water (Table 2). Studies describing the typical TP values found in water samples from various limnetic ecosystems show that such concentrations do not exceed 0.01-0.04 mgP/l (Snoeying & Jenkins, 1990). The TP values found in Lake Maracaibo lie far outside of this range, with a total average phosphorus concentration of between 0.28 and 0.52 mgP/l.

3.2. Phosphorus in overlying water in batch system

Fig. 2 shows the evolution of the TP transfer from sediment to water in the years 1976, 1983, 1998, and 2009. All of the TP concentrations increase until approximately day 20. The experiments in the years 1976, 1983, and 2009 produced uniform results, with growth until day 20, followed by stabilization. This stabilization is presumed to be the result of reaching an equilibrium between sediment and water. The data recorded in 1983 followed this same trend, although there were instances of twofold and threefold increase between days 50 and 70. The combined effects of rapid adsorption and desorption of P may cause a sharp gradient in soluble P to be sustained in the sediment-water interface of aquatic systems, which could result in a significant flux of P to the water column. This occurrence was observed in the instances of greater increases, particularly in 2009 and after day 50 in 1983.

Table 1: Average Composition of the Lake Maracaibo Sediments at the Beginning of the Experiments

Parameter	1976	1983	1998	2009
Dry matter (%)	25.50±2.25	43.80±3.20	25.80±1.70	ND
Total-P (mg/g DW)	1.00±0.05	1.19±0.04	1.21±0.01	2.63±0.03
Total-N (mgN/g DW)	8.70±0.52	14.50±0.80	5.47±0.25	2.68±0.02
Ammonium (mgN/g DW)	0.10±0.05	0.19±0.01	0.03±0.00	0.02±0.00
Total-Fe (mgFe/g DW)	23.50±0.40	ND	36.53±1.10	51.49±0.39
<i>n</i>	5	5	5	3

ND: non-determined.

Table 2: Average Characteristics of Overlying Water in Lake Maracaibo

Parameter	1976	1983	1998	2009
pH	7.64±0.15	8.30±0.10	6.84±0.07	6.80±0.02
Salinity (pus)	5.66±1.15	5.09±0.40	7.8±0.30	8.90±0.03
Total-P (mgP/l)	0.28±0.01	0.43±0.02	0.47±0.02	0.52±0.02
Total-N (mgN/l)	ND	2.40±0.02	1.46±0.03	ND
Orthophosphate (mgP/l)	0.19±0.02	0.15±0.06	0.34±0.01	0.50±0.02
Ammonium (mgN/l)	0.35±0.02	1.68±0.06	0.68±0.00	0.10±0.01
Dissolved oxygen (mg/l)	0.01±0.00	0.01±0.00	0.02±0.00	0.00±0.00

Chlorophyll ($\mu\text{g/l}$)	2.00 ± 0.03	2.40 ± 1.10	0.76 ± 0.05	ND
<i>n</i>	3	3	3	3

ND: non-determined.

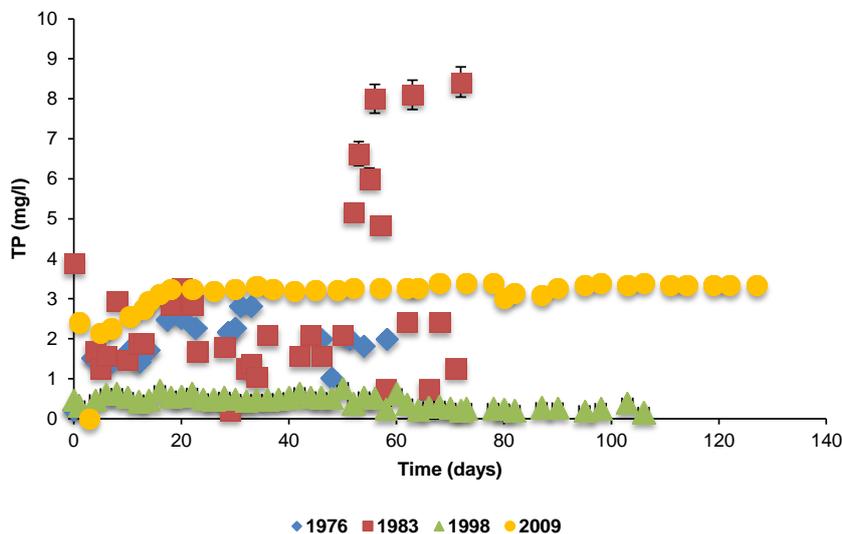


Fig. 2: Temporal Sedimentary Total Phosphorus (TP) Release in the Batch System

3.3. pH in overlying water

The greatest quantity of phosphorus release was 0.655 mgP/l, which was observed at pH 8 (Fig. 3). The phosphorus release at pH 8 was four times higher than that at pH 5.8, which was 0.159 mgP/l. The operational scheme of P fractionation includes P reactive to metal oxides; NaOH-extractable P (Fe/Al-P, P bound to Al, Fe and Mn oxides and hydroxides); reductant soluble reactive P (BD-P), which represents the redox-sensitive P fraction and mainly included P bound to Fe-hydroxides and Mn compounds; calcium-bound P; and HCl-

extractable P (Ca-P, P associated with Ca). High pH promotes the release of NaOH-P and BD-P, and low pH promotes the release of HCl-P (Shengrui et al., 2006; Xiangcan et al., 2006).

The rate of P release in these laboratory experiments increased as pH increased from 5.7 to 8. In sediments from Lake Maracaibo, the contribution of NaOH-P was 18.77%, that of BD-P was 35.67%, and that of HCl-P was 34.16% (Torres 2012). At alkaline pH, NaOH-P and BD-P can be easily released in sediments and were the main P release fractions. NaOH-P and BD-P contributed over

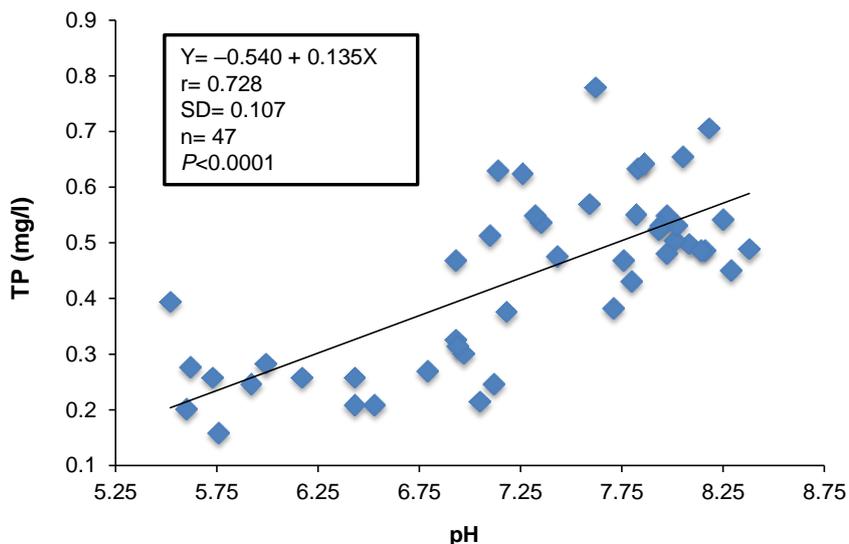


Fig. 3: Correlation between Total Phosphorus (TP) and pH in the Batch System

50% of the total P released from the sediments to the overlying water. This is consistent with the results found by Torres (2012) who showed that Al, Fe, Mn and Ca were 51.428, 66.871, 2.991 and 4.880 mg/kg, respectively, meaning that Al and Fe (NaOH-P and BD-P) were higher than Ca (HCl-P). A linear regression analysis indicated that pH data positively correlated with TP (Fig. 3):

$$Y = -0.540 + 0.135X, r = 0.728, n = 47, P < 0.0001 \quad (1)$$

3.4. Redox conditions in overlying water

Redox potential had a critical influence on the release of phosphorus. A potential interval of -80.3 to 82.0 mV was found. In general, the release rates were higher under

reductive redox conditions (-80 mV) and high pH values. Under anoxic conditions, Fe(III) is reduced to Fe(II). Phosphorus has a strong affinity to iron oxide, aluminum, and manganese (Roy et al., 2012). The reduction and oxidation (redox) of these metals regulate the dynamics of phosphorus in sediments. The mechanisms of phosphorus mobilization are explained by the reductions of insoluble metal oxides, such as Fe(III) to soluble Fe(II) in sediments or water (Chistophoridis & Fytianos, 2005). Linear regression analysis indicated that redox potential was negatively correlated with TP:

$$Y = 0.397 - 0.0024X, r = -0.7303, n = 47, P < 0.0001 \quad (2)$$

There was an increase in the concentration of phosphorus in relation to the decrease in redox potential (Fig. 4).

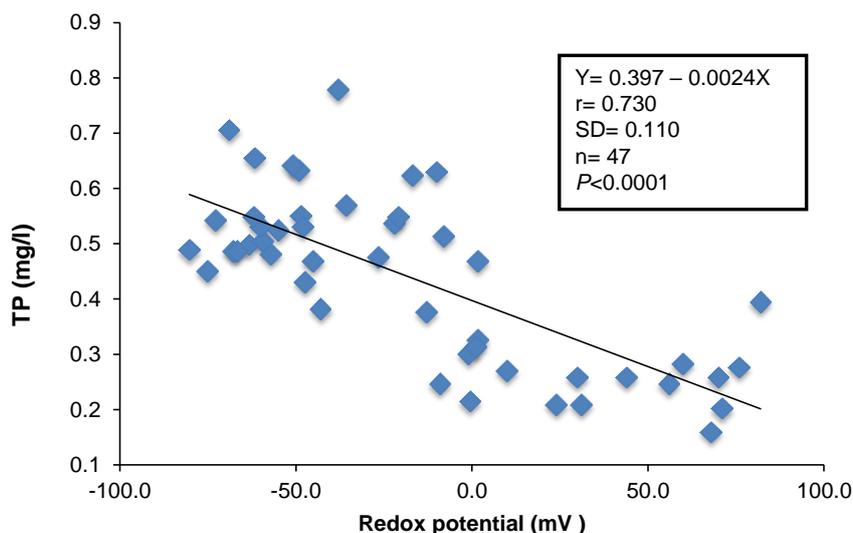


Fig. 4: Correlation between Total Phosphorus (TP) and the Redox Potential in the Batch System

3.5. Total iron in overlying water

There is a close correlation between the concentrations of phosphate and iron in their different states of oxidation in overlying water. In this study, TFe slightly increased with increasing TP, reaching 0.35-16.44 and 0.16-0.78 mg/l, respectively. It is well known that at low oxygen concentrations, phosphate is adsorbed by Fe(III) to form solid complex iron-phosphate hydroxide. When the redox potential decreases, iron is reduced to Fe(II) and phosphate is released (Sundby et al., 1992). Fig. 5 shows a very weak relationship between TP and TFe:

$$Y = 0.376 + 0.0147X, r = 0.353, n = 47, P = 0.0150 \quad (3)$$

This suggests that a large variation existed. The phosphorus and iron dynamics are demonstrated by the molar ratio of Fe to PO_4^{-3} at the end of the anoxic incubation (Fe:P release ratio). The release of phosphorus from sediment was investigated in shallow and eutrophic Lake Blankensee by Ramm & Scheps (1997); they reported that when the TFe:TP ratio (by weight) is greater

than 21 in the sediment, phosphorus release is blocked. Jensen et al. (1992) reported that if the Fe:P ratio (by weight) is above 15, it may be possible to control internal P-loading by keeping the surface sediment oxidized. Although the sedimentary iron content must be higher than the concentration of phosphorus, iron phosphate formation is regulated by the concentration of sulfates and the formation of iron sulfides (Cooke et al., 1993). Smolders et al. (2017), suggests that internal loading of the P coming from sediments explains the soluble P ions concentrations which are most pronounced at low dissolved oxygen concentrations and in regions where the P/Fe ratio in sediment is large. In this study, the TFe:TP ratio fluctuated between 19 and 173 in the sediment. The TFe concentrations of the sediment samples ranged from

23 to 51 mg/g. This great variability in the Fe:P ratio explains the weak relationship between Fe and P in the overlying water, as shown in Fig. 5.

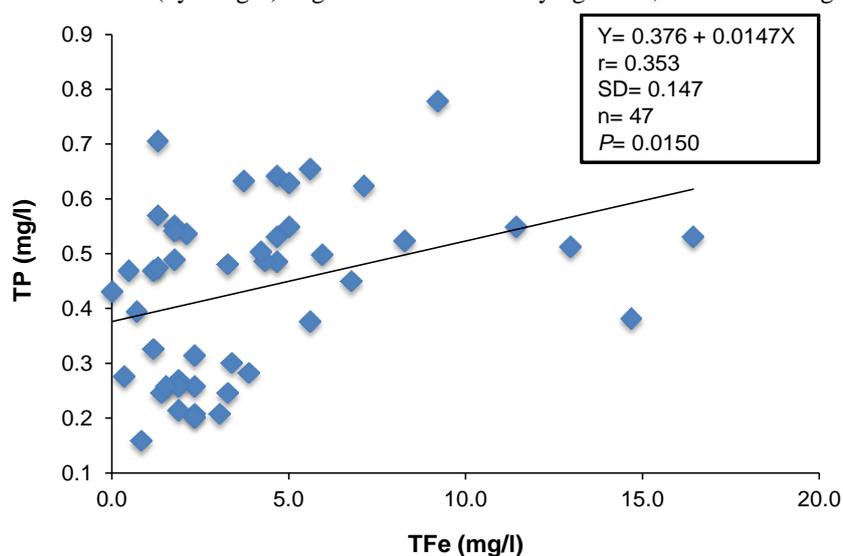


Fig. 5: Correlation between Total Phosphorus (TP) and Total Iron (TFe) in the Batch System

3.6. Phosphorus release flux estimated with the batch system and regression models

The phosphorus concentrations in water in the batch system were determined to quantify the amount of

phosphorus released by the sediment to the water column in Lake Maracaibo (1976, 1983, 1998 and 2009), while those for 2023 were estimated with regression models. This P fluxes calculated are presented in Table 3.

Table 3: Estimates of Total Phosphorus Loading to Lake Maracaibo ($\text{kg/year} \times 10^6$)

Total phosphorus	1976	1983	1998	2009	2023
Estimated in Lake Maracaibo	43.73 ^a	27.5 ^c	15.44 ^d	15.29 ^d	33.52 ^f
Contribution from sediments	4.87 ^b	4.84	7.85	8.14 ^e	9.20 ^f
% sediment contribution	11.13	17.6	28.55	52.72	27.45

^aParra-Pardi (1979), ^bLedo (1979), ^cHansen et al. (2001), ^dTroncone et al. (2006a), ^eTorres (2012), ^fRegression models.

In the batch systems was estimated that 34 to 44% of the TP was released in the first 40 to 50 days and approximately 80% was released over the course of three months. Hupfer & Lewandowski (2005) estimated that approximately 60% of the settling particulate P is released within 2 weeks, approximately 80% is released within 0.5 year, and 85% is released during the total diagenesis. Based on the hypolimnetic P accumulation rates, the potentially mobile P in the sediment would be exhausted within three months. The release of P is generated by a continuous flux of settling phosphorus from the epilimnion rather than by a large inventory of temporary P stored in the sediment. Diagenesis in the upper sedimentary layers is so rapid that it prevents an accumulation of potentially mobile P. The results of this work are in agreement with those of Hupfer & Lewandowski (2005) regarding the rapid TP release from sediment; however, the phosphorus release rate from the Lake Maracaibo sediments was lower than that obtained by Hupfer & Lewandowski (2005) in Lake Arendsee, Germany.

A multiple linear regression model to describe the relationship between TP (dependent variable) and pH, TFe, and the redox potential (independent variables) was performed. The R-squared value indicates that the model, as fitted, explains 54.69% of the variability in TP. The equation of the fitted model is:

$$TP = 1.18327 - 0.11551 * pH + 0.00495242 * TFe - 0.00430484 * \text{redox potential} \quad (4)$$

The analysis revealed significant relationships between variables at the 95.0% confidence level ($P < 0.05$). Because the p -value in the ANOVA table is lower than 0.05, there is a statistically significant relationship between the variables at the 95.0% confidence level. Predictive estimates through regression models, in order to know the TP contribution from sediments at the present time (2023), exhibited the following equations:

Estimated in Lake Maracaibo:

$$y = 0.0437x^2 - 175.16x + 175333, R^2 = 0.9904 \text{ (\% error 0.96)} \quad (5)$$

Contribution from sediments:

$$y = -0.0011x^2 + 4.6651x - 4756.7, R^2 = 0.9085 \text{ (\% error 9.15)} \quad (6)$$

Comparing the value of the release rate found in Lake Maracaibo with those of other lakes around the world, different release rates are observed for lakes with different degrees of eutrophication. For example, Lake Onondaga (USA) is a hypereutrophic lake (3-38 mgP/m².d) (Penn et al., 2000), Lake Tiefer (Germany) is considered a low eutrophic lake (3.04 mgP/m².d) (Selig & Schlunbaum, 2003), Lake Beaver (USA) is bordering on eutrophic

conditions (0.57 mgP/m².d) (Sen et al., 2004), Lake Dudinghausen (Germany) is considered mesotrophic (0.35 mgP/m².d) (Selig & Schlunbaum, 2003), and Roundaway Lake (USA) is a hypereutrophic system (-3.7-3.3 mgP/m².d) (Evans et al., 2021). Based on the results of this study, Lake Maracaibo (Venezuela) is considered hypereutrophic (1.03 to 1.70 mgP/m².d).

3.7. Annual contribution to internal loads in Lake Maracaibo

The annual contribution of sedimentary phosphorus to the P content of the overlying water in anaerobic conditions was estimated based on the TP flux (between 1.03 and 1.70 mgP/m².d) and the sediment area in Lake Maracaibo (12,958 km²). The contribution was found to be between 4.87 and 8.04x10⁶ kg of P per year. The estimated annual loadings from external sources in Lake Maracaibo are shown in Table 3. The estimated sedimentary contribution to lake water between 1976 and 2023 comprises between approximately 11.13 and 52.72% of the external loading.

The results show a reduction in the external loading of phosphorus between 1976 and 2009 as a result of phosphorus resuspension from the sediments. The ICLAM (Instituto para el Control y Conservación del Lago de Maracaibo) used a mass balance model to conduct a study of Lake Maracaibo during the period between 1996 and 2006. Based on the amount of phosphorus in the model, it was observed that inflow from tributary rivers is the source of higher nutrients in Lake Maracaibo. The model could not measure the contribution of nutrients from the hypolimnion (the main internal source of nutrients) to the water column. Under this constraint, a concentration of available phosphorus in the lake of 15.44x10⁶ kg/year was obtained, and subsequently, 6.39x10⁶ kg/year of TP was estimated to be trapped in the sediment (Troncone et al., 2006a). The value of 15.44x10⁶ kg/year was taken for the year 1998, as shown in Table 3. The amount of phosphorus loading from sediment in this laboratory experiment in 1998 was estimated to be 7.85x10⁶ kg/year, which is similar to the value of 6.39x10⁶ kg/year estimated by ICLAM using the mass balance model. In 2006, Troncone et al. (2006a) estimated that 100% of the wastewater flow to Lake Maracaibo would be treated between 2007 and 2012; assuming a 100% reduction in the available phosphorus in the lake, that would be 15.29x10⁶ kg/year. This was the estimated value for 2009, as shown in Table 3.

The behavior of TP internal charges seems to reveal a cyclical phenomenon in this ecosystem, whose concentrations regain strength according to the predictions for 2023 (Table 3). These abrupt increases in TP concentrations could explain the temporary planktonic

blooms observed in the lake, for example during 2004-2005 and July-2023 where excessive growths of the *Lemna obscura* (Kiage & Walker, 2009; NASA, 2023) and the *Microcystis* sp. (Esconusted, 2023) were reported, respectively. These events highlight the increase in nutrient concentrations in the water as a result of the discharge of untreated wastewaters and the increase in river flows due to excessive rainfall this year (El Niño effect), which contribute nutrients from agricultural land south of the lake. This increase in flows of tributaries that push the water masses towards the lake center acts as a trigger to erode the structure of hypolimnetic cone, causing the release of nutrients confined in the sediments of this area (Parra-Pardi, 1979), among others factors.

3.8. Comparison of phosphorus values in the batch system and *in-situ* in Lake Maracaibo

The concentrations of phosphorus at the beginning and at the end of the batch system experiment were 0.251 and 0.253 mg/g, respectively. The values of these phosphorus concentrations are quite similar, which indicates that the batch system successfully simulated the natural conditions of the lake. Using the batch system is a convenient way to evaluate phosphorus adsorption and release processes in sediments.

IV. CONCLUSIONS

The parameters with the greatest influence on P release in sediments from the hypolimnetic cone in Lake Maracaibo are the iron concentration and redox potential. These two variables explain the 54.69% of the TP variability in the overlying water. The release of sedimentary TP in Lake Maracaibo is a rapid process. It was estimated that approximately 80% of the TP may be released from sediments over the course of three months. Under anaerobic conditions, the annual contribution of the released phosphorus to the P content of overlying water ranged from 4.84 to 8.14×10^6 kgP/year, accounting for approximately 11.13-52.72% of the external P loading. The cycling phenomenon observed in the external loading of phosphorus between 1976 and 2023 with increases in 1976 and 2023 and decreases in 1998 and 2000, causes great variability in the P concentrations in the lake water, which results mainly P release from sediments. The study of phosphorus transfer across the water-sediment interface in the Lake Maracaibo system, particularly internal phosphorus loading, provides additional valuable data for implementing measures to mitigate the acceleration of the process of eutrophication in tropical reservoirs. The batch system used in this work successfully simulated the natural conditions of the lake.

ACKNOWLEDGEMENTS

The authors wish to thank ICLAM, especially M.Sc. Federico Troncone, for providing the water and sediment samples for some experiments.

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