



Research Paper

Phosphorus distribution pattern in sediments of natural and constructed wetlands



G.A. Di Luca*, M.A. Maine, M.M. Mufarrege, H.R. Hadad, M.C. Pedro, G.C. Sánchez, S.E. Caffaratti

Química Analítica, Instituto de Química Aplicada del Litoral (IQAL), Facultad de Ingeniería Química, Universidad Nacional del Litoral (UNL)-Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Santiago del Estero 2829, Santa Fe, 3000, Argentina

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ABSTRACT

Two constructed wetlands for treating industrial and sewage effluents (CW1 and CW2) and two natural wetlands (NW1 and NW2), located in Argentina, were studied. The aims of the study were (1) to assess the accumulation and distribution pattern of P in the surface sediments of both natural and constructed wetlands, and (2) to evaluate P long-term retention in sediment. In the sediment of all study sites, inorganic P fractions were dominant. Similar incoming water composition was determined between NW2 and CW1 and between NW1 and CW2. Water composition governed P concentration and distribution in sediment, being mainly P bound to CaCO_3 in CW1 and NW2 and bound to $\text{Fe}(\text{OOH})$ in NW1 and CW2. According to water and sediment characteristics, the four wetlands will continue removing P from water. Studied wetlands are efficient and sustainable in terms of P retention.

1. Introduction

Wetlands have the ability to reduce contaminant loadings in water. Mitsch and Gosselink (2007) named them “kidneys of the landscape” because they receive wastewater and purify them. Phosphorus reaches aquatic ecosystems from diffuse (especially agriculture) and point sources (treated and untreated sewage and industrial effluents). Studies indicate that most of the P present in wetlands is retained within sediments (Reddy et al., 1999; Ogrinc and Faganeli, 2006; Maine et al., 2009). Sediment physicochemical characteristics are crucial for P retention capacity. Phosphorus in sediments is present both in inorganic and organic forms. Such forms include precipitated forms, physically adsorbed onto mineral surfaces, biologically assimilated in cells and in detritus (Richardson, 1999; Mitsch and Gosselink, 2007; Kadlec and Wallace, 2009). Therefore, mineralization of organic matter and reduction of iron can remobilize P bound to sediment. Phosphorus retention in a wetland can occur over a short or a long period. As such, sediment can also be an internal source of P and in general it may play an important role in buffering P concentrations in the overlying water column. Chemical, biological and physical processes are involved in the exchange of P between water and sediment (Boström et al., 1988; Baldwin, 1996; Clavero et al., 1997; Clavero et al., 1999; Clavero et al., 2000). Biotic uptake of inorganic P by plants and microorganisms is considered to be short-term and rapid. Abiotic processes (co-

precipitation with minerals, settling, sedimentation, sorption and burial) are considered to be 50–70% of the permanent P reservoir (Richardson, 1999). Thus, P removal process in wetlands is complex and interrelated with the biotic and abiotic components. Speciation of total phosphorus (TP) in different forms is necessary to understand the phosphate exchange mechanisms by sediments, and its potential removal or release from the water column.

Wetlands are complex systems where the biological, chemical and physical processes interact to remove contaminants from water. Constructed wetlands (CWs) are designed to optimize the processes that occur naturally in wetland vegetation, sediment or substrate and associated microorganisms, in order to improve the efficiency of the system in water purification. They are extensively used for P removal from different types of effluents such as domiciliary and municipal sewage, stormwater, agricultural runoff and industrial effluent (Calheiros et al., 2007; Vymazal, 2007; Maine et al., 2007, 2009; Kadlec and Wallace, 2009; Di Luca et al., 2011; Gagnon et al., 2013; Menon and Holland, 2013; Dotro et al., 2015).

Two natural and two constructed wetlands with different characteristics were studied. The aims of this work were (1) to compare the accumulation and distribution pattern of P in surface sediments of both natural and constructed wetlands, and (2) to evaluate the long-term retention of P in sediments.

* Corresponding author.

E-mail address: gdiluca@fiq.unl.edu.ar (G.A. Di Luca).

2. Materials and methods

2.1. Study sites

Two natural wetlands (NW1 and NW2) and two constructed wetlands (CW1 and CW2) were studied. All study sites were located in Argentina.

NW1 is a wetland located in the floodplain of the Middle Paraná River in Santa Fe, Argentina (31° 32' 45" S, 60° 29' 37" W). The Paraná River, the sixth largest in the world, is the second largest watershed of South America covering an area of 3.1×10^6 km². Paraná River has an irregular hydrological regime. During the first six months of the year the river is at high stage, with maximum peaks in March–April. Low waters occur in the second half of the year, with minimum flows in September–October. About 30% of the Paraná floodplain is covered by a wide variety of temporary and permanent lakes. During the largest floods, they tend to merge into a continuous sheet of water that covers the whole floodplain. However, at low river levels, processes such as the growth and decay of primary producers (mainly macrophytes) and the mixing and resuspension of bottom sediments govern lake metabolism. Owing to the river and floodplain dynamics, the thousands of shallow lakes vary considerably in shape and size. Water bodies are colonized by floating and rooted macrophytes and are generally small (100–500 m wide 500–3000 m long), shallow (1–6m), turbid and productive (Hadad and Maine, 2007).

NW2 is located in Laguna Mar Chiquita (30° 37' 41" S, 62° 33' 32" W). It is the largest saline lake in South America, with an area that ranges between 2000 and 6000 km² according to water level, and one of the biggest in the world, retaining a wild and slightly altered physiognomy (Bucher and Bucher, 2006). Laguna Mar Chiquita is a Guarani Aquifer outcrop, and also three main rivers pour their waters into this lake: (i) The Suquia (or Primero) River; (ii) The Xanaes (or Segundo) River (total length 340 km and average discharge of $14.5 \text{ m}^3 \text{ s}^{-1}$); and (iii) The Dulce River (total length of 812 km and an average discharge of $80 \text{ m}^3 \text{ s}^{-1}$), which is the biggest one. Surrounding lands are subject to floods from the Dulce River, generating hydromorphic soil conditions and conditioning the biological dynamics of the region. The geological fault on which the lake is formed is the Salinas Grandes, which is the reason for its salinized waters. Salinity fluctuates in relation to water level; varying within a range of 22–274 g L⁻¹ (Bucher and Curto, 2012). The predominant salts are sodium chloride, sodium sulfate, calcium sulfate and magnesium sulfate. The predominant vegetation is halophytic by the shores, but nearby there are native forests. The main sources of pollution in the area include urban and industrial waste and agrochemicals.

CW1 and CW2 are free water surface (FWS) wetlands constructed for the treatment of the effluents of two metallurgical factories. In both CWs, industrial wastewater and sewage from the factory are treated together. Industrial and the sewage effluents receive primary treatment before reaching the CWs.

CW1 was constructed in a tool factory in Santo Tomé, Santa Fe, Argentina (31° 40' S, 60° 47' W). It is 50 m long, 40 m wide and 0.3–0.6 m deep, with a central baffle dividing it into two identical sections. The wetland was rendered impermeable by means of bentonite. Mean wastewater discharge was $100 \text{ m}^3 \text{ d}^{-1}$. Water residence time ranged from 7 to 12 d. Wastewater and sewage from the factory were treated together. After flowing through the CW, the effluent was discharged into a 1.5 ha pond. Emergent and floating, locally abundant, macrophyte species were transplanted into the wetland at the beginning of the operation period, in 2003, but only *Typha domingensis* persisted. Currently, *T. domingensis* cover is about 80%. *T. domingensis* aerial parts are harvested annually to ensure an optimal growth after the winter season. Further design and operation details were provided by Maine et al. (2007).

CW2 is located in another metallurgical industry in the city of Santo Tomé, Santa Fe, Argentina (31° 39' 52.08" S, 60° 49' 0.74" W). It has an

area of 7 m x 20 m (wide x length) and an average water column of 0.2–0.7 m. It was waterproofed with a geomembrane. The mean inlet flow is $10 \text{ m}^3 \text{ d}^{-1}$. All factory effluents (industrial effluent, sewage, storm water and cooling water), go through an equalization chamber and then reach the wetland. Minimum residence time in the wetland is 7 days. The treated effluent leaves the wetland by a waterfall to be dumped into a concrete pool which is 4 m x 2 m, 40 cm deep, and it is subsequently conducted to a pond on the same factory site. The species selected for this wetland was *T. domingensis*, reaching a cover of 80%. CW2 has been in operation since 2009. *T. domingensis* aerial parts are harvested annually to ensure an optimal growth after the winter season (see Maine et al., 2017 for further details).

2.2. Analysis

Sediment and water samples were collected seasonally in natural wetlands (total number of samplings: 24) and bimonthly at the inlet and outlet areas of the CWs (total number of samplings: 36), in the period 2009–2014. In CW1 samples were collected in the inlet (1 m away from the effluent discharge) and outlet (100 m from the effluent discharge) areas of the wetland. In CW2 samples were collected in the inlet (1 m away from the effluent discharge) and outlet (20 m from the effluent discharge, before the waterfall) areas of the wetland. Samplings in NW2 were carried out on the Laguna Mar Chiquita shore (30° 55' S- 62° 41' W). This point is about 5 Km from the nearest incoming affluent (Xanaes River). In NW1, sampling point is located on the Middle Paraná River floodplain (31°33'53.3"S 60°33'02.4"W) about 1 Km from a smaller channel of the Paraná River system.

Samples were taken by triplicate in all wetlands. Water characterization of the wetlands was performed following APHA et al. (2012). Water samples were filtered through a 0.45 mm membrane filter for dissolved soluble reactive phosphorus (SRP) determination, while TP was measured after a sulfuric acid-nitric acid digestion. P in filtered and digested samples was measured colorimetrically by the ascorbic acid method (Murphy and Riley, 1962).

Surface sediment samples (0–3 cm depth) were collected using a 3-cm diameter PVC corer and stored at 4 °C until they were analyzed. Sediment pH was measured in a 1:2.5 sediment:water suspension. Redox potential (Eh) (Ag/AgCl electrode) and pH were measured *in situ* with an Orion mV-meter. Eh measurements were corrected by adding 200 mV to the field voltage (value of the Ag/AgCl reference electrode at 20 °C). Organic matter (OM) was determined by weight loss on ignition at 550 °C for 3 h. Sediment samples were oven-dried at 45 °C until constant weight, grounded using a mortar and pestle, and sieved through a 63 mm sieve. TP in sediment was determined after acid digestion with a HClO₄:HNO₃:HCl (7:5:2) mixture (Maine et al., 2005) followed by P determination in the digested samples (Murphy and Riley, 1962). In addition, a sequential extraction of sediment P was performed in each sample (Golterman, 1996). This method allows to determine iron-bound phosphate (Fe(OOH)-P), calcium bound phosphate (CaCO₃-P), and two organically bound P-fractions, acid soluble organic phosphate and alkali soluble organic phosphate (org-P-acid and org-P-alk). SRP in the extracts was measured using the acid ascorbic method with some modifications suggested by Golterman (1996). Acid-washed polyethylene centrifuge tubes (50 mL) were used for the extraction to minimize sediment loss. P sequential extraction was performed using fresh sediment and results were expressed as dried weight. For each P fraction, 5 years mean values (and standard deviation) from each study site were calculated.

Primary and secondary minerals in the sediment were determined by X-ray Diffraction Analysis (XRD) (SHIMADZU model XD-D1). Working conditions were Cu Ka monochromatic radiation, 40 mA and 30 kV. Samples were run at a speed of $1^\circ 2\theta \text{ min}^{-1}$ (10–80). Crystalline phases were identified using DP-D1 system software.

2.3. Statistical analysis

Analysis of variance (ANOVA) was used to determine whether significant differences existed in P concentration or in P fractions in sediment of different study sites ($p < 0.05$). The normality of residuals was analyzed graphically and Bartlett's test was used to check the homogeneity of variances ($p < 0.05$). P fraction concentrations were transformed (log) to achieve homogeneity of variances and normality ($p < 0.05$). Duncan's test was used to differentiate means where appropriate ($\alpha = 0.05$). Calculations were performed using the Statgraphics Plus 5.0 software.

2.4. QA/QC

All glassware was cleaned and washed with 2N HNO₃ prior to each use. All reagents were of analytical grade. Replicate analyses (at least ten times) of the samples showed a precision of typically less than 4% (coefficient of variation).

3. Results and discussion

3.1. Water

In both CWs contaminant removal efficiencies were successful during the study period (Table 1). The concentrations measured were significantly lower at the outlet than at the inlet, indicating high removal efficiency, as it can be seen in Table 1. CWs presented removal efficiencies comparable to those reported by other authors. In FWS CWs removal efficiency for nitrogen is typically 40–50% (Vymazal, 2007), depending on many factors including inflow concentration, chemical form of nitrogen, water temperature, season, organic carbon availability, and dissolved oxygen concentration (Kadlec and Wallace, 2009). FWS CWs provide sustainable removal of phosphorus but at relatively slow rates ranging from 40 to 90% (Vymazal, 2007).

Conductivity showed a wide range of variability in the inlet effluent of both CWs (CW1: 3910–7900 mmho cm⁻¹ and CW2: 1124–4520 mmho cm⁻¹) while in the outlet area conductivity decreased not only in its mean value but also in its variability (CW1: 1860–2500 mmho cm⁻¹ and CW2: 1058–1477 mmho cm⁻¹). In CW1, alkalinity is mainly due to CO₃²⁻ while in CW2 is due to HCO₃⁻. The decrease in alkalinity and Ca²⁺ concentrations and the high-water pH at the inlet suggest calcium carbonate precipitation in this area of CW1. This fact was confirmed by DRX analysis (Fig. 1a).

SRP and TP concentrations were significantly higher in CW2 than in CW1 (Table 1). Also, mean removal percentage of both parameters was significantly higher in CW2 than in CW1. This could be explained by

several factors. P adsorption in sediments increases with increasing P water concentration, until all sorption sites are occupied (Reddy and DeLaune, 2008). Also, DO in water influences P removal, CW2 showed significantly higher DO in water than CW1 allowing Fe(OOH)_n formation and P binding in its surface. On the other hand, it is known that pH strongly influences P adsorption equilibrium in sediments. In the majority of systems, as pH increases and surface charge becomes more negative, the sorption of anions like phosphate decreases. Zhou et al. (2005) found that when pH is greater than 8, high free OH⁻ concentration will compete with SRP to adsorb onto sediment surface, as in the case of CW1, where pH ranged between 10.8 and 12.9 (Table 1). As the pH increases, oxidation-reduction potential (ORP) decreases, Fe(III) was reduced and the competition from OH⁻ mentioned above would interfere with P adsorption onto sediment.

NW2 presented extremely high conductivity (Table 1). Oroná et al. (2010) found salinity values exceeding 30 g L⁻¹ in the Mar Chiquita Lake, close to those found in sea water. This data along with the chemical composition of water allowed its classification as saline, sodium-chlorinated. In NW1, pH, conductivity and concentrations of all the variables measured, except Fe and NH₄⁺ are significantly lower than in NW2, in accordance with a freshwater system. TP concentration in water was significantly higher in NW2 than in NW1. However, both wetlands can be classified as hypereutrophic since TP was greater than 100 mg L⁻¹ (Reddy and DeLaune, 2008).

Wetlands can operate as regulators for P retention between uplands and nearby aquatic systems such as lakes, streams and estuaries. They may behave as both phosphorus source and sink; thus, it is important to understand the biogeochemical processes that regulate its availability and retention in wetlands.

3.2. Sediment

In the inlet and outlet sediment of CWs, the pH values measured were slightly alkaline and in the NWs they were circumneutral (Table 2), in accordance with the lower pH values registered in the water of natural wetlands in comparison with the constructed wetlands. The sediments of CWs and NW2 were reduced, the Eh measured varied over a quite narrow range (approximately -127.34 and -42.02 mV), whereas in NW1 the sediment was moderately reduced (150.83 mV) (Table 2). The Eh measured at the outlet of both CWs was lower than the Eh measured at the inlet areas.

According literature, most P entering wetlands accumulates within the system, being sediments the major P reservoirs (Richardson, 1985; Reddy and DeLaune, 2008; Kadlec and Wallace, 2009). P retention is considered one of the most important attributes of natural and constructed wetlands, particularly those that receive nonpoint source

Table 1

Water physicochemical characterization of the studied wetlands. Mean values, ranges (Min.-Max.) and estimated mean removal efficiencies (%) in the studied constructed wetlands. Parameter concentrations are expressed as mg L⁻¹, and conductivity as mmho cm⁻¹.

Parameter	NW1	NW2	CW1		Removal	CW2		Removal
			Inlet	Outlet		Inlet	Outlet	
pH	7.0 (6.5–7.3)	7.1 (7.0–8.2)	11.0 (10.8–12.9)	8.6 (8.1–8.9)	–	7.7 (7.4–8.1)	7.8 (7.6–8.2)	–
Conductivity	110 (70–200)	51550 (20000–85000)	5327 (3910–7900)	2166 (1860–2500)	–	1728 (1124–4520)	1200 (1058–1477)	–
DO	8.21 (6.7–9.0)	7.7 (6.3–9.1)	3.62 (2.38–5.7)	0.99 (0.40–1.95)	–	6.0 (3.2–7.4)	6.4 (4.2–7.8)	–
Alkalinity	103.2 (100.1–105.7)	257.8 (236.3–279.3)	777.2 (299.4–1431.4)	295.1 (193.3–376.9)	62.0	588.7 (101.7–1647.0)	367.3 (167.9–474.1)	37.6
Cl ⁻	7.1 (4.2–10.1)	18160.3 (7405–29102)	698.4 (256.9–1569.4)	233.5 (162.9–285.9)	66.6	32.7 (22.6–42.5)	22.5 (7.1–29.4)	31.2
SO ₄ ²⁻	6.5 (5.0–8.7)	7559.5 (4500–12000)	785.8 (460.0–1872.9)	422.6 (199.9–714.4)	46.2	456.1 (43.1–2781.0)	138.9 (67.0–218.7)	69.5
Ca ²⁺	7.1 (6.4–9.7)	526.65 (430.1–715)	377.7 (136.7–856.7)	48.9 (44.9–54.6)	87.1	90.5 (76.8–120)	65.2 (48.0–88.8)	27.9
Fe	0.46 (0.21–0.84)	0.20 (0.14–0.32)	8.27 (0.824–17.4)	0.870 (0.087–2.69)	92.2	0.350 (0.005–0.505)	0.108 (0.050–0.221)	69.1
SRP	0.041 (0.010–0.099)	0.067 (0.051–0.094)	0.034 (0.05–0.079)	0.030 (0.05–0.057)	12.5	0.899 (0.247–1.370)	0.436 (0.140–0.728)	51.5
TP	0.160 (0.100–0.198)	0.317 (0.217–0.400)	0.318 (0.072–0.889)	0.197 (0.103–0.391)	38.0	2.328 (0.642–3.7)	0.686 (0.398–1.080)	70.5
NO ₂ ⁻	0.002 (0.001–0.005)	0.061 (0.05–0.120)	1.24 (0.88–2.33)	0.241 (0.151–0.372)	80.6	0.038 (0.004–0.087)	0.017 (0.002–0.033)	75.3
NO ₃ ⁻	2.4 (1.6–3.1)	10.2 (1.7–25)	20.09 (1.17–50.6)	9.89 (5.24–13.9)	50.8	2.588 (0.271–7.2)	0.531 (0.158–1.500)	93.3
NH ₄ ⁺	1.056 (0.315–1.587)	0.230 (0.05–0.469)	9.18 (0.88–17.1)	5.55 (0.63–11.2)	39.5	16.0 (0.957–26.8)	2.27 (0.477–5.070)	85.8

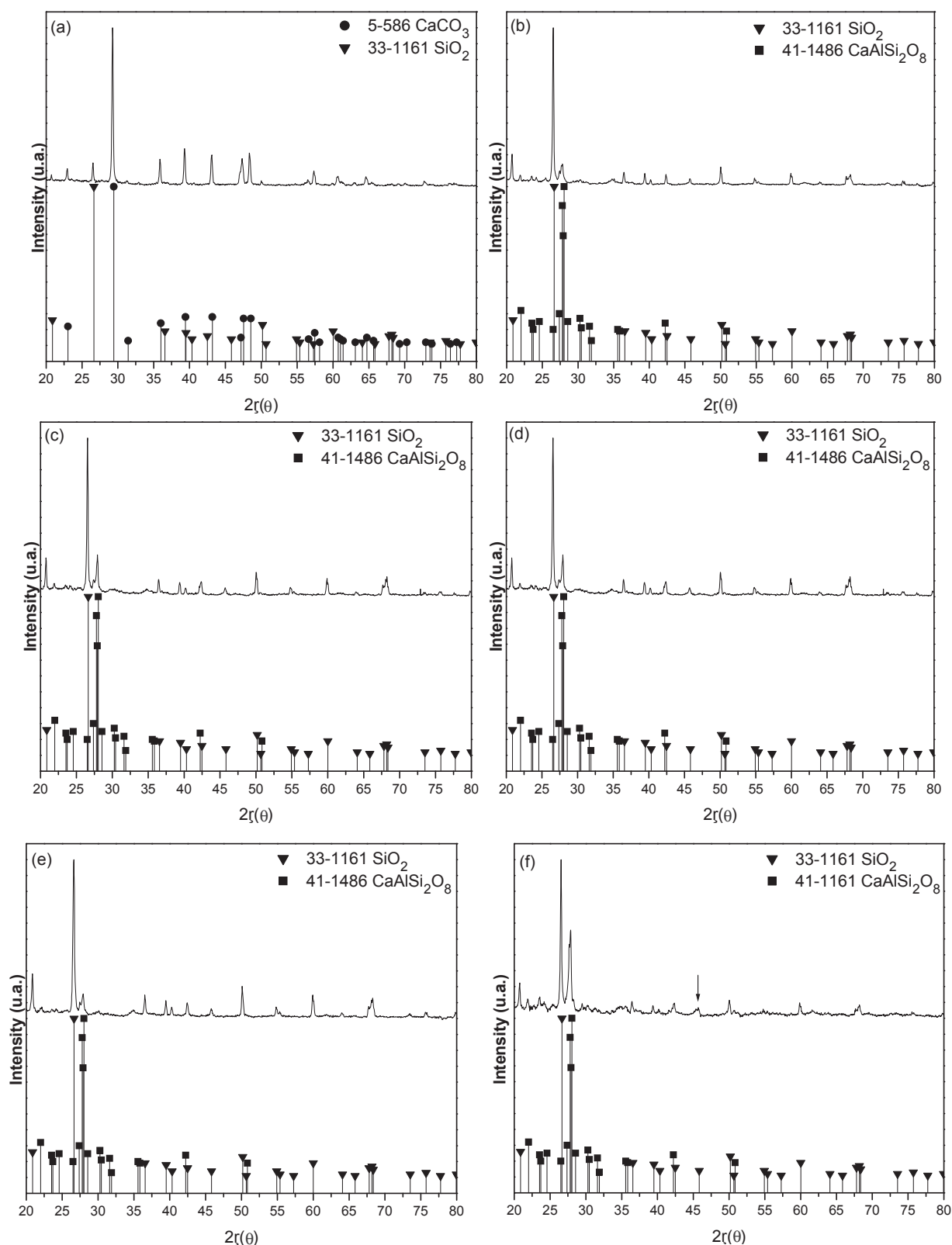


Fig. 1. Surface sediment layer (0–3 cm) XRD spectra of the wetlands studied. (a) CW1 inlet, (b) CW1 outlet, (c) CW2 inlet, (d) CW2 outlet, (e) NW1, and (f) NW2.

pollution or wastewater. Sediment TP concentration was significantly higher in NW2 and in the inlet of CW1 than in the other wetlands studied (Fig. 2). In the case of NW2, the main tributary of this wetland, the Primero River, suffers a slight but progressive deterioration in water quality as it passes through a densely populated area. Also, the effluents from the municipal wastewater treatment plant from the City of

Córdoba affect it seriously. P concentration in the sediment of the inlet area of CW1 was comparable to P concentration in NW2.

In both CWs, P concentration was significantly higher in the inlet than in the outlet sediment, showing that it was efficiently retained in the inlet (Fig. 2). Generally, P concentration in water decreased as long as the nutrient flows through the wetland. The lowest P concentration

Table 2
Mean values of organic matter (OM), Redox Potential (Eh) and pH in surface sediments at the different studied wetlands.

Wetland	Area	% OM	Eh (mV)	pH
NW1		13.72	150.83	6.34
NW2		6.07	-88.80	7.53
CW1	Inlet	2.96	-65.61	8.20
	Outlet	3.81	-127.34	7.97
CW2	Inlet	5.50	-42.02	8.28
	Outlet	4.04	-56.07	8.25

in sediment was found in the outlet of CW1. The concentration in the outlet area of this CW showed no significant differences with initial concentration when CW1 began operation. At that moment, P concentration was low and uniform across the wetland ($P = 0.378 \text{ mg g}^{-1}$; Maine et al., 2017), suggesting that, after 13 years of operation, P retention capacity of this wetland was not saturated. In the case of NW1, P concentration in sediment could be due to manure deposits that of animals pasturing there.

Notwithstanding, P concentration in the influent water of CW2 and P removal percentages were higher than in CW1 (Table 1). P concentration in the sediment of the inlet area of CW2 was lower than in the CW1 sediment (Fig. 2). This fact could be explained by several factors. One is that the operation time of CW2 is lower than CW1. Another factor might be that a dense *T. domingensis* litter deposited on the sediment of CW2, which accumulated high P concentration ($P = 1.090 \text{ mg g}^{-1}$), preventing P from reaching the sediment. This litter was composed mainly of dead leaves that remain after the winter, as part of the annual cycle of macrophytes. It is important to highlight

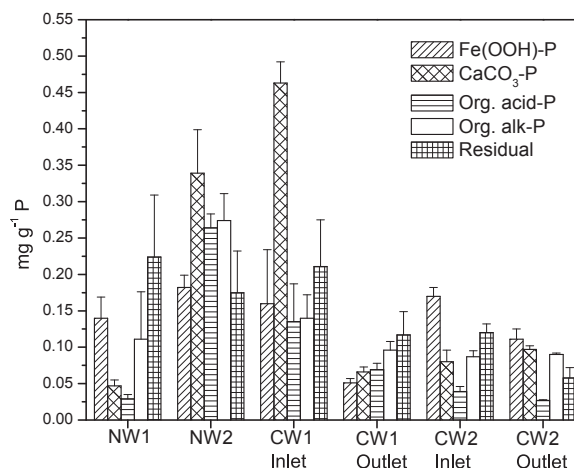


Fig. 3. Mean P fractionation (Fe(OOH)-P, $\text{CaCO}_3\text{-P}$, Org. acid-P, Org. alk-P and residual P).

that even dead, macrophytes continue retaining contaminants, and due to their slow degradation, they can be simply removed from the CW for final placement. In fact, macrophyte harvest and dead plant removal from the bottom is rendered periodically. This is an important advantage for CW management. The portion of detritus that is not removed constitutes the sediment after accretion. The concentration in the outlet area of this CW showed no significant differences with initial concentration when CW2 began operation ($P = 0.392 \text{ mg g}^{-1}$; Maine et al., 2017).

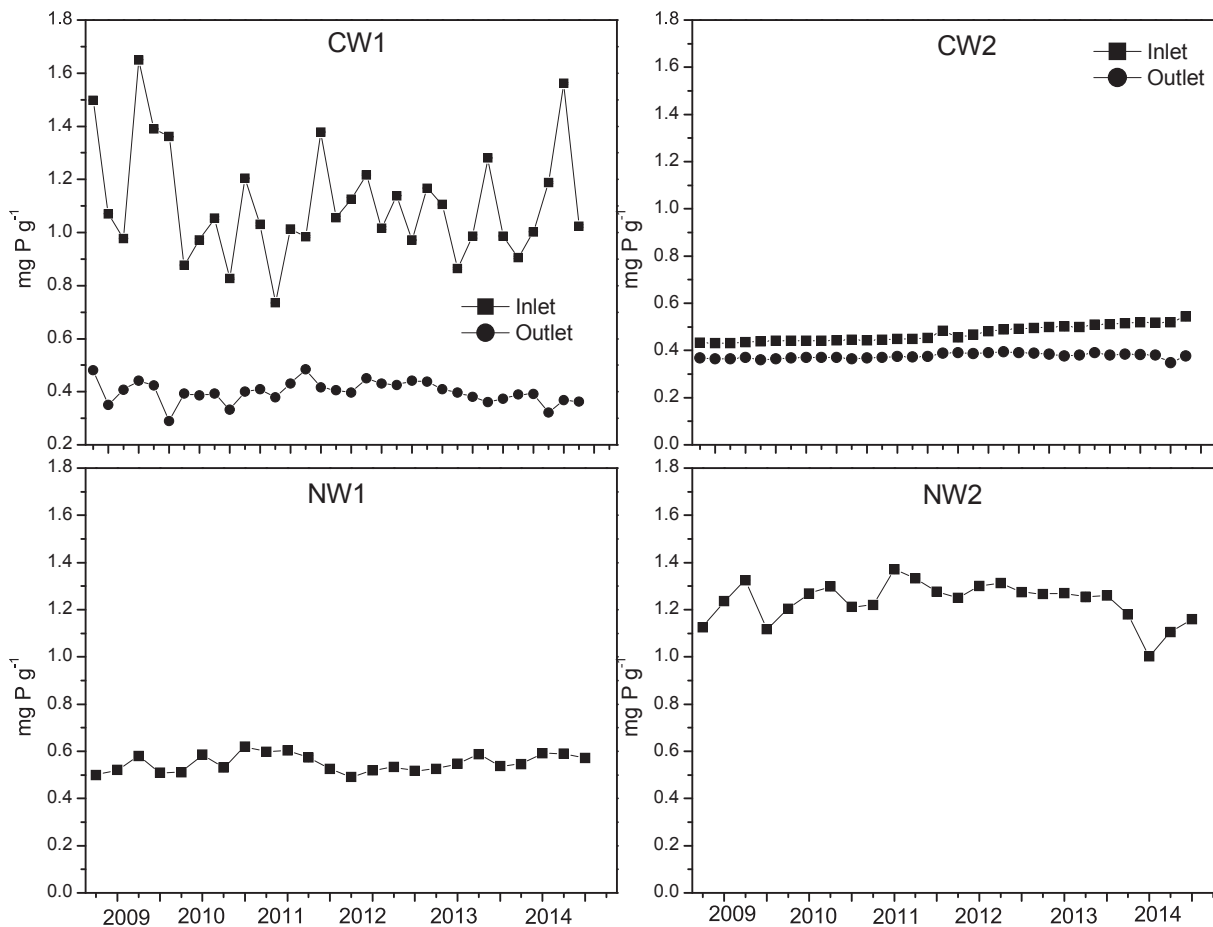


Fig. 2. 5-years TP concentration (mg g^{-1}) in surface sediment layer (0–3 cm) of the studied wetlands. Concentrations are expressed in mg g^{-1} .

The distribution of P in sediment is mainly controlled by hydrological factors, sediment composition and redox conditions (Andrieux-Loyer and Aminot 2001; Kim et al., 2003; Wang et al., 2006; Álvarez-Rogel et al., 2007; Jordan et al., 2008). P sequential extraction showed that sediments were dominated by P inorganic fractions in all wetlands (Fig. 3). It is important to note that NW2 and the inlet zone of CW1 showed a similar pattern of distribution of the P fractions. In these sites, the formation of calcium phosphate compounds of different solubility can occur due to the high concentrations of Ca^{2+} and alkalinity. Calcite saturation indices were calculated taking into account the chemical composition of water (APHA et al., 2012), being values positive on sites NW2 and at the CW1 inlet. These results indicate that calcite is supersaturated so its precipitation is thermodynamically favored. Moreover, the presence of CaCO_3 in the inlet area of CW1 was corroborated by the XDR analysis (Fig. 1a). Consequently, at these sites, P accumulated mainly bound to CaCO_3 ($\text{CaCO}_3\text{-P}$) (Fig. 1). Several calcium phosphate compounds could precipitate on the surface of calcite (calcium phosphate, dicalcium phosphate, beta-tricalcium phosphate, octacalcium phosphate, and hydroxyapatite). When water pH is below 4, phosphorus bound to calcium is likely to be released. This pH value is practically impossible to occur in these wetlands due to the high buffering capacity of the systems.

As in the case of inlet area of CW1 and NW2, P distribution in CW2 and NW1 could be linked. In both areas of CW2, the main P fraction was $\text{Fe}(\text{OOH})\text{-P}$ (Fig. 3). Whereas in NW1, $\text{Fe}(\text{OOH})\text{-P}$ was a very important P fraction (Fig. 3). It is known that Eh influences the biogeochemical cycling of P in sediment. Generally, oxidized sediment retains P while an increase in water P concentrations is observed under reducing conditions of the sediment. This fact has been closely referring to adsorption effects. $\text{Fe}(\text{III})$ -oxyhydroxides acts as a sink for P in oxidized sediments, such as in the case of NW1 sediment. Numerous studies have linked the release of P under reducing conditions due to the dissolution of $\text{Fe}(\text{III})$ oxides (Mortimer, 1941; Hutchison and Hesterberg, 2004). However, several studies found high P sorbed in sediment at low Eh, as in CW2 sediments, and a decrease in water P concentration (Kuo and Mikkelsen, 1979; Sah and Mikkelsen, 1986; Sah et al., 1989a, 1989b; Zhang et al., 1993). The formation of amorphous or poorly crystalline compounds of $\text{Fe}(\text{II})$ could explain this ostensible contradiction. Reduced Fe compounds have larger surface areas, thus many more sorption sites than ferric forms. Reddy and DeLaune (2008) stated that the binding energy for phosphate in sorption sites is lower in reduced than in aerobic sediment. Therefore, reduced sediment will adsorb a large amount of P with a low binding energy. Furthermore, XDR analysis showed that the crystalline phases identified in the outlet area of CW1, both areas of CW2 and in both NWs, were SiO_2 (PDF # 33–1161) and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (PDF # 41–1161) (Fig. 1b, c and d). The absence of peaks corresponding to $\text{Fe}(\text{OOH})$ in the XDR analysis (Fig. 1) in all study sites, indicate that these oxides are in amorphous or poorly crystalline state.

Organic phosphorus is that bonded in some way with organic matter. This bond is usually covalent. An important proportion of TP exists in organic forms in all sites studied (Fig. 2). However, only a small portion, the Org acid-P, may be biologically active. This fraction represents easily mineralizable organic phosphorus and is composed by nucleic acids, phospholipids, and sugar phosphates. Org. alk-P was larger than Org. acid-P in all sites. This fraction represents more resistant forms of organic P, involved in the long-term transformations of P and consists mainly in inositol phosphates (IHPs), phytin and humic acids (Reddy and DeLaune, 2008).

In NW1 and in the outlet area of CW1, P was mainly accumulated in the residual fraction (Fig. 2). Concentrations of residual P showed that these systems are operating as long-term sinks of P (Reddy and DeLaune, 2008).

Finally, it is important to note scarce variation of P distribution in sediment of the study wetlands along five years, reflected by low standard deviations of P fractions, in agreement with the fact that physicochemical characteristics of water and sediments govern P

distribution patterns in sediments.

4. Conclusion

Physico-chemistry of sediments and incoming water (mainly pH, Eh, and conductivity) determined different P retention mechanisms in each study wetland. P was retained mainly in inorganic fractions in all study sites and those forms. In CW1 and NW2, high alkalinity and Ca^{2+} concentrations in water determine that precipitation reactions on the CaCO_3 surface were responsible of the major P removal. In the case of NW1 and CW2, due to the more oxidized conditions, the main contribution to the P binding comes from a ligand-exchange process on the Fe-OH_2^+ and Fe-OH sites. Both, the low sediment OM content and the predominance of metal-bound P forms indicate that the P mobility is low. P distribution in sediment of the study wetlands remained stable along five years. It is important to highlight that P concentration did not increase in the sediment of the outlet area of the CWs studied; therefore, sediment of these CWs could continue accumulating P. Finally, the wetlands studied are efficient and sustainable in terms of P retention.

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