Research Paper

Phosphorus distribution pattern in sediments of natural and constructed wetlands

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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 Fe(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.

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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 km^2. Paraná River has an irregular hydrological regime. During the first six months of the year the river is at high stage, with mSaximum 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 km^2 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 Suquía (or Primero) River; (ii) The Xanaes (or Segundo) River (total length 340 km and average discharge of 14.5 m^3 s^{-1}); and (iii) The Dulce River (total length of 812 km and an average discharge of 80 m^3 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 m^3 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 m^3 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 HClO$_4$:HNO$_3$: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 (CaCO$_3$-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, 5years 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° 2q min^{-1} (10–80). Crystalline phases were identified using DP-D1 system software.