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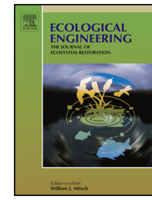

Long-term performance of two free-water surface wetlands for metallurgical effluent treatment

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ABSTRACT

The aim of this study was to evaluate the efficiency of two constructed wetlands (CW1 and CW2) for the wastewater treatment of metallurgical industries and determine if contaminants are retained by the sediment or the plants, key knowledge for suitable wetland management. Both systems are free water surface CWs and were designed to treat industrial wastewater (with high pH and salinity containing Cr, Ni and Zn) and sewage together. Wastewaters receive a primary treatment before reaching the wetlands. CW1 and CW2 have been operating for 14 and 7 years, respectively. Wastewater, sediment and plants were sampled monthly in the inlet and outlet zones of both CWs. In both CWs, removal efficiencies were satisfactory. *T. domingensis*, the dominant species, is tolerant to metallurgical wastewaters and efficient in metal accumulation. Metals and P were efficiently removed in both CWs, being metals retained mainly in sediment, and P was retained in sediment and plants of the inlet zone. Metal concentration in macrophyte tissues is related to influent concentration while metal concentration in sediment depends not only on influent concentration but also on the time of operation of the CWs. Metals are bound to sediment fractions that can be considered steady under chemical and environmental conditions of the wetlands. Since the conditions for metal removal are largely provided by the influents (high pH, alkalinity, Fe, Ca and ionic concentrations), the sediment will continue retaining metals as far as the composition of the influents remain the same.

1. Introduction

Constructed wetlands (CWs) have been widely studied for the treatment of various types of wastewater such as domestic sewage, agricultural, industrial, mine drainage, leachate, urban runoff, etc. (Maine et al., 2006, 2007, 2009; Kadlec and Wallace, 2009; Vymazal, 2011; Brix, 1993; Brix and Arias, 2005; Shubiao et al., 2014; Zhang et al., 2014; Wu et al., 2015). There are hundreds of CWs operating in Europe, Asia, United States and Australia. In Latin America, in countries such as Mexico, Colombia, Peru and Bolivia, this technology has been widely used for the depuration of sanitary effluents of small villages, tourist resorts, university campus, etc. In Argentina, even though the environmental conditions are favourable with a great availability of low cost marginal and several macrophytes adapted to the climate, CWs are not widely implemented. In our country, as in other countries in Latin America, there are companies that construct wetlands without having performed the necessary previous studies and subsequent monitoring for control and optimization. This causes malfunctioning of the wetland system and, consequently, encourages the idea that such technology is not efficient. In particular, in the case of industrial effluent treatment, it is important to carry out specific previous studies for each case and monitor the systems along time, not only to understand depuration mechanisms, but also to optimize system operation.

Our research group designed two wetlands for the final wastewater treatment of two metallurgical manufacturing plants. Both systems are free-water surface constructed wetlands. As the chemical composition of the wastewaters and the volumes to be treated are different, CWs have different design characteristics. Wastewater from the industrial processes and sewage from the factory were treated together, after a primary treatment. We thought that high nutrient concentrations could improve the ability of macrophytes to take up heavy metals from wastewater. This hypothesis was corroborated by our research group (Hadad et al., 2007; Hadad et al.,

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2010; Mufarrege et al., 2016). We have studied these wetlands since they began operating. The aim of this work was to compare the efficiency of CWs and to determine if the contaminants (Cr, Ni, Zn, and P) were retained by the sediment or by plants, key knowledge for a suitable wetland management.

1.1. Wetland description

Both systems are free-water surface CWs. They were constructed for the final treatment of the wastewaters of two metallurgical manufacturing plants. In both wetlands, wastewater and sewage from the factories were treated together. Both wastewaters received a primary treatment before discharging into the wetlands.

CW1 started operating 14 years ago. It is 50 m long, 40 m wide and 0.4–0.5 m deep, with a central baffle forcing the wastewater to cover double the distance (Fig. 1a). The wetland was rendered impermeable by means of bentonite (5 compacted layers, total depth: 0.6 m, to reach hydraulic conductivity: 10^{-7} m s^{-1}). Soil (1 m) was placed on top of the bentonite layer. Locally available floating (*Pistia stratiotes*, *Eichhornia crassipes* and *Salvinia rotundifolia*) and emergent macrophytes (*Panicum elephantipes*, *Pontederia cordata*, *Typha domingensis* and *Hydrocotyle ranunculoides*) were transplanted into the wetland.

During the first stage of the wetland operation (from October 2002 to February 2003) only diluted sewage of the factory was treated (the composition of the influent was 25 m^3 d^{-1} of sewage + 75 m^3 d^{-1} of pond water). Sewage consisted of wastewater from 750 factory employees. Later (March 2003), industrial wastewater and sewage were treated together (25 m^3 d^{-1} of sewage + 75 m^3 d^{-1} of industrial wastewater). Mean wastewater discharge was 100 m^3 d^{-1}. Water residence time ranged from 7 to 12 days. After flowing through the CW, the effluent was discharged into a 1.5 ha pond.

CW2 has been in operation since 2009. It is 20 m long, 7 m wide and 0.3–0.7 m deep. It was waterproofed with a geomembrane. A layer of 1.5 m of soil was placed on top of the geomembrane. *T. domingensis* plants growing in a pond located on the same site were transplanted to CW2, in order to ensure the plant growth. Plants were pruned to a height of approximately 30 cm keeping their rhizomes. Three plants per square meter were transplanted and they were irrigated without flooding the wetland, until robust growth. To enhance plant growth in deeper zones and to increase wastewater circulation through the CW, baffles of 0.50 m width with plants were constructed transversally to the wastewater circulation. On leaving the wetland the effluent fell into a concrete pool simulating a waterfall and then was led to a pond by a channel (Fig. 1b). This wetland treats all the plant wastewaters: the chrome plating bath effluents and sewage, storm water and cooling water. The two first effluents receive a previous primary treatment. Wastewaters reach an equalizing chamber and then enter the wetland. During the first year of operation, only sewage (with previous primary treatment), storm water and cooling circuit effluents were discharged into the CW. After this period, also the industrial wastewater began to be discharged. Mean wastewater discharge is approximately 10 m^3 d^{-1}. Water residence time is 7–10 days.

2. Materials and methods

2.1. Sampling and analytical determinations

Wastewater, sediment and plants were sampled monthly in the inlet and outlet zones of both CWs. Efficiency was determined from the influent and effluent contaminant concentrations. Samples were collected in triplicate.

Conductivity, pH and dissolved oxygen (DO) were determined in water *in situ*. Conductivity was measured with an YSI 33 conductometer, pH with an Orion pH-meter and DO with a Horiba OM-14 portable meter. Refrigerated water samples were sent to the lab. For metal analysis, samples were acidified to pH < 2. Samples were filtered through Millipore membrane filters (0.45 μm) for soluble reactive phosphorus (SRP) and N determinations (APHA, 2012). Chemical analyses were performed following APHA (2012). NO_2^- was determined by coupling diazotation followed by a colorimetric technique. NO_3^- and NH_4^+ by potentiometry (Orion ion selective electrodes, sensitivity: 0.01 mg L^{-1} of N, reproducibility: ±2%). SRP was determined by the colorimetric molybdenum blue method (Murphy and Riley, 1962). In the case of total phosphorus (TP), non-filtered water samples were digested with sulphuric acid-nitric acid. SRP was determined in the digested samples (Murphy and Riley, 1962). Ca^{2+} was determined by EDTA titration. Alkalinity was measured by HCl titration. SO_4^{2-} was assessed by turbidimetry. Chemical oxygen demand (COD) was determined by the open reflux method and biochemical oxygen demand (BOD) by the 5-day BOD test. Total Fe, Cr, Ni and Zn concentrations were determined in water samples by atomic absorption spectrometry (by flame or electrothermal atomization, according to sample concentration, Perkin Elmer AAnalyst 200), previous acid digestion with nitric acid-hydrochloric acid (APHA, 2012).

Surface sediment samples were collected using a 3-cm diameter PVC corer at a depth of 0–3 cm and stored at 4 °C until analysis. For metal fractionation, a sequential extraction proposed by Tessier et al. (1979) was carried out. Sediment samples were oven-dried at 45 °C until constant weight was reached, and ground using an agata mortar. They were sieved through a 63 μm sieve prior to sequential extraction of metals. For metal analyses, samples were digested using a $HClO_4$:HNO_3:HCl (7:5:2) mixture. These digests and the extracts obtained from the sequential extraction procedure were analysed for Cr, Ni and Zn by atomic absorption spectrometry (Perkin Elmer, AAnalyst 200). TP in sediment was determined as SRP (Murphy and Riley, 1962) in the digested samples.

In both CW, *T. domingensis* plants were sampled and separated into above-ground (stems and leaves) and below-ground parts (roots and rhizomes). The below-ground parts were washed with tap water in order to separate the attached sediment. In CW2 dead plants pieces (detritus) were sampled by hand. TP, Cr, Ni and Zn in above and below-ground parts and detritus were determined in the same way as in the sediment samples. Plant cover was estimated measuring the area occupied by aerial (visible) parts in the wetland.

To estimate where contaminants are retained, it is necessary to take into account not only concentration but also mass of each compartment. Cr, Ni and Zn amounts (mg) were estimated by multiplying each contaminant concentration in plant tissue or sediment (mg g^{-1} dry weight) or in water (mg L^{-1}) by biomass (g dry weight) or volume (L). In sediment, an active layer of 3 cm was considered (Di Luca et al., 2011a,b). To estimate biomass plants were collected with a square frame of 50 cm each side, in five replicates. At the laboratory, the plants collected were separated into above-ground and below-ground parts. The roots were carefully rinsed with distilled water to remove sediment residues. In order to measure dry weight, plant material was dried at 105 °C until a constant weight was reached (APHA, 2012).

A paired test was used to corroborate statistical differences between the inlet and outlet contaminant concentrations in water, and sediment and plant tissues. ANOVA was carried out to determine if there were significant differences in contaminant concentrations among plant tissues (leaves and roots) and sediment, and among the different sediment fractions. Duncan's test was used to differentiate means where appropriate. A level of $p < 0.05$ was used in all comparisons.