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Ecological Engineering

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

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ARTICLE INFO

Article history:

Received 15 January 2016

Received in revised form 13 June 2016

Accepted 6 July 2016

Available online xxx

Keywords:

Metals

Phosphorus

Typha domingensis

Sediment

Industrial wastewater

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.

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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 $25 \text{ m}^3 \text{ d}^{-1}$ of sewage + $75 \text{ m}^3 \text{ d}^{-1}$ of pond water). Sewage consisted of wastewater from 750 factory employees. Later (March 2003), industrial wastewater and sewage were treated together ($25 \text{ m}^3 \text{ d}^{-1}$ of sewage + $75 \text{ m}^3 \text{ d}^{-1}$ of industrial wastewater). Mean wastewater discharge was $100 \text{ m}^3 \text{ d}^{-1}$. 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 $10 \text{ m}^3 \text{ d}^{-1}$. 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 $\text{pH} < 2$. Samples were filtered through Millipore membrane filters ($0.45 \mu\text{m}$) for soluble reactive phosphorus (SRP) and N determinations (APHA, 2012). Chemical analyses were performed following APHA (2012). NO_2^- was determined by coupling diazotization 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: $\pm 2\%$). 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 $63 \mu\text{m}$ sieve prior to sequential extraction of metals. For metal analyses, samples were digested using a $\text{HClO}_4:\text{HNO}_3:\text{HCl}$ (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.



Fig. 1. Aerial picture of the CW1 (a) and satellite image of the CW2 (b). A general map shows the location of the studied wetlands with a little square.

2.2. QA/QC

All glassware was washed with 2 M HNO₃ before each experiment. Analytical grade reagents and Milli-Q water were used to prepare all solutions. Certified standard solutions were used. Replicate analyses of the samples showed a precision of typically less than 5% (coefficient of variation). For water, detection limits were 2, 2, 3 and 5 $\mu\text{g L}^{-1}$ for Ni, Cr, Zn and P, respectively. For macrophyte tissues and sediment, detection limits were 30, 20, 30 and 5 $\mu\text{g g}^{-1}$ for Ni, Cr, Zn and P, respectively.

3. Results and discussion

Table 1 shows the mean concentration and the range of the parameters measured and estimated removal efficiencies obtained in the CW1 and CW2 respectively, during normal operation. High pH and conductivity were determined in the wastewater to be treated in both CWs. pH and conductivity were higher in CW1 than in CW2, but in CW2 some conductivity peaks were registered. The chemical composition of the wastewater to be treated presented high variability, a common characteristic of industrial wastewaters. However, after flowing through the CWs, the outlet effluent presented not only lower concentrations but also lower variability of the parameters measured than the inlet effluent, proving the buffer capacity of the CWs.

Metals were efficiently removed from the wastewater. It is important to highlight that these CWs were final treatments and metal concentrations were low. At the inlet, Cr and Zn concentrations were significantly higher in CW2 than in CW1, while Ni exhibited the highest concentrations in the CW.

Contaminant removal efficiencies were satisfactory, except for SRP and NH₄⁺ in CW1 probably due to low DO concentration. A waterfall in the outlet zone was disposed to increase DO, but removal efficiencies did not increase significantly. In CW2, DO concentration was higher and SRP and NH₄⁺ removal efficiencies were higher. An important decrease of sulphate was also observed. In both CWs, wastewaters showed high sulphate concentrations, due to its use in the primary treatments. CWs performances were steady over the operation periods, allowing concentrations to meet the regulatory limits set by law.

As it was said, several macrophytes were transplanted to CW1 initially, being *E. crassipes*, *P. cordata* and *T. domingensis* those showing a larger cover (Fig. 2). According to literature, the use of a high diversity of plants has advantages, such as a higher efficiency in contaminant removal, disturbance resilience, better habitat, etc. (Brisson, 2013). *E. crassipes* showed a fast growth becoming the dominant macrophyte and covering 80% of the CW for 2 years. However, its cover decreased after this period. New specimens

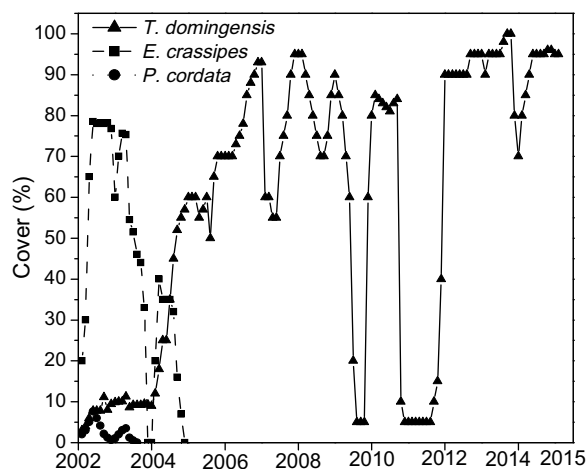


Fig. 2. Plant cover registered in CW1 throughout the studied period.

were transplanted but *E. crassipes* did not tolerate the wastewater (Maine et al., 2007). High pH and salinity were the cause of disappearance of floating macrophytes (Hadad et al., 2007), but when *E. crassipes* cover decreased, *T. domingensis* cover began to increase. To enhance *T. domingensis* growth, CW1 water level was decreased and baffles of 0.50 m wide were constructed transversally to the wastewater circulation. *T. domingensis* was the dominant species during the last 10 years. Contaminant accumulation in plants and sediment were estimated and compared between floating macrophyte dominance and emergent macrophyte dominance periods (Table 2). It can be seen that during the *E. crassipes* dominance, contaminants were retained in the macrophyte biomass. During *T. domingensis* dominance stage, metals were retained mainly in sediment and P was retained in sediment and macrophyte biomass. Harvest of floating macrophytes would allow metal and P removal from the system. However, plants have to be safely disposed. Emergent macrophytes favour metal accumulation in the sediment, phytostabilization them.

Fig. 2 shows the decrease in macrophyte cover in time. Certain cover decrease was due to plant pruning to enhance growth. Then, the most important decrease occurred in 2009 and 2011, when a population of capybaras (*Hydrochoerus hydrochaeris*) caused the depredation of the aerial parts of macrophytes of CW1. Capybaras, the largest amphibious rodent known in the world, weigh 80 kg on average. The CW looked like a pond without macrophytes. However, the roots and rhizomes of *T. domingensis* were not damaged and CW1 continued retaining contaminants during the predation period (Maine et al., 2013). The wetland was fenced with wire to

Table 1
Mean, minimum and maximum values of the measured parameters in the influent and effluent, and removal (%) of the CW1 and CW2. pH, Conductivity ($\mu\text{mho cm}^{-1}$, 25 °C) and concentrations (mg L^{-1}).

Parameters	CW1			CW2		
	Influent	Effluent	Removal	Influent	Effluent	Removal
pH	10.8 (10.4–12.2)	8.3 (7.9–9.3)	–	7.9 (7.4–8.3)	8.0 (8.0–8.1)	–
Conductivity	5113 (3890–8700)	1955 (1400–2500)	–	3213 (975–10060)	1203.6 (1058–1358)	–
DO	3.40 (0–6.2)	2.1 (0.3–5.2)	–	6.0 (3.2–7.4)	6.4 (4.2–7.8)	–
NO_3^-	50.6 (15.4–98.2)	9.9 (3.6–24.2)	80.4	0.945 (0.271–1.28)	0.364 (0.158–0.484)	74.4
NO_2^-	2.22 (0.281–6.21)	0.352 (0.017–0.766)	84.1	0.112 (0.004–0.223)	0.037 (0.030–0.053)	71.2
NH_4^+	0.88 (0.15–2.6)	0.77 (0.05–2.14)	11.8	6.15 (0.957–15.6)	2.08 (0.722–3.89)	66.1
SRP	0.030 (0.005–0.079)	0.026 (0.005–0.334)	13.3	0.692 (0.247–0.903)	0.307 (0.291–0.350)	58.1
TP	0.396 (0.064–1.38)	0.309 (0.129–0.696)	22.0	0.889 (0.642–1.322)	0.425 (0.398–0.442)	52.8
SO_4^{2-}	1872.9 (991.4–2316.1)	626.4 (412.1–884.1)	66.5	1428.8 (56.3–2781)	133.7 (75.3–181.3)	90.6
Alkalinity	553.2 (114.6–750.4)	224.1 (156.8–332.3)	36.5	690.0 (101.7–1647.0)	283.0 (167.9–378.2)	63.2
Ca	219.6 (92.3–305.2)	81.3 (51.1–101.2)	61.7	90.5 (76.8–120)	65.2 (48.0–88.8)	36.9
Fe	0.824 (0.052–2.54)	0.087 (0.05–0.230)	89.4	0.350 (0.151–0.561)	0.110 (0.061–0.173)	70.4
Cr	0.092 (0.023–0.204)	0.014 (0.002–0.033)	84.7	0.310 (0.012–1.45)	0.022 (0.019–0.025)	92.9
Zn	0.041 (0.022–0.070)	0.020 (0.015–0.050)	51.2	0.072 (0.006–0.145)	0.031 (0.003–0.067)	51.7
Ni	0.048 (0.004–0.101)	0.023 (0.004–0.082)	69.5	0.018 (0.004–0.032)	0.004 (0.004–0.006)	77.5
COD	85 (27.9–154.0)	37.1 (13.9–42.9)	74.6	57.1 (21.3–160)	12.4 (2.0–27.2)	78.2
BOD	31.3 (9.8–30.9)	9.97 (3.0–20.1)	73.2	45.3 (10.2–55.5)	8.6 (3.2–17.6)	82.5

Table 2
Estimated contaminant retention by macrophytes tissues and sediment in the inlet area of CW1 (%).

Dominant species	Cr		Ni		Zn		TP	
	sediment	tissues	sediment	tissues	sediment	tissues	sediment	tissues
<i>E. crassipes</i>	11	89	7	93	5	95	2	98
<i>T. domingensis</i>	73	27	87	13	71	29	62	38

stop animals from approaching, which allowed the recovery of the vegetation. Subsequently, *T. domingensis* reached a cover of 80% after 90 days. This luxuriant growth was enhanced by the growth season.

Regarding CW2, *T. domingensis* was selected taking into account the experience with CW1 (Fig. 3). *T. domingensis* cover reached a value of 90% after a few months. However, the plant cover decreased during 2012, as a result of an occasional dumping with high Cr(VI) concentrations. The wetland was closed to avoid an effluent outflow. Cr concentration in water decreased after 30 days. The wetland was emptied, plant detritus containing high Cr concentrations was removed and new specimens of *T. domingensis* were planted in the inlet area. Four months after the dump, the wetland was operating normally. Both CWs suffered the decrease in plant cover due to different events, but they were able to recover their performance demonstrating the robustness of these systems.

Table 3 shows Cr, Ni and Zn (from the industrial wastewaters) and TP (from the sewage) concentrations in *T. domingensis* tissues of plants sampled in the inlet and outlet areas of both CWs. In both CWs, TP concentrations in tissues were significantly higher in the plants from the inlet area than those of the outlet area. P is retained in roots and above-ground parts. The same can be seen for metals:

concentrations in plant tissues taken at the inlet area were significantly higher than those of the outlet area. Contrarily, metals are

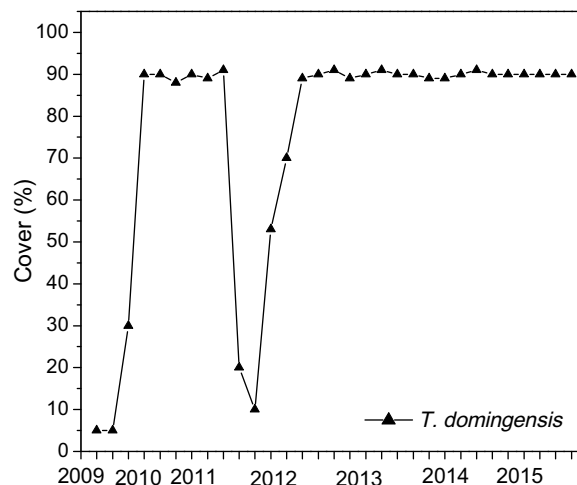
**Fig. 3.** Plant cover registered in CW2 throughout the studied period.

Table 3Cr, Ni, Zn and TP concentrations (mg g^{-1}) measured in tissues of *T. domingensis* grown in CW1 and CW2 at the end of the study.

CW1	Cr		Ni		Zn		TP	
	Leaves	Roots	Leaves	Roots	Leaves	Roots	Leaves	Roots
Inlet Zone	0.023	0.356	0.014	0.199	0.034	0.090	2.24	1.84
Outlet Zone	0.010	0.034	0.006	0.030	0.035	0.086	1.16	1.02
CW2								
Inlet Zone	0.053	0.764	0.009	0.019	0.034	0.199	2.48	1.87
Outlet Zone	0.033	0.195	0.007	0.013	0.014	0.054	1.76	1.29
Detritus (<i>T. domingensis</i>)	2.29		0.013		0.206		1.09	

Table 4Cr, Ni, Zn and TP concentrations (mg g^{-1}) measured in sediments of CW1 and CW2 at the end of the study and initial values.

Sample	CW1				CW2			
	Cr	Ni	Zn	TP	Cr	Ni	Zn	TP
Inlet zone	1.582	0.960	0.146	0.996	0.865	0.017	0.056	0.586
Outlet zone	0.047	0.039	0.063	0.379	0.016	0.011	0.024	0.388
Initial	0.038	0.028	0.060	0.378	0.016	0.011	0.024	0.392

retained in roots. Low translocation from roots to aerial parts is an advantage because metals are not available for herbivorous animals. Metals remain immobilized in the CW sediment. Despite the longer operation time of CW1, Cr and Zn concentrations in tissues were significantly lower than in CW2. This is probably due to the higher Cr and Zn concentrations in CW2 influent than in CW1 influent. Ni concentrations in tissues were significantly higher in CW1 than in CW2 due to this metal low concentration in the influent of CW2 (Table 1). It is important to highlight that the emergent macrophytes also have an influence on the biogeochemical cycles of the sediment affecting the redox potential because of their ability to transport oxygen from the root to the rhizosphere zone (Barko et al., 1991; Sorrell and Boon, 1992). Quantitatively, this oxygenated layer can be visualized by the red color associated with the iron oxidized forms on the root surface and surrounding sediment.

Detritus from *T. domingensis* was accumulated at the inlet of the CW2. Detritus are constituted by dead leaves that remain in decomposition after winter, as part of the annual cycle of plant growth. High metal concentrations were determined in detritus (Table 3). Contaminants are not only sorbed by live plants. Schneider and Rubio (1999) demonstrated at laboratory scale that the dead biomass of three floating macrophytes (*Potamogeton lucens*, *Salvinia herzogii* and *E. crassipes*) was an excellent metal biosorbent. Similar results were reported for dead biomass of *Spirodela intermedia*, *Lemna minor* and *P. stratiotes* using a multimetal solution (Miretzky et al., 2006). This can be an important advantage for CW management. When plants die, since their degradation is slow (Hammerly et al., 1989), they continue retaining metals in the CW, as it was determined in our work. Detritus is mineralized and becomes part of the sediment. If necessary, detritus can be easily removed from the CW for final disposal.

In both CWs, the inlet sediment showed significantly higher Cr, Ni, Zn, and P concentrations than those registered in the outlet zone (Table 4). The outlet sediment concentrations were not significantly different from the initial concentrations (measured at the beginning of the study), showing that contaminants are retained in the inlet area. Metal and P concentrations were higher in the sediment of CW1 probably due to the longer time of operation. Ni concentration was not significantly accumulated at the inlet of the CW2 because the treated wastewater contained low concentrations of this metal.

According to the mass balance (Fig. 4), P was retained by plants and sediment. Sediment was the main accumulation compartment of metals in the studied free water surface CWs with

emergent macrophytes. This is an advantage since metals were phytostabilized within the treatment system. Sediment sorption is considered the main long-term contaminant accumulation mechanism (Machemer et al., 1993; Wood and Shelley, 1999; Maine et al., 2009). However, the sediment could release the contaminants if the environmental conditions changed (Boström et al., 1985). In order to determine the perdurability of the contaminant retention in the sediment of both CWs, a fractionation of sediment was carried out to assess which compounds had retained metals in the sediment. Table 5 shows Cr, Ni and Zn fractionation in sediments at the end of the studied period in the CW1 and CW2. The extraction sequence can be seen as an inverse scale of relative availability of metals, being the exchangeable fraction the most labile and bioavailable, showing in all cases a concentration significantly lower than the other concentrations. In both CWs, Cr and Ni are mainly bound to Fe-Mn oxides and organic matter. Fe-Mn oxides fraction represents sinks of metals. Organic matter has the ability to form complexes and adsorb cations due to the presence of negatively charged groups (Laveuf and Cornu, 2009). The low Ni concentration in the different fractions of the CW2 sediment confirmed the low concentrations of this metal in the wastewater, indicating that there was no accumulation in sediment. Zn was bound to the Fe-Mn oxides and carbonates fraction. The calcium carbonate precipitation is thermodynamically favored and Zn can co-precipitate with it. These fractions can be considered steady under the chemical and environmental conditions of the wetland. Since the conditions for metal removal are largely provided by the wastewaters (high pH,

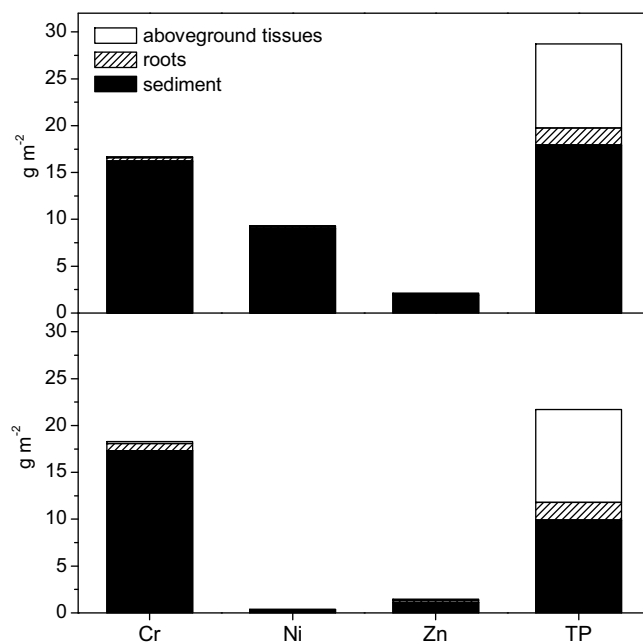


Fig. 4. Accumulation of Cr, Ni, Zn and P (g m^{-2}) in sediment and plant tissues in the inlet area of the CW1 (upper) and the CW2 (lower).

Table 5
Cr, Ni and Zn concentrations (mg g^{-1}) of the different sediment fractions of CW1 and CW2 at the end of the study.

Fraction	Exchangeable	Bound to Carbonates	Bound to Fe–Mn oxides	Bound to OM	Residual
Cr					
WC1	0.001	0.064	0.930	0.205	0.302
WC2	0.002	0.004	0.812	0.080	0.008
Ni					
WC1	0.007	0.134	0.609	0.083	0.233
WC2	0.001	0.002	0.008	0.002	0.004
Zn					
WC1	0.001	0.074	0.054	0.004	0.013
WC2	0.001	0.038	0.028	0.004	0.001

alkalinity, Fe, Ca and ionic concentrations), the sediment may be expected to continue retaining metals as far as the composition of the influent remains the same.

4. Conclusions

- Removal efficiencies were satisfactory in both CWs allowing effluents to comply with regulations.
- *T. domingensis* is a suitable species for the treatment of the studied metallurgical wastewaters.
- Metals and P were efficiently removed in both CWs, being accumulated in the inlet zone. Metals were retained mainly in sediment, while P was retained in sediment and plants.
- In FWS wetlands, metal concentration in macrophyte tissues is related mainly to influent concentration, while metal concentration in sediment depends not only on influent concentration but also on time of operation of the CWs.
- Metals were bound to sediment fractions that would not release them to water while the chemical and environmental conditions of the systems remained the same.
- The CWs faced with accidental events were capable of recovering their performance, demonstrating their robustness.
- In both CWs, the conditions for metal removal are largely provided by the inlet influent chemical compositions (high pH, alkalinity, Fe, Ca and ionic concentrations). In consequence, the inlet area sediments will continue retaining metals as far as the influent compositions remain the same.
- CWs outlet area sediments have not begun to accumulate contaminants, suggesting wetland potential for long term performance.

Acknowledgements

The authors thank *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET)*, *Universidad Nacional del Litoral (UNL)-CAI+D Project* and *Agencia de Promoción Científica y Tecnológica* for providing funds for this work.

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