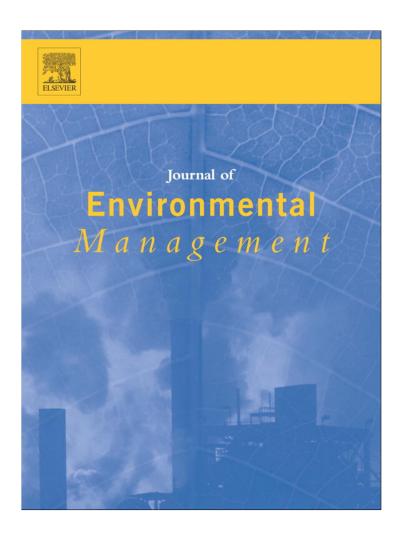
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## Sustainability of a constructed wetland faced with a depredation event

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### ABSTRACT

A free water surface constructed wetland (CW) designed for effluent treatment was dominated by the emergent macrophyte Typha domingensis reaching a cover of roughly 80% for 5 years. Highly efficient metal and nutrient removal was reported during this period. In June 2009, a population of approximately 30 capybaras (Hydrochoerus hydrochaeris) caused the complete depredation of the aerial parts of macrophytes. However, plant roots and rhizomes were not damaged. After depredation stopped, T. domingensis showed a luxuriant growth, reaching a cover of 60% in 30 days. The objective of this work was to evaluate the sustainability of the CW subjected to an extreme event. Removal efficiency of the system was compared during normal operation, during the depredation event and over the subsequent recovery period. The CW efficiently retained contaminants during all the periods studied. However, the best efficiencies were registered during the normal operation period. There were no significant differences between the performances of the CW over the last two periods, except for BOD. The mean removal percentages during normal operation/depredation event/recovery period, were: 84.9/73.2/74.7% Cr; 66.7/ 48.0/51.2% Ni; 97.2/91.0/89.4% Fe; 50.0/46.8/49.5% Zn; 81.0/84.0/80.4% NO3; 98.4/93.4/84.1% NO2; 73.9/ 28.2/53.2% BOD and 75.4/40.9/44.6% COD. SRP and TP presented low removal efficiencies. Despite the anoxic conditions, contaminants were not released from sediment, accumulating in fractions that proved to be stable faced with changes in the operating conditions of the CW. T. domingensis showed an excellent growth response, consequently the period without aerial parts lasted a few months and the CW could recover its normal operation. Plants continued retaining contaminants in their roots and the sediment increased its retention capacity, balancing the operating capacity of the system. This was probably due to the fact that the CW had reached its maturity, with a complete root-rhizome development. These results demonstrated that faced with an incidental problem, this mature CW was capable of maintaining its efficiency and recovering its vegetation, demonstrating the robustness of these treatment systems.

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### 1. Introduction

CWs have been used for the treatment of industrial effluents, urban and agricultural stormwaters, mine waters, etc. (Hammer, 1989; Kadlec and Knight, 1996; Kadlec and Wallace, 2009; Maine et al., 2007, 2009; Moshiri, 1993; Song et al., 2006; Vymazal et al., 1998; Vymazal, 2011).

Sediment is the main responsible for contaminant removal from waters in wetlands (Di Luca et al., 2011a,b; Golterman, 1995; Machemer et al., 1993; Maine et al., 2009; Wood and Shelley, 1999). However, sediment can release or retain contaminants according to environmental conditions (Boström et al., 1985). The availability of

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metal and P retained in sediment depends on redox conditions, pH (Boström et al., 1985; Gambrell et al., 1991; Lefroy et al., 1993; Maine et al., 1992), organic matter content (Wood and Shelley, 1999), etc. Contaminant dynamics also depends on the chemical forms in which they are retained by sediment, which are studied by sequential extraction schemes.

In addition to the importance of sediment, macrophytes are key components of natural and constructed wetlands. Emergent macrophytes are able not only to take up contaminants in their tissues but also to influence the biogeochemical cycles of the sediment, due to their capacity to transport oxygen to the rhizosphere influencing the sediment redox conditions (Barko et al., 1991; Sorrel and Boon, 1992). Many studies comparing planted and unplanted systems were carried out, but they often led to conflicting results regarding the importance of plants (Calheiros et al., 2007; Lee and Scholz, 2007; Vymazal, 2011).

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Wetland plants are exposed to animal depredation. A wide variety of mammals reside in or visit treatment wetlands (Kadlec and Wallace, 2009). Small rodents, most of which are herbivorous species that graze on plants, are commonly found in CWs. However, it is larger rodents, as muskrats, that have been proven problematic in many treatment wetlands. Muskrats (Ondatra zibethica) cut large number of emergent herbaceous plants (Latchum, 1996). This grazing can change treatment wetland areas from densely vegetated to a patchwork of open and emergent areas (Kadlec et al., 2007). Nutrias (Myocastor coypus) cause problems as muskrats do. However, no designed research studies have been conducted to quantify the effects of rodent depredation on wetland performance (Kadlec and Wallace, 2009). In this paper, the removal efficiency of a free water surface CW planted with Typha domingensis was compared considering normal operation, an herbivorous depredation event and the subsequent recovery period. In the CW studied, *T. domingensis* became the dominant species covering 80% (55–95%) of the wetland surface for approximately 5 years. Highly efficient metal and nutrient removal was reported during this period (Maine et al., 2009). In June 2009 a population of approximately 30 capybaras (Hydrochoerus hydrochaeris) caused the complete depredation of the aerial part of the macrophytes. Capybaras are pig-sized tailless South American amphibious rodents, which are the largest rodent known in the world, with a mean weight of 80 kg. The wetland looked like a scarce vegetated pond (5% plant cover). However, the roots and rhizomes of *T. domingensis* were not damaged. In November 2009, the wetland was fenced with wire to stop animals from approaching. Subsequently, T. domingensis showed a luxuriant growth that was also enhanced by the growth season, reaching a cover of 80% after 30 days. The objective of this work was to compare wetland efficiency in contaminant removal considering the normal operation period (Feb. 2005-May 2009), the depredation period with plants without aboveground parts (Jun. 2009-Nov. 2009) and the subsequent recovery period (Dec. 2009-Sep. 2010).

### 1.1. Study site

A free-water surface wetland was constructed at a metallurgic plant located in Santo Tomé, Santa Fe, Argentina (S 31° 40′; W 60° 47′). The wetland covers an area of 2000 m² with a water residence time ranging was 7 days. Mean wastewater discharge was 100 m³ d $^{-1}$ . Further details were provided by Maine et al. (2007). Emergent and floating, locally abundant macrophyte species were transplanted into the wetland at the beginning of the operation period, in 2003, but only *T. domingensis* persisted. *T. domingensis* aerial parts have been harvested annually to ensure an optimal growth after the winter season. Industrial wastewater and sewage are treated together (25 m³ d $^{-1}$  of sewage + 75 m³ d $^{-1}$  of industrial wastewater), to improve the ability of macrophytes to take up heavy metals from wastewater (Hadad et al., 2006, 2007).

### 2. Materials and methods

The study was divided in three periods: 1) normal operation (Feb. 2005—May 2009), 2) depredation period without aerial parts of *T. domingensis* (Jun. 2009—Nov. 2009) and 3) recovery (Dic. 2009—Sep. 2010).

### 2.1. Water

Monthly samplings of the influent and effluent were performed. Samples were collected in triplicate. Conductivity was measured with an YSI 33 conductimeter, dissolved oxygen (DO) with a Horiba OM-14 portable meter and pH with an Orion pH-meter. Water

samples were filtered through Millipore membrane filters (0.45  $\mu$ m) for soluble reactive P (SRP) and N determinations. Chemical analyses were performed following APHA (1998); NO<sub>2</sub>was determined by coupling diazotation followed by a colorimetric technique. NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> 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). Total phosphorous (TP) was determined after sulfuric acid-nitric acid digestion followed by SRP determination in the digested samples. Ca<sup>2+</sup> was determined by EDTA titration. Alkalinity (carbonate and bicarbonate) was measured by HCl titration. Cl<sup>-</sup> was determined by the argentometric method. SO<sub>4</sub><sup>2</sup> 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 the sample concentration, Perkin Elmer AAnalyst 200).

### 2.2. Sediment

Sediment samples were collected monthly using a 3-cm diameter PVC corer and stored at 4 °C until analysis. Redox potential (Eh) and pH of the bulk sediment layers were measured in situ with an Orion pH/mV-meter. Organic matter (OM) was determined by weight loss on ignition at 550 °C for 3 h. Each sediment sample was analyzed according to the sequential extraction proposed by Golterman (1996) for P fractionation and by Tessier et al. (1979) for metal fractionation. Sediment samples were oven-dried at 45 °C until constant weight was reached and ground using a mortar and pestle. Subsequently, they were sieved through a 53 µm sieve prior to sequential extraction of metals. For TP or metal analyses, samples were digested with a HClO<sub>4</sub>:HNO<sub>3</sub>:HCl (7:5:2) mixture. These digests and the extracts obtained from the sequential extraction procedure were analyzed for Cr, Ni and Zn and by atomic absorption spectrometry (Perkin Elmer, AAnalyst 200) using an air-acetylene flame. In the case of TP, SRP was determined in the extracts and in the digested samples (Murphy and Riley, 1962).

### 2.3. Macrophytes

Macrophytes were sampled monthly. Four replicates were taken randomly at the inlet in each sampling. The macrophytes were then separated between above (stems and leaves) and belowground parts (roots and rhizomes). TP, Cr, Ni and Zn in above and belowground parts were determined in the same way as in the sediment samples. Plant cover was estimated measuring the area occupied by the aerial (visible) parts in the wetland.

### 2.4. Statistical analysis

ANOVA analysis was performed to evaluate the difference in contaminant removal efficiencies among the three periods studied. ANOVA was also carried out to determine if there were significant differences among the periods for contaminant concentrations in plant tissues (leaves and roots) and sediment. Duncan's test was used to differentiate means where appropriate. A level of p < 0.05 was used in all comparisons.

### 2.5. QA/QC

All glassware was pre-cleaned and washed with 2 M  $HNO_3$  prior to each experiment. All reagents were of analytical grade. All solutions were prepared with Milli-Q water. Certified standard solutions were used. Replicate analyses (performed at least ten times)

of the samples showed a precision of typically less than 8% (coefficient of variation). The detection limits were 30, 20, 3 and 5 µgg <sup>-1</sup> for Gr. Ni, Zn and P, respectively. The accuracy of the sequential extraction procedure was also evaluated comparing the sum of the concentrations determined for five fractions with total concentration data.

# 3. Results and discussion

T. domingensis cover ranged from 55% in late winter and early spring to 95% in summer from February 2005 to May 2009 (Fig. 1). As it can be seen, macrophyte cover presented seasonal variations, which did not affect the removal efficiency of the system (Maine et al., 2009). However, in June 2009 a population of approximately 30 capybaras caused the complete depredation of the aerial part of macrophytes. The wetland looked like a plant-free pond but the roots and rhizomes of T. domingensis were not damaged. In November 2009, the wetland was fenced with wire to stop the animals from approaching, which allowed the recovery of the vegetation. Subsequently, T. domingensis showed a luxuriant growth that was also enhanced by the growth season, reaching a cover of 60% after 30 days and 80% after 60 days.

# 3.1. Contaminant removal from water

Table 1 shows the mean concentration of the measured parameters and estimated removal efficiencies. In the three periods, removal efficiencies were satisfactory. Notwithstanding, the significantly highest efficiencies were registered during the normal operation period. Removal efficiencies did not present significant differences between the two last periods, except in the case of BOD and COD, which showed lower removal efficiently removed in the different periods. SRP, TP and NH<sub>4</sub><sup>+</sup> were not efficiently removed in the different periods, probably due to the fact that the DO concentration was low at the inlet and at the outlet, close to exhaustion in roughly half of the samplings. Ca<sup>2+</sup> and alkalinity decreased, suggesting calcium carbonate precipitation. NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> removal was likely to be caused by diffusion from the water column toward the anoxic sediments. Denitrification seemed to cause the main nitrate loss. SO<sub>4</sub><sup>2-</sup> and Fe reductions at the outlet suggest

**Fig. 1.** *T. domingensis* cover in the wetland throughout the periods studied (normal operation, depredation event, and recovery).

Apriloto Apr

Mar Jun Cover (%)

50

20

30

10

60

100

80 90

70

Table 1

Inlet and outlet mean concentrations, ranges (Min.—Max.), and estimated removal efficiencies in the periods studied (normal operation, depredation event, and recovery). Concentrations are expressed in mg L<sup>-1</sup>.

Period Parameter	Normal operation			Depredation event			Recovery		
	Inlet	Outlet	Rem. (%)	Inlet	Outlet	Rem. (%)	Inlet	Outlet	Rem. (%)
Temperature (°C)	20.5 (10.2-29.6)	18.1 (6.6-27.5)	_	21.3 (19.5-28.9)	18.7 (14.8-29.2)	_	19.5 (14-23.9)	17.6 (12.5-23)	_
DO (mg L <sup>-1</sup> )	2.21 (0-9.5)	1.34 (0-7.5)	_	2.93 (0.2-5.32)	1.79 (0.1-4.53)	_	3.40 (0-6.2)	2.12 (0.3-5.2)	_
Conductivity (umho cm <sup>-1</sup> )	4653.3 (1500-8500)	2413.9 (1400-5500)	-	6450 (4800-10,000)	2242.5 (1950-2570)	-	5113.3 (3890-7700)	1955.6 (1400-2500)	-
pH	10.2 (6.5-12.6)	8.05 (7.1-9.1)	_	10.9 (10.5-11.4)	8 (7.9-8.3)	_	10.8 (10.4-11.5)	8.3 (7.9-9.3)	_
NO <sub>3</sub>	37.3 (3.3-153.7)	7.09 (0.3-45.5)	81.0	59.5 (33.5-103.6)	9.5 (5.7-16.7)	84.0	50.6 (15.4-98.2)	9.9 (3.6-24.2)	80.4
NO <sub>2</sub> -	2.612 (0.061-28)	0.041 (0.005-0.33)	98.4	1.183 (0.38-2.61)	0.078 (0.005-0.166)	93.4	2.221 (0.258-6.22)	0.352 (0.017-0.766)	84.1
NH <sub>4</sub> +	3.04 (0.16-15.0)	2.65 (0.265-10.6)	12.8	2.12 (0.65-4.5)	1.94 (0.146-3.31)	8.5	0.88 (0.154-2-67)	0.77 (0.05-2.14)	11.8
TP	0.435 (0.028-2.08)	0.333 (0.032-1.51)	23.4	0.514 (0.041-1.59)	0.379 (0.167-0.33)	20.4	0.396 (0.064-1.38)	0.309 (0.129-0.696)	22.0
SRP	0.074 (0.003-0.346)	0.065 (0.005-0.273)	12.1	0.104 (0.015-0.215)	0.093 (0.014-0.078)	10.6	0.030 (0.005-0.079)	0.026 (0.005-0.334)	13.3
SO <sub>4</sub> <sup>2-</sup>	1711.3 (248.4-3598.5)	765.9 (203.5-2238.3)	65.2	2380.1 (2447-6917)	736.5 (480.2-911.6)	54.0	1872.9 (991.4-2316.1)	626.4 (412.1-884.1)	66.5
Alkalinity	555.2 (71.2-1647.2)	292.9 (167.9-427.1)	47.2	327.7 (224.3-403.2)	263.2 (168.4-313.6)	19.7	353.2 (114.6-750.4)	224.1 (156.8-332.3)	36.5
Ca <sup>2+</sup>	187.8 (6.8-642)	76.3 (17.3-349.4)	65.3	252.1 (35.9-617.5)	93.2 (58.5-111.6)	63.4	136.1 (99.4-358.8)	47.5 (30.9-75.6)	65.1
Fe	8.833 (0.05-72.3)	0.249 (0.001-2.1)	97.2	1.051 (0.09-2.49)	0.095 (0.05-0.19)	91.0	0.824 (0.05-2.54)	0.087 (0.05-0.230)	89.4
Cr	0.053 (0.002-0.4)	0.008 (0.001-0.045)	84.9	0.041 (0.01-0.079)	0.011 (0.01-0.014)	73.2	0.092 (0.023-0.204)	0.014 (0.002-0.033)	84. 7
Ni	0.054 (0.004-0.748)	0.018 (0.003-0.049)	66.7	0.025 (0.01-0.047)	0.017 (0.01-0.039)	48.0	0.041 (0.022-0.070)	0.020 (0.015-0.050)	51.2
Zn	0.04 (0.01-0.146)	0.02 (0.003-0.09)	50.0	0.019 (0.01-0.039)	0.012 (0.01-0.033)	36.8	0.038 (0.004-0.101)	0.023 (0.004-0.082)	49.5
BOD	124.9 (6.7-405)	32.6 (3-297)	73.9	34.1 (9.6-78.6)	24.5 (5-56.9)	28.2	21.3 (9.8-30.9)	9.97 (3.0-20.1)	53.2
COD	322.7 (44.3-1238)	79.4 (7.5-470)	75.4	88.6 (15.7-158.6)	52.4 (10.5-78.4)	40.9	85 (27.9-154.0)	47.1 (13.9-72.9)	44.6

pyrite formation in the bottom sediment. Cr, Ni and Zn were efficiently retained.

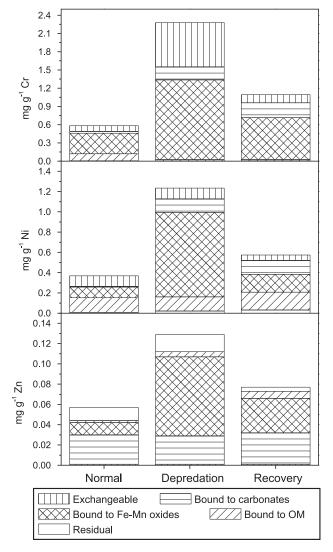
### 3.2. Sediment

In sediment, pH was alkaline and the Eh revealed anoxic conditions in the three periods studied (Table 2). During the depredation period, both pH and Eh values were significantly lower than the ones registered in the other periods. Emergent macrophytes are capable of altering local soil pH conditions through assimilation/ production of anions/cations through root exudates (Nye, 1981) and stabilizing and oxidizing bottom sediments due to their capacity to transport oxygen from roots into the rhizosphere (Barko et al., 1991; Brix and Schierup, 1990; Dunbabin et al., 1988; Jacob and Otte, 2003). Plant associated microbial processes can stimulate alkalinity-generating redox reactions such as ferric iron or sulfate reduction which can enhance metal retention (Vile and Wieder, 1993). However, organic material associated with plant growth, senescence and root exudates, directly affects microbial activity (Dunbabin and Bowmer, 1992), increases soil oxygen demand (Rovira, 1956), and can decrease soil pH (Roane et al., 1996), as it can be seen during the depredation period. Researchers have reported generally higher soil Eh in vegetated than in plant-free soil (Reina et al., 2006; Negrin et al., 2011). Changes in root oxygen diffusion or dying roots supply a source of energy for microbe respiration and thus intensify the reducing conditions (Armstrong et al., 1990). This can be observed in this study, where the measured Eh values were higher in the normal operation and recovery periods than in the depredation period. The organic matter content in sediment increased in the last two periods, probably due to plant material degradation.

Cr, Ni, Zn and TP concentrations in the outlet sediment did not present significant differences among the three periods studied (data not shown). These concentrations were significantly higher in the inlet than in the outlet sediment along the study, demonstrating that they were efficiently retained in the wetland.

At the inlet sediment, TP and metal concentrations presented the highest values during the depredation period when plant cover decreased, thereby maintaining the overall retention capacity of the system. In the recovery period, total metal concentrations decreased in the inlet sediment probably due to plant uptake. However, these concentrations were significantly higher than those measured in the normal operation period. TP concentrations decreased significantly during the recovery period, probably due to the high macrophyte productivity.

Metal partitioning in the bottom sediment of the outlet did no present significant differences among the three periods studied (data not shown). In the inlet sediment (Fig. 2), Cr was mainly associated with Fe—Mn oxides and, to a lesser extent, with the carbonate fractions. In the depredation period, a significant increase in Cr bound to Fe—Mn oxides was observed. Ni and Zn were accumulated mainly bound to carbonates in the normal operation period and mainly bound to Fe—Mn oxides in the depredation period, whereas they were found bound in both fractions, without significant differences, in the recovery period. This behavior shows that the system tended to recover its normal conditions.



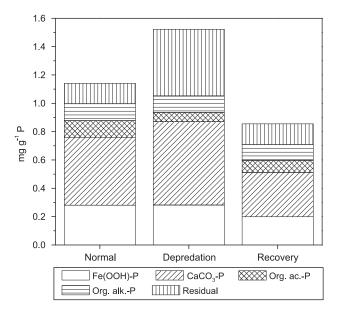
**Fig. 2.** Exchangeable, Bound to Carbonates, Bound to Fe—Mn oxides, Bound to OM and Residual fractions in the inlet area during the periods studied (normal operation, depredation event, and recovery).

In the case of P, in the inlet sediment, the  $CaCO_3$ —P fraction was significantly higher than the others in the three periods studied (Fig. 3). This could be explained by the high pH of this area and by the high  $Ca^{2+}$  and  $CO_3^{2-}$  loads in the effluent which led to P coprecipitation with  $CaCO_3$  (calcite saturation indices greater than 1). This P fraction showed a significant increase when the TP increased during a depredation period. The second important P-fraction was Fe(OOH)—P.

The four contaminants studied were accumulated mostly bound to Fe—Mn oxides in the inlet sediment during the depredation period. This fraction is pH and Eh sensitive, since the stability of  $Fe^{2+}$  and Fe (hydr)oxides primarily depends on a combination of Eh and pH of the sediment. A general thought is that under anoxic

**Table 2**Redox potential (mV), pH and OM (%) in the inlet and outlet sediment during the periods studied (normal operation, depredation event, and recovery).

	Eh (mV)			pН			OM (%)	OM (%)			
	Normal	Depredation	Recovery	Normal	Depredation	Recovery	Normal	Depredation	Recovery		
Inlet Outlet	-229.3 -336.5	-283.6 -387.0	-193.6 -285.9	9.23 9.24	8.04 7.95	8.25 7.98	5.1 5.4	6.1 8.0	6.8 6.2		



**Fig. 3.** Fe(OOH)–P, CaCO<sub>3</sub>–P, org acid-P, org alk-P, and Residual P fractions in the inlet area during the periods studied (normal operation, depredation event, and recovery).

conditions as those found during the three periods studied, and particularly during the depredation period, contaminants bound to Fe—Mn oxides were released. However, the nearly amorphous Fe(OH)<sub>3</sub> minerals (ferrihydrite) are reduced at a higher Eh for a given pH than it happens with crystalline minerals of FeOOH (goethite) or Fe<sub>2</sub>O<sub>3</sub> (hematite). Therefore, contaminants initially released due to the transformations of Fe were then re-adsorbed on amorphous or poorly crystalline Fe-oxides and mixed Fe(II)Fe(III)-hydroxy compounds (Gale et al., 1994; Reddy et al., 1999). It is also possible that occluded Fe<sup>3+</sup> covered with organic matter (mainly humic compounds) may be protected from reduction (Peng et al., 2007).

### 3.3. Plants

Throughout the study, metal concentrations in plants were higher in roots and rhizomes than in aerial parts, suggesting scarce translocation (Table 3). The toxic elements such as Cr, Ni, and Zn are taken quickly and retained in the root system (Hadad et al., 2007; Maine et al., 2004; Suñé et al., 2007). The binding of positively charged metal ions to the negative charges on the cell walls of roots or chelation to phytochelatins followed by accumulation in vacuoles has been reported to reduce the transport mechanisms of

metals to the aerial parts (Göthberg et al., 2004) thus increasing the tolerance of plants (Poschenrieder et al., 2006).

Metal concentrations increased in the belowground parts of *T. domingensis* during the depredation period and they remained constant or continued increasing in the recovery period. Taking into account the high macrophyte productivity, metal concentrations would be expected to decrease in roots during the recovery period. It can be proposed that plants may act as pumps sucking metals, "cleaning the sediment". The increase of concentrations in the belowground parts is in agreement with the decreasing concentrations in sediment during the recovery period.

Metal concentrations studied in the aerial parts did not show significant differences between the normal operation and the recovery periods. It can be proposed that the bioaccumulation of metals in the aerial parts is not a key factor in the retention mechanism. However, the aerial parts translocate oxygen to the roots and sediment, playing an important role in the retention mechanism.

Regarding P, the highest concentrations in belowground tissues were found in the recovery period, in agreement with the decreasing P concentration in sediment. This might happen because plants, faced with a scarcity of P, absorb this nutrient and translocate it to the leaves, whereas when there is a large availability of P, plants absorb it, translocate it to the leaves up to a certain concentration, and subsequently start to accumulate it in roots producing a "luxury consumption". This is probably a growth strategy for further biomass development. Macronutrients such as P are taken quickly by the roots and translocated to the aerial parts to carry out photosynthesis. In this case study, *T. domingensis* could probably survive without aerial parts because the depredation event lasted a short time.

These results demonstrated that faced with an incidental problem a mature CW planted with T. domingensis is capable of maintaining its efficiency and to recover its vegetation, demonstrating the robustness of the free surface constructed wetlands. This was probably because the CW had reached its maturity, with a complete root-rhizome development. The root-rhizome system of the emergent plant plays a key role in contaminant removal. Kadlec et al. (2000) proposed that a complete root-rhizome development for a newly CW may require 3-5 years and the CW performance improves with wetland maturity (Kadlec et al., 2000; Maine et al., 2009). Vymazal and Krópfelová (2005) reported that for Phragmites sp., three to four seasons are usually needed to reach maximum standing crop but in some systems it may take even longer. The CW studied has been dominated by T. domingensis for the last five years. Probably this treatment system could continue in efficient operation due to the fact that it has reached its maturity.

**Table 3**Contaminant concentrations in the above and belowground parts of *T. domingensis* during the periods studied (normal operation, depredation event, and recovery).

Period	Normal operation			Depredation event			Recovery		
Contaminant	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
P									
Aboveground	2.242	0.787	4.91	_	_	_	2.598	1.81	3.54
Belowground	1.839	0.66	4.58	1.498	1.04	1.86	2.466	1.81	4.3
Cr									
Aboveground	0.023	< 0.001	0.285	_	_	_	0.023	0.010	0.079
Belowground	0.265	0.015	1.97	0.520	0.215	1.27	0.795	0.401	1.63
Ni									
Aboveground	0.014	< 0.001	0.129	_	_	_	0.017	0.004	0.053
Belowground	0.199	0.005	1.14	0.525	0.217	1.32	0.527	0.202	1.06
Zn									
Aboveground	0.034	0.006	0.177	_	_	_	0.053	0.015	0.161
Belowground	0.090	0.022	0.319	0.096	0.062	0.323	0.109	0.068	0.307

### 4. Conclusions

Cr, Ni, Zn and P were efficiently retained in the CW during the three periods studied. This was probably because the CW had reached its maturity, with a complete root-rhizome development. Despite the anoxic conditions, contaminants were not released from sediment, accumulating in fractions which proved to be stable faced with changes under normal operating conditions for the CW. T. domingensis showed an excellent response regarding growth and propagation, consequently the period without aerial parts lasted a few months and the CW could resume its normal operation. Plants continued retaining contaminants in their roots and the sediment increased its retention capacity, balancing the operating capacity of the system. These results demonstrated that faced with an incidental problem, this mature CW was capable of maintaining its efficiency and recovering its vegetation, demonstrating the robustness of these treatment systems.

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### References

- APHA. 1998. Standard Methods for the Examination of Water and Wastewater. American Public Health Association/American Water Works Association/Water Environment Federation, New York, p. 1268.
- Armstrong, W., Armstrong, J., Beckett, P.M., 1990. Measurement and modelling of oxygen release from roots of Phragmites australis. In: Cooper, P.F., Findlater, B.C. (Eds.). Proceedings of the International Conference on the Use of Constructed Wetlands in Water Pollution Control, Cambridge, UK, 24 -8 September. Pergamon Press, Oxford, pp. 41–51.
  Barko, J.W., Gunnison, D., Carpenter, S.R., 1991. Sediment interactions with sub-
- mersed macrophyte growth and community dynamics. Aquat. Bot. 41, 41-65.
- Boström, B., Ahlgren, L., Bell, R., 1985. Internal nutrient loading in a eutrophic lake, reflected in seasonal variations of some sediment parameters. Verhandlungen IVI. 22, 3335-3339.
- Brix, H., Schierup, H.H., 1990. Soil oxygenation in constructed reed beds: the role of macrophyte and soil-atmosphere interface oxygen transport. In: Cooper, P., Findlater, B. (Eds.), Constructed Wetlands in Water Pollution Control. WRc Swindon, Wiltshire, UK, pp. 53–65. Calheiros, C.S.C., Rangel, A.O.S.S., Castro, P.M.L., 2007. Constructed wetland systems
- vegetated with different plants applied to the treatment of tannery wastewater. Water Res. 41 (8), 1790-1798.
- Luca, G.A., Maine, M.A., Mufarrege, M.M., Hadad, H.R., Sánchez, G.C., Bonetto, C.A., 2011a. Metal fractionation in the sediment of a constructed wetland for industrial wastewater treatment. Ecol. Eng. 37, 1267–1275.
- Di Luca, G.A., Mufarrege, M.M., Sánchez, G.C., Hadad, H.R., Maine, M.A., 2011b. P distribution in different sediment fraction of a constructed wetland. Water
- Sci. Technol. 63 (10), 2374–2380.

  Dunbabin, J., Pokorny, J., Bowmer, K., 1988. Rizhosphere oxidation by *Typha domi*ngensis Pers. in miniature artificial wetly filters for metal removal from wastewater. Aquat. Bot. 29, 303–317.
- Dunbabin, J., Bowmer, K., 1992. Potential use of constructed wetlands for treatment
- of industrial wastewaters containing metals. Sci. Tot. Environ. 111, 151–168. Gale, P.M., Reddy, K.R., Graetz, D.A., 1994. Phosphorus retention by wetland soils used for treated wastewater disposal. J. Environ. Qual. 23, 370-377.
- Gambrell, R., Wiesepape, J., Patrick Jr., W., Duff, M., 1991. The effects of pH, redox, and salinity on metal release from a contaminated sediment. Water Air Soil Pollut. 57-58, 359-367.
- Golterman, H.L., 1995. The labyrinth of nutrient cycles and buffers in wetlands: results based on research in the Camargue (Southern France). Hydrobiologia 315, 39-58.
- Golterman, H.L., 1996. Fractionation of sediment phosphate with chelating compounds: a simplification, and comparison with other methods. Hydrobiologia
- Göthberg, A., Greger, M., Holm, K., Bengtsson, B.E., 2004. Influence of nutrient levels on uptake and effects of mercury, cadmium and lead in water spinach. J. Environ. Qual. 33, 1247–1255.
- Hadad, H.R., Maine, M.A., Bonetto, C., 2006. Macrophyte growth in a pilot-scale constructed wetland for industrial wastewater treatment. Chemosphere 63 (10), 1744-1753.

- Hadad, H.R., Maine, M.A., Natale, G.S., Bonetto, C., 2007. The effect of nutrient addition on metal tolerance in Salvinia herzogii. Ecol. Eng. 31 (2), 122-131.
- Hammer, D.A., 1989. Constructed Wetlands for Wastewater Treatment. Lewis Publishers Inc., Chelsea, MI.
- Jacob, D., Otte, M., 2003. Conflicting processes in the wetland plant rhizosphere: metal retention or mobilization? Water Air Soil Pollut. 3, 91–104.
- Kadlec, R.H., Knight, R.L., 1996. Treatment Wetlands. Lewis Publishers Inc., Boca Raton, Florida.
- Kadlec, R.H., Knight, R.L., Vymazal, J., Brix, H., Cooper, P., Haberl, R., 2000. Constructed Wetlands for Pollution Control: Processes, Performance, Design and Operation. IWA Specialist Group on use of Macrophytes in Water Pollution Control. IWA Publishing, p. 156.
- Kadlec, R.H., Pries, J.H., Mustrad, H., 2007. Muskrats (Ondatra zibethicus) in treatment wetlands. Ecol. Eng. 29 (2), 143-153.
- Kadlec, R.H., Wallace, S.D., 2009. Treatment Wetlands, second ed. CRC Press, Boca Raton, Florida.
- Latchum, J.A., 1996. Ecological Engineering Factors of a Constructed Wastewater Wetland. University of Maryland, College Park, Maryland. (M.S. Thesis)
- Lee, B.H., Scholz, M., 2007. What is the role of *Phragmites australis* in experimental constructed wetland filters treating urban runoff? Ecol. Eng. 29, 87-95.
- Lefroy, R., Samsoir, S., Blair, G., 1993. The dynamics of sulfur, phosphorus and iron in flooded soils as affected by changes in Eh end pH. Aust. J. Soil Res. 32, 493-508.
- Machemer, S., Reynolds, J., Laudon, L., Wildeman, T., 1993. Balance of S in a constructed wetland built to treat acid mine drainage, Idaho Springs, Colorado, USA. Appl. Geochem. 8, 587-603.
- Maine, M.A., Leguizamon, M., Hammerly, J., Pizarro, M., 1992. Influence of the pH and redox potential on phosphorus activity in the Parana Medio system. Hydrobiologia 228, 83-90.
- Maine, M.A., Suñé, N., Lagger, S.C., 2004. Chromium bioaccumulation: comparison
- of the capacity of two floating aquatic macrophytes. Water Res. 38, 1494–1501. Maine, M.A., Suñé, N., Hadad, H.R., Sánchez, G., Bonetto, C., 2007. Removal efficiency of a constructed wetland for wastewater treatment according to vegetation dominance. Chemosphere 68, 1105-1113.
- Maine, M.A., Hadad, H.R., Sánchez, G., Caffaratti, S., Bonetto, C., 2009. Influence of vegetation on the removal of heavy metals and nutrients in a constructed wetland. J. Environ. Manage. 90, 355–363.
- Moshiri, G.A., 1993. Constructed Wetlands for Water Quality Improvement. CRC Press, Boca Raton, Florida.
- Murphy, J., Riley, J., 1962. A modified single solution method for determination of phosphate in natural waters. Anal. Chim. Acta 27, 31-36.
- Negrin, V.J., Spetter, C.V., Asteasuain, R.O., Perillo, G.M.E., Marcovecchio, J.E., 2011. Influence of flooding and vegetation on carbon, nitrogen, and phosphorus dynamics in the pore water of a Spartina alterniflora salt marsh. J. Environ. Sci. 23 (2), 212-221.
- Nye, P.H., 1981. Changes of pH across the rhizosphere induced by roots. Plant Soil 61, 7–26.
- Peng, J.F., Wang, B.Z., Song, S.H., 2007. Adsorption and release of phosphorus in the in the surface sediment of a wastewater stabilization pond. Ecol. Eng. 31, 92-97.
- Poschenrieder, C., Tolrá, R., Barceló, J., 2006. Can metal defend plants against biotic stress? Trends Plant Sci. 11 (6), 288–295.
- Reddy, K.R., Kadlec, R.H., Flaig, E., Gale, P.M., 1999. Phosphorus retention in streams and wetlands: a review. Crit. Rev. Environ. Sci. Technol. 29, 83-146.
- Reina, M., Espinar, J.L., Serrano, L., 2006. Sediment phosphate composition in relation to emergent macrophytes in the Doñana Marshes (SW Spain). Water Res. 40, 1185-1190.
- Roane, T.M., Pepper, I.L., Miller, R.M., 1996. Microbial remediation of metals. In: Crawford, R.L., Crawford, D.L. (Eds.), Bioremediation: Principles and Applications. Cambridge University Press, pp. 312-340.
- Rovira, A.D., 1956. Plant root excretions in relation to the rhizosphere effect: I. The
- nature of root exudate from oats and peas. Plant Soil 7 (2), 178–194.
  Song, Z., Zheng, Z., Li, J., Sun, X., Han, X., Wang, W., Xu, M., 2006. Seasonal and annual performance of a full-scale constructed wetland system for sewage treatment in China. Ecol. Eng. 26, 272-282.
- Sorrell, B.K., Boon, P.L., 1992. Biogeochemistry of billabong sediments. II seasonal variations in methane production. Freshwater Biol. 27, 435-445.
- Suñé, N., Maine, M.A., Sánchez, G., Caffaratti, S., 2007. Cadmium and chromium removal kinetics from solution by two aquatic macrophytes. Environ. Pollut. 145, 467-473.
- Tessier, A., Campbell, P., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51 (7), 844-851.
- Vile, M.A., Wieder, R.K., 1993. Alkalinity generation by Fe(III) reduction versus sulfate reduction in wetlands constructed for acid mine drainage treatment. Water Air Soil Pollut. 69, 425-441.
- Vymazal, J., 2011. Constructed wetlands for wastewater treatment: five decades of experience, Environ, Sci. Technol, 45, 61-69.
- Vymazal, J., Brix, H., Cooper, P.F., Green, M.B., Haberl, R., 1998. Constructed Wetlands for Wastewater Treatment in Europe. Backhuys Publishers, Leiden.
- Vymazal, J., Krópfelová, L., 2005. Growth of Phragmites australis and Phalaris arundinacea in constructed wetlands for wastewater treatment in the Czech Republic. Ecol. Eng. 25, 606-621.
- Wood, T., Shelley, M.A., 1999. Dynamic model of bioavailability of metals in constructed wetland sediments. Ecol. Eng. 12, 231-252.