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Removal and accumulation of Cu, Ni and Zn in horizontal subsurface flow constructed wetlands: Contribution of vegetation and filling medium

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ABSTRACT

This study investigated the accumulation and removal of Cu, Ni and Zn in two horizontal subsurface flow constructed wetlands for domestic wastewater treatment, which differ by shape, presence of macrophytes and water depth. Between March and December 2007, the three metals were measured in the influent and effluents of the two systems. Average percentage removal rates were extremely low for Cu (3% and 9% in the two beds) and higher for Zn and Ni (between 25 and 35%). Under higher Zn influent concentrations, it was found to be between 78–87%, which is in agreement with other literature data.

During the peak standing crop season (August), biomasses of the different parts of *Phragmites australis* (stems, leaves and flowers, roots and rhizomes) were analysed in terms of weight and heavy metal concentration in order to assess heavy metal distribution among the tissues. It was found that the plants contribute to total heavy metal removal to a lesser extent than the filling medium. Aboveground tissues remove 34% of Cu, 1.8% of Ni and 6.2% of Zn % and, once harvested, their disposal does not appear to pose a problem for the environment. If heavy metals are present at high concentrations in the horizontal subsurface flow bed influent, over time, their accumulation in the filling medium could necessitate special care in the bed's management to avoid release into the surrounding environment.

1. Introduction

Constructed wetlands with a horizontal subsurface flow (H-SSF) are commonly used for domestic wastewater treatment, but there are further applications for other types of wastewaters such as effluents from food processing, abattoirs, pulp and paper production, and textile industries as well as municipal solid wastes (MSW) landfill leachate. In general, H-SSF systems are extensively monitored for macropollutants, including BOD_5, COD, suspended solids, nitrogen and phosphorus compounds and bacteria (Kadlec and Knights, 1996; Vymazal et al., 1998; Sundaravadivel and Vigneswaran, 2001).

Fewer studies have looked at trace elements in H-SSF systems, although lately there has been a growing interest in evaluating such systems ability and reliability in removing micropollutants, particularly heavy metals (HMs), from domestic and industrial wastewaters (Scholz and Xu, 2002; Vymazal and Krasa, 2003; Ranieri, 2004), MSW landfill leachate (Peverly et al., 1995; Yalcuk and Ugurlu, 2009), and acid mine drainage (Mays and Edwards, 2001; Deng et al., 2004).

In recent years, some studies have investigated the behaviour of plants in the presence of HMs. Among them, Miretzky et al. (2004) and Hassan et al. (2007) examined the removal rates of some elements, Drost et al. (2007) investigated the toxicity of HMs on plants, Dunbabin and Bowmer (1992) analysed the use of these plants as biofilters for polluted waters, Cardwell et al. (2002) evaluated biomonitoring of metals, Deng et al. (2004) and Mishra et al. (2008) investigated HMs uptake by duckweed (*Lemna minor*), water hyacinth (*Eichoria crassipes*), Salix, cattail (*Typha latifolia*) and common reed (*Phragmites australis*).

The HM concentration ranges vary depending on the origin of the wastewaters. Table 1 shows the observed ranges of HMs concentrations in raw domestic and industrial wastewaters (mainly refinery, chemical and plastic factories), in different types of surface runoff (parking areas, roofs, roads), MSW landfill leachate, and acid mine drainage.

The main difficulty in treating wastewaters containing HMs is due to the fact that they cannot be *destroyed* or *degraded*. HMs can accumulate in binding sites within the filling medium or precipitate during their passage through the plant.

H-SSF beds are dynamic micro-systems in which many physical, chemical and biological mechanisms may occur simultaneously. These mechanisms are strictly correlated to filling medium conditions (*i.e.*: structure, chemical composition, biofilm and sediments characteristics), environmental conditions (mainly aerobic/anaerobic/anoxic conditions, temperature and pH), and operational conditions (mainly water chemical characteristics and flow rate) which may change over time.

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Table 1
Heavy metal concentration ranges observed in different kinds of wastewater. The interval for domestic wastewater refers to daily average values, for rain water refers to average values of runoff of water from different kinds of surfaces (parking lots, roads and roofs), for industrial wastewater and MSW landfill leachate refers to daily average values and for mine drainage refers to monthly average values.

Parameter	Domestic wastewater	Rain water	Industrial wastewater	Landfill leachate	Mine drainage
Cd, μg/L	0.10–6.12	0.09–19	620	0.5–140	10–50
Cr, μg/L	3–111	0.1–5.6	90–350	15–1600	1300
Cu, μg/L	25–556	2.2–452	400–1450	4–10000	150
Fe, μg/L	900–2417	3–9	270	100000–500000	30000–300000
Hg, μg/L	0.15–4.28	0.4–2	n.a.*	10–160	n.a.*
Mn, μg/L	80–200	n.a.*	n.a.*	400–3700	2000–134000
Ni, μg/L	5–98	0.7–8.2	520–2760	20–13000	70–2000
Pb, μg/L	4–165	0.4–190	1560	10–8450	2–6
Zn, μg/L	40–770	6–1991	2000–10000	260–120000	10–7100

*n.a. = not available.
The ranges are based on: Ehrig, 1989; Mulamoottil et al., 1999; Gillespie et al., 2000; Mays and Edwards, 2001; Kjeldsen et al., 2002; Batty and Younger, 2004; Bertanza and Papiri, 2006; Rule et al., 2006; Lesage et al., 2007; Abe et al., 2008; Mishra et al., 2008; Khan et al., 2009; Kropfelova et al., 2009; and Yalcuk and Ugurlu, 2009.

HMs removal mechanisms in H-SSF systems are complex and include different pathways: (i) binding to sediments and soils (through sedimentation, flocculation, adsorption, cation and ion-exchange, complexation, oxidation and reduction); (ii) precipitation and co-precipitation as insoluble salts and (iii) plant uptake and, to a lesser extent, microbial metabolism (Kadlec and Knights, 1996; Deng et al., 2004; Kosopolov et al., 2004; Ujang et al., 2005).

HMs accumulation in *soil and sediments* is quite variable: fine-textured sediments containing an appreciable amount of organic matter tend to accumulate metals (Gambrell, 1994), whereas coarse-textured materials are generally not contaminated due to their low affinity for metals (Deng et al., 2004; Lesage et al., 2007). The existence of aerobic and anaerobic microzones within the medium of the horizontal beds causes a complex shift in the equilibrium of the oxi-reduction reactions in which HMs take part. In fact, in anaerobic conditions, they tend to precipitate as insoluble salts (mainly sulphides and oxyhydroxides), whereas in aerobic ones they tend to be released into the water due to the formation of sulphates (Gambrell, 1994; Kropfelova et al., 2009).

HMs accumulate *in plants* through the following stages: mobilization and uptake from the soil, compartmentalization and sequestration within the root, efficiency of xylem loading and transport, distribution between metal sinks in the aerial parts and sequestration and storage in leaf cells (Clemens et al., 2002). Plant species, growth stage of the plants, pH and HMs concentration in the water all affect the accumulation mechanisms (Jackson et al., 1993; Deng et al., 2004; Mishra et al., 2008).

Once in the leaf tissue, contaminants may be released back into the environment, either directly by excretion from the leaves (Burke et al., 2000; Batty and Younger, 2004; Weis et al., 2004) or indirectly when leaves become detritus, thereby raising metal bioavailability in the soil (Windom et al., 1976). Periodic harvestings of the aboveground (ABG) parts of the plants can reduce the HMs presence in the site.

This paper investigates the removal of three HMs (Cu, Ni and Zn) in two different H-SSF pilot plants: one vegetated with *P. australis*, the other only by spontaneous plants and grass on turf. These trace elements were selected because they may be found in wastewaters, often at high concentrations, (see Table 1). If a wastewater treatment sequence includes a H-SSF constructed wetland, HMs retention and accumulation within the filling medium of the bed could result in a potential contamination of the site. In some countries, such as Italy, the Netherlands and Norway, specific regulations set threshold concentrations for many micropollutants, including HMs, which once reached, mandate specific studies or risk analyses and identification of remediation actions.

An experimental campaign was carried out in order to evaluate (i) removal and accumulation rates of the three trace elements in the two beds, (ii) HMs distribution among the tissues of *P. australis*, after one year of working life of the bed, (iii) environmental risk for *P. australis* and for the filling medium due to HMs accumulation in the macrophytes and the substratum during the bed lifetime in case the feed is a (typical) secondary domestic wastewater or a stream with a high HM content.

2. Materials and methods

2.1. Pilot plants

This study took place at the experimental station located within the grounds of the municipal wastewater treatment plant (WWTP) for the town of Ferrara, Northern Italy (44°83'N and 11°62'E). Two H-SSF beds, which differ in shape, water depth, vegetation and hydraulic retention time, were investigated from March to December 2007. Their main characteristics are reported in Table 2. Fig. 1 shows the layout of the pilot plant (not to scale). Meteorological conditions during the investigation period were: outside temperature ranging between −5 and 38 °C, with an average of 17 °C, maximum solar radiation ranging between 200 and 1200 W m^{-2}. Total precipitation for the period March–December 2007 was 600 mm. Average annual precipitation for the period 2003–2008 was 720 mm $year^{-1}$.

Bed 2 was planted with *P. australis* in June 2006, and so the plants were well developed (1.5–2 m high) by the time of the study, with their roots penetrating to the bottom of the gravel filter. Removal of dead plant material was not necessary during the observation period. In the other cell, spontaneous vegetation and grass grew luxuriantly,

Table 2
Main geometrical, physical and design characteristics of the investigated H-SSF constructed wetlands together with treatment performance of the two systems based on COD, BOD_5 and SS average concentrations found in the influent and in the two beds' effluents during the whole observation period.

Parameter	Bed 1	Bed 2
Length L, m	28	12
Width W, m	1	2.5
Aspect ratio, L:W	28:1	12:2.5 = 4.8
Water depth, m	1.2	0.6
Filling material, mm	Gravel, 8–10	Gravel, 8–10
Porosity, %	33	33
Plants	Spontaneous plants and grass on turf	*Phragmites australis*
Total volume, m^3	33.6	18
Gravel volume, m^3	22.5	12.6
Flow rate, m^3 day^{-1}	8	8
Design p.e.*	53	50
Treatment performance (in/out)		
COD, mg L^{-1}	45/11	45/13
BOD_5, mg L^{-1}	18/3	18/7
SS, mg L^{-1}	25/4	25/6

* A *per capita* water requirement of 250 L $p.e.^{-1}$ day^{-1} is assumed.