

IRON AND MANGANESE IN SEDIMENTS OF CONSTRUCTED WETLANDS WITH HORIZONTAL SUBSURFACE FLOW TREATING MUNICIPAL SEWAGE

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ABSTRACT

In 2008, concentrations of iron and manganese in the sediments of seven constructed wetlands with horizontal subsurface flow in the Czech Republic were evaluated. The surveyed constructed wetlands varied in the length of operation between two and sixteen years at the time sampling. In each constructed wetland three samples of sediment were taken in the inflow, middle and outflow zones to the depth of 0.6 m. The sample was divided into top (0–20 cm) and bottom (20–60 cm) sections, resulting in a total number of 18 samples in each system. In each sample the amount of sediment on dry mass basis was evaluated and concentrations of Fe and Mn in the sediment were determined using ICP–MS. The results indicated that the concentrations of manganese were substantially higher in the new systems which have been in operation only for two years as compared to other systems which have been in operation between five and sixteen years. Concentrations of iron were lower in systems which have been in operation for more than eight years. The results also revealed that the concentration of sediments increases with the length of operation. As a result, accumulation of iron and manganese increases with the length of operation.

KEYWORDS

Constructed wetlands, iron, manganese, sediment, wastewater

INTRODUCTION

Iron and manganese are common constituents in municipal wastewaters. Both elements are usually present in sewage in concentrations which do not represent any environmental risks. However, chemistry of both elements is very important for other wastewater constituents such as phosphorus and heavy metals. The primary sorption mechanism for phosphorus in wetlands is thought to be ligand exchange, by replacement of surface hydroxyls on soil Al and Fe oxyhydroxides (Schwertmann and Taylor, 1989). Hydrous Fe and Mn oxides sorb or co-precipitate trace metals under oxidizing conditions while these metals could be released after Fe/Mn hydrous oxides reduction under reducing conditions. Under reducing conditions soluble Mn and Fe compounds may form insoluble sulfides (Kosolapov et al., 2004). Also, iron and manganese compounds serve as important electron acceptors during organic matter decomposition when dissolved oxygen and nitrate have been depleted (Reddy et al., 1986).

The objective of this study was to evaluate the amount of sediments and the concentration of iron and manganese in the sediments of constructed wetlands (CWs) with horizontal subsurface flow with different length of operation.

MATERIALS AND METHODS

Seven constructed wetlands with horizontal subsurface flow (HF CWs) treating municipal sewage with time of operation varying between 2 and 16 years (Table 1) were sampled in 2008. In each constructed wetland samples were taken in the inflow, middle and outflow zones (3 samples in each zone). Gravel or crushed rock samples were taken using the reinforced stainless steel soil sampler (so called "Russian corer") which was driven into the filtration substrate to a depth of 60 cm. Samples were divided into surface (0–20 cm) and bottom (20–60 cm) sections in order to evaluate vertical distribution of sediments. In the laboratory, samples were cleaned from roots and freeze-dried under low pressure and temperature. Dried sediment material was weighed, homogenized and passed through a 0.5 mesh sieve. After drying both sediment and filtration material volume were determined in order to calculate the volume ratio between sediment and filtration material. 500 mg of the dry sediment was digested in reverted (Löfelft) aqua-regia (4.5 ml HNO₃ and 1.5 ml HCl) under high pressure and temperature in microwave apparatus (MARS-5, CEM, USA) according to the modified U.S. EPA method 3052 (U.S. EPA, 1995). After digestion, the sample was filtered in order to obtain a clear sample. Iron and manganese were analyzed by ICP-MS (PQ-ExCell, VG-Thermo Elemental, Winsford, Cheshire, UK) according to U.S. EPA method 200.8 (U.S. EPA, 1994).

Table 1. Length of operation, filtration material and vegetation of constructed wetlands included in the survey. *P. arundinacea* = *Phalaris arundinacea*, *P. australis* = *Phragmites australis*

Locality	Length of operation	Filtration material	Vegetation
Čejkovice	2	rock (4–16 mm)	<i>P. arundinacea</i>
Libnič	2	rock (4–8 mm)	<i>P. arundinacea</i>
Břehov	5	gravel (4–8 mm)	<i>P. arundinacea</i> + <i>P. australis</i>
Slavošovice	7	gravel (4–32 mm)	<i>P. australis</i>
Mořina	8	rock (4–8 mm)	<i>P. arundinacea</i> + <i>P. australis</i>
Příbraz	9	gravel (4–8 mm)	<i>P. arundinacea</i> + <i>P. australis</i>
Spálené Poříčí	16	gravel (0–16 mm)	<i>P. australis</i>

RESULTS AND DISCUSSION

Results in Table 2 indicate that the manganese concentrations in the sediment decreased with the length of operation. A possible explanation for this phenomenon may come from the fact that older systems become usually more anaerobic and manganese is washed out from these systems. The increase in Mn concentration in the outflow has been reported for CWs Břehov, Slavošovice and Mořina (Kröpfelová et al., 2009) and similar results were reported from Belgium (Lesage et al., 2007a). The concentrations in the sediment are comparable with Mn concentration of 434 mg/kg reported by

Vymazal and Krása (2003) for another HF CWs in the Czech Republic. Also, Lesage et al. (2007a) reported similar Mn concentrations in a HF CWs in Flanders, Belgium (261–947 mg/kg). The concentrations are also comparable with values reported for natural wetland stands (Vymazal and Krása, 2003).

Iron concentrations in the sediment exhibited a similar trend but the highest concentrations were measured in CW Slavošovice. The high concentrations may be affected by the fact that the system is sealed by clay with high Fe content and the laboratory experiments indicated that under anaerobic conditions Fe is washed out (Kröpfelová et al., 2009). The higher values measured in our study were comparable with those reported by Lesage et al. (2007b) from Belgium (19 000 – 21 000 mg/kg) but lower than those reported by Lesage et al. (2007a) for another HF CW in Belgium (23 458 – 35 351 mg/kg). Vymazal (2003) reported much lower Fe concentration of 440 mg/kg for a HF CW in the Czech Republic. Also Eckhard et al. (1999) reported lower Fe concentrations of 500 – 2 700 mg/kg for the HF CW treating landfill leachate in New York. On the other hand, Zuiderwaard (1996) and Haberl and Perfler (1990) reported a comparable average Fe concentrations of 14 000 mg/kg for four HF CWs in the Czech Republic and 16 500 – 22 200 mg/kg for a HF CW in Austria, respectively.

Results in Table 3 indicate that the concentration of sediments in the filtration beds increases with the length of operation from less than 1% to about 11% on dry mass basis. As a result the amount of accumulated Mn and Fe increases with the length of operation despite decreasing concentration.

Table 2. Manganese and iron concentration in sediments of surveyed constructed wetlands. Different letters indicate significant difference at $\alpha = 0.05$ between the means.

	Mn (mg/kg)	Fe (mg/kg)
Čejkovice	507 ^a ± 161	18 028 ^a ± 1127
Libnič	625 ^a ± 303	17 585 ^a ± 3 917
Břehov	221 ^b ± 65	19 694 ^{ac} ± 5 312
Slavošovice	253 ^b ± 164	21 567 ^c ± 3 399
Mořina	213 ^b ± 35	11 773 ^b ± 1553
Příbraz	266 ^b ± 78	16 412 ^a ± 3 373
Spálené Poříčí	127 ^c ± 116	8 659 ^b ± 6 872

Table 3. Concentration of sediments in the filtration material and the amount of Mn and Fe accumulated in the filtration bed.

	Sediment (% DM)	Sediment (g /dm ³)	Mn (mg/dm ³)	Fe (mg/dm ³)
Čejkovice	0.66 ± 0.55	8.90 ± 7.37	4.5	160
Libnič	0.40 ± 0.18	6.40 ± 3.01	4.0	113
Břehov	3.32 ± 1.53	40.6 ± 10.7	9.0	799
Slavošovice	2.26 ± 1.57	34.8 ± 25.3	8.8	751
Mořina	3.05 ± 2.34	39.0 ± 26.5	8.3	459
Příbraz	3.22 ± 2.06	38.9 ± 14.2	10.4	638
Spálené Poříčí	10.6 ± 4.10	134 ± 34.7	17.0	1160

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