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Original Scientific Article

Removal of Mercury from Wastewater Using a Constructed Wetland

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Abstract. Removal of mercury from municipal wastewater using a constructed wetland was studied. Wastewater, wetland plant, and sediment samples were analyzed using an advanced mercury analyzer AMA-254. Average concentrations of total mercury in inflow and outflow water were 0.157 and 0.057 μg L^{-1}, respectively. Significant fraction of mercury (38.2 %) was removed from wastewater during pretreatment. Mercury concentrations in vegetation (*Phragmites australis*) varied in the range of 0.0099−0.0105 and 0.0079−0.0086 mg kg^{-1} for the above and belowground biomass, respectively. Total mercury concentrations in the constructed wetland sediments were 0.151 and 0.103 mg kg^{-1} at distances 1 and 10 m from the inflow zone. Mercury can be precipitated and deposited at the initial part of the wetland bed and thus removed from wastewater. The formation of volatile mercury species is another mechanism of its removal. On the other hand, assimilation of Hg in wetland plants does apparently not contribute to mercury removal from wastewater.

Keywords: environmental analytical chemistry, heavy metals, wastewater treatment, reed bed, atomic absorption spectrometry

INTRODUCTION

Wastewater treatment using constructed wetlands is an appealing method of water quality improvement suitable mainly for small villages.[1] Constructed wetland treatment systems reduce level of many contaminants (*e.g.*, organic compounds, suspended solids, nitrogen, phosphorus, and pathogens). This reduction occurs through diverse physical, chemical, and biological mechanisms.[2] Although wetlands are characterized by anaerobic and reducing properties that result from flooding of the soil, layers with oxidative properties due to the wetlands' aeration by vegetation roots also are present in many flooded systems. Steep redox-potential gradients that are extraordinarily important with respect to those processes taking place during wastewater treatment are found at the root-sediment interface.[3]

Mercury is one of the most toxic pollutants occurring in industrial, agricultural and municipal wastewater.[4] Burning of fossil fuels represents another important source of mercury pollution. This metal has the ability to accumulate mostly in fish[5] and some species of wild growing mushrooms.[6] Mercury contamination of wetland and aquatic ecosystems may have negative consequences for the resident species (*e.g.*, birds that feed within aquatic environments).[7]

Biosorption and bioaccumulation can be used to remove metals from wastewater. Diverse microorganisms are able to concentrate metals to levels that are substantially higher than those encountered in the environment.[8] Dissimilatory sulfate reduction and the subsequent precipitation of metal sulfides belong among the most important processes in removal of metals from wastewater.[9,10] Redox transformations also contribute to the metal disposal.[11] Fe^{II} and Mn^{II} may be oxidized in aerobic zones of a vegetation bed (aeration due to the plants) and precipitated as insoluble oxides and hydroxides if constructed wetlands are used to treat wastewater.[12,13] Other metal ions may be coprecipitated during this process.

The biomethylation of Hg with the production of volatile dimethylmercury is a well-known phenomenon[11] mediated by range of aerobic and anaerobic bacteria. The arising compound may be eliminated from the aquatic environment by evaporation. On the other hand, it exhibits a high toxicity since it is lipophilic and biologically active.[14] Formation of methylmercury (monomethylmercury cation and dimethylmercury)

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naturally appears to be a potential way of mercury removal in constructed wetlands. However, it may be accumulated by aquatic organisms and transferred to higher trophic levels as well.[15] Gustin *et al.*[16] concluded that hydraulic retention time and flow rates of water in a wetland system affected the efficiency of Hg removal since significant fraction of mercury was bound to the fine clay-sized particulate matter. They highlighted in their study the benefits of a constructed wetland used for wastewater treatment, such as removal of nutrients, suspended solids, and mercury. However, they accented the risk of highly toxic methylmercury production in wetland systems that had to be taken into account. Haarstad *et al.*[17] similarly pointed out that a wetland could serve as a methylmercury source. They estimated that methylmercury concentrations could reach 15 % of total mercury. They also specified the risk of the Hg accumulation in fish. Chavan *et al.*[18] characterized a small-scale constructed wetland as a system that behaved as a sink of methylmercury during the winter months and as a source of methylated mercury forms in summer.

While most of the marsh plant species should be similar in metal uptake patterns and in accumulation of metals primarily in roots, some species may redistribute a greater proportion of metals into aboveground tissues, especially to leaves. *Phragmites australis* sequesters more metals belowground than *e.g. Spartina alterniflora* that allocates higher metal amounts in leaves. Thus, the replacement of *Spartina alterniflora* by *Phragmites australis* would lead to a reduction in mercury bioavailability. This information is important for the use of wetlands for phytoremediation as well as for marsh restoration efforts. Furthermore, the excretion of metals by leaves is also greater for *Spartina alterniflora* than for *Phragmites australis* probably because of the presence of salt glands in the former species.[19] Correia *et al.*[20] observed that *Eichhornia Crassipes* had mechanisms of Hg retention in roots. Their results suggested this macrophyte promoted changes in the Hg cycle since it attracted most Hg present in water and reduced Hg volatilization. Zhang *et al.*[21] studied in detail distribution of heavy metals among sediments, a water body, and plants in Hengshuihu Wetland. The metal distributions among these compartments were significantly different; the highest amounts of heavy metals were detected in sediments while the lowest level in water. The distribution of Hg indicated that it entered the wetland mainly from the outside water bodies and the atmosphere. The concentration of heavy metals in plants decreased in order: root, leaf, and stem.

Mercury removal in a wetland treatment system was studied by King *et al.*[22] They observed the average total mercury concentration decrease of 50 % in a wetland planted with *Scirpus californicus*. Kröpfelová *et al.*[23] studied removal of trace elements in three horizontal sub-surface flow constructed wetlands in the Czech Republic. They found Hg removal efficiencies in the range of 29.4−47.4 %. These efficiencies were determined based on mercury concentrations in inflowing and outflowing water.

This article is a sequel to previous works concerning the operation of the Slavošovice constructed wetland.[3,12,23,24] Its goal is to examine in detail the fate of mercury in this wetland used for the treatment of municipal wastewater. Water samples were taken not only at the inflow and outflow; but moreover from the inflow zone and from three selected sampling sites in the vegetation bed. It enables a description of the gradual decrease in mercury concentration in the profile of the wastewater treatment plant and an assessment of the extent of individual processes participating in mercury removal (precipitation and deposition in the wetland bed, assimilation by plants). Therefore, concentrations of Hg in wetland plants (*Phragmites australis*; above and belowground biomass) and in sediments were also determined and mercury distribution into these compartments was studied. The study should comprehensively evaluate the possibilities of alternative wastewater treatment systems with respect to mercury removal.

EXPERIMENTAL

General

An advanced mercury analyzer AMA 254 (Altec, Prague, Czech Republic) was used to determine total mercury content both in liquid and solid samples. All samples were analyzed without previous mineralization by the cold vapor method. Wastewater samples were acidified with concentrated nitric acid (Analpure, Merck, Darmstadt, Germany) after the sampling. A stock standard solution of Hg^{II} (1000 mg L^{-1}, Analytika, Prague, Czech Republic) was used to validate the analytical method. Calibration standard solutions were prepared in deionized distilled water (Milli-Q Element System, Merck Millipore, Billerica, USA).

Study Site

The studied system was a constructed wetland with horizontal subsurface flow designed for treatment of municipal wastewater and located in the village of Slavošovice, 15 km east of České Budějovice (South Bohemia, Czech Republic, 48°57′40.814′′N, 14°39′31.017′′E). This wastewater treatment plant had begun operations in August 2001. The system consists of a storm overflow, pretreatment (screens, horizontal sand trap, and sedimentation basin), and two vegetated beds planted with common reed (*Phragmites australis* (CAV.), TRIN. ex. STEUDEL). Each reed bed is 17 m

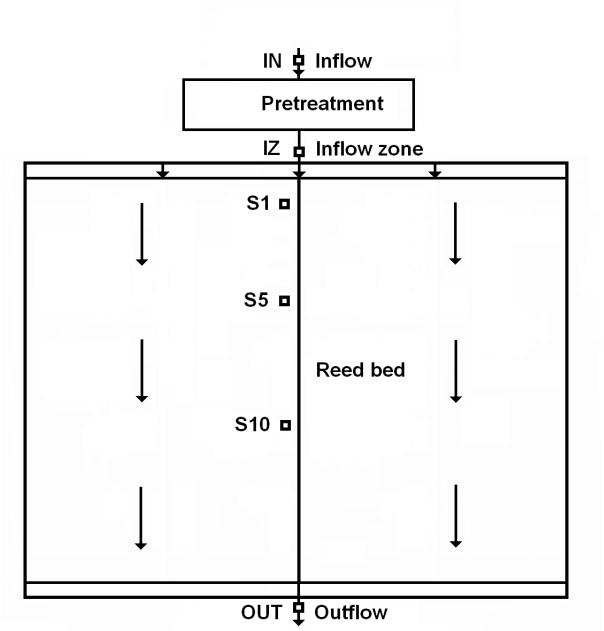

Figure 1. Schematic of the constructed wetland with individual sampling sites marked by squares. Wastewater is treated as it flows through the wetland bed after pretreatment (screens, horizontal sand trap, and sedimentation basin). IN - inflow; IZ - inflow zone; S1, S5, S10 - sampling sites at distances 1, 5, and 10 m from the inflow zone (central longitudinal transect); OUT - outflow.

long, 22 m wide, and 0.9 m deep. The constructed wetland substrate is gravel (1.0−2.0 cm). The wetland was designed for 150 person equivalents (PEs), with an area per PE of 5 m^2. The wetland actually serves just 120 PE. Schematic of the constructed wetland with individual sampling sites is shown in Figure 1; properties of treated water (inflow rates and temperatures measured for individual sampling days) are summarized in Table 1. Main characteristics of wastewater (pH, chemical and biochemical oxygen demand, total dissolved solids, total N, P, and S) are listed in Table 2.

Table 1. Properties of treated water monitored *in-situ*

Date	Inflow / L s^{-1}	T_1 / °C[(a)]	T_{10} / °C[(a)]
April 24	0.251	8.4	8.2
June 13	1.039	15.1	15.0
July 9	0.808	16.4	16.9
August 6	0.492	19.4	17.7
September 2	0.143	15.6	14.7
September 23	0.102	14.1	12.9
October 30	0.089	12.0	10.8

[(a)] T_1 and T_{10} - temperatures measured in the central longitudinal transect at distances 1 and 10 m from the inflow zone (IZ) at 10 cm depth.

Table 2. Main characteristics of treated wastewater

Parameter	Inflowing water	Outflowing water
pH	7.65 ± 0.92	6.68 ± 0.84
COD_{Cr}[(a)] (mg L^{-1})	322.0 ± 38.2	43.7 ± 5.1
BOD_5[(b)] (mg L^{-1})	170.0 ± 30.0	13.3 ± 2.1
Total N (mg L^{-1})	43.7 ± 19.3	16.9 ± 5.2
Total P (mg L^{-1})	3.79 ± 0.95	2.29 ± 0.51
Total S (mg L^{-1})	14.3 ± 5.6	3.0 ± 2.2
TDS[(c)] (mg L^{-1})	838.2 ± 276.6	480.1 ± 129.6

[(a)] COD_{Cr} - chemical oxygen demand.
[(b)] BOD_5 - biochemical oxygen demand.
[(c)] TDS - total dissolved solids.

Sampling and Sample Pretreatment

Wastewater was sampled at the inflow (IN), from the inflow zone (IZ), at the outflow (OUT), and from selected sampling sites along a central transect running the length of the wetland bed (Figure 1). Samples from the vegetated bed were taken at 40 cm depth. Individual sampling sites were designated at 1, 5, and 10 m from the inflow zone. Samples were not filtered before the analysis. All liquid samples were acidified with 1.0 mL of concentrated HNO_3 per 250 mL of a sample. They were analyzed as soon as possible (within two days) after the sampling. They were stored refrigerated.

Samples of sediments were always dried at laboratory temperature (at least for 10 days) and properly powdered and homogenized using a mortar. Then they were sieved (0.5 mm pore size) and prepared for the analysis. Samples of wetland plants (*Phragmites australis*; above and belowground parts) were dried at the laboratory temperature as well. Then they were ground and homogenized using a laboratory mill (VIPO, Partizánske, Slovak Republic).

Total Mercury Determination

Using a nickel weighing boat (the spectrometer accessory), 100 μL of water or 25 mg of a dried solid sample (weight measured using the analytical balance) were introduced to the mercury analyzer. The preset drying and decomposition times were 60 and 150 s, respectively. The characteristics of the analytical method were assessed prior to the analysis of real samples. Limits of detection (0.016 μg kg^{-1}) and quantification (0.052 μg kg^{-1}) were determined based on 3σ and 10σ criteria; sensitivity (0.002 kg μg^{-1}) was found as a slope of the calibration (correlation coefficient of 0.996). Accuracy (96.78 %) was determined using the Light sandy soil 7001 certified reference material (Analytika, Prague, Czech Republic). Precision (0.48 %) was expressed as repeatability.

RESULTS AND DISCUSSION

Mercury Determination in Treated Water

Samples were taken in the profile of the constructed wetland seven times in 2013 from spring to autumn (April 24, June 13, July 9, August 6, September 2, September 23, and October 30). They were taken at the inflow and outflow, from the inflow zone, and from sites in the wetland bed at distances of 1, 5, and 10 m from the inflow zone. Removal of total mercury is shown in Figure 2. Mercury concentrations at the inflow and outflow were 0.157 ± 0.045 and 0.057 ± 0.021 μg L^{-1}, respectively. They systematically decreased in the profile of the wetland. The average mercury removal efficiency was 63.7 %. This efficiency is comparable or even higher than reported by King *et al.*[22] and Kröpfelová *et al.*[23] who observed the decrease in mercury concentration using a wetland treatment system by approximately 50 %. On the other hand, Nelson *et al.*[25] observed the mercury removal efficiency in excess of 80 % for their treatment wetland.

A significant fraction (38.2 %) of mercury was already removed during pretreatment in the section of the wastewater treatment plant where no wetland vegetation grew. A possible mercury removal mechanism is precipitation (*e.g.*, as insoluble HgS) and sedimentation in the constructed wetland vegetation bed. It corresponds to higher Hg concentrations detected in sediments at the beginning of the wetland bed (1 m from the inflow zone) compared to sediment samples taken in distances 5 and 10 m form the inflow zone (see below). The pH values measured for treated wastewater were close to neutral (7.65 ± 0.92 for inflowing water, 7.09 ± 0.81 for water sampled in the wetland bed 1 m from the inflow zone, and 6.68 ± 0.84 for outflowing water; see Table 2). Treated water is slightly acidified as it flows through the vegetated bed. It can be due to the formation of acid products of the organic matter decomposition. Therefore, the increase in HgS solubility due to the formation of $[HgS_2]^{2-}$ complex is not probable. Furthermore, mercury may also be removed due to the formation of volatile Hg^0 or dimethylmercury as described by Haarstad *et al.*[17] Microbial methylation runs easily in the acidic environment.[26] However, Matilainen and Verta reported no effect of pH in the range of 4.9−6.9 on the methylation of Hg.[27] The horizontal subsurface flow constructed wetland was capable of removing mercury from treated water with the reasonably high efficiency.

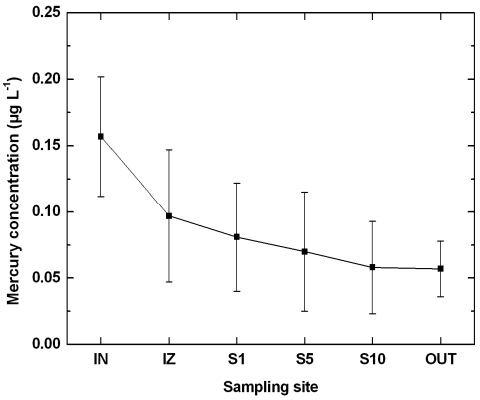

Figure 2. Mercury removal from treated water in the profile of the constructed wetland.

Mercury Determination in Wetland Plants

Total mercury concentrations were determined in dried wetland plant samples (*Phragmites australis*, both the above and belowground biomass) taken from the Slavošovice constructed wetland. Hg concentrations in samples taken from the wetland bed (1 m from the inflow zone) were 0.0105 ± 0.0027 and 0.0081 ± 0.0026 mg kg^{-1} for the above and belowground biomass, respectively; Hg concentrations in samples taken from other sampling sites were almost the same. The results are summarized in Table 3. There is no correlation with the decrease of Hg concentration in water in the profile of the wetland. There is no obvious evidence of mercury assimilation by wetland plants as a mechanism contributing to the Hg removal in the constructed wetland (*cf.* 38.2 % of Hg removed during pretreatment in the absence of wetland plants). It is in contrast to conclusions presented by Weis and Weis.[19] No influence of retention time on assimilation of Hg by *Phragmites australis* was observed during the present study. Previous research revealed that retention time during the vegetative period was significantly longer (14.0 days) than during the non-vegetative period of the year (8.1 days) due to evapotranspiration in the reed stand.[28] However, no trend in Hg assimilation and Hg concentrations measured for wetland plant samples was registered during the monitoring period at the Slavošovice constructed wetland. Weis and Weis[19] similarly conclude that assimilation of mercury depends on many other factors (*e.g.*, the character of sediments, presence of microbial symbionts, translocation and distribution to aboveground tissues) rather than on retention time. They

Table 3. Mercury in wetland plants (*Phragmites australis*)

Sampling site	Aboveground / mg kg^{-1}[(a)]	Belowground / mg kg^{-1}[(b)]
S1[(c)]	0.0105 ± 0.0027	0.0081 ± 0.0026
S5[(c)]	0.0102 ± 0.0038	0.0086 ± 0.0019
S10[(c)]	0.0099 ± 0.0037	0.0079 ± 0.0039

[(a)] Hg concentration in dried aboveground biomass (leaves and stems).
[(b)] Hg concentrations in dried belowground biomass (roots and rhizomes).
[(c)] For S1, S5, and S10 see Figure 1.

Table 4. Mercury in wetland sediments

Sampling site	Hg concentration / mg kg^{-1}
S1[(a)]	0.151 ± 0.040
S5[(a)]	0.090 ± 0.042
S10[(a)]	0.103 ± 0.032

[(a)] For S1, S5, and S10 see Figure 1.

advert to a great variability of changes in metal levels determined in wetland plants and remark that individual leaves acquire higher concentrations of metals over their life span.

Mercury Determination in Sediments

The sediments were sampled from the Slavošovice constructed wetland at distances of 1, 5, and 10 m from the inflow zone at 10 cm depth. The obtained results are summarized in Table 4. The highest total mercury concentration (0.151 ± 0.040 mg kg^{-1}) was determined for the sample taken 1 m from the inflow zone, *i.e.*, at the beginning of the vegetation bed. It indicates that mercury can be partially removed from inflowing water by precipitation and sedimentation here. The processes participating in wastewater treatment are generally the most effective at the initial section of the wetland vegetation bed. In accord with our previous results,[3] the major part of diverse contaminants is removed from treated water during its flow through the first meter of the bed.

CONCLUSION

The present study describes the fate of mercury in the horizontal subsurface flow constructed wetland used for the treatment of municipal wastewater. Mercury was shown to be removed from treated water with the efficiency of 63.7 %. More than a half of the removed mercury fraction (38.2 %) was disposed during the pretreatment in the section where no wetland plants grew (horizontal sand trap, sedimentation basin). Thus, the effect of vegetation on the mercury removal was ambiguous. Mercury can be removed from wastewater by volatilization (Hg^0; formation of dimethylmercury) and mainly by sedimentation of precipitated Hg forms (HgS) in the constructed wetland bed. The concentrations of mercury in wetland sediments were 0.151 ± 0.040 mg kg^{-1} and 0.103 ± 0.032 mg kg^{-1} for samples taken 1 and 10 m from the inflow zone. Mercury was preferably removed at the beginning of the vegetation bed. It corresponds to degradation and removal of other pollutants, *e.g.*, organics, nitrogen, or phosphorus.[3] The constructed wetland with horizontal subsurface flow is capable of removing mercury from treated water with the fair efficiency.

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