Behavior of Zinc in a Constructed Wetland System Receiving Domestic Wastewater

Kaoru ABE*, Akihito OOKUMA**, Michio KOMADA***, Sunao ITAHASHI*, Kennji BANZAI*

* National Institute for Agro-Environmental Sciences, 3-1-3, Kannondai, Tsukuba 305-8604, Japan

** Koibuchi College of Agriculture and Nutrition, 5965, Koibuchimachi, Mito 319-0323, Japan

*** National Agricultural Research Center, 3-1-1, Kannondai, Tsukuba 305-8666, Japan

ABSTRACT

In Japan, environmental quality standards for Zn pollution were enacted recently because of the toxicity of Zn to aquatic ecosystems. A free-water-surface constructed wetland (500 m²) planted with *Zizania latifolia* Turcz. received secondary-treated wastewater from a dormitory (60 to 100 residents) at the Koibuchi College of Agriculture and Nutrition in Japan, to remove nutrient salts before the discharge of the water to a pond for agricultural use. We examined the removal efficiencies of Zn and its behavior in this constructed wetland within 3 years and discussed the mechanism of Zn removal. The constructed wetland was effective in treating wastewater with low Zn concentrations. The T-Zn concentration in secondary-treated domestic wastewater (average T-Zn: 0.048 mg/L) decreased by 51% during passage through the constructed wetland. Most of the dissolved Zn was removed, but only a little particulate Zn was removed. The increase in Zn concentration in the wetland soil corresponded to 69.8% of the Zn removed by the wetland. However, the amount of Zn accumulated in the aboveground parts of *Z. latifolia* corresponded to only 9.8% of the Zn removed by the wetland. Thus, Zn was removed mainly by adsorption onto the wetland soil, including soil particles and organic matter.

Keywords: constructed wetland, domestic wastewater, secondary-treated, soil, *Zizania latifolia*, Zn

INTRODUCTION

Environmental quality standards for zinc (Zn) pollution were recently enacted in Japan because of the toxicity of Zn to aquatic ecosystems. These standards have been set at 0.03 mg/L for Zn in rivers and lakes and 2 mg/L in wastewater. Zn is used in various human activities, and the sources of Zn loading in the aquatic environment are quite varied. Zinc is an essential micronutrient for mammals, and many foods contain it. Some commodities such as shampoos and cosmetics also contain Zn. Nakanishi *et al.* (2008) estimated that, in Japan, 468 t/year of Zn is loaded from domestic wastewater to the aquatic environment and 1172 t/year is loaded from domestic wastewater to sewage treatment systems. The Zn load from factories to the aquatic environment was estimated to be 700 t/year. Domestic wastewater is therefore a major source of Zn pollution of aquatic ecosystems.

In recent years, considerable attention has been directed toward constructed wetlands, because of their low cost and ease of operation (Brix, 1993; Cooper, 2007; Vymazal, 2007). Most studies of heavy metal treatment in constructed wetland systems have examined heavily contaminated wastewater from mine drainage and industries

Address correspondence to Kaoru Abe, Soil Environment Division, National Institute for Agro-Environmental Sciences, Email: abekaoru@affrc.go.jp
Received June 17, 2010, Accepted July 14, 2010.

(Gillespie *et al.*, 2000; Mays and Edwards, 2001). There have been few studies on the removal of heavy metals from wastewaters containing low concentrations of these metals, such as domestic wastewater, by constructed wetland systems.

Wastewater from a dormitory at the Koibuchi College of Agriculture and Nutrition (KCAN) in Ibaraki Prefecture, Central Japan, is first treated by a combined household wastewater treatment facility that uses primary and secondary treatment processes. The secondary-treated effluent is then polished by a free-water-surface-flow constructed wetland to remove nutrient salts before the effluent is discharged to a pond for agricultural use. In the previous study, we have already reported the year-round N, P, and Zn removal efficiencies of the constructed wetland system (Abe *et al.*, 2008). Here, we examined Zn removal efficiencies and Zn behavior in the constructed wetland within 3 years and discussed the mechanism of Zn removal.

MATERIALS AND METHODS

Free-water-surface-flow Constructed Wetland

The constructed wetland is 16 m wide and 30 m long, with a water depth of 0.1 m (Fig. 1). It was built on a fallow paddy field at KCAN in 2004. The wetland soil is a humic gleyed andosol. A barrier of plastic boards has been installed around the wetland to prevent percolation of water. Flow-correction boards are installed every 7.5 m inside the wetland to prevent shortcut flow. Although *Phragmites australis* (reed) is commonly used in constructed wetlands, this species rapidly extends strong rhizomes that could puncture the bunds of the paddy field adjacent to the wetland. Therefore, this wetland has been planted with *Zizania latifolia* Turcz. (Manchurian wild rice), which, unlike reeds, causes little damage to the paddy field and has a high biomass production rate. The wetland receives about 10,000 to 30,000 L/day of secondary-treated wastewater from 60 to 100 dormitory residents. The average water retention time in the wetland is 2.6 days.

Fig. 1 - Free-water-surface-flow constructed wetland system.

Measurements

The volume of wastewater inflow was measured with an integration flow meter. The effluent water volume was calculated as the sum of inflow and rainfall minus evapotranspiration. Because the paddy field had a hardpan (impermeable layer) under the plow layer (i.e., the topsoil) and the groundwater level was high in the biotope area, water leaching was considered to be negligible. For convenience, the typical rate of evapotranspiration from a Japanese paddy field (4.0-6.5 mm/d) (Kaneko, 1973) was used to represent that of the constructed wetland except for any rainy days (0 mm/d for rainy days).

Influents and effluents were collected weekly from May 2006 through October 2009 (inflow was stopped after this time) and the acid-soluble Zn concentration was measured. Total zinc (T-Zn) and dissolved Zn concentrations were measured once or twice a month. To measure the acid-soluble Zn concentration, water samples were adjusted to pH 1 with nitric acid (HNO₃) just after sampling. To measure the dissolved Zn concentration, water samples were filtered with a 0.2 µm membrane filter just after sampling. To measure the T-Zn concentration, water samples (25 mL) were digested with concentrated HNO₃ (2 mL) in Teflon beakers on a hot plate at 200-250 °C.

Aboveground parts of *Z. latifolia* growing over an area of 1 m² were harvested from four to eight sampling points in the constructed wetland every year. Samples were dried at 80°C for 3 days. Soil core samples at 10 cm depth were taken from eight sampling points (illustrated in Fig. 1) in the constructed wetland in November 2006 and January 2010, after several weeks of drainage. They were then air-dried and passed through a 2-mm mesh sieve. The *Z. latifolia* (0.2 g) or finely ground soil (0.2 g) was digested with concentrated HNO₃ (2 mL), followed by hydrogen fluoride (HF) (5 mL) and perchloric acid (HClO₄) (1mL) in Teflon beakers on a hot plate at 200-250 °C. To quantify the soluble Zn, the air-dried and sieved soil was shaken with 0.1 mol/L HCl solution at a 1:5 soil to solution ratio for 1 h at 200 rpm (Japanese Society of Soil Science and Plant Nutrition, 1995).

The Zn concentration in the solutions prepared as described above were measured with an inductively coupled plasma optical emission spectrometer (Vista-Pro, Varian Inc., Palo Alto, CA, USA) or inductively coupled plasma mass spectrometer (Agilent 7500cs, Agilent Technologies, Santa Clara, CA, USA)

RESULTS AND DISCUSSION

The relationship between the acid-soluble Zn concentration and T-Zn concentration in the influents (secondary-treated domestic wastewater) and effluents is shown in Fig. 2. The acid-soluble Zn concentration was almost the same as the T-Zn concentration. The slope of the linear regression between T-Zn and acid-soluble Zn concentrations in the influents was 0.962, which is quite close to 1 ($r^2 = 0.980$). That of the effluents, however, was 0.875 ($r^2 = 0.910$), which is a little lower. It was considered that the wetland soil which contained Zn flowed out with water. The T-Zn concentrations in the influents and effluents within 3 years were calculated from the acid-soluble Zn concentrations by using each regression equation.

Fig. 3 illustrates the concentrations of T-Zn in the influent and effluent of the constructed wetland. The average T-Zn in the influent was 0.048 mg/L while the average T-Zn concentration in the effluent was 0.023 mg/L implying a 51% decrease. Our findings indicated that the constructed wetland was useful for treating wastewater with a low Zn concentration; the system decreased the Zn concentration to a level below the limit required by the Japanese water quality standard (0.03 mg/L) and this level is unlikely to have negative effects on aquatic organisms downstream.

Fig. 2 - Relationship between T-Zn concentration and acid-soluble Zn concentration in the influent and effluent of the constructed wetland.

Fig. 3 - Changes in T-Zn concentration in the influent and effluent of the constructed wetland.

Fig. 4 illustrates the fractionation of Zn in the influent and effluent. More than 80% of the Zn in the influent was in the dissolved form. This result is in agreement with that of Isozaki *et al.* (2006), who reported that about 90% of Zn in treated sewage water is in the dissolved form. About 90% of the dissolved Zn was removed by the constructed wetland system. The particulate Zn (T-Zn minus dissolved Zn) concentration hardly decreased but rather increased while the effluent was passing through the wetland, because soil in the wetland flowed out with the water.

Fig. 5 illustrates the fractionation of Zn in soils in the constructed wetland. The T-Zn concentration in the wetland soil in 2010 was higher than that in 2006. An increase in soluble Zn (0.1 mol/L HCl extractable form) concentration was the main reason for this T-Zn increase.

The Zn balance of the wetland within 3 years (from November 2006 to October 2009) is shown in Table 1. The Zn loading from the secondary effluent was 1.811 g/m^2 ($1.65 \times 10^{-3} \text{ g/m}^2/\text{day}$). The amount of Zn removed was 0.870 g/m^2 ($7.95 \times 10^{-4} \text{ g/m}^2/\text{day}$), and the percentage removal rate was 48.0%. Atmospheric deposition was one of the Zn sources for the aquatic environment. Zinc loading from atmospheric deposition in Japan was estimated to be $6.3 \times 10^{-5} \text{ g/m}^2/\text{day}$ (Nakanishi *et al.*, 2008). As this value corresponded to only 3.7% of Zn loading from the secondary effluent in this constructed wetland, it was considered to be negligible for discussing Zn removal efficiency and its mechanisms in this constructed wetland. The increase in the amount of Zn in the top 10 cm of wetland soil corresponded to 69.8% of the Zn removed by the constructed wetland system. Eighty percent of the Zn increase in the soil was due to the increase in the soluble (0.1 mol/L HCl extractable) form. The amount of Zn accumulated in the aboveground parts of *Z. latifolia* corresponded to only 9.8% of the Zn removed by the constructed wetland system. Zinc removal by other pathways was considered to include Zn accumulation in the roots of *Z. latifolia* and the biomass of other species.

These results indicated that the Zn in the secondary-treated domestic wastewater was removed mainly by adsorption onto the wetland soil. One of the mechanisms for Zn removal was considered to be adsorption of Zn^{2+} onto the minus charge of clay minerals and organic matter (like humic substances) in wetland soil. Humic gleyed andosol is rich in humic substances, therefore we think that the wetland soil adsorbed Zn^{2+} effectively. Isozaki *et al.* (2006) reported that the fraction of free ion in dissolved Zn in effluents from the sewage treatment plants was 12-47%. They also suggested that residual fraction in dissolved Zn was Zn-DOM (zinc and dissolved organic matter) complex. Further studies on the reaction of dissolved Zn with wetland soil are needed.

Fig. 4 - Fractionation of Zn in the influent and effluent of the constructed wetland. (The concentration of Zn was measured once a month.)

Fig. 5 - Fractionation of Zn in wetland soil in November 2006 and January 2010. (The average Zn concentrations of soil samples were taken from each block in the wetland, and the soil sampling points and block numbers are illustrated in Fig. 1.)

Table 1 - Zinc balance from November 2006 to October 2009 in free-water-surface constructed wetland planted with *Z. latifolia*

	Inflow	Removal				Outflow	
		Accumulation in soil (top 10cm)	(Soluble form)	Plant uptake	Removal for other reason	Total removal	
Zn [g/m ²]	1.811	0.607	(0.571)	0.086	0.224	0.870	0.941
% to inflow	100	33.5	(31.5)	4.7	9.8	48.0	52.0
% to total removal	-	69.8	(65.6)	9.8	20.4	100	-

CONCLUSIONS

- (1) The constructed wetland was useful for treating wastewater with a low Zn concentration; the system decreased the Zn concentration to a level below the water quality standard.
- (2) Most of the dissolved Zn was removed by the constructed wetland system, but little particulate Zn was removed.
- (3) The increase in Zn concentration in the wetland soil corresponded to 69.8% of the Zn removed by the wetland system. The Zn increase in the wetland soil was mainly due to an increase in the soluble (0.1 mol/L HCl extractable) form. The amount of Zn accumulated in the aboveground parts of *Z. latifolia* corresponded to only 9.8% of the Zn removed by the wetland.
- (4) Our results indicated that Zn was removed mainly by adsorption onto both soil particles and organic matter of the wetland soil.

REFERENCES

- Abe K., Komada M. and Ookuma A. (2008). Efficiency of removal of nitrogen, phosphorus and zinc from domestic wastewater by a constructed wetland system in rural areas: a case study, *Wat. Sci. Technol.*, **58**, (12), 2427-2433.
- Brix H. (1993). Wastewater treatment in constructed wetland: system design, removal

- process, and treatment performance. In: *Constructed Wetlands for Water Quality Improvement*, G. A. Moshiri (ed.), CRC Press Inc., Boca Raton, FL, pp. 9-22.
- Cooper P. (2007). The constructed wetland association UK database of constructed wetland systems, *Water Science and Technology*, **56**(3), 1-6.
- Gillespie W. B., Hawkins W. B., Rodgers J. H. Jr., Cano M. L. and Dorn P. B. (2000). Transfers and transformations of zinc in constructed wetlands: mitigation of a refinery effluent, *Ecological Engineering*, **14**, 279-292.
- Isozaki Y., Nakajima F. and Furumai H. (2006). Speciation of zinc, copper and nickel in domestic wastewater treatment process and in receiving river water, *Environmental Science*, **19**(5), 445-452 (in Japanese with English summary).
- Japanese Society of Soil Science and Plant Nutrition (ed.) (1995). *Methods for the Analysis of Soil Environments (Dojyou Kannkyou Bunnseki Hou)*. Hakuyuu-sha, Tokyo, Japan (in Japanese).
- Kaneko R. (1973). *Hydrology Course 12; Agricultural Hydrology*, Kyoritsu Shuppan Co., Ltd, Tokyo (in Japanese).
- Mays P. A. and Edwards G. S. (2001). Comparison of heavy metal accumulation in a natural wetland and constructed wetlands receiving acid mine drainage, *Ecological Engineering*, **16**, 487-500.
- Nakanishi J., Naito W. and Kamo M. (2008). *Risk Assessment Document Series 20: Zinc*, Maruzen, Tokyo, Japan (in Japanese).
- Vymazal J. (2007). Removal of nutrients in various types of constructed wetlands, *Science of the Total Environment*, **380**, 48-65.