Chapter 17
Transformation of Chloroform in Constructed Wetlands

Yi Chen, Yue Wen, Qi Zhou, and Jan Vymazal

Abstract Chloroform is a volatile organic contaminate widely detected in groundwater, surface water and wastewater effluent, thus its fate in the natural treatment systems is of great importance to the environment and human's health. In this study, the transformation processes were studied for six model constructed wetlands (CWs), for treating chloroform in the secondary effluent. Contaminate fate was investigated in the respective water, plant, litter, gravel and atmosphere. Results showed that sorption and biodegradation were the main chloroform removal processes in litter-added CWs, while sorption and plant uptake were the primary contributors to chloroform removal in planted CWs. Volatilization flux of chloroform was always low (2.0–2.5 %) in CWs likely due to the limitation of water–air transfer via diffusion in the SSF CWs. Overall, this study makes the quantitative evaluation of chloroform distribution (i.e. aqueous phase, gaseous phase, vegetation, and bed substrate) and multiple removal pathways (i.e. destructive versus nondestructive processes) in CWs. This will benefit for opening the "black box" of the treatment processes and make people better understand the transformation of trace volatile organic pollutants in natural treatment systems.

Keywords Constructed wetlands • Chloroform • Transformation • Plant litter • *Typha latifolia*

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17.1 Introduction

Chloroform is a volatile organic contaminate widely detected in the environment. Previous studies showed that it is frequently detected in groundwater, wastewater effluent and surface water, thus its fate in the natural treatment systems is of great importance to the environment and human's health. Considering the slow degradation and great health concern of chloroform, its fate and remediation approach is a hot topic (Carter et al. 2012; Chan et al. 2012; Justicia-Leon et al. 2014). Gupta et al. (1996b) found that the removal efficiency of chloroform could achieve 99 % in the methanogenic enriched culture under anaerobic condition. In aerobic environment, some microbes can also transform choloform to CO_2 using different primary substrates (Kim et al. 2000; Wahman et al. 2007; Frascari et al. 2012). However, the high cost of the biotechnology limited the wide application in the field.

Constructed wetlands (CWs) are ecosystems connecting between terrestrial and aquatic systems, and it acts as a "lung of earth" to store and purify the contaminants in the wastewater (Vymazal 2011a). Various types of wastewater and contaminants have been successfully treated in different types of CWs (Vymazal 2007). However, the fate of chloroform has not been evaluated in the wetland systems due to the complexity of wetlands. The wetland systems are ecosystems where four spheres (hydrosphere, biosphere, lithosphere and atmosphere) overlap and thus more heterogeneous and complicated than other natural and engineered systems. The presence of plant which can interact with these spheres makes the wetland systems even more complicated and unique (Vymazal 2011b). Thus, the transformation of contaminants and the related treatment process in wetland systems is always considered as a "black box" for decades (Garcia et al. 2010). This is especially the case for the chloroform investigated in this study, because its trace concentration (ng/L-μg/L) and highly volatile nature make the quantitative evaluation of pollutants distribution (i.e. aqueous phase, gaseous phase, vegetation, and bed substrate) and multiple removal pathways (i.e. destructive versus nondestructive processes) analytically difficult. As mentioned above, the investigation of chloroform removal in CWs will benefit for opening the "black box" of the treatment processes and make people better understand the transformation of trace volatile organic pollutants in natural treatment systems.

The objective of this study was to assess the fate of chloroform in different lab-scale CWs, including unplanted and planted CWs with or without plant litter. Furthermore, a mass balance of chloroform in CWs was established.

17.2 Materials and Methods

17.2.1 Design and Operation of the SSF CW

The subsurface flow (SSF) CW microcosms (length: 0.3 m, width: 0.3 m, height: 0.5 m) were located in a temperature controlled greenhouse. These CWs were operated as batch systems for 5 years to treat the nitrate and sulfate in the secondary effluent. Details of the microcosm design were illustrated in our previous study (Lin et al. 2008; Wen et al. 2010). All the microcosms were filled with gravel (ϕ 8–13 mm, porosity = 0.4) and planted with cattail (*Typha latifolia*). Cattail litter was cut into pieces (1–2 cm) and was used as a potential bio-adsorption material and electron donor for the reductive de-chlorination of chloroform in this study. The collection and preparation of the cattail litter has been described in our previous literatures (Chen et al. 2011).

Six sequencing batch SSF CW microcosms were applied in the study. i.e. unplanted and non-litter added unit (W0), unplanted and litter-added unit (W1, 100 g cattail litter), unplanted and double litter-added unit (W2, 200 g cattail litter), planted and non-litter added unit (W3, 22 plants/m^2), densely planted and non-litter added unit (W4, 40 plants/m^2), planted and litter-added unit (W5, 22 plants/m^2, 100 g cattail litter). The feed water of the CWs was the secondary effluent from a neighboring wastewater treatment plant with chlorine disinfection. The concentration of the chloroform was 52 ± 18 μg L^{-1}. The batch wetland microcosm was fed with the secondary effluent every 5 days (nominal HRT 5d), and the water level was set to 45 cm, resulting in a vadose zone of 5 cm. All treatments (W0 ~ W5) were triplicated and the duration of each experiment was 100 days which included 20 periods (each period lasted for 5d).

17.2.2 Sampling Procedure and Analysis of Aqueous, Solid and Gaseous Samples

Water samples were collected between 0 and 120 h every 5 days. Water samples were collected from each microcosm at a depth of 20 cm using a 100 ml syringe, and were analyzed in duplicate for chloroform concentration by a gas chromatograph (GC) (Agilent 7890A) with an electron capture detector (ECD). The column used was an HP-5 phenyl Methyl Siloxan column (30 m × 0.32 mm I.D. with 0.25 um film thickness). The injector, ECD and GC oven temperature programs for chloroform were: injector of 200 °C; ECD of 300 °C; oven of an initial temperature of 45 °C for 2 min, ramping to 120 °C at 8 °C/min and holding for 2 min. Passive samplers (RADIELLO®, RAD130, Supelco) were used to measure the emission of chloroform in each wetland microcosm. According to the preliminary experiments, the measurements were performed at 10 cm in the air above the centre of each wetland surface for 5 days of exposure time. Background concentrations of chloroform

outside the greenhouse were also measured during the 5 days of exposure time. The RADIELLO® passive sampler was composed of a diffusive body (a semi-permeable membrane) and an adsorbing cartridge packed with activated charcoal with particle size 35–50 mesh. After sampling, chloroform trapped in the adsorbing cartridge was recovered by carbon disulfide, analysis was performed by GC-ECD system. For solid samples, the adsorbed chloroform was extracted using hexane and acetone mixture (50:50) for 5 min, and 1.5 mL of the supernatant was used for analysis.

17.3 Results and Discussion

17.3.1 Sorption

In order to reveal the effect of sorption on chloroform removal in CWs, the sorption rates of gravel, litter and plant were investigated in this study. As shown in Fig. 17.1, all the components of CWs (gravel, litter and plant) could adsorb chloroform to some extent. The litter-added CWs showed the highest sorption rates, followed by the planted and control CWs. Plant litter and gravel was found to be the main sorption sites of chloroform in CWs. This was likely due to the hydrophobic interactions between chloroform and organic carbon attached to litter and gravel (biofilm). Previous studies also found that organic-rich biomass had a good performance for chloroform sorption (Adachi et al. 2002; Cunha et al. 2010). Compared with the blank system (W1), the sorption driven by gravel was lower in litter added CWs. This was probably due to the competitive sorption of chloroform between litter and gravel, which decreased the sorption by gravel.

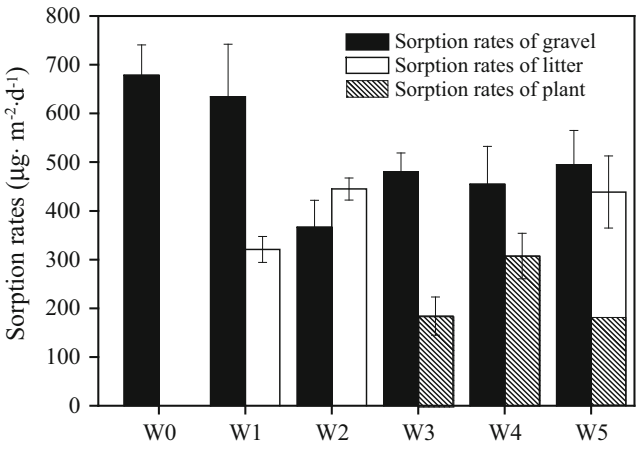

Fig. 17.1 The sorption rates of chloroform on gravel, litter and plant in W0 ~ W5 microcosms

Table 17.1 Total mass and concentration of chloroform on plant tissue in W3 and W4 microcosms

		Leaves	Stems	Roots
Mass (μg)	W3	284.5	291.6	1079.9
	W4	485.9	529.9	1749.8
Concentration (μg/g)	W3	27.6	18.7	65.8
	W4	38.9	29.0	88.4

17.3.2 Plant Uptake

As shown in Fig. 17.1, the plant uptake contributes to the chloroform removal in CWs. Previous studies indicated that the organic contaminates were removed by plant through root uptake and transpiration-driven to aboveground biomass (Imfeld et al. 2009). In general, organic contaminates with high log K_{ow} benefit for their sorption on roots but hinder the transportation inside the plants. Previous studies have suggested that direct uptake of organics by plants via transpiration is generally indicated by low to intermediate log K_{ow} values ranging from 0.5 to 3 (Seeger et al. 2011). In this study, chloroform is a compound of moderate hydrophobicity with log K_{ow} value of 1.97, indicating that it could be entered and easily translocated within the wetland plant. In order to understand the distribution and transportation of chloroform inside the wetland plants, the plant was harvested at the end of the experiment, and the content and concentrations of chloroform were detected in plant tissues. As shown in Table 17.1, chloroform was detected in both belowground and aboveground of plant, and chloroform content in belowground was significantly higher than those in aboveground biomass. The results also showed that chloroform was mainly stored in the roots, and less than 40 % was transported from belowground to aboveground biomass. The low chloroform content in the aboveground biomass was likely due to the following reasons: (1) the transpiration is relatively low, resulting in inefficient driving force to transport chloroform from belowground to aboveground biomass, (2) the strong sorption between chloroform and roots hindered the transportation of chloroform inside the plant tissues, (3) significant phytodegradation in the aboveground biomass, (4) significant phytovolatilization from stems and leaves. Firstly, transpiration rates in this study was expected to be high according to the massive water loss in CWs. Secondly, phytodegradation of chloroform was expected to play a minor role in CWs, because very limited metabolite (i.e. dichloromethane) was detected in the plant tissues. Thirdly, volatilization was very limited (see the next section) in planted CWs, so phytovolatilization of chloroform from stems and leaves was expected to be low compared with its content. As mentioned above, the strong sorption of chloroform on the plant roots might be the obstacle preventing its transportation from belowground to aboveground biomass (Table 17.1).

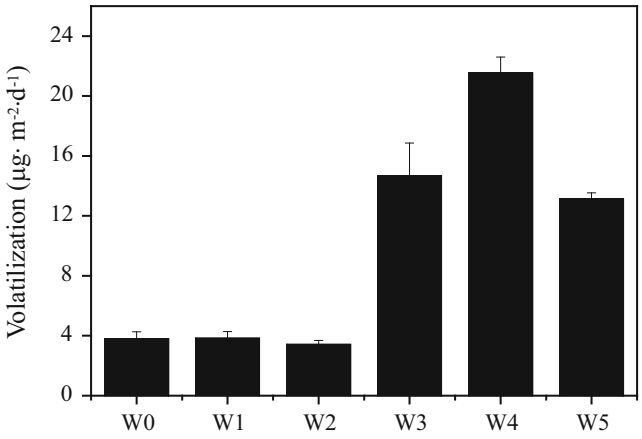

Fig. 17.2 The chloroform volatilization rates in W0 ~ W5 microcosms

17.3.3 Volatilization

As an important component of CWs, plant can remove the volatile organic contaminates from volatilization (Imfeld et al. 2009). In this study, the chloroform emission was detected using the passive samplers. As shown in Fig. 17.2, the calculated volatilization rates were much higher in planted CWs than those in unplanted CWs, and the emission increased as the plant density. This indicated that plant could promote the chloroform volatilization in CWs. According to the mass balance calculation, chloroform removed via volatilization only accounted for 2.0–2.5 % of the total chloroform in the influent. This suggested that volatilization plays a minor role in the chloroform removal process in planted CWs. By contrast, volatilization was considered to be a main pathway for chloroform removal in SF-CWs likely due to the direct and efficient contact between water and air (Rostad et al. 2000). The low volatilization observed in this study was likely the consequence that the water level is below the medium surface in SSF-CWs, resulting in hindered water–air transfer via diffusion in the SSF CWs. Seeger et al. (2011) and van Afferden et al. (2011) also found that the contribution of volatilization on volatile organic compounds (i.e. benzene and MTBE) removal was marginal in planted CWs. Previous study revealed that transpiration-driven uptake of volatile compounds can be well estimated based on Dettenmaier model (Dettenmaier et al. 2009). In this study, the model based uptake rates of chloroform was lower than the detected uptake rates. This indicated that Dettenmaier model could estimate the chloroform uptake by wetland plants to some extent, though it could not include the complete uptake pathways. Dettenmaier model calculated uptake rate is based on transpiration rates and the log K_{ow} values of target organic compounds, and some other uptake pathways (i.e. gas-phase transport) are not included in this model.

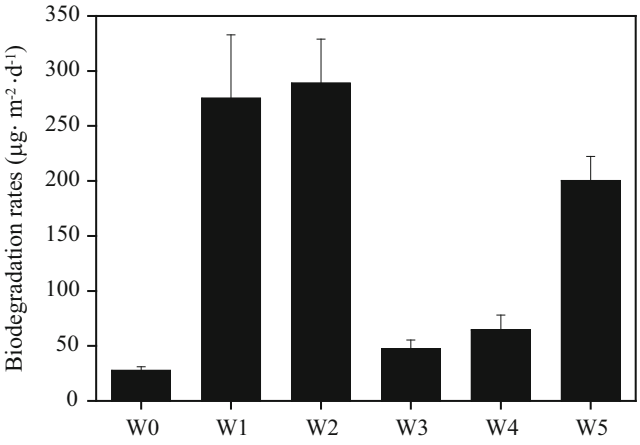

Fig. 17.3 The chloroform biodegradation rates in W0 ~ W5 microcosms

17.3.4 Biodegradation

The biodegradation rates were calculated from the mass balance equation, and the results are shown in Fig. 17.3. The biodegradation rates in litter-added CWs were much higher than those in the other CWs (Fig. 17.3). This suggested that the plant litter could significantly improve the biodegradation of chloroform. Previous studies reveal that redox potential, microbes community and carbon sources are the most important factors for chloroform biodegradation (Gupta et al. 1996b; Pavelic et al. 2006; Wahman et al. 2011). In this study, the redox potential in litter-added CWs were between −200 ~ −100 mV, suggesting that the anaerobic and sulfate reducing environment were achieved in the litter-added CWs. Previous study showed that the anaerobic reductive dechlorination of chloroform was promoted under the sulfate reducing environment (Gupta et al. 1996a), supporting the efficient biodegradation of chloroform observed in this study. Sulfate-reducing bacteria and methanogens were identified to be the key microbes responsible for chloroform degradation (Gupta et al. 1996a, b). In the litter-added CWs, both microbes were detected and their abundance was correlated with the chloroform degradation rates (Chen et al. 2015). In addition to anaerobic environment and the related degrading microbes, carbon source is also a critical factor for chloroform degradation. In the litter-added CWs, the carbon source is mainly produced during litter decomposition. Firstly, the lignocellulose is hydrolyzed to reducing sugars, and then the monosaccha-rides are converted to volatile fatty acids (i.e. acetic acid) through the anaerobic microbial metabolism (Chen et al. 2012). Acetic acid has been demonstrated to be primary substrate driving chloroform degradation through cometabolism (Gupta et al. 1996a). Thus, the accumulation of acetic acid in litter-added CWs provided the carbon source for chloroform degradation.

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