ABSTRACT

The performance and removal mechanisms of a hybrid constructed wetland (HCW) followed by a willow planted filter (WPF) were evaluated for the treatment of a leachate contaminated by wood pole preservatives (pentachlorophenol (PCP) and chromated copper arsenate) to reach the storm sewer discharge limits. The HCW aimed to dechlorinate the PCP and polychlorodibenzo-p-dioxins/polychlorodibenzofurans (PCDD/F) and to remove metals by adsorption and precipitation. The HCW was efficient in removing PCP (>98.6%), oil, arsenic (99.4%), chromium (>99.2%), copper (>99.6%) and iron (29%) to under their discharge limits, but it was unable to reach those of Mn and PCDD/F, with residual concentrations of 0.11 mg Mn/L and 0.32 pg TEQ/L. Iron and manganese could be removed but were subsequently released by the HCW due to low redox conditions. No dechlorination of PCDD/F was observed since its chlorination profile remained the same in the different sections of the HCW. Adsorption was the most probable removal mechanism of PCDD/F. The WPF was able to remove some residual contamination, but it released Mn at a gradually decreasing rate. Total evapotranspiration of the leachate by a larger fertilized WPF and the construction of an underground retention basin are proposed to prevent any discharge of PCDD/F traces in the environment.

Key words | adsorption, constructed wetland, dechlorination, evapotranspiration, PCDD/F, willow filter

ABBREVIATIONS

CCA   Chromated copper arsenate
CWs   Constructed wetlands
HCW   Hybrid constructed wetland
GC-MS Gas chromatography coupled with mass spectrophotometer
HSSF  Horizontal sub-surface flow
OCDD  Octachlorodibenzo-dioxin
PCDD/F Polychlorodibenzo-p-dioxins/polychlorodibenzofurans
PCP   Pentachlorophenol
TCDD  Tetrachlorodibenzo-p-dioxin
TEQ   Toxic equivalent
WPF   Willow planted filter
ZVI   Zero valent iron

INTRODUCTION

Wood is widely used for industrial purposes in Canada, such as cross-ties and poles for electrical or communication lines support. They are usually treated with preservatives such as pentachlorophenol (PCP) or chromated copper arsenate (CCA) to prevent fungi and insects and extend their life expectancy (EPRI 2002). When newly treated and old wood poles are stored together outside in stockpiles, they come into contact with rainfall, creating a leachate that can contaminate the environment (Sudell et al. 1992).

The leachate treatment technology installed next to a wood pole stockpile site consists of a system of constructed wetlands (CWs) and a willow planted filter (WPF) designed to treat the targeted contaminants, especially polychlorodibenzo-p-dioxins/polychlorodibenzofurans (PCDD/Fs), an impurity of PCP-based preservatives.
PCDD/Fs, also known as ‘dioxins and furans’ are molecules made of two benzene rings attached by one or two oxygen atoms and surrounded by one to eight chlorines (Gibson & Skett 1986). Among 210 congeners of PCDD/Fs, 17 are considered toxic and subject to environmental regulations. Congeners are weighted by a toxic equivalent (TEQ) factor and summed to calculate the TEQ, which is the regulated parameter (Van den Berg et al. 2006). A non-detect congener is not considered in the TEQ calculation.

The objective of this field study was to compare various extensive CW technologies to treat the wood pole stockpile leachate and meet municipal storm sewer discharge limits (CMM 2008). These discharge limits were 1 mg/L for arsenic, chromium and copper, 15 mg/L for iron, 0.1 mg/L for manganese, 15 mg/L for total oil and grease and 60 μg/L for PCP. For PCDD/Fs, the reference criterion was 0.0031 pg TEQ/L, which is meant for the safety of piscivorous birds and mammals (Fenner 1995; MDDEFP 2013).

This paper focuses on the performances of one of the CWs, which consisted of four sections, and of the WPF to propose a final concept of a full-scale wood preservative leachate management strategy.

**METHODOLOGY**

Four different wetlands with intermediate sampling points were used to treat the leachate in parallel systems (sampling points P3 to P11; see Figure 1). Then, those pretreated effluents were mixed into one connecting point (P12) to be pumped into a WPF for polishing. The effluent of the WPF (P13) was then sent to a storm sewer as illustrated in Figure 1, a flow diagram of the wetland system from the wood pole stockpile (P1) to the storm sewer (P14).

The treatment system was operated from May to November through 2012 to 2015. The system was hibernated from December to April due to the cold climate, which freezes the soil and leachate. A concentrated leachate made from wood pole embedment ends, macerated in water, was spiked to the leachate (6% v/v) in 2012 at P2 to reach the end of life of the system more quickly. From July 2013, only the leachate was pumped into the system.

The wood stockpile area has a surface area of 2,240 m² and receives approximately 1 m of precipitation every year. Under the poles, a storage volume of 514 m³ is available. Throughout the year, the leachate volume varies depending on the precipitation and evaporation in the basin, and on the treatment capacity of the wetland system.

The wetland under study (CW C) consisted of a 0.8 m deep and 40 m² horizontal subsurface flow (HSSF) hybrid constructed wetland (HCW) receiving 1 m³/d and consisting of four sequential sections, one wetland and three filters, separated by empty permeable plastic sampling boxes (Figure 2). The first section was filled with sand (52%), blond peat (40%) and zero valent iron powder (ZVI; 25 μm; 8%v), and was maintained under anaerobic conditions by a geomembrane cover. The function of this section was to dechlorinate highly chlorinated congeners of PCP and PCDD/Fs. The second section was filled with sand (75%), black peat (25%) and calcined clay (5%), equipped with forced aeration, and planted with Phragmites australis. This wetland section (identified as ‘aerobic’ in Figure 2) aimed to oxidize contaminants and dechlorinate the lower chlorinated congeners of PCP and PCDD/Fs. The third section was filled with electric arc furnace steel slag to remove metals, especially ZVI, escaping from the first section. The fourth section was made of 100% blond peat to neutralize the high pH arising from the steel slag section.

![Figure 1](https://iwaponline.com/wst/article-pdf/76/1/164/451855/wst076010164.pdf)  
**Figure 1** | Flow diagram of the wetland system from the wood poles stockpile (P1) to the storm sewer (P14). Only one of the constructed wetlands (CW C) and the WPF are reported in this paper. P1 to P14 are sampling points.
The HSSF WPF (Salix miyabeana SX67) was 48 m², 1.5 m deep and filled with sand (80%) and brown peat (20%). Its function was to treat the residual contamination and to evaporate some of the 3.7 m³/d of leachate coming from the four HCWs.

Monitoring was done twice a month to collect data for pH, redox potential (ORP), temperature and conductivity. Sampling campaigns for potential pollutants were made three to four times per year (a total of 14 campaigns) at every intermediate point (P2, P7D, P7F, P7H, P7K, P12 and P13; Figures 1 and 2). Measures and sampling were made at approximately mid-water depth. Analyses included As, Cr, Cu, Fe, Mn, total oil and grease, PCP, PCDD/Fs, and many other parameters that are not presented in this paper, all of which were analyzed in a certified laboratory. Plant biomass from the HCW and WPF was sampled in October 2013 for analyses of As, Cr, Cu, PCP and PCDD/Fs. Roots were rinsed with tap water, while aerial parts had no special treatment before being stored in a glass jar at 4 °C (Demers 2015). The substrate in each section of the HCW was also sampled for PCDD/Fs contamination in 2015 to determine if it had to be managed as contaminated soils.

Considering the initially high detection limits and many non-detects (or censored data), statistical analysis of the data for metals included modelling of left censored data with regression on order statistic model using R software, and especially the NADA package (Helsel, 2012). This statistical treatment was made on datasets having successfully passed a Shapiro test to conclude about the normality or log normality of their distribution. The datasets that failed the Shapiro test were compared but no modeled data were generated. To determine the difference between two sets of data, the function cendiff and/or Wilcox test was used (p-value < 0.05; Lee 2013).

PCDD/Fs are measured by gas chromatography coupled with a high resolution mass spectrophotometer (GC-HRMS) by a standard governmental method (CEAEQ 2011). The detection limit is different for every congener and for every sample because it is based on the final extraction volume, the recovery rate of standards, the extraction column performance and other parameters. For the analysis of the PCDD/F removal, only the eight chlorine dioxin congener (OCDD) was used to measure the performance of the process because the others were often under their detection limit and could not be modelled. The removal efficiency was calculated either on the basis of an arithmetical removal or the log removal.

**Arithmetic removal formula**

\[
\text{% removal} = \left(\frac{[\text{Metal}]_{\text{in}} - [\text{Metal}]_{\text{out}}}{[\text{Metal}]_{\text{in}}}\right) \times 100\%
\]

**Log removal formula**

\[
\text{Log removal} = \log_{10} [\text{OCDD}]_{\text{in}} - \log_{10} [\text{OCDD}]_{\text{out}}
\]

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**RESULTS AND DISCUSSION**

**Operating conditions**

The leachate showed an average pH of 6.4 and an ORP of ~67 mV. Throughout the HCW, the ORP decreased in the anaerobic section (P7D) and became positive in the aerobic one (P7F). Downstream from point P7F, the ORP gradually decreased to ~170 mV at the HCW effluent point (P7K). The pH was neutral in the first section, but variable in the aerobic section (7.0 to 10.6), probably due to some backmixing from the slag section. The peat was able to neutralize the pH from 11.0 in the slag section to 7.7 on average, during the whole duration of the experiment.
The flow of leachate pumped into the four wetlands was not constant in the 4 years of operation due to variation of the precipitation, and thus, the total quantity of leachate to treat. The leachate flow ranged from 0.5 m$^3$/d to 1.0 m$^3$/d and the rain falling directly into the HCW contributed 0.1 m$^3$/d to the flow on average. Extremes of 2.5 m$^3$/d to 4.5 m$^3$/d of pre-treated effluent and rain were filtered through the WPF depending on the weather. There was no sign of surface runoff or clogging in the first 4 years of operation.

The evapotranspiration in the HCW was observed through the variation of up to 36% of the outflow between hot summer days and nights, but could not be precisely evaluated due to a lack of recorded data of the inflow. The expected mean evapotranspiration in summer is around 3 mm/d for *Phragmites australis* (Burba et al. 1999; Borin et al. 2011) which represents 0.14 m$^3$/d or 17% of the inflow in the HCW. For the WPF, 5.3 mm/d is expected to be evacuated by evapotranspiration on average (Guidi et al. 2008; Curneen & Gill 2015), which represents a potential of 0.25 m$^3$/d or 7% of the total 3.5 m$^3$/d theoretically pumped influent.

**Metals and metalloids**

Metal analysis of the leachate showed that the macerated water did not have a significant influence on the CCA concentrations (As, Cr, Cu). An increased concentration of CCA would be useful to estimate the limitations of the HCW treatment capacity, which were not reached in this study.

The arsenic (As) mean concentration in the leachate was 0.77 mg/L and was removed at a level of 96.2% by the first anaerobic section (Figure 3(a) – P7D). This removal was attributed to chemisorption onto peat, in particular with humic substances (Palmer et al. 2015). The aerobic section, brought the removal of up to 99.5% (P7F). Downstream from this point, there was no significant change in As concentration in the slag and peat sections (Figure 3(a)). The four parallel wetlands together were able to remove 88.5% of As. The WPF was able to treat 81.8% of the residual As contamination with a final average concentration of 0.016 mg/L over 4 years. The As concentration was not significantly different throughout each season or year of the study.

Chromium (Cr) and copper (Cu) were removed by the first two sections like arsenic, but were below the detection limit (0.001 mg/L) in points P7F to P7K. From an influent concentration of 0.13 mg/L and 0.26 mg/L, respectively, Cr and Cu were removed at 95.6% and 91.7% in the anaerobic section. The four parallel wetlands together removed 89.9% of the chromium and 89.7% of the copper. The WPF removed 68.6% and 81.5% of the residual Cr and Cu with a final average concentration of 0.004 mg/L and 0.005 mg/L during the 4 years of operation.

There are three main removal mechanisms for As, Cr and Cu in the HCW and the WPF: adsorption onto peat, co-precipitation with Fe and Mn oxyhydroxides and bioaccumulation. The adsorption onto peat is used for the retention of diverse contaminants in water treatment and wetlands, including As, Cr and Cu (Sen Gupta et al. 2009; Hu et al. 2010; Palmer et al. 2015). This removal mechanism...
is efficient until the saturation of the media, which depends on the amount of adsorption sites. The adsorption rates depend on the cation exchange capacity and the contaminant concentration. Since most of the treatment is made in the first two sections, which contain peat, adsorption is probably occurring in the HCW. The diminution of the efficiency of the anaerobic section would be a sign of saturation of the media and must be monitored.

Precipitation and co-precipitation of CCA contaminants with iron and manganese hydroxide can occur in wetland systems and can be a problem if they dissolve further in anaerobic conditions (Keon et al. 2001; Kadlec & Wallace 2009; Pedescoll et al. 2015). In this pilot experiment, no dissolution of As, Cr and Cu were observed even though Fe and Mn release were occurring in the last section of the HCW and in the WPF; hence, co-precipitation may not be the main removal mechanism. The bioaccumulation of As, Cr and Cu are observed in treatment wetlands, but it could not be confirmed in the present study due to high detection limits (Bragato et al. 2009; Demers 2015). The HCW and WPF were able to treat the contamination efficiently from CCA preservative under the discharge criteria and did not reach their end of life after 4 years of operation.

The Fe concentration in the HCW increased occasionally at the end of the AN section, probably because of leaching from the ZVI powder. The subsequent sections (OX and Slag) were efficient to remove iron and it was below the detection limit of 0.07 mg/L in the effluent (Figure 5(b)).

The main removal mechanism of Fe in the OX section was probably oxidation due to the forced aeration, favouring precipitation. The peat section released Fe, giving a mean effluent concentration of 1.2 mg/L. The proposed explanation for this was the solubilization of the blond peat or of iron oxide precipitates retained in it. Globally, the HCW did not affect the Fe concentration, since P2, P7D and P7K were not statistically different.

The manganese (Mn) average concentration in the influent leachate was 0.21 mg/L, which exceeded the discharge limit criteria of 0.1 mg/L. The anaerobic section was able to remove 57% of the Mn, the aerobic section brought the removal efficiency up to 83% and the slag section to 99%. Just like for the iron, the redox and pH conditions were considered responsible for the removal of Mn. The peat section (P7K) released increasing concentrations of manganese such that the total removal of the HCW was 47% (effluent of 0.11 mg/L) over 4 years. The blond peat may be aging or oxidizing over time. At the junction of the wetlands (P12), the Mn was twice the initial concentration and the WPF released even more Mn as shown by its average of 1.3 mg/L effluent concentration (P13). The brown peat in the substrate of the WPF and other wetlands must have released Mn. Contrarily to the HCW, the WPF showed a gradual decrease in Mn release over time from 2.1 mg/L in 2012 to 0.4 mg/L in 2015. The Mn may be drained from the substrate and/or translocated into the willow’s biomass. The maximum heights of willows recorded were 2.65 m in 2012, 2.85 m in 2013 and 2.6 m in 2014 while the number of stem was 3, 11 and 14 for the same years with a medium diameter of 2 cm. All individuals survived (Demers 2015).

Iron and manganese release is often observed in HSSF CWs, because of their redox sensitivity that tends to decrease in time and stages of the wetlands, enhancing the re-dissolution of oxyhydroxides precipitates (Kadlec & Wallace 2009; Pedescoll et al. 2015). Hence, the addition of forced aeration at the end or in the WFP may be enough to address the Mn exceeding concentrations. The efficiency of a slag filter for the retention if iron could not be evaluated clearly in the HCW, since the aerobic section was sufficient to treat it. However, the slag section was the most effective process for the removal of Mn and it is considered promising for the retention of Fe and Mn in wetland systems.

Organic contaminants

The addition of macerated water resulted in a high concentration of organic contaminants in the influent as indicated by average values of 210 μg PCP/L and 700 pg TEQ/L of PCDD/F in 2012, compared to 2.7 μg PCP/L and 130 pg TEQ/L of PCDD/F after 2012. With or without the spiked influent, however, PCP, hydrocarbons, oil and grease were easily removed by the first anaerobic section (P7D; <1 μg PCP/L; <0.1 mg/L C10-C50 hydrocarbons; <5 mg/L of total oil and grease).

The PCDD/F TEQ was almost always over the discharge criterion at every stage of the system, whether the influent leachate was spiked with a concentrated leachate or not. To reach the criterion of 0.0051 pg TEQ/L, a total of 4.9 log removal (99.998%) of PCDD/F would have been required on average.

Most of the OCDD was removed at the beginning of the HCW in the anaerobic and aerobic sections (Figure 4). The slag section had a small negative impact on the removal of OCDD and the peat section a positive one, bringing the total removal of the HCW to 3.3 log removal (99.95%). The WPF was also able to retain some of the residual OCDD (87.1%), but the final concentration is similar to
the anaerobic section. Overall, the wetland system could not reach the objective of 4.9 log removal. On some occasions, the criterion of 0.0031 pg TEQ/L was reached, but this was essentially attributed to occasional higher detection limits, bringing the TEQ calculation of a congener to zero in the case of non-detection. The removal efficiency of OCDD remained relatively constant over the 4 years of operation.

Although PCDD/Fs dechlorination was first assumed to be an important removal mechanism, it appeared that adsorption may have been the dominant removal mechanism during the study for three main reasons: most of the removal was achieved at the beginning of the HCW (Figure 4), the chlorination profile was stable throughout the sections of the HCW and the same profile was found in the different phases (water, soil and biomass) of the HCW (Figure 5). The adsorption rate is directly correlated with the concentration, which is always higher upstream in the treatment. If the ZVI in the anaerobic section was able to remove chlorine from the highly chlorinated congeners, they would be found at lower concentrations while the lower chlorinated congeners would increase in concentration, especially when the OCDD is much more present than the Tetrachlorodibenzo-p-dioxin (10,000:1). Instead, the profile keeps the same slope and the ratio of contamination (anaerobic relative to leachate) is stable for every isomer (Figure 5). The symmetry of the water contamination in the soils and in the biomass of macrophytes confirms those conclusions. The substrate of the HCW is decreasingly contaminated (from the first to the last sections) and the PCDD/F profile is the same in substrates, the biomass and the water, showing no degradation of the highly chlorinated congeners or increase in the lowest chlorinated congeners.

Removal by adsorption also means that PCDD/Fs are accumulating in the substrate rather than being degraded. Thus, the saturation of the anaerobic section substrate is expected, but the end of life could not be predicted. The saturation is observed when the efficiency starts to decrease in the first sections. The management of the substrates at the dismantlement of the pilot must also consider soil contamination. The few measures of biomass and media contamination show that the accumulation of PCDD/F

Figure 4 | The most efficient sections for removing OCDD are the first two sections of the HCW and the WPF because they are receiving the highest concentrations.

Figure 5 | The PCDD isomers concentration profile is the same in the leachate and the anaerobic section effluent, in the substrate of the four sections and the biomass of the CW. Note: the same profile was observed for furan isomers.
was not sufficient to consider them as hazardous waste according to the applicable regulation.

**Full-scale implementation**

Since the PCDD/F removal objective could not be achieved by the treatment system studied, the total evapotranspiration of the leachate by the WPF was considered. This pilot scale study was able to demonstrate the capacity of willows to survive and grow in a pre-treated effluent. Further studies on willow evapotranspiration capacity should lead to a full-scale conception with a larger WPF able to respond to the needs of the site. These studies could include the impact of fertilization, of pruning of the willows and of a free surface flow design on the evapotranspiration potential of a WPF.

For a full-scale implementation, other elements should be taken in consideration, especially the construction of a retention basin to manage the total amount of leachate and the separation of the CCA and PCP treated wood pole to create two distinct leachates. CCA treated wood pole leachate could be treated by an HCW with added aeration without polishing by a WPF, while PCP treated wood pole leachate could be treated by a simpler HCW composed of anaerobic and aerobic sections followed by an underground retention basin upstream of a larger total evapotranspiration WPF.

**CONCLUSION**

The in situ treatment system consisting of an HCW and a WPF was able to treat a mixed wood preservative leachate and meet discharge criteria for chromium, copper, arsenic, iron, PCP and oil, but not for manganese or PCDD/Fs. Most metals were removed by oxidation, precipitation or adsorption onto the substrate. The main removal mechanism for PCDD/Fs was adsorption and not dechlorination as initially hypothesized. Considering this, a prospective decline in removal efficiency is expected in years to come and the substrate should be monitored to comply with regulations before dismantlement. As a short-term solution to remove the excess manganese, passive or forced aeration added in or after the WPF is proposed.

For the implementation of a full-scale leachate management system, it would be advisable to separate the PCP and CCA pole storage areas to be able to manage them differently. CCA leachate would be treated with the same configuration of HCW without WPF, while PCP leachate would be first sent to a system composed of anaerobic and aerobic zone CWs followed by underground retention basins upstream of a total evapotranspiration WPF.

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