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Distribution and Removal of Cadmium and Lead in a Constructed Wetland Receiving Urban Runoff

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Urban wastewater carries a variety of organic and inorganic compounds that must be reduced or biodegraded to a safe level before the water can be discharged or reused. The use of constructed wetlands to treat urban runoff is an emerging technology in the UK (Cooper et al. 1996, Shutes et al. 1997, Scholes et al. 1998). The Environment Agency of England and Wales has constructed a number of experimental wetlands to investigate their applications and efficiencies in treating different types of runoff. One of the full-scale wetlands was built in 1995 at Dagenham, East London, UK, where this study was carried out.

The process of water purification occurs in a highly engineered environment where vegetation, microbial communities, soil and sediments, flow rates and other parameters are carefully controlled to maximise the efficiency of the treatment process and reduce its variability. The design of a constructed wetland greatly influences its efficiency. Different processes can be decoupled and isolated in individual cells so that the treatment applied may be specific to particular pollutants.

Heavy metals are major inorganic components in urban runoff. Constructed wetlands remove heavy metals by several processes such as precipitation, uptake by living organisms, adsorption and complexation. Relatively little information was available regarding the efficiency of metal removal and the distribution of heavy metals in a constructed wetland. This paper aims to address these issues by examining the metal contents in water and sediments over a six-month period including data collected during a storm event.

MATERIALS AND METHODS

The Dagenham wetland (Figure 1) is a constructed system on the Wantz stream in East London, UK. The system was planned mainly for the purification of water from road runoff. The Wantz stream receives substantial urban discharges within its catchment area. The wetland is 250 m long and 7 m wide. It consists of a settlement tank and a series of three wetlands, separated by weirs to control the

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flow. The wetland has a surface flow system and is planted mainly with *Typha latifolia* in reedbed 1 and *Phragmites australis* in reedbeds 2 and 3. The settlement tank was built at the beginning of the wetland system to retain coarse materials that are sometimes thrown into the Wantz watercourse. The water residence time in the system is of 120 min in dry weather (Ozsturk, personal communication) and 50 min during storm events (Scholes et al. 1999). Background water analysis carried out by the Environment Agency identified elevated levels of BOD (up to 69.4 mg L^{-1}), Pb (up to 285 $\mu g\ L^{-1}$) and Zn (up to 550 $\mu g\ L^{-1}$).

A sampling programme was carried out from September 1998 to February 1999 to evaluate the behaviour of Cd and Pb in the wetland system. Five sampling stations were selected along the wetland (D1 to D5). Station D1 was situated at the beginning of the wetland, D2 at the settlement tank, D3 and D4 were located between the settlement tank and the end of reedbed 3, and D5 at the end of the system. In total, four sampling visits were conducted: at the end of September 1998; in early November during a storm event; in the end of November, after the water from the storm event had receded; and in January 1999.

Surface oxic sediments were collected using a scoop, dried at room temperature and carefully sieved through a 2 mm mesh before analysis. Water samples were collected in sampling bottles and filtered using Whatman GF/C filters in the laboratory. The filtered samples were stored at -20 °C if not immediately analysed.

The sediment pH was determined by rehydrating 5 g of sediment in 10mL of double distilled water. The pH reading was taken after the suspension was allowed to settle for 10 min. The organic content of the samples was determined by ignition at 550 °C for 1 h (Bjorklund et al. 1984).

Heavy metals in sediments were measured using the three-step sequential extraction and acid-digestion methods described by Carapeto and Purchase (2000). Metal concentrations in the water samples were determined by digesting 100 mL of water with 10 mL concentrated HNO_3. Trace metal analyses in sediment and water were carried out using inductively-coupled plasma atomic emission spectroscopy (ICP-AES; Perkin-Elmer Model Plasma 40 Spectrometer, Perkin-Elmer Ltd, New Barn Lane, Seer Green, Buckinghamshire, HP9 2QP, UK) and graphite furnace atomic absorption spectroscopy (GF-AAS; Perkin-Elmer Model Zeeman 4110ZL Spectrometer, Perkin-Elmer Ltd) respectively. For ICP-AES, the flow rates of the Ar carrier gas and the samples were 12 and 0.004 L min^{-1} respectively. The emission wavelengths were between 160-800 nm and the temperature was 5000 °C. For GF-AAS, 20 μL of sample was injected and atomised at 2450 °C for 3 seconds. The current was set at 25 ma. All analyses were carried out in triplicates.

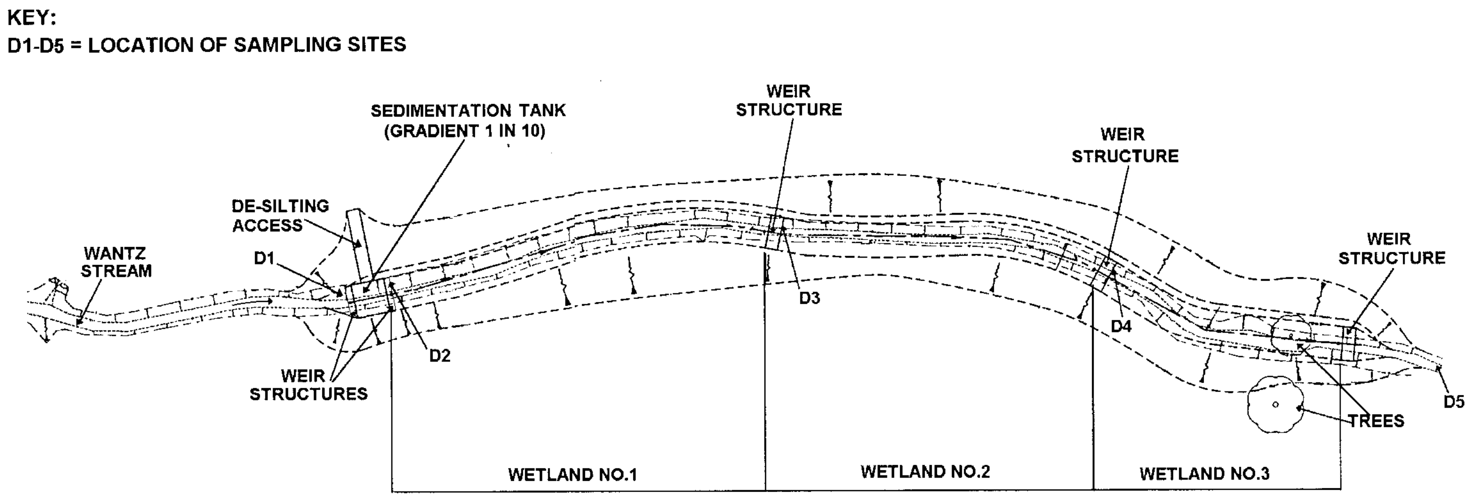

Figure 1. Diagrammatic representation of the Dagenham wetland and the locations of the sampling stations (D1-5).

RESULTS AND DISCUSSION

During the storm event, it was only possible to collect sediments from station D5. The raised water level in the wetland made the other sampling sites inaccessible.

The average sediment pH values, organic matter content and metal concentrations obtained by sequential extraction and acid digestion are shown in Table 1. Data obtained from the storm event is also listed. The pH values of the sediment collected in dry weather were relatively consistent between the sampling stations (7.0–7.2). However, the pH value recorded at station D5 during the storm event fell significantly to 5.8. The average organic matter content varied from 11.4 to 18.9% in dry condition. The organic matter at D5 increased from the average 11.7% to 16.8% during the storm event suggesting mixing and resuspension of sediments.

The mean values of Cd, and Pb reported in this study are similar to that observed by Scholes et al (1998, 1999). The Swedish Environmental Protection Agency published a classification table for lakes and watercourses according to the level of metals present in water, sediments and biota (SEPA, 1991). Based on this classification, the wetland at Dagenham can be regarded as to be contaminated with very high levels of Cd (above 5 $\mu g\ g^{-1}$ dry weight) and high levels of Pb (100-400 $\mu g\ g^{-1}$ dry weight).

In general, the concentrations of Cd and Pb in sediments decreased from station D1 to D5, which is expected in free-flowing water systems unless there are sub-superficial currents in the opposite direction. The levels of Cd and Pb were found to be higher at D4 than D3, however, these values were not significant at the 95% confidence interval. The mean total concentrations for Cd and Pb in the outlet sediments decreased by 28 and 32% respectively compared to the metal concentrations in the inlet sediment (Table 1). The reduction suggested a limited degree of metal removal during dry conditions. Due to the scarcity of the sediment samples, it was not possible to determine the metal removal efficiency in the sediment during the storm event.

The mean concentrations of dissolved metals in water collected in dry weather and storm events are shown in Figure 2. The dissolved metal concentrations in the outlet water (D5) were lower than that of the inlet water (D1), indicating the removal of heavy metals. However, the efficiency varied from metal to metal and dry to storm conditions. In dry condition, approximately 54% of dissolved Cd was removed. It is not possible to comment on the removal efficiency of Pb as its levels were below the detection limit (0.18 $\mu g\ L^{-1}$). During the storm event, the removal efficiency of Cd increased to 64%, but only 3% of Pb was removed. The dissolved Cd and Pb levels in the water samples obtained from D4 were noticeably higher than those from D3. It is interesting to note that a similar trend was also observed with the sediment samples (Table 1), although the differences

Table 1. The mean pH values, organic matter content (%), metal contents ($\mu g\ g^{-1}$) in sediments fractions and total metal content from acid digestion (± Standard Deviation) The data shown are the mean of 18 samples per site for the dry weather and 6 for the storm event.

Station	pH	Organic matter (%)	Cd ($\mu g\ g^{-1}$ dry weight) Fraction I	Cd Fraction II	Cd Fraction III	Cd Total metal concentration	Pb ($\mu g\ g^{-1}$ dry weight) Fraction I	Pb Fraction II	Pb Fraction III	Pb Total metal concentration
D1	7.2	16.3	1.55 (±1.10)	2.89 (±0.34)	7.03 (±1.11)	8.56 (±2.95)	8.53 (±6.93)	221.71 (±28.79)	147.16 (±26.33)	361.66 (±56.51)
D2	7.1	17.9	1.77 (±1.59)	2.94 (±0.27)	6.13 (±0.81)	8.57 (±2.46)	8.88 (±6.17)	184.40 (±19.17)	119.62 (±17.49)	314.91 (±32.70)
D3	7.1	11.4	1.54 (±1.40)	2.11 (±0.59)	3.72 (±1.68)	6.22 (±3.29)	9.44 (±6.43)	127.68 (±85.72)	50.55 (±42.46)	172.72 (±125.11)
D4	7.0	18.9	1.46 (±1.27)	2.98 (±0.35)	6.04 (±2.18)	7.77 (±1.56)	9.32 (±7.00)	159.05 (±11.13)	81.11 (±26.18)	237.55 (±23.98)
D5	7.1	11.7	1.48 (±1.33)	2.15 (±1.00)	4.55 (±2.07)	6.18 (±3.89)	10.0 (±6.62)	131.39 (±74.64)	67.60 (±54.43)	197.67 (±131.68)
D5 *	5.8	16.8	3.05 (±0.16)	1.42 (±0.21)	5.83 (±0.51)	10.28 (±0.72)	7.29 (±0.12)	105.92 (±13.22)	51.18 (±3.32)	122.00 (±1.49)

Fraction I = Exchangeable Fraction
Fraction II = Organically Bound Fraction
Fraction III = Residual Fraction
* = Storm event

were not statistically significant. This phenomenon may be attributed to the short-circuiting effect caused by grazing animals damaging part of the reedbed. The storm water had been observed to flow unimpeded from one station to the next, resulting in greatly reduced retention time (Ozturk, personnel communication). The damage to the reedbed may also explain the relatively low removal efficiency observed in this study.

In addition to the total metal concentrations, this study also examined the distribution and speciation of heavy metals in the sediments. The relative amount of Cd detected in the sediment samples were as follows: residual fraction > organically bound fraction > exchangeable fraction. Although the majority of Cd was present in the residual phase, a significant proportion (35-46%) of the total Cd was found in the exchangeable and organically bound fractions. Cadmium present in the organically bound and residual fractions can be mobilised under acidic condition, changes in water ionic composition and oxidation of organic matter. Sediments collected during the storm event showed reduction in Cd level in the organically bound phase (Table 1). As the pH decreased to 5.8, a significant amount of Cd was mobilised into the exchangeable phase and subsequently the aqueous phase. As the exchangeable Cd can be readily taken up by macrophytes and microbes in the constructed wetland, this may explain the 100% removal of Cd observed by Scholes et al. (1998) during a storm event. However, it is not possible to confirm this observation in this study due to the scarcity of the inlet samples.

The order of Pb concentration found in the sediments was as follows: organically bound fraction > residual fraction > exchangeable fraction. The high levels of Pb found in the organically bound fraction are expected as Pb is more strongly sorbed by organic matter than Cd. The Pb species are likely to be tetramethyl and tetraethyl lead, originated from the exhausts of motor vehicles. The low level of Pb found in the aqueous phase probably reflects the general insolubility of Pb compounds and the relatively small proportion of Pb present in the exchangeable fraction of the sediment (Table 1). The removal of Pb via uptake of macrophyte microorganisms may be limited as a result.

Constructed wetlands are designed to mimic the sediment and nutrient removal processes occurring in natural wetlands. General design principles are based on holding or slowing the passage of water through the wetland where a range of physical, chemical and biological processes can operate to store, transform or and remove various pollutants. These processes can be optimised through the control and manipulation of the hydraulic regime, including retention time. The design of the wetland at Dagenham is very simple and it appeared that the system functions best during storm events, when the Wantz stream overflows and its margins work as a sponge and a filter for the storm water. Under normal conditions, the whole system behaves as a normal stream with reeds planted on its margins and the metal removal efficiency of the system is much reduced. In addition, the reedbeds

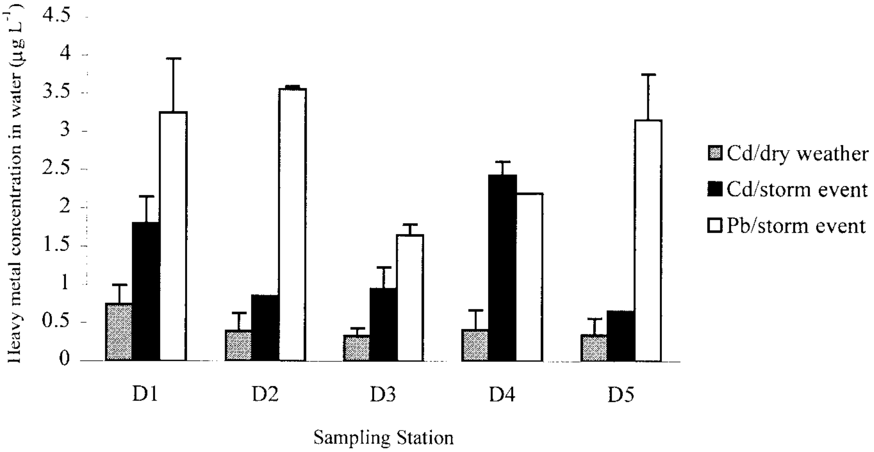

Figure 2. Heavy metal concentrations in water samples (μg L^{-1}) in dry weather conditions and the storm event. The Pb concentration in dry weather was below the detection limit (0.18 μg L^{-1}). The data shown are the mean of 18 samples per site for the dry weather and 6 for the storm event. The error bars denote the standard deviation.

at Dagenham have suffered a number of problems since the beginning of construction (Scholes et al. 1999). Heavy rain resulted in flooding of the beds and preventing the *Phragmites* to be established. Grazing animals caused further damage to the reedbed that affected the overall size of the wetland and the development of a litter layer. All these factors contributed to the reduction in the overall performance of the wetland. It is recommended that future design of constructed wetlands should include a proper settlement tank and several cells. The reedbeds should be secured to prevent excess damage leading to short-circuiting.

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