#### ARTIFICIAL WETLANDS AND THEIR IMPORTANCE FOR WATER QUALITY

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#### ABSTRACT

The efficiency of a constructed wetland to remove Cd, Ni and Pb was studied over a sixmonth period. The distribution of these metals in the sediments was examined using a sequential extraction method. Results showed that high levels of Cd and Pb were present and that each metal has a characteristic distribution in the sediment. There was a significant difference in the removal efficiency of metals during dry weather and during storm events. Although, the removal of Ni and its distribution did not show any consistent trend, it was evident that a significant amount of Ni was removed during the storm event.

#### INTRODUCTION

Natural wetlands are extremely balanced and productive ecosystems. They can be used to control floods, recharge underground water systems, and maintain wildlife habitats, and it is an extremely efficient and cost effective way to treat wastewater. In constructed wetlands the purification process occurs in a controlled environment where the vegetation, microbial communities, soil, sediments, speed of water as well as other parameters are set to maximise the efficiency of the water treatment. However, the designs of constructed wetlands vary which influence their efficiencies in pollutant removal.

Urban runoff carries a great variety of pollutants (e.g. heavy metals) that need to be removed or biodegraded before it can be discharged or reutilised. Many heavy metals are essential micronutrients; others are non-essential to life and may be toxic at trace quantities. Heavy metals mobilised by different anthropogenic activities may be transported to terrestrial or aquatic ecosystems through urban and industrial effluents or, by atmospheric transportation.

Many elements show a tendency to form complexes with organic substances that remain in the particulate form or are deposited in the sediments (Baeyens et al, 1995). The use of sediments to determine the degree of contamination is therefore useful, especially for metals that are known to settle and accumulate in this compartment. They offer integrated information on spatial as temporal contamination. Several studies showed that these tendencies vary with space and time owing to a complex assemblage of factors (Vasconcelos et al, 1997). Sudden changes in the pattern of water flux, as for

example during storm events, may redistribute and alter the contamination profiles. One of the most important factors affecting the distribution of heavy metals is found to be the nature of the sediments which determines the characteristics of adsorption, and is influenced by the organic matter content (Pereira, 1992).

The removal of metals, both dissolved and in suspension, by wetlands involves several processes such as precipitation, absorption by living organisms, adsorption and complexation. The use of constructed wetlands for treatment of urban wastewater is an emerging technology in the United Kingdom (Scholes et al, 1998, 1999). The Environment Agency of England and Wales has constructed a number of experimental wetlands to investigate their application and efficiency in the treatment of several types of runoff. One of these wetlands was built in 1995 at Dagenham, east of London (UK) where the present study took place.

This study aims to contribute to the understanding of the efficiency of metal removal, as well as on metal distribution, in constructed wetlands by analysing metal concentration in the water and in the sediments over a six-month period, including samples collected during a storm event.

### MATERIALS AND METHODS

The constructed wetland at Dagenham (Figure 1) is built on the Wantz stream in east London, UK, for treating road runoff. The wetland is 250 m x 7m, comprises a settlement tank and a series of three wetlands, separated by weirs to control the 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. A settlement tank was built at the beginning of the system to retain any coarse materials discarded into the stream.



Figure 1. DIAGRAMMATIC REPRESENTATION OF THE DAGENHAM WETLAND AND THE LOCATIONS OF THE SAMPLING STATIONS (D1 - 5)

The water residence time in the system is 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 indicated elevated levels of BOD (up to 69.4 mg L<sup>-1</sup>), Pb (up to 285  $\mu$ g L<sup>-1</sup>) and Zn (up to 550  $\mu$ g L<sup>-1</sup>).

The behaviour of Cd, Pb and Ni in the wetland system was studied from September 1998 to February 1999. Five sampling stations (D1 - 5) were selected - 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, 3 in dry conditions and 1 during storm event.

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 organic content and pH of sediment was determined. The total concentration of metals in the sediments and their speciation were analysed using acid digestion and a sequential extraction technique respectively (Carapeto and Purchase, 1999).

### RESULTS

During the storm event the raised water level in the wetland render sampling sites D1 - D4 inaccessible. The pH values of the sediments were relatively constant during the dry conditions. However, the pH value at D5 significantly decreased during the storm event (Table 1). In addition, the organic matter at D5 also increased from the average 11.7% to 16.8% during the storm event suggesting mixing and resuspension of sediments.

Station		р	Н		Organic matter (%)			
	Date of Collection				Date of Collection			
	29/9/98	*3/11/98	25/11/98	8/1/99	29/9/98	*3/11/98	25/11/98	8/1/99
D1	7.2	-	7.2	7.3	16.8	-	16.4	15.7
D2	7.2	-	7.2	7.0	20.3	-	16.2	17.3
D3	7.3	-	7.0	7.0	8.4	-	19.3	6.5
D4	7.1	-	7.0	7.0	14.2	-	16.3	26.1
D5	7.1	5.8	7.1	7.0	3.4	16.8	16.9	14.9

## Table 1 – AVERAGE pH VALUES AND ORGANIC CONTENT OF SEDIMENTS

\* Storm event

Heavy Metals in the Sediments

Concentrations of Cd and Pb significantly increased after the storm event. In general, the concentrations of Cd and Pb in sediments decreased from station D1 - 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 at D3, however, these values were not significant at the 95% confidence interval. Figures 2a - c show the concentration of heavy metals in the sediments.

The difference in Ni concentration between D3 and D4 was significant. Moreover, after the storm event Ni showed a significant decrease in its concentration in the sediments at sampling stations D1, D2 and D4 while there was a significant increase at D3 and D5.

The mean total concentrations for Cd and Pb in the outlet sediments decreased to 27 and 45% respectively compared to the metal concentrations in the inlet sediments. 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 sequential extraction data indicated that Cd and Pb were found predominantly in the residue and organically bound fractions respectively (Table 2). The levels of Ni detected in the three fractions were highly variable (data not shown) and no observable trend can be deduced.

Table 2 – MEAN VALUES FOR Cd AND Pb IN DIFFERENT SEDIMENT FRACTIONS AT DAGENHAM IN DRY WEATHER AND DURING THE STORM EVENT. NUMBER OF SAMPLES AT EACH SITE EQUALS 18 FOR DRY WEATHER AND 6 DURING THE STORM EVENT. STANDARD DEVIATION IN BRACKETS.

		Cd (µg/g dry wei	ight)	Pb (µg/g dry weight)			
Station	Fraction I	Fraction II	Fraction III	Fraction I	Fraction II	Fraction III	
D1	1.55 (± 1.10)	2.89 (± 0.34)	7.03 (± 1.11)	8.53 (± 6.93)	221.71 (± 28.79)	147.16 (± 26.33)	
D2	1.77 (± 1.59)	2.94 (± 0.27)	6.13 (± 0.81)	8.88 (± 6.17)	184.40 (± 19.17)	119.62 (±17.49)	
D3	1.54 (±1.40)	2.11 (± 0.59)	3.72 (±1.68)	9.44 (± 6.43)	127.68 (± 85.72)	50.55 (± 42.46)	
D4	1.46 (± 1.27)	2.98 (± 0.35)	6.04 (± 2.18)	9.32 (± 7.0)	159.05 (± 11.13)	81.11 (± 26.18)	
D5	1.48 (±1.33)	2.15 (± 1.00)	4.55 (± 2.07)	10.0 (± 6.62)	131.39 (± 74.64)	67.60 (± 54.43)	
D5 *	3.05 (± 0.16)	1.42 (± 0.21)	5.83 (± 0.51)	7.29 (± 0.12)	105.92 (± 13.22)	51.18 (± 3.32)	

Fraction I = Exchangeable fraction

Fraction II = Organically bound fraction

Fraction III = Residual fraction

\* = Storm event

#### **Total Cd in sediments**



Total Pb in sediments





Fig. 2 – TOTAL CONCENTRATION OF Cd, Pb AND Ni (µg/g DRY WEIGHT) IN SEDIMENTS FROM SAMPLING STATIONS DURING THE STUDY PERIOD STORM EVENT: 03-11-1998

(a)

(b)

Heavy Metals in the Water

Mean concentrations of Cd and Pb in the water are showed in Figure 3. Dissolved metal concentration increased significantly during the storm event. During dry weather sampling values for Pb were always below detection limit. It is worth mentioning that the increase in dissolved metals concentration during the storm event was followed by an increased concentration in the sediments in the next sampling period (25-11-98) (Figures 2a and b).

In general the dissolved metal concentrations in the outlet water (D5) were lower than that of the inlet water (D1), indicating the removal of heavy metals (Figure 3). 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<sup>-1</sup>). 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 (Figure 2), although the differences were not statistically significant. This phenomenon may be attributed to the short-circuiting effect where part of the reedbed was damaged by grazing animals. 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.

Ni showed a different behaviour and during the storm event its concentration in the water was always significantly lower than that observed in dry periods (Figure 4).



Sampling stations

Figure 3 - Cd AND Pb CONCENTRATION (μg/l) IN WATER DURING DRY WEATHER AND STORM EVENT



Sampling stations Figure 4 - Ni CONCENTRATION ( $\mu g/l$ ) IN WATER DURING DRY WEATHER AND STORM EVENT

### DISCUSSION

According to the classification criteria for lakes and watercourses published by the Swedish Environmental Protection Agency (1991), the wetland at Dagenham is contaminated with very high levels of Cd (above 5  $\mu$ g/g dry weight), high levels of Pb (100-400  $\mu$ g/g dry weight) and moderately high levels of Ni (30-75  $\mu$ g/g dry weight).

The mean values of Cd and Pb reported in this study are similar to that observed by Scholes et al (1998, 1999). This study also showed that the majority of Cd was detected in the residual phase, a significant proportion 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 conditions, changes in water ionic composition and oxidation of organic matter. Sediments collected during the storm event showed a reduction in Cd level in the organically bound phase (Table 2). 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.

In relation to Pb, the majority of the metal was detected in the organically bound fraction followed by a high concentration in the residual fraction (Table 2). Similar pattern was observed by Hlavay & Polyak (1998) analysing sediment samples from Lake Balaton. The Pb species are likely to be tetramethyl and tetraethyl lead, originated from the exhausts of motor vehicles.

Cadmium and Pb levels in the runoff water did not exceed the values established by the European Community Water Quality Standards (5  $\mu$ g/l and 125  $\mu$ g/l for dissolved Cd and Pb respectively; EC 1976). The reduction of pH during storm event may also mobilise Cd into fraction I and consequently into the aqueous phase which could be accumulated by macrophytes and microorganims. Removal of Pb could be relatively limited as Pb and its related compounds are comparatively less soluble.

Nickel is an essential micronutrient for the growth of some animals but becomes toxic at elevated concentrations. The concentration of Ni did not decrease with increasing distance from the input source during dry weather although that pattern could be observed in the storm event. Crites et al (1997) observed that while other metals showed a reduced concentration in the water with increasing distance from the source, nickel did not partition favourably and did not follow the same trend.

During dry weather, metal removal rate in the wetland was below 46% in the sediments and 54% in the water. However, during the storm event removal of dissolved Cd increased to 64%. Also during the storm event it was possible to observe a marked increase in the concentration of dissolved Cd and Pb at sampling station D4. This increase may have been a consequence of the short-circuiting effect observed at this station since the reedbed was partially damaged by grazing animals. As a result, the storm water flows unimpeded from one station to the next, resulting in greatly reduced retention time as mentioned previously. The damage to the reedbed may also explain the relatively low removal efficiency observed in this study.

During the storm event the percentage of removal for Ni averaged 61%. This reduction rate is well within the averages reported by Sinicrope et al (1992).

Constructed wetlands are built with the purpose to mimic the natural processes of sedimentation and nutrient retention that are present in the natural ones. The design of these systems is based on the principle of retention or slowing the flux of water through the system allowing, in this way, a variety of physical, chemical and biological processes to take place leading to the transformation and/or retention of pollutants. These processes may be optimised by changes in the hydrologic regime, namely retention time. The wetland at Dagenham has a very simple design and it seems to work better during stormy periods 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.

For a higher efficiency the construction of artificial wetlands should include a sedimentation tank with specific characteristics and several cells in the design of the whole system. The maintenance of reedbeds should be constant in order to avoid the short-circuiting effects and to maintain the retention time. Furthermore, the

maintenance of healthy reedbeds will provide a variety of substrates for different types of microorganisms, which help in the purification process of water.

### CONCLUSION

The constructed wetland at Dagenham is an efficient system for the removal of Cd and Pb form road runoff during storm events. In these periods, metals bound to the organic fraction may be mobilised. Analysis for Ni showed variable results but during the storm event removal of dissolved Ni was considerable. The maintenance of healthy reedbeds will help to increase water retention time allowing a more efficient transformation of metals and removal by emergent wetland plants.

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### REFERENCES

# GLOBAL AND REGIONAL MERCURY CYCLES: SOURCES, FLUXES AND MASS BALANCES

Baeyens, W.; Ebinghaus, R.; Vasiliev, O. (Editores), 1995, NATO ASI Series, Kluwer Academic Publishers, 563pp.

# MERCURY IN SWEDISH LAKES – ITS REGIONAL DISTRIBUTION AND CAUSES

Bjorklund I.; Borg H.; Johansson K., 1984, Ambio, **13**:118-121.

# THE USE OF SEQUENTIAL EXTRACTION FOR ANALYSIS OF HEAVY METALS IN SEDIMENT SAMPLES

Carapeto, C.; Purchase, D. 1999, Bulletin of Environmental Contamination and Toxicology, **64**(1), 51-58

## REMOVAL OF METALS AND AMMONIA IN CONSTRUCTED WETLAND

Crites, R.W.; Dombeck, G.D.; Watson, R.C.; Williams, C.R. 1997, Water Environment Research, **69**(2): 132-135

# CHEMICAL SPECIATION OF ELEMENTS IN SEDIMENT SAMPLES COLLECTED AT LAKE BALATON

Hlavay, J. & Polyak, K. 1998, Microchemical Journal, 58: 281 - 290.

# SOME ASPECTS OF MERCURY AND SELENIUM DISTRIBUTION IN THE TAGUS AND MERSEY ESTUARIES

Pereira, C.M.C. 1992, PhD Thesis, King's College, University of London

# THE TREATMENT OF METALS IN URBAN RUNOFF BY CONSTRUCTED WETLANDS

Scholes L, Shutes RBE, Revitt DM, Forshaw M, Purchase D. 1998, *Science of the Total Environment*, **214**: 211-219

# THE REMOVAL OF URBAN POLLUTANTS BY CONSTRUCTED WETLANDS DURING WET WEATHER,

Scholes LNL, Shutes RBE, Revitt DM, Purchase D, Forshaw M., 1999, Water Science and Techonoly, **40**: 333-340.

### METAL REMOVAL BY WETLAND MESOCOSMS SUBJECTED TO DIFFERENT HYDROPERIODS

Sinicrope, T.L.; Langis, R.; Gersberg, R.M.; Busanardo, M.J.; Zedler, J.B. 1992, Ecol. Eng., **1**(4): 309-322

### QUALITY CRITERIA FOR LAKES AND WATERCOURSES: A SYSTEM FOR CLASSIFICATION OF WATER CHEMISTRY AND SEDIMENT AND ORGANISM METAL CONCENTRATIONS

Swedish Environmental Protection Agency, 1991, Publisher: Swedish Environmental Protection Agency [Statens naturvardsverk], 32 pp

# COMPARISON OF AVAILABILITY OF COPPER (II) COMPLEXES WITH ORGANIC LIGANDS TO BACTERIAL CELLS AND TO CHITIN

Vasconcelos, M.T.S.D.; Azenha, M.A.O.; Cabral, J.P.S. 1997, Environmental Toxicology and Chemistry, **16**(10): 2029-2039