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Constructed Wetlands: Treatment of Concentrated Storm Water Runoff (Part A)

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ABSTRACT

The aim of this research was to assess the treatment efficiencies for gully pot liquor of experimental vertical-flow constructed wetland filters containing *Phragmites australis* (Cav.) Trin. ex Steud. (common reed) and filter media of different adsorption capacities. Six out of 12 filters received inflow water spiked with metals. For 2 years, hydrated nickel and copper nitrate were added to sieved gully pot liquor to simulate contaminated primary treated storm runoff. For those six constructed wetland filters receiving heavy metals, an obvious breakthrough of dissolved nickel was recorded after road salting during the first winter. However, a breakthrough of nickel was not observed, since the inflow pH was raised to eight after the first year of operation. High pH facilitated the formation of particulate metal compounds such as nickel hydroxide. During the second year, reduction efficiencies of heavy metal, 5-days at 20°C N-Allylthiourea biochemical oxygen demand (BOD) and suspended solids (SS) improved considerably. Concentrations of BOD were frequently <20 mg/L. However, concentrations for SS were frequently >30 mg/L. These are the two international thresholds for secondary wastewater treatment. The BOD removal increased over time due to biomass maturation, and the increase of pH. An analysis of the findings with case-based reasoning can be found in the corresponding follow-up paper (Part B).

Key words: storm runoff; gullies; constructed wetlands, biochemical oxygen demand; suspended solids; conductivity

INTRODUCTION

CONSTRUCTED WETLANDS in the United States and Europe are usually soil or gravel based horizontal-flow systems planted with *Typha latifolia* L. (cattail) and/or *Phragmites australis* (Cav.) Trin. ex Steud. (com-

mon reed). They are used to treat storm runoff, domestic and industrial wastewater (Cooper *et al.*, 1996; Kadlec and Knight, 1996; Scholz, 2003), and have also been applied for passive treatment of mine wastewater drainage (Mungur *et al.*, 1997; Mays and Edwards, 2001).

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Storm runoff from urban areas has been recognized as a major contributor to pollution of the receiving urban watercourses (Park and Yoon, 2003). The principal pollutants in urban runoff are 5-day at 20°C N-Allylthiourea [biochemical oxygen demand (BOD)], suspended solids (SS), heavy metals, deicing salts, hydrocarbons, and fecal coliforms (Scholz and Martin, 1998; Scholz and Zettel, 2004).

Although various conventional methods have been applied to treat storm water (Cooper *et al.*, 1996; Park and Yoon, 2003), most technologies are not cost-effective or too complex. Constructed wetlands integrated into a best management practice concept are a sustainable means of treating storm water and proved to be more economical (e.g., construction and maintenance) and energy efficient than traditional centralized treatment systems (Kadlec *et al.*, 2000). Furthermore, wetlands enhance biodiversity and are less susceptible to variations of loading rates (Cooper *et al.*, 1996; Scholz and Trepel, 2004).

Contrary to standard domestic wastewater treatment technologies, storm water (gully pot liquor and effluent) treatment systems have to be robust to highly variable flow rates and water quality variations. The storm water quality depends on the load of pollutants present on the road, and the corresponding dilution by each storm event (Park and Yoon, 2003; Scholz, 2003).

In contrast to standard horizontal-flow constructed treatment wetlands, vertical-flow wetlands are flat, intermittently flooded, and drained, allowing air to refill the soil pores within the bed (Cooper *et al.*, 1996; Green *et al.*, 1998; Gervin and Brix, 2001). When the wetland is dry, oxygen (as part of the air) can enter the top layer of debris and sand. The following flow of wastewater will absorb the gas and transport it to the anaerobic bottom of the wetland. Furthermore, aquatic plants such as macrophytes transport oxygen to the rhizosphere. However, this natural process of oxygen enrichment is not as effective as the previous engineering method (Kadlec and Knight, 1996; Karathanasis *et al.*, 2003).

While it has been recognized that vertical-flow constructed wetlands usually have higher removal efficiencies with respect to organic pollutants and nutrients in comparison to horizontal-flow wetlands, denitrification is usually less efficient in vertical-flow systems (Luederits *et al.*, 2001).

Heavy metal removal

Heavy metals within storm water are associated with fuel additives, car body corrosion, and tire and brake wear. Common metal pollutants from cars include copper, nickel, lead, zinc, chromium, and cadmium. Freshwater quality standards are most likely to be exceeded by

copper (Cooper *et al.*, 1996; Kadlec and Knight, 1996; Scholz *et al.*, 2002; Tchobanoglous *et al.*, 2003).

Metals occur in soluble, colloidal, or particulate forms. Heavy metals are most bioavailable when they are soluble, either in ionic or weakly complexed form (Cooper *et al.*, 1996; Wood and Shelley, 1999; Cheng *et al.*, 2002).

There have been many studies on the specific filter media within constructed wetlands to treat heavy metals economically, such as limestone, lignite, activated carbon, peat, and leaves (Scholz and Martin, 1998; Scholz *et al.*, 2002). Metal bioavailability and reduction are controlled by chemical processes including acid volatile sulfide formation and organic carbon binding and sorption in reduced sediments of constructed wetlands (Obarska-Pemkowiak and Klimkowska, 1999; Wood and Shelley, 1999; Kadlec, 2002). It follows that metals usually accumulate in the top layer (fine aggregates, sediment, and litter) of vertical-flow and near the inlet of horizontal-flow constructed treatment wetlands (Cheng *et al.*, 2002; Scholz and Xu, 2002; Vymazal and Krasa, 2003).

Physical and chemical properties of the wetland soil and aggregates affecting metal mobilization include particle size distribution (texture), redox potential, pH, organic matter, salinity, and the presence of inorganic matter such as sulfides and carbonates (Backstrom *et al.*, 2004).

The cation exchange capacity of maturing wetland soils and sediments tend to increase as texture becomes finer because more negatively charged binding sites are available. Organic matter has a relatively high proportion of negatively charged binding sites. Salinity and pH can influence the effectiveness of the cation exchange capacity of soils and sediments because the negatively charged binding sites will be occupied by a high number of sodium or hydrogen cations (Knight *et al.*, 1999).

Sulfides and carbonates may combine with metals to form relatively insoluble compounds. Especially the formation of metal sulfide compounds may provide long-term heavy metal removal, because these sulfides will remain permanently in the wetland sediments as long as they are not reoxidized (Cooper *et al.*, 1996; Kadlec and Knight, 1996).

Project purpose

The major purpose of this study is to improve the design, operation, and management of vertical-flow constructed treatment wetlands to secure a high wastewater treatment performance during all seasons. The objectives are to assess

1. the performance of vertical-flow constructed treatment wetland filters, combined with a treatment pond (above the litter zone) for gully pot liquor treatment;



Figure 1. Constructed treatment wetland rig (The King’s Buildings campus; The University of Edinburgh) in May 2004.

2. the compliance with water quality standards in terms of the reduction efficiencies of BOD, SS, nickel, copper, and nitrate;
3. the impact of environmental conditions, such as variations of salt concentrations, pH, and the temperature on the treatment performance of constructed wetlands during all seasons;
4. the feasibility of conventional chemical pH adjustment to prevent heavy metal leaching during winter; and
5. the overall role of adsorption media and *P. australis*.

EXPERIMENTAL PROTOCOLS

Study site

F1

Twelve wetland filters (Fig. 1) were located outdoors at The King’s Buildings campus (The University of Edinburgh, Scotland) to assess the system performance in a cold climate (09/09/02 to 21/09/04). The 12 first days of operation were not analyzed because the water quality was not representative. Inflow water, polluted by road runoff, was collected from randomly selected gully pots on the campus, the nearby predominantly housing estates

and two major roads. After mixing both the sediment and the water phase within the gully pot, water was collected by manual abstraction with a 2-L beaker.

Filter design, media composition, and limitations

Round drainage pipes were used to construct the aboveground filters. All 12 vertical-flow wetland filters (Fig. 1) were designed with the following dimensions: height = 83 cm and diameter = 10 cm. The relatively small size of these wetlands makes them vulnerable to environmental changes. However, a literature search has revealed that the use of small wetlands for experimental purposes is common to simulate industrial-scale systems, and that data variation is similar between small and large systems (Karathanasis *et al.*, 2003; Scholz *et al.*, 2002; Wießner *et al.*, 2004; Zhao *et al.*, 2004).

Aboveground filters experience higher temperatures and associated data variations than below-ground filters in summer. It follows that performance data might be “overly optimistic” for this season. However, above-ground filters are exposed to severe conditions such as relatively low temperatures in winter in comparison to below-ground systems that are insulated by the (frozen) soil, debris, litter, and potentially snow (Picard *et al.*, 2004; Scholz and Xu, 2002). Moreover, the macrophytes and most of the microbial biomass are usually inactive during winter. Therefore, freezing and thawing events have little impact on the filtration performance (Cooper *et al.*, 1996; Kadlec and Knight, 1996).

Different packing order arrangements of filter media and plant roots were used in the wetland filters (Tables

Table 1. Systematic and stratified experimental setup of filter content and operation.

Filter	Planted	Media ^a	Metals ^b	Aerated	Highloading ^c
1	No	1	No	No	No
2	No	1	Yes	No	No
3	No	2	No	No	No
4	Yes	2	No	No	No
5	No	3	No	No	No
6	Yes	3	No	No	No
7	No	2	Yes	No	No
8	Yes	2	Yes	No	No
9	No	3	Yes	No	No
10	Yes	3	Yes	No	No
11	Yes	3	Yes	Yes	No
12	Yes	3	Yes	Yes	Yes

^a1=no media, 2=standard, 3=addition of Filtralite (light expanded clay) and Frogmat (barley straw), see also Table 2; ^baddition of hydrated copper and nickel nitrate; ^cFilter 12 received approximately 153% additional inflow in comparison to Filter 11 (Table 3), for example.

T1
T2

1 and 2). The outlet of each constructed wetland comprised a valve at the bottom of each filter. In September 2002, the calculated empty filter bed volumes were approximately 6.2, 6.4, 4.0, 4.1, 3.8, 4.1, 3.8, 4.0, 3.8, 4.0, 4.0, and 4.0 L for Filters 1 to 12, respectively. The filter volume capacities were measured by draining the filters entirely.

The inflow waters of Filter 2 and Filters 7 to 12 were dosed with hydrated copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and hydrated nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Filters 1 and 2 (controls) are similar to wastewater stabilization ponds or gully pots (extended storage) without a significant amount of filter media (Table 2). In comparison, Filters 3, 5, 7, and 9 are similar to gravel and slow sand filters, and Filters 4, 6, 8, and 10 are typical reed bed filters. The reed bed filters contain gravel and sand substrate and native *Phragmites australis* (Cav.) Trin. ex Steud. (common reed), all of similar total biomass weight during planting and from the same local source. However, Filters 5, 6, 9, and 10 also contain adsorption media. Additional natural adsorption media (Filtralite and Frogmat) were used. Filtralite [containing 3% of calcium

oxide (CaO)] with diameters between 1.5 and 2.5 mm is associated with enhanced metal and nutrient reduction (Brix *et al.*, 2001; Scholz and Xu, 2002). Furthermore, Frogmat (natural product based on raw barley straw) has a high adsorption area, and is therefore likely to be associated with a high heavy metal reduction potential. The use of other filter media with high adsorption capacities such as activated carbon (Scholz and Martin, 1998; Scholz *et al.*, 2002) and oxide-coated sand (Sansalone, 1999) has been discussed elsewhere.

Filters 11 and 12 are more complex in their design and operation (Table 1). The top water layer of both filters is aerated (with air supplied by air pumps) to enhance oxidation (minimizing zones of reducing conditions) and nitrification (Green *et al.*, 1998; Obarska-Pempkowiak and Klimkowska, 1999; Cheng *et al.*, 2002). Filter 12 receives about 153% of Filter 11's mean annual inflow volume and load (Table 1). The hydraulic regime of Filter 12 differs from that of Filters 1 to 11 to identify the best filtration performance. A higher hydraulic load should result in greater stress on *P. australis* and biomass.

Table 2. Packing order of vertical-flow wetland filters (F).

Height (cm)	F1	F2	F3	F4	F5	F6
61–83	W	W	W	W	W	W
56–60	W	W	6	6+P	7	7+P
51–55	W	W	6	6+P	6	6+P
36–50	W	W	4	4+P	5	5+P
31–35	W	W	3	3	5	5
26–30	W	W	3	3	4	4
21–25	W	W	2	2	3	3
16–20	W	W	2	2	2	2
11–15	2	2	2	2	2	2
0–10	1	1	1	1	1	1
Height (cm)	F7	F8	F9	F10	F11	F12
61–83	W	W	W	W	AW	AW
56–60	6	6+P	7	7+P	7+P	7+P
51–55	6	6+P	6	6+P	6+P	6+P
36–50	4	4+P	5	5+P	5+P	5+P
31–35	3	3	5	5	5	5
26–30	3	3	4	4	4	4
21–25	2	2	3	3	3	3
16–20	2	2	2	2	2	2
11–15	2	2	2	2	2	2
0–10	1	1	1	1	1	1

Abbreviations: W, water, P, *Phragmites australis* (Cav.) Trin. ex Steud.; (common reed); AW, aerated water; 1, stones; 2, large gravel; 3, medium gravel; 4, small gravel; 5, Filtralite (light expanded clay product); 6, sand (0.6–1.2 mm); 7, Frogmat (barley straw).

Environmental conditions and operation

The filtration system was designed to operate in batch flow mode to reduce pumping and computer control costs. All filters were periodically inundated with pre-treated inflow gully pot liquor and drained to encourage air penetration through the aggregates (Cooper *et al.*, 1996; Gervin and Brix, 2001; Scholz and Xu, 2002).

Since 22 September 2003, the pH value of the inflow has been artificially raised by addition of sodium hydroxide (NaOH) to the sieved gully pot liquor to prevent a breakthrough of metals (see below and Tchobanoglous *et al.*, 2003). It follows that the inflow pH was therefore increased from a mean pH 6.7 to pH 8.1 (Table 3).

Metal nitrates

Copper and nickel were selected as additional heavy metals for investigation because they are commonly occurring contaminants from road vehicles and are not easily bioavailable (Cooper *et al.*, 1996; Kadlec and Knight, 1996; Scholz and Xu, 2002). It follows that these metals are likely to accumulate within the sediment and debris of constructed wetlands. As the buildup continues, metal toxicity increases as does the risk of severe pollution due to leaching (Scholz *et al.*, 2002).

Some heavy metals do accumulate easily in constructed wetlands but may be released if environmental conditions change; for example, road gritting (containing

Table 3. Primary treated gully pot effluent: water quality variables after contamination with hydrated copper nitrate and hydrated nickel nitrate.

22/09/02–21/09/03						
<i>Variable</i>	<i>Unit</i>	<i>Number of samples</i>	<i>Mean</i>	<i>SD^a</i>	<i>Mean (winter)</i>	<i>Mean (summer)</i>
Nickel (dissolved)	mg/L	57	1.06	0.143	1.08	1.09
Copper (dissolved)	mg/L	58	1.03	0.036	1.04	1.02
BOD ^b	mg/L	58	61.1	49.29	43.8	86.9
Nitrate-nitrogen	mg/L	63	1.45	1.008	1.43	1.12
Ammonia-nitrogen	mg/L	63	1.65	2.058	1.72	2.11
<i>Ortho</i> -phosphate-phosphorus	mg/L	62	0.06	0.149	0.05	0.03
Suspended solids	mg/L	70	335.7	377.75	743.7	160.7
Total solids	mg/L	66	2,995.5	6,793.27	9,403.9	376.5
Turbidity	NTU	71	311.7	479.65	690.6	162.1
Dissolved oxygen	mg/L	68	4.70	2.493	5.70	3.16
pH	—	71	6.69	0.411	6.89	6.72
Redox potential	mV	62	142.5	112.72	165.5	2.7
Conductivity	μS	71	5,139.1	11,182.22	15,311.6	501.0
Temperature (air)	°C	70	12.3	5.96	7.2	17.9
Temperature (gully pot)	°C	69	10.7	5.78	4.8	18.0
22/09/03–21/09/04 (artificial increase of pH after 21/09/03)						
<i>Variable</i>	<i>Unit</i>	<i>Number of samples</i>	<i>Mean</i>	<i>SD^a</i>	<i>Mean (winter)</i>	<i>Mean (summer)</i>
Nickel (dissolved)	mg/L	68	1.02	0.042	1.01	1.02
Copper (dissolved)	mg/L	66	1.02	0.018	1.01	1.02
BOD ^b	mg/L	73	89.2	55.5	89.7	66.6
Nitrate-nitrogen	mg/L	72	1.38	1.220	1.19	1.14
Ammonia-nitrogen	mg/L	72	1.45	1.934	1.89	1.35
<i>Ortho</i> -phosphate-phosphorus	mg/L	72	0.10	0.136	0.07	0.16
Suspended solids	mg/L	75	853.9	1,420.85	1,955.2	366.7
Total solids	mg/L	71	2,141.8	3,219.84	5,296.4	794.7
Turbidity	NTU	78	274.5	358.57	546.2	143.6
Dissolved oxygen	mg/L	78	3.07	1.49	3.41	3.22
pH	—	78	8.07	1.082	8.25	8.73
Redox potential	mV	78	44.4	93.44	31.8	64.1
Conductivity	μS	78	2,227.2	4,620.82	6,191.7	403.6
Temperature (air)	°C	155	13.7	6.46	7.1	20.6
Temperature (gully pot)	°C	75	12.0	5.65	6.0	18.9

^aStandard deviation; ^b5-day at 20°C N-Allylthiourea biochemical oxygen demand. Abbreviation: na, not available.

Table 4. Mean and standard deviation of outflow water quality variables.

<i>Mean (22/09/02–21/09/03)</i>							
<i>Variable</i>	<i>Unit</i>	<i>Filter 1</i>	<i>Filter 2</i>	<i>Filter 3</i>	<i>Filter 4</i>	<i>Filter 5</i>	<i>Filter 6</i>
BOD ^a	mg/L	37.2	43.4	16.4	30.7	23.3	33.5
Suspended solids	mg/L	174.6	189.0	120.8	130.4	132.4	127.3
Total solids	mg/L	2,772.8	3,602.5	2938.7	3,266.2	2,949.1	3,990.4
Turbidity	NTU	79.8	89.0	15.0	39.0	35.4	25.6
Conductivity	μS	5,148.5	6,827.7	5,920.8	5,392.6	5,809.9	5,797.7
<i>Variable</i>	<i>Unit</i>	<i>Filter 7</i>	<i>Filter 8</i>	<i>Filter 9</i>	<i>Filter 10</i>	<i>Filter 11</i>	<i>Filter 12</i>
BOD ^a	mg/L	12.7	22.0	21.8	37.6	20.1	19.8
Suspended solids	mg/L	96.7	92.5	85.8	79.1	73.2	163.5
Total solids	mg/L	2,375.6	2,118.4	1,717.1	1,808.8	1,779.0	2,941.7
Turbidity	NTU	11.2	20.6	27.3	34.3	17.5	43.5
Conductivity	μS	4,912.2	4,346.8	3,808.8	3,667.8	3,528.5	5,941.4
<i>Mean (22/09/03–21/09/0404; artificial increase of pH after 21/09/03)</i>							
<i>Variable</i>	<i>Unit</i>	<i>Filter 1</i>	<i>Filter 2</i>	<i>Filter 3</i>	<i>Filter 4</i>	<i>Filter 5</i>	<i>Filter 6</i>
BOD ^a	mg/L	30.2	30.4	3.1	2.3	4.4	4.4
Suspended solids	mg/L	434.6	9,07.5	76.6	65.8	130.4	82.7
Total solids	mg/L	1,690.3	1,931.8	1,379.6	1,398.9	1,372.9	1,430.7
Turbidity	NTU	118.6	117.8	6.0	4.8	8.6	6.0
Conductivity	μS	2,268.2	2,356.0	2,339.9	2,260.3	2,220.0	2,507.6
<i>Variable</i>	<i>Unit</i>	<i>Filter 7</i>	<i>Filter 8</i>	<i>Filter 9</i>	<i>Filter 10</i>	<i>Filter 11</i>	<i>Filter 12</i>
BOD ^a	mg/L	2.3	2.7	2.8	3.5	3.6	7.6
Suspended solids	mg/L	147.3	78.1	83.4	71.7	89.9	102.8
Total solids	mg/L	1,390.3	1,497.3	1,509.4	1,804.7	1,578.5	1,647.4
Turbidity	NTU	9.6	6.9	10.2	4.9	7.4	20.1
Conductivity	μS	2,199.2	2,484.2	2,450.6	2,459.6	2,534.5	2,495.3
<i>Standard deviation (22/09/02–21/09/03)</i>							
<i>Variable</i>	<i>Unit</i>	<i>Filter 1</i>	<i>Filter 2</i>	<i>Filter 3</i>	<i>Filter 4</i>	<i>Filter 5</i>	<i>Filter 6</i>
BOD ^a	mg/L	39.89	41.95	13.09	31.24	22.74	30.33
Suspended solids	mg/L	365.53	440.59	265.83	252.75	249.34	273.44
Total solids	mg/L	7,273.37	10,821.20	6,886.58	6,585.16	6,216.36	8,318.42
Turbidity	NTU	96.15	73.83	24.21	61.19	46.64	28.45
Conductivity	μS	13,473.42	19,920.19	13,442.84	11,789.78	12,286.69	12,860.16
<i>Variable</i>	<i>Unit</i>	<i>Filter 7</i>	<i>Filter 8</i>	<i>Filter 9</i>	<i>Filter 10</i>	<i>Filter 11</i>	<i>Filter 12</i>
BOD ^a	mg/L	13.88	25.03	20.08	35.76	14.04	17.63
Suspended solids	mg/L	225.06	197.81	168.08	166.03	144.40	307.73
Total solids	mg/L	5,948.07	4,720.47	3,580.56	3,648.16	3,659.61	6,450.13
Turbidity	NTU	18.95	30.18	42.51	54.91	18.07	86.23
Conductivity	μS	11,672.86	9,431.98	6,319.37	6,683.83	7,077.11	11,479.77

(continued)

Table 4. Mean and standard deviation of outflow water quality variables. (CONTINUED)

Standard deviation (22/09/03–21/09/0404; artificial increase of pH after 21/09/03) (Continued)							
Variable	Unit	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6
BOD ^a	mg/L	21.24	37.06	7.23	3.11	8.11	6.66
Suspended solids	mg/L	449.80	3,580.34	96.29	79.97	263.65	107.28
Total solids	mg/L	1,507.80	2,417.22	1,722.92	1,601.87	1,445.83	1,714.86
Turbidity	NTU	90.33	258.22	6.89	4.44	8.38	4.48
Conductivity	μS	2,945.92	3,000.52	2,839.88	2,565.04	2,476.56	2,857.82
Variable	Unit	Filter 7	Filter 8	Filter 9	Filter 10	Filter 11	Filter 12
BOD ^a	mg/L	3.86	3.83	4.00	4.49	4.24	7.83
Suspended solids	mg/L	228.84	82.75	96.24	86.77	133.64	138.81
Total solids	mg/L	1,623.29	1,538.09	1,716.03	2,553.49	1,905.64	2,426.29
Turbidity	NTU	18.79	7.76	19.59	4.24	10.94	37.18
Conductivity	μS	2,611.49	2,572.43	2,840.91	2,741.12	3,069.47	3,638.43

^aFive-days at 20°C N-Allylthiourea biochemical oxygen demand.

salt) in winter. Such transformation processes are not well understood (Norrstrom and Jacks, 1998).

Copper nitrate and nickel nitrate were added to the inflow water of Filter 2 and Filters 7 to 12 to give total concentrations of dissolved copper and nickel of approximately 1 mg/L for each metal, comparable to figures reported for urban water heavily contaminated with heavy metals and mine wastewater (Cooper *et al.*, 1996; Kadlec and Knight, 1996; Mungur *et al.*, 1997; Scholz and Xu, 2002).

Concerning the dosed inflow water, the background concentration for nitrate-nitrogen (including nitrite-nitrogen) was only approximately 0.497 mg/L. Therefore, introduced nitrate-nitrogen contributed to 65% (or approximately 0.917 mg/L) of the overall nitrate-nitrogen (including nitrite-nitrogen) load.

The filter volumes available for influent water differ among the filters due to different filter media compositions (Table 2) and hydraulic regimes (Table 1). The mean annual total loading rates for the contaminated filters were therefore between 96 and 187 mg for each metal.

Metal determinations

Metal concentrations were determined in the raw gully pot liquor, sieved (pore size of 0.25 mm) gully pot liquor (partially used as actual inflow water for some filters), contaminated (added metal nitrates) sieved gully pot liquor (partially used as actual inflow water for some filters) and the outflow waters from the experimental rig (Table 1). Raw gully pot liquor was sieved to simulate preliminary and primary treated storm water. This procedure is in line with common practice in the wastewater industry (Cooper *et al.*, 1996; Tchobanoglous *et al.*, 2003).

A Varian Spectr AA 400 Atomic Absorption Spectrometer with a GTA-96 graphite furnace tube atomizer was used for the standard analysis of nickel and copper. Notched GTA partition tubes (coated) were applied, and the carrier gas was argon.

BOD, nutrient, and other determinations

The BOD was determined in all water samples with the OxiTop IS 12–6 system, a manometric measurement device, supplied by the Wissenschaftlich-Technische Werkstätten (WTW), Weilheim, Germany. Nitrification was suppressed by adding 0.05 mL of 5 g/L N-Allylthiourea (WTW Chemical Solution No. NTH 600) solution per 50 mL of sample water.

Nitrate was reduced to nitrite by cadmium and determined as an azo dye at 540 nm (using a Perstorp Analytical EnviroFlow 3000 flow injection analyzer) following diazotization with sulfanilamide and subsequent coupling with N-1-naphthylethylenediamine dihydrochloride (Allen, 1974).

Ammonia-nitrate and *ortho*-phosphate-phosphorus were determined by automated colorimetry in all water samples from reaction with hypochlorite and salicylate ions in solution in the presence of sodium nitrosopentacyanoferrate (nitroprusside), and reaction with acidic molybdate to form a phosphomolybdenum blue complex, respectively (Allen, 1974). The colored complexes formed were measured spectrometrically at 655 and 882 nm, respectively, using a Bran and Luebbe autoanalyzer (Model AAIII).

Composite water samples were analyzed on Mondays, Wednesdays, and Fridays. All other analytical procedures were performed according to the American standard methods (1995).

EXPERIMENTAL RESULTS AND DISCUSSION

Inflow water quality

T3 Table 3 summarizes the water quality of the inflow to those filters artificially contaminated with heavy metals after the first and second year of operation. The pH of the inflow was artificially raised to assess its influence on the treatment performance and particularly on the potential breakthrough of heavy metals during the second winter (Table 3).

Raw gully pot liquor was sieved (pore size of 2.5 mm) to simulate preliminary treatment (Tchobanoglous *et al.*, 2003). Sieving resulted in a mean annual reduction of BOD and SS by approximately 12 and 22%, respectively.

The inflow data set was divided into two subsets (winter and summer) to assess the effect of seasonal variations (e.g., temperature) and road management (e.g., road gritting and salting) on the water quality. Most variables including BOD (except for the first year of operation), SS, total solids (TS), turbidity, and conductivity are high in winter compared to summer (Table 3).

Comparison of annual outflow water qualities

T4
T5
F2 The overall filtration performance figures are summarized in Tables 4 and 5. Figure 2 shows selected inflow and selected outflow concentrations for nickel and copper. Concerning BOD removal, the performances of all filters (except for Filters 1 and 2; extended storage) improved greatly over time. The reductions in BOD were also satisfactory for most filters if compared to minimum American and European standards (<20 mg/L) for the secondary treatment of effluent (Tables 3 to 5).

Furthermore, the artificial increase of pH after the first year of operation had no apparent influence on the treatment performance of BOD. There is no obvious difference in performance between Filters 8 and 11, indicating that aeration did not contribute significantly to the removal of BOD (Tables 3 and 4).

Negative reduction rates for TS and conductivity were predominantly caused by road salting in late autumn and winter. Any conventional filter system including constructed wetlands is unable to retain salts in high concentrations. Therefore, salts cannot be retained after a certain loading threshold that is associated with a lag period is exceeded. The lag period is predominantly a function of the buffering capacity of the biomass and the batch-flow operational mode (see above). It follows that after an initial positive removal period, the removal efficiencies are becoming negative (Norrstrom and Jacks, 1998). Furthermore, the dissolved solids fraction increases as microbial biomass mineralizes the organic contaminants.

Conductivity correlates well with dissolved solids that contribute to a large proportion of the TS mass (Cooper *et al.*, 1996; Scholz *et al.*, 2002).

In contrast to previous researchers who reported the worst seasonal performance for BOD removal during winter (Karathanasis *et al.*, 2003), all filters with the exception of Filters 1 and 2 showed high BOD removal figures (>94%) in the second winter. This suggests that soil microbes still have the capacity to decompose organic matter in winter.

Concerning other variables, reduction rates for SS increased also in the second year although outflow concentrations frequently exceeded the threshold of 30 mg/L throughout the year except for summer. Turbidity values of the outflow decreased greatly over time. Despite the artificial increase of pH in the inflow, the pH of the outflow was approximately neutral and comparable to the first year of operation. Moreover, the pH of the outflow was relatively stable in the second year (standard deviation of approximately 0.18).

Heavy metal treatment

Heavy metal removal efficiencies improved during the second year of operation (Fig. 2). However, the reduction in metals was not sufficient to comply with American standards for secondary wastewater treatment. Dissolved nickel and dissolved copper concentrations should not exceed 0.0071, 0.0049 mg/L, respectively (Tchobanoglous *et al.*, 2003).

The decomposition of aquatic plants after fall, reducing soil conditions, road gritting, and salting during periods of low temperatures and acid rain contribute to increases of metal concentrations in the outflow (Norrstrom and Jacks, 1998; Sasaki *et al.*, 2003). For example, high levels of conductivity were recorded in the filter inflow and outflows (Tables 3 to 5), and the breakthrough of dissolved nickel was observed during the first winter (Fig. 2a).

Concerning the effect of retention time on the treatment efficiency of metals, the heavy metal outflow concentrations of Filter 12 (higher loading rate) were slightly higher than the corresponding concentrations for the other filters. According to previous studies (Kadlec and Knight, 1996; Wood and Shelley, 1999), metal removal efficiencies for wetlands are highly correlated with influent concentrations and mass loading rates. Moreover, it was suggested that the formation of metal sulfides was favored in wetlands with long retention times. This may lead to a more sustainable management of constructed treatment wetlands.

Link between pH and treatment of metals

After the increase of the inflow pH, mean reduction efficiencies for nickel increased during the second win-

Table 5. Removal (%) per wetland filter^a of outflow variables.

22/09/02-21/09/03

Variable	Filter 1			Filter 2			Filter 3			Filter 4			Filter 5			Filter 6		
	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d
BOD ^e	43	13	82	32	3	80	76	59	85	51	40	84	65	49	88	49	44	86
SS ^f	52	40	81	44	25	78	67	53	92	65	54	86	64	54	92	66	52	88
TS ^g	9	N	N	N	N	21	4	N	6	N	1	N	3	N	N	N	N	N
Turb ^h	78	86	65	71	86	51	96	98	95	90	94	94	90	96	91	93	95	93
Condi ⁱ	2	N	N	N	N	2	N	N	N	N	N	N	N	N	N	N	N	N

22/09/03-21/09/0404 (artificial increase of pH after 21/09/03)

Variable	Filter 7			Filter 8			Filter 9			Filter 10			Filter 11			Filter 12		
	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d
BOD ^e	79	53	94	66	32	92	67	51	93	43	2	89	69	68	89	69	65	84
SS ^f	72	60	98	73	62	91	75	71	95	77	70	92	78	71	88	51	35	86
TS ^g	20	15	25	29	32	N	42	48	19	39	45	2	40	43	N	2	N	28
Turb ^h	96	97	99	93	95	96	91	94	98	89	90	93	94	96	94	86	85	92
Condi ⁱ	4	N	N	15	11	N	26	36	N	28	32	N	31	29	N	N	N	N

22/09/02-21/09/03

Variable	Filter 1			Filter 2			Filter 3			Filter 4			Filter 5			Filter 6		
	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d
BOD ^e	66	69	76	63	44	71	97	100	96	97	99	94	95	99	96	95	99	93
SS ^f	49	74	52	15	N	76	91	91	98	92	92	98	85	91	97	90	91	97
TS ^g	25	36	37	15	23	56	38	40	65	38	42	58	39	50	64	36	38	49
Turb ^h	57	77	48	61	68	62	98	99	95	98	99	98	97	97	96	98	99	98
Condi ⁱ	N	7	18	N	8	N	N	12	N	N	18	N	0	22	N	N	9	N

22/09/02-21/09/03

Variable	Filter 7			Filter 8			Filter 9			Filter 10			Filter 11			Filter 12		
	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d	A ^b	B ^c	C ^d
BOD ^e	97	99	95	97	99	91	97	99	96	96	99	90	96	98	90	91	94	88
SS ^f	81	89	99	90	91	96	91	90	99	91	91	98	89	87	97	87	87	98
TS ^g	39	42	72	34	46	50	34	43	71	21	22	53	31	36	56	28	24	34
Turb ^h	97	98	99	98	98	98	97	99	98	98	99	99	98	97	99	93	93	97
Condi ⁱ	3	16	N	N	17	N	N	16	N	N	15	N	N	9	N	N	2	N

^aChange (%) = $\frac{(in - out) \times 100}{in}$, where in = inflow and out = outflow; ^boverall mean; ^cmean of the winter; ^dmean of the summer; ^e5-days at 20°C N-Allylthiourea biochemical oxygen demand (mg/L); ^fsuspended solids (mg/L); ^gtotal solids (mg/L); ^hturbidity (NTU); ⁱconductivity (μ S); in italics: BOD > 20 mg/L and SS > 30 mg/L (outflow values). Abbreviation: N, negative removal (i.e., more output than input).

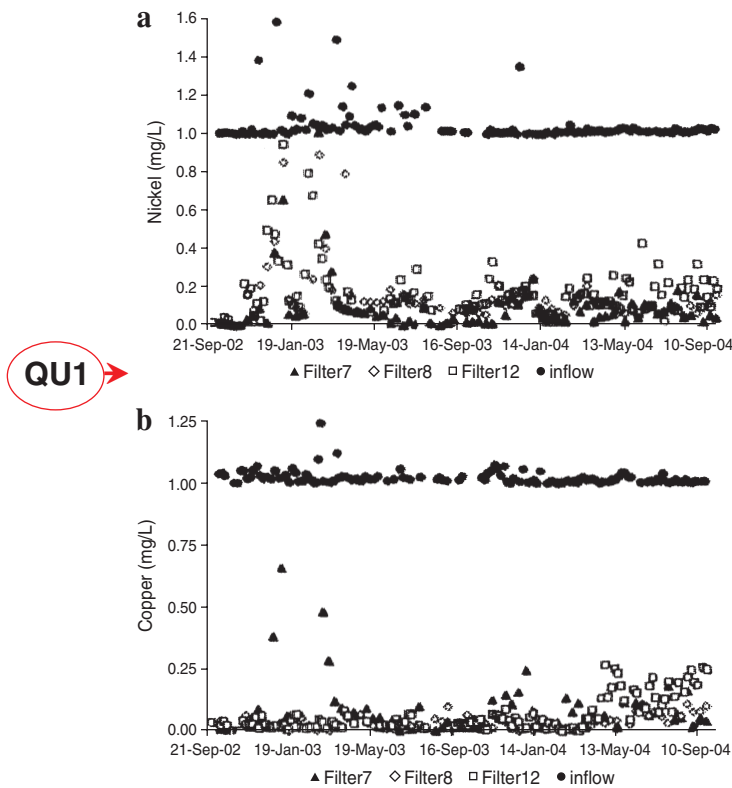


Figure 2. Daily (a) nickel and (b) copper concentrations (mg/L) in the inflow and outflows of Filters 7 (unplanted), 8 (planted), and 12 (planted and high loading).

ter compared to the first winter; for example, 90 and 65%, respectively, for Filter 7 (Fig. 2a). Moreover, an obvious breakthrough of nickel was not observed during the second winter despite the presence of high salt concentrations in the inflow. This is likely to be due to the artificial increase of pH. A high pH facilitates nickel precipitation. For example, nickel hydroxide ($\text{Ni}(\text{OH})_2$) may precipitate at pH 9.1 if the corresponding metal concentration is 1 mg/L (Tchobanoglous *et al.*, 2003), which is similar to the inflow concentrations of spiked filters. Moreover, dissolved copper did not break through any constructed wetland filters throughout the study (Fig. 2b).

All filters acted as pH buffers after pH increase, and pH levels were subsequently reduced. It can be assumed that this buffering capacity is greatly enhanced by the presence of active biomass rather than macrophytes (Kadlec and Knight, 1996; Sasaki *et al.*, 2003). However, the outflow pH values for the planted filters recorded were slightly lower than those for the unplanted filters. For example, the overall mean pH value for Filter 7 (unplanted filters) is 7.31, and the corresponding value for Filter 8 (planted filters) is 6.98 during the second year of operation.

Analysis of variance and case-based reasoning

An analysis of variance has shown that all filters containing aggregates are relatively similar to each other with respect to most of their outflow variables. It follows that some filters could be considered as replicates (e.g., Filter 7 is a replicate of Filter 3) despite the differences in filter setup (Tables 1 and 2). The p -values of the pairs for Filter 3 and 7 are 0.20, 0.95, and 0.98 for BOD, SS, and turbidity, respectively. Pairs of data associated with $p \geq 0.05$ can be regarded as statistically similar.

The absence of filter replicates is not a serious issue considering that the filter performances are similar (see above), and that the standard deviations (Table 4) of most outflow variables are comparable with large-scale systems (Cooper *et al.*, 1996; Kadlec and Knight, 1996; Vymazal, 2002; Karathanasis *et al.*, 2003). Moreover, a more detailed experimental study with three replicate filters, for example, would not be justified in terms of costs and potential scientific benefit.

Furthermore, case-based reasoning of the experimental data set has been applied by Lee *et al.* (2005). The purpose of this follow-up paper is to show how case-based reasoning can be applied for water quality control purposes.

CONCLUSIONS

Despite the highly variable water quality of road runoff, the novel filters showed great treatment performances particularly with respect to the 5-day at 20°C N-Allylthiourea biochemical oxygen demand (BOD) reduction in a cold climate. Removal efficiencies for SS in particular improved over time and dissolved copper was removed satisfactorily in comparison to values obtained from the literature. However, a breakthrough of dissolved nickel during the first winter of the first year of operation was observed. After creating an artificially high inflow pH of approximately 8 after 1 year of operation, nickel was successfully treated despite vulnerability to leaching when exposed to a high salt concentration during the second winter.

A high pH was apparently also linked to high removal efficiencies. The elevated pH had no apparent negative effect on the biomass including macrophytes. Moreover, filters showed a great pH buffering capacity. Findings indicate that conventional pH adjustment can be successfully applied to constructed wetland systems for storm water treatment.

The presence of Filtralite (adsorption filter media) and *Phragmites australis* (Cav.) Trin. ex Steud., common reed (macrophyte), did not result in an obvious reduction of metal concentrations in outflow waters. Operational conditions such as inflow pH and retention time were more important for the heavy metal treatment.

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