Retention of heavy metals and poly-aromatic hydrocarbons from road water in a constructed wetland and the effect of de-icing

Karin Tromp [a,1], Ana T. Lima [b], Arjan Barendregt [c], Jos T.A. Verhoeven [a,*]

[a] *Ecology and Biodiversity, Department of Biology, Utrecht University, Padualaan 8, 3584 CA Utrecht, The Netherlands*
[b] *Geochemistry, Dept. of Earth Science, Utrecht University, P.O. Box 80021, 3508 TA Utrecht, The Netherlands*
[c] *Interfacultary Institute for Risk Assessment Science, Toxicology Division, Utrecht University, P.O. Box 80177, 3508 TD Utrecht, The Netherlands*

ARTICLE INFO

ABSTRACT

A full-scale remediation facility including a detention basin and a wetland was tested for retention of heavy metals and Poly-Aromatic Hydrocarbons (PAHs) from water drained from a motorway in The Netherlands. The facility consisted of a detention basin, a vertical-flow reed bed and a final groundwater infiltration bed. Water samples were taken of road water, detention basin influent and wetland effluent. By using automated sampling, we were able to obtain reliable concentration averages per 4-week period during 18 months. The system retained the PAHs very well, with retention efficiencies of 90–95%. While environmental standards for these substances were surpassed in the road water, this was never the case after passage through the system. For the metals the situation was more complicated. All metals studied (Cu, Zn, Pb, Cd and Ni) had concentrations frequently surpassing environmental standards in the road water. After passage through the system, most metal concentrations were lower than the standards, except for Cu and Zn. There was a dramatic effect of de-icing salts on the concentrations of Cu, Zn, Cd and Ni, in the effluent leaving the system. For Cu, the concentrations even became higher than they had ever been in the road water. It is advised to let the road water bypass the facility during de-icing periods.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Run-off from road surfaces is polluted with Poly-Aromatic Hydrocarbons (PAHs) and heavy metals, which arise from car tires, exhausts and metal structures in light poles and crash barriers. Mostly these substances drain off to the road margins, where they may become deposited, bound to soil particles or infiltrate towards the groundwater [1–4]. Large stretches of roads, have sewer systems to collect the runoff from fly-overs or viaducts. These systems create point sources of hazardous pollutants which periodically may reach concentrations harmful for the environment [5,6].

In many parts of the European Union, the material used for road surfaces during the last decades is increasingly the so-called "Pervious Coated Macadam", which has relatively large pores that effectively drain the storm water during heavy rain showers. The downside of such road surfaces is that the pores easily accumulate particulate material with high concentrations of heavy metals and PAHs. Torrential rain storms may flush out these accumulated pollutants and create periodical peaks in runoff concentrations [7].

Measures to reduce these emissions include periodic road sweeping, where the pollutants are flushed out of the pores and collected in a truck, and the use of gully pots in sewer systems, where polluted particles accumulate and can be periodically removed [8].

Road de-icing with salt (NaCl) has been found to release particulate as well as dissolved pollutants from the road surface. This creates problems particularly in Northern countries, where seasonal frosts may be frequent and of long duration. For instance in Sweden, large amounts of trace elements are mobilized in roadside soils every year due to the use of NaCl as de-icing agent, threatening many of the shallow drinking water eskers [9,10]. When a sewer system is involved, where large amounts of particulate pollutants accumulate at road surfaces or in gully pots, de-icing can similarly provoke the release of pollutants to the surrounding environment [8]. In the Netherlands, national and regional governments have already set standards for receiving surface waters and groundwater bodies with respect to point sources of storm water runoff [11].

A constructed natural ecosystem involving phytoremediation [12,13] could serve as a buffer for such pollution sources. Constructed wetlands have been previously used to purify point sources of road runoff before it enters the environment [6,14,15]. Retention of contaminants does occur, due to sedimentation and adsorption [16,17]. Studies of the effects of first flush phenomena and de-icing on the retention capacity and the outflow pollutant concentrations have shown quite variable results, with potential
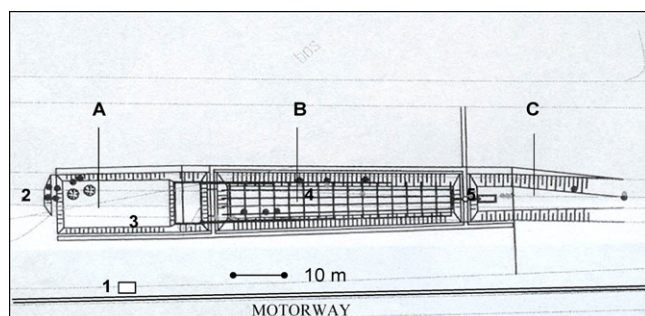
Fig. 1. Road water remediation facility along the A1 near Laren, The Netherlands. A, Detention basin; B, Vertical-flow wetland with Common reed; C, Infiltration ditch. 1, Road verge, location of road water samplers; 2, Precipitation collector; 3, Inflow pipe with discharge meter and influent sampler; 4, Perforated tubes for wetland inflow and outflow; 5, Effluent sampler.

mobilization of copper, zinc and lead as a result of contact with salt water [10,18–20].

This study is addressing the performance of a vertical-flow constructed wetland designed for purifying stormwater runoff from a motorway stretch drained by a sewer system. The wetland was constructed with the objective to comply with the standards for groundwater in a sandy drinking water protection zone, which were imposed by the provincial government of North Holland. The wetland was a full-scale research object equipped with automated sampling devices for measuring discharge and water quality. We investigated the following research questions: (1) What are the reductions in concentrations going from road runoff via the sewer system (gully pots) towards the wetland and finally to the groundwater recharge point? (2) To what extent is there a first flush related to rainfall events? (3) What are the effects of road management measures (sweeping, de-icing)? (4) What is the 'best practice' for the road and wetland management?

2. Materials and methods

2.1. Location and design

This study was carried out along the A1 motorway from Amersfoort to Amsterdam, near the exit Laren, The Netherlands. This 4-lane motorway stretch has heavy traffic and runs through the soil and drinking water protection area "'t Gooi". The Province of North Holland has set strict limitations for the occurrence point sources from roads in this particular area, to prevent pollution by water rich in heavy metals and organic micropollutants. To comply with these rules, the drained motorway sections near fly-overs need facilities to minimize point source pollution. The investigated system encompassed a sewer system draining 1.8 ha of motorway and channeling the water to a series of gully pots which collect sediment; it ended in an engineered remediation facility in a trench beside the motorway (Fig. 1).

The remediation facility consisted of a water detention basin (A in Fig. 1) with a hard surface (area 228 m^2, of which 40 m^2 of gravel bed; volume 79 m^3) to store the water from large rain showers. From here, the water entered by gravity into two perforated tubes on top of a vertical-flow wetland (B) with a surface area of 250 m^2. The wetland was underlain by a plastic lining sealing it off from the sandy soils beneath and was planted with Common reed (*Phragmites australis*). The substrate was about 90 cm thick and consisted of 20 cm gravel with perforated inflow tubes, underlain by 40 cm of sand, root cloth, then another 20 cm of gravel with 4 parallel outflow drains and finally 10 cm of sand on top of the plastic lining. The water drained into a clean-water well with a retention capacity of 0.5 m^3 and an overflow draining finally into an infiltration ditch (C) of 41 m^2, where the water could drain towards the groundwater. The discharge of influent into the vertical-flow wetland amounted to approximately 3700 cm/year, while rainfall was 89 cm/year (values are means of two annual periods, data not shown). The facility had overflows that directed excess water at times of exceptional rainfall straight into the final infiltration ditch. This happened twenty times during the 18-month study period and about 10% of the total hydraulic load bypassed the wetland this way.

Road water was collected in funnels connected to sample barrels in a narrow box sunken into the road verge (1 in Fig. 1). Rain water was collected in rain gauges (2). Water flowed from the sewer into the detention basin (3), where its flow rate was continuously monitored with a discharge meter and volume-proportional samples were taken of this influent (20 mL for each 100 L), which were collected in sampling bottles in a metal box (automated sampling device ISCO 6712). The effluent was sampled at the end of the vertical-flow wetland (5), where time-proportional samples were collected (one 50-mL sample per 2 h). Flow rate and sampling, as well as water levels in the detention basin and wetland, were continuously monitored with Diver water level loggers. Water samples (barrels and flasks) were collected from the outside storage cupboards every week and transferred to the laboratory at Utrecht University. pH was measured in the field of each sample that contained water (influent bottles remained empty in weeks without rain).

2.2. Sampling procedure and laboratory analysis

The monitoring period was 27 January 2003 through 5 September 2004. In this period, 80 weekly samples of road water, remediation facility influent (measured at the inflow of the detention basin) and effluent (measured at the outflow of the wetland) were collected and refrigerated (4 °C). Samples for four consecutive weeks were combined by thorough mixing, so that finally 20 mixed samples for 4-week periods for each of these three water types were analysed. The mixing procedure was carried out separately for samples to be analysed for heavy metals, PolyAromatic Hydrocarbons (PAHs) and chloride.

For heavy metals, two 100-mL subsamples from each weekly sample were taken immediately after collection. One of the subsamples was filtered over a 0.45 μm membrane filter and contained the dissolved fractions of the metals, the other subsample remained unfiltered and contained the total concentrations of the metals. Both subsamples were acidified with a mixture of nitric acid (65%) and hydrochloric acid (35%); four weekly subsamples of both categories were mixed thoroughly for each period. The mixed samples were diluted 1:10 with nitric acid (45%) and measured for Cd, Cr, Cu, Ni, Pb and Zn with Inductive Coupled Plasma Mass Spectrometry (ICP-MS).

For PAHs, 200-mL subsamples from four weekly samples were thoroughly mixed. The mixed samples were extracted with the organic solvent cyclohexane according to the 'reflux' method, by which the cyclohexane extract was evaporated after separation from the water phase. The residue was dissolved in acetonitril and analysed for PAHs with an HPLC Fluorescence meter in the laboratory of the Institute for Risk Assessment Sciences of Utrecht University. 11 PAHs were analysed, which are all part of the group of 16 EPA priority PAHs, i.e., phenantrene, anthracene, fluorantene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluorantene, benzo[k]fluorantene, benzo[a]pyrene, dibenz[a,h]anthracene and benzo[ghi]perylene.

For chloride, 10-mL subsamples from each weekly sample were filtered over a 0.45 μm membrane filter and combined to a mixed sample for a 4-week period; chloride concentrations were measured with a Skalar continuous-flow auto-analyzer.

Table 1
Contaminant concentrations in μg/L. Values are minimum, maximum and average values ± SD of 20 monthly samples.

	Runoff (μg/L)			Influent (μg/L)			Effluent (μg/L)			Dutch Standards (μg/L)[a]	EU Standards (μg/L)[b]	EPA standards (μg/L)[c]
	Min.	Average	Max.	Min.	Average	Max.	Min.	Average	Max.			
Cd	0.1	0.6 ± 1.2	5.5	0.1	0.4 ± 0.4	1.3	0.1	0.6 ± 1.1	4.3	2	0.4	0.08–0.25	0.25
Cr	0.8	4.1 ± 2.8	10.5	1.0	2.7 ± 1.3	6.1	0	1.2 ± 0.6	2.2	84	1.0	–	74/11
Cu	21.7	117.1 ± 101.8	445	36	103.5 ± 89.2	405	12.3	113.0 ± 215.4	980	3.8	15	–	1–1000[d]
Ni	1.3	3.8 ± 2.7	12.5	1.1	2.1 ± 0.9	5.1	2.9	6.1 ± 3	16.2	6.3	15	20	52
Pb	7.4	29.3 ± 18	71.7	2.7	7.1 ± 4.1	19.8	0	5.1 ± 4.3	15	220	15	7.2	2.5
Zn	115	289.8 ± 171	602	62	115.3 ± 44.3	256	15.1	67.8 ± 83	378	40	65	–	120
Anthracene	0.004	0.021 ± 0.02	0.08	0	0.003 ± 0.002	0.009	0	0.0009 ± 0.0013	0.004	0.08	0.0007	0.1	40,000
Phenanthrene	0	0.20 ± 0.22	0.77	0	0.08 ± 0.12	0.39	0	0.02 ± 0.06	0.24	0.3	0.003	–	–
Fluoranthene	0	0.78 ± 0.95	3.65	0	0.06 ± 0.07	0.24	0	0.004 ± 0.012	0.05	0.5	0.003	–	140
Benzo(a)anthracene	0.04	0.19 ± 0.2	0.89	0	0.02 ± 0.02	0.07	0	0.0013 ± 0.0014	0.0034	0.03	0.0001	–	0.018
Chrysene	0.09	0.44 ± 0.51	2.17	0	0.05 ± 0.04	0.16	0	0.006 ± 0.010	0.039	0.9	0.003	–	0.018
Benzo(k)fluoranthene	0.03	0.12 ± 0.12	0.46	0.004	0.02 ± 0.01	0.05	0	0.0017 ± 0.0015	0.006	0.2	0.0004	0.003	0.018
Benzo(a)pyrene	0.06	0.25 ± 0.23	0.84	0.009	0.03 ± 0.02	0.11	0	0.0018 ± 0.0024	0.01	0.2	0.0005	0.05	0.018
Benzo(g,h,i)perylene	0.09	0.36 ± 0.34	1.27	0.01	0.06 ± 0.05	0.19	0	0.008 ± 0.009	0.03	0.5	0.0004	0.002	–

[a] Dutch standards regarding total contents for surface waters/target values for shallow groundwater (Normen voor het waterbeheer, 2000).
[b] Quality standards for annual average concentrations for inland surface waters listed in the European Directive 2008/105/EC.
[c] Freshwater chronic level for priority contaminants according to the water quality criteria by EPS for the US.
[d] EPA Report "Aquatic life ambient freshwater quality criteria - Copper", EPA Washington DC, 2007.

2.3. Data analysis

The sampling procedure resulted in a range of concentration data over time for the road water, the influent to the detention basin and the effluent of the vertical-flow wetland. Although some of the pollutant retention in the remediation facility may have occurred by sedimentation in the detention basin, the residence time of water in that basin is so much lower than that of the vertical-flow wetland, that most retention will have occurred in the latter. We have no data on the performance of these two parts of the total system and will refer to the detention basin plus vertical-flow wetland as 'wetland' in the further paper. Although there are 20 sampling points in time, each giving a representative value for the concentrations of pollutants over the 4-week interval, these cannot be seen as replicates, because there are seasonal dynamics related to rainfall and the application of de-icing salts. Therefore, the data have not been tested statistically, but rather analysed by comparing the means, SD and highest and lowest value for the PAHs and heavy metals for the road water, the wetland influent and wetland effluent. The comparison of the former two water types gives the retention of the sewer system draining the road water towards the wetland, while the comparison of the latter two water types gives the retention of the wetland. As we found distinct dynamics related to de-icing salt application for the heavy metals, we presented these data graphically as well.

The retention efficiency of the sewer system and the wetland were further analysed by calculating the removal percentages on the basis of concentration changes. For the sewer system, this was calculated as $(C_{\mathrm{road\ water}} - C_{\mathrm{influent}}) \times 100\%/C_{\mathrm{road\ water}}$, for the wetland system as $(C_{\mathrm{influent}} - C_{\mathrm{effluent}}) \times 100\%/C_{\mathrm{influent}}$.

3. Results

3.1. Metals

The average concentrations of the metals studied were generally highest in the road runoff, intermediate in the wetland influent (after passage of the road sewer system) and lowest in the wetland effluent (Table 1). This behaviour is evident for zinc, lead and chromium. Concentrations for lead and chromium were continually highest in the road runoff, with a strong decline towards the wetland influent and a further reduction towards the wetland effluent (Fig. 2A and B). Zinc showed a similar pattern but had a distinct peak in influent and effluent concentrations in March 2004, when the wetland effluent even surpassed the road runoff concentrations (Fig. 2C). The concentrations for copper (Fig. 2D) were continuously lowest in the wetland effluent, except for the period January–March 2004, when the concentration in the wetland effluent reached a very high peak, beyond any values measured in the road runoff or wetland influent. The peaks for copper and zinc coincided with a peak in the chloride concentration in the road runoff as a result of de-icing salt (Fig. 3). There is no obvious relation between the temporal patterns and the rainfall patterns, or with the occurrence of road sweeping actions. The pH in the three water types did not fluctuate much and was mostly in the range between 7.0 and 8.2 (Fig. 4). It was slightly lower in the road water than in the wetland influent and effluent.

The comparisons of concentrations during passage of the system showed a totally different picture for nickel and cadmium. Both elements showed a decline in average concentration going from road runoff to wetland influent but then an increase again during passage through the wetland, for nickel to even higher values than in the original road runoff (Table 1). The temporal patterns of concentrations for nickel showed that the concentrations in runoff were highest in the wetland effluent most of the time, with a prominent
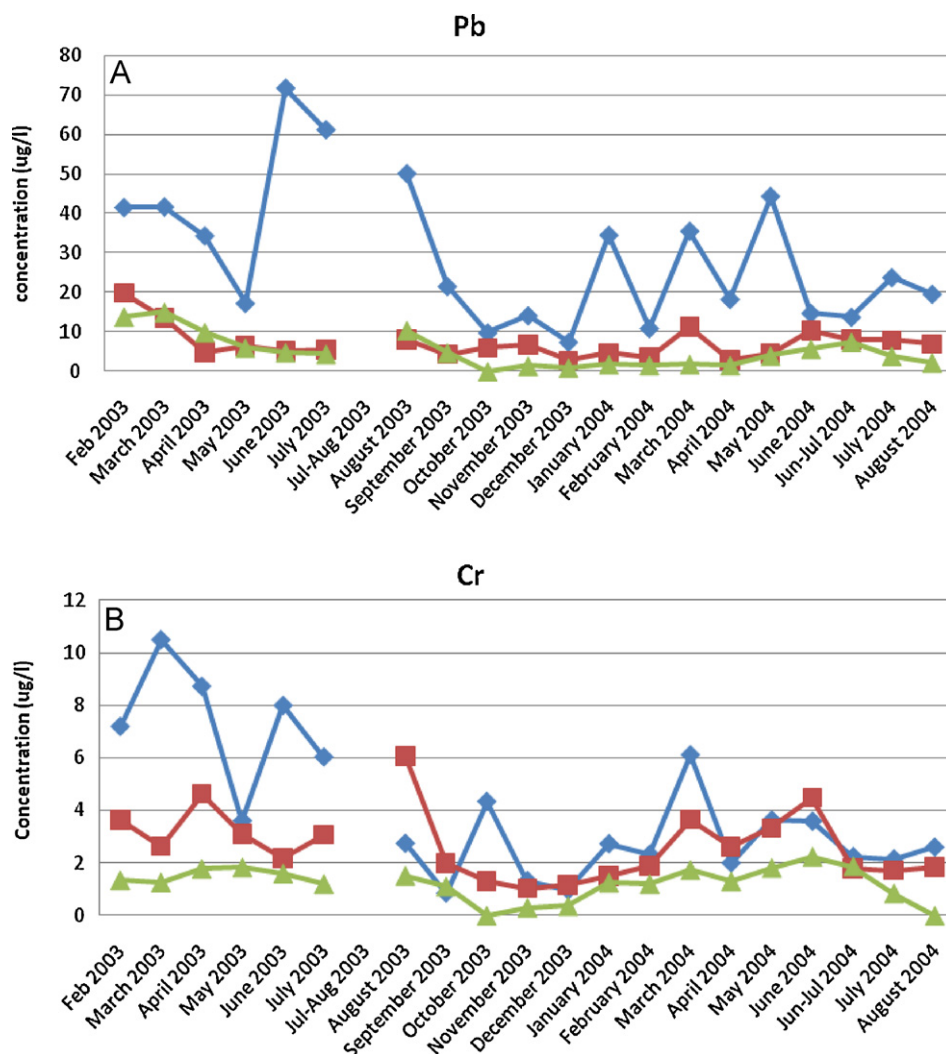
Pb

Cr

Fig. 2. (A–F) Concentrations of metals in road runoff, detention basin influent and wetland effluent in the course of the study period. Values represent total concentrations in monthly integrated samples.

Table 2
Percentages of particulate and dissolved fractions in road runoff, detention basin influent and wetland effluent. Values are averages of 20 monthly samples.

	Cd	Cr	Cu	Ni	Pb	Zn
Road water						
Particulate	31	64	30	49	91	55
Dissolved	69	36	70	51	9	45
Influent						
Particulate	22	23	8	14	58	26
Dissolved	78	77	92	86	42	74
Effluent						
Particulate	8	19	4	5	27	7
Dissolved	92	82	96	95	73	93

peak at the same moment as copper and zinc (Fig. 2E). Cadmium was mostly very low in the wetland effluent, except for peaks in the winter periods, again most distinctly in March 2004 (Fig. 2F). The peaks in the January–March 2004 period coincide with the period of de-icing salt application (Fig. 3).

The values presented in Table 1 and Fig. 2A–F are total concentrations. Particulate and dissolved fractions in road runoff differ for the various metals (Table 2). Cadmium and copper have high dissolved fractions (about 70%), nickel and zinc are about fifty-fifty and chromium and lead have low dissolved fractions. The partitioning changes towards higher dissolved fractions during passage through the system. After passage through the sewers, all metals had dissolved fractions higher than 70% except for lead. Finally, after passage through the wetland, 4 of the metals had dissolved fractions higher than 90% and all were higher than 70%.

When compared to environmental standards for surface water, it is clear that only the concentrations of chromium remain below the standards at all times for all three water types, whereas this element does surpass the Dutch standard for shallow groundwater regularly (Table 1). For nickel, the averages remain below the standards, although the value for the wetland effluent comes close to the Dutch surface water standard. Peak values for this element occasionally surpass this standard. The concentrations for lead stay permanently below the Dutch standard, but quite regularly surpass the stricter EU standard for surface water, in particular in the road runoff and the wetland influent. Cadmium concentrations surpass the Dutch standards occasionally, even in the wetland effluent, and go very often beyond the EU standards (Table 1). The largest problems in terms of surpassing environmental standards are formed by copper and zinc. Both elements often reach values that are much higher than the standards for surface water as well as shallow groundwater in The Netherlands. The very high peaks in the wetland effluent in the winter (at times of road de-icing) are a potential environmental hazard.
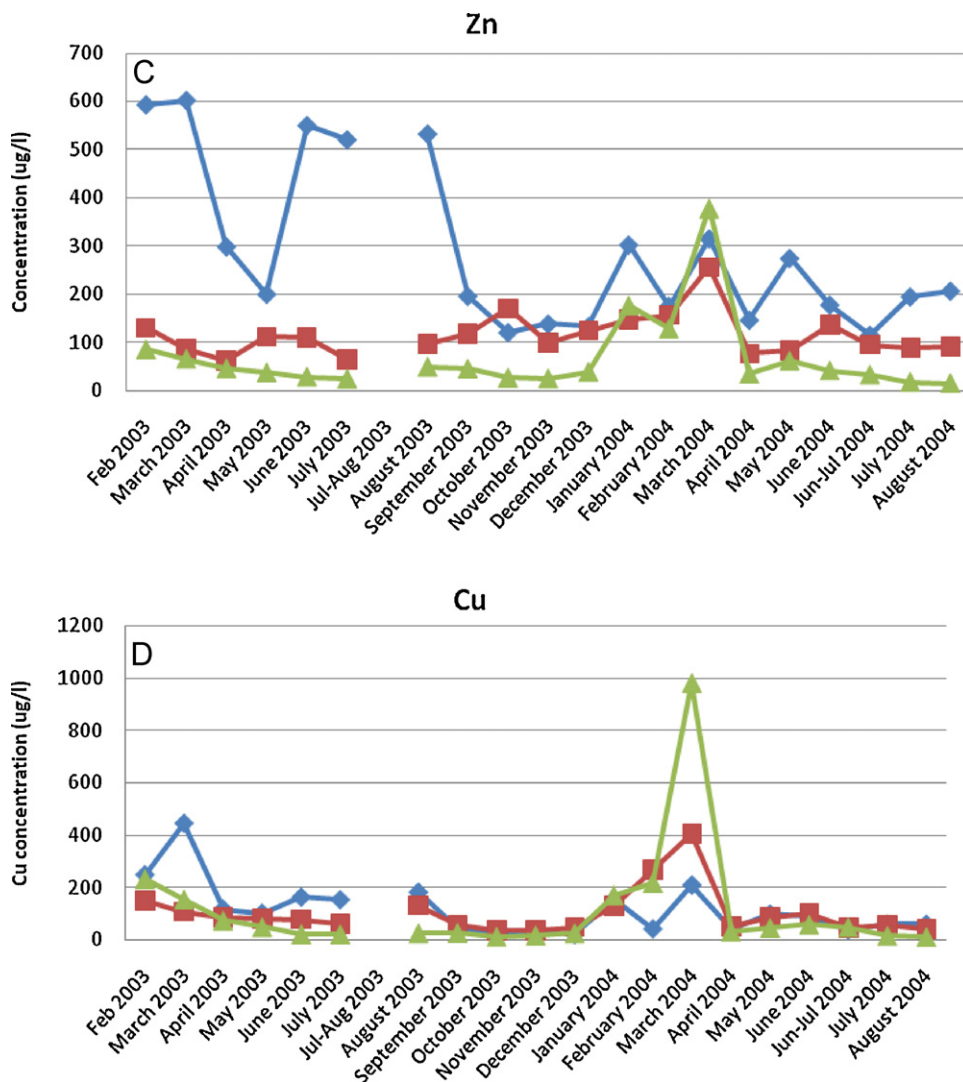
Fig. 2. (*Continued*).

3.2. Poly-aromatic hydrocarbons

All eight PAHs studied showed the same pattern for comparisons between the concentrations at different stages during passage through the roadside system: highest values for road runoff, intermediate values for wetland influent and lowest values for wetland effluent (Table 1). The final average concentration in wetland effluent was at least 10–20 times, often even 50–100 times lower than the original concentrations in road runoff. Both steps in the process (sewer system and wetland) contributed significantly to these decreases. It is clear that the standard deviations of means are commonly high, indicating considerable concentration changes in time. However, the seasonal patterns of concentrations were not related to rainfall or salt use (data not shown).

The average concentrations in road runoff surpassed the Dutch environmental standards for surface water for three of the studied PAHs, i.e. fluoranthene, benzo[a]pyrene and benzo[a]anthracene; the average concentration of the last compound was 6 times higher than the standard (Table 1). The concentrations in wetland influent and effluent never surpassed these standards for any of the compounds studied. However, the average concentrations of benzo[k]fluoranthene and benzo[g,h,i]perylene in road runoff as well as wetland influent did surpass the much stricter standards put forward by the EU. All eight compounds did not entirely meet

target values for groundwater set by the Dutch government, even in wetland effluent, although most target values were approached there while the values were much higher in the influent and road runoff (Table 1).

4. Discussion

4.1. Performance of the facility

The engineered system along the motorway A1, consisting of (1) the sewer system including gully pots and (2) the remediation facility (the detention basin plus vertical-flow wetland), generally retained PAHs and heavy metals quite well. The retention took place both in the sewer system and in the remediation facility (indicated as 'wetland' from here on). Sedimentation of particles was probably the major mechanism for organic pollutants as well as metals, in both sections of the total system. The general pattern of average concentrations: highest in the road water, intermediate in the wetland influent and lowest in the wetland effluent (the end discharge of the system) was found for all 8 PAHs studied and for the metals zinc, lead, chromium and copper. Only nickel and cadmium showed a quite low retention; both elements showed seasonally high concentrations in the water leaving the systems, sometimes even higher than road water concentrations. The only
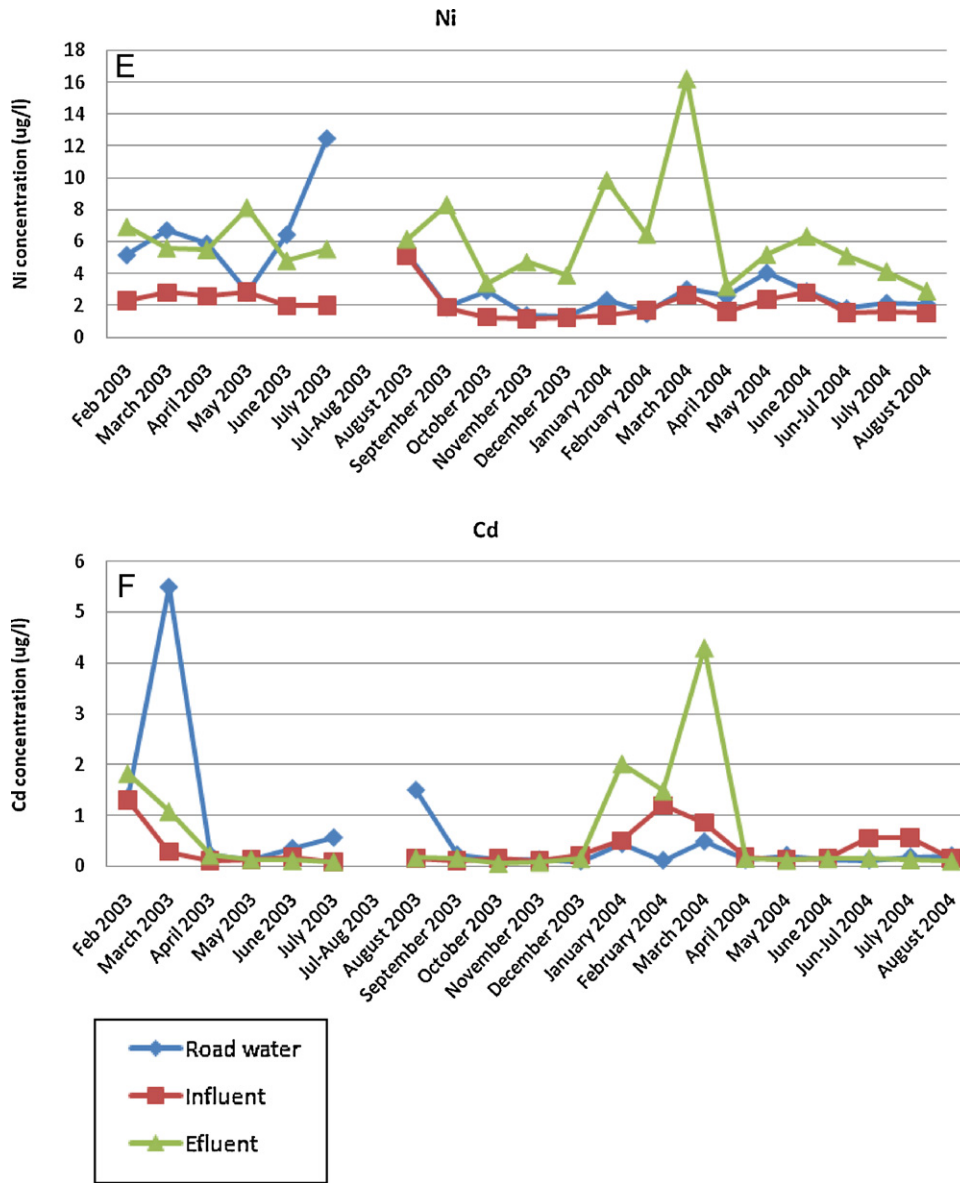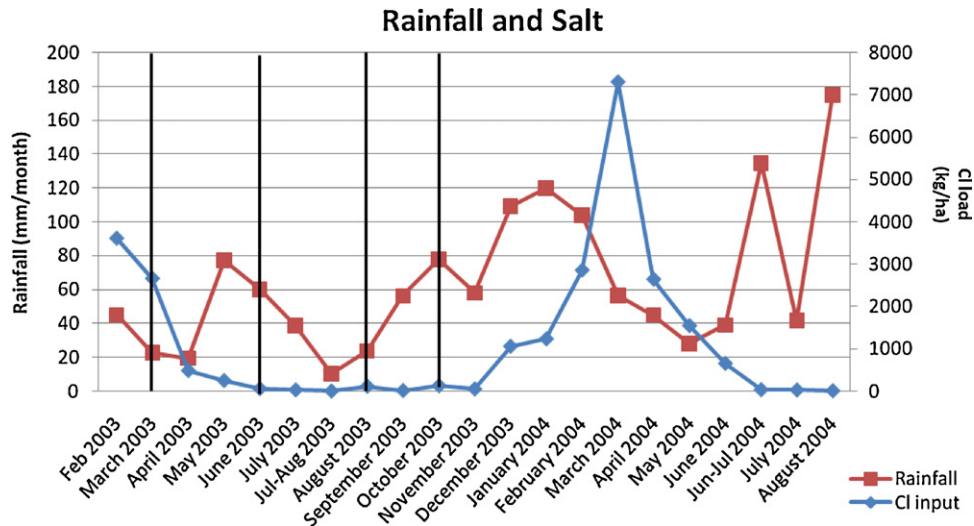
Fig. 2. (*Continued*).

Fig. 3. Rainfall (mm) and chloride input (kg/ha) for each monthly period at the A1 near Laren; the 4 thick vertical lines represent the sweeping events.
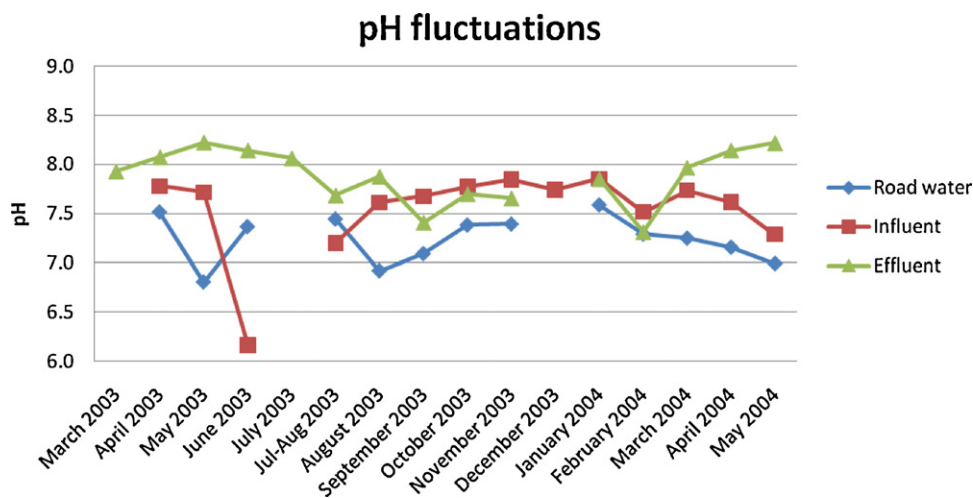
Fig. 4. pH changes in the sampled water throughout the year.

clear mechanism explaining the periodically high peaks in the concentrations of copper, zinc, cadmium and nickel is the leaching of metals due to high sodium and chloride concentrations after application of de-icing salts in winter.

Efficiency calculations based on concentration changes summed for a one-year period showed that high PAH retention percentages were reached in the sewer system as well as in the wetland (Table 3). All efficiencies are above 60% and by far the most are above 80%. This means that total efficiencies for the whole system are generally over 90–95%. This is in accordance with previous studies [21]. However, some authors have found that the growth of wetland plants was significantly influenced by PAHs regardless of the medium (water or soil) and PAH types [22]. Nevertheless, *Phragmites australis* formed a healthy vegetation in our wetland and we detected no visible damage. For the metals the situation is more complicated. Some laboratory studies, and smaller scale constructed wetlands, show a high retention of metals [23,24]. Here we have to distinguish between the particulate and the dissolved fractions (Table 3). Removal percentages were always positive for particulate fractions, but positive as well as negative for dissolved fractions. This means that both parts of the total system did function as traps for particles for all six metals studied (except for nickel in the wetland). The sewer system showed high particulate removal percentages for all metals, but negative values for dissolved chromium, copper and lead. These three metals did

settle as particulates but were partly leached out, mostly in de-icing periods. The wetland showed this pattern even more strongly for cadmium and nickel, which showed net leaching percentages over 100% and moderately also for copper and lead (leaching percentages 15–37%). This led to an overall net loss from the wetland of nickel (213% of the input), cadmium (74%) and copper (11%). The other metals showed positive total retention percentages in the wetland.

Although net loss of dissolved metals primarily occurred in de-icing periods, for nickel the net leaching from the wetland occurred all year around. Nickel leaching from road surfaces and sewer systems has been found to be associated with pH values lower than 8 [25]. The role of the reed vegetation in mobilizing metals, particularly nickel, in planted treatment wetlands has been suggested in other studies [26,27]. The acidifying effect of decomposing litter has been suggested as a mechanism. In our system, however, pH in the wetland effluent was even higher than that in the influent, while both were in the pH range where nickel is rather soluble [25]. It may be assumed that the sand or gravel used to build up the wetland bottom had relatively high nickel contents and these were slowly leached from the system. For the other metals, it is probable that the reed vegetation has contributed to the retention by taking up dissolved species in the roots and rhizomes. Such removal mechanisms involving plant uptake have been shown for chromium, zinc and copper [28,29]. Even if the net annual balance for dissolved fractions of copper and zinc in the wetland is negative, these uptake mechanisms will have contributed to their (temporary) retention. Easy leaching of dissolved species has been found regularly in studies of roadside soils and urban runoff, in particular for cadmium, zinc and copper [18,30].

The addition of NaCl in order to facilitate de-icing, has provoked the release of previously retained metals towards the effluent, which happened particularly in the wetland. The de-icing through salinization is indeed a drawback, decreasing the wetland's efficiency as an attenuator of micro-pollutants, in particular copper, zinc, cadmium and nickel. The net release of these metals evidences that they had not been adsorbed by the plants to a great extent, but had been accumulating in the soil and in the plant litter.

De-icing effect on metal release is well documented [30,31], where low pH and displacement of the cations by Na$^+$ are indicated as the main causes. In the present study, no significant pH fluctuations were observed throughout the investigated period, so that pH cannot have played a major role (Fig. 4). Therefore, the main cause for the observed behaviour must have been the exchange of cations at charged surface sites, such as clays and (plant-derived)

Table 3
Removal percentages of heavy metals and PAHs in the sewer system (incl. gully pots) and in the remediation facility, based on concentration changes. Positive values indicate removal, negative values a release. The percentages refer to the input into the sewer system (road runoff) and the remediation facility, respectively.

	Cd	Cr	Cu	Ni	Pb	Zn
Heavy metals removal % in sewer system						
Total	40	39	13	48	76	60
Particulate	57	79	77	85	85	81
Dissolved	32	−33	−15	11	−14	34
Heavy metals removal % in the remediation facility						
Total	−74	51	−11	−213	28	42
Particulate	30	34	47	−13	67	84
Dissolved	−105	49	−15	−337	−37	24

Phen	Anth	Fla	Pyr	B(a)A	Chry	B(b)F	B(k)F	B(a)P	DIB(a,h)A	B(g,h,I)P	Sum
PAH removal % in sewer system											
60	86	92	87	89	89	87	85	88	82	84	86
PAH removal % in the remediation facility											
69	70	94	91	94	88	93	91	94	93	87	87

organic matter. When metals are readily released by salts they are considered to be in an exchangeable form, i.e. adsorbed to hydrated iron oxides, manganese oxides or humic acids [32]. When NaCl was introduced into the wetland where the heavy metals had been accumulating and had become adsorbed to these exchange sites, the very high concentrations of Na+ then substituted the heavy metals, mobilizing them to the soil pore water, a well-known mechanism [33].

Humic substances proliferate in a wetland and play an important role in these environments [34,35]. Amrhein et al. [20] observed elevated Cr concentrations that were correlated with dissolved organic matter concentrations. They concluded that the mobilization of Cu, Ni, Cr, Pb, and Fe from roadside soils was mostly controlled by organic matter mobilization [20]. In our system, most of the heavy metals were found to be primarily in the particulate fraction, both in road water and in wetland influent (Table 3). Due to the relatively high pH (Fig. 4), the dissolved fractions of the metals are not expected to have been in the toxic ionic form, but rather in a form where they are bound to dissolved organic matter. Since the most substantial salt-provoked releases for copper, zinc and cadmium were observed in the wetland, it is likely that the main compound adsorbing these metals had been the non-soluble organic matter at the wetland bottom. Apart from direct substitution of metals by Na+, the salt most probably also led to organic matter solubilization and this resulted in an even higher release of the heavy metals. Recent authors stated that once the organic matter has been solubilized under the influence of road salt and thereafter leached, it is gone from the system, and 'once it has gone, it is gone', implying that with the organic matter solubilization, part of the adsorption capacity for metals is flushed out of the system [31].

4.2. 'Best management practice' for the road and the engineered system

Although there have been quite some studies investigating the functioning of wetland systems for road water treatment, the set-up designed here is in various aspects unique and has not been tested before. Most earlier studies have been done on wetlands as part of urban and/or road storm water detention structures [16,17,29,36] or on roadside soils and small trenches bordering roads and parking lots [4,9,30,31]. To the best of our knowledge, this is the first study where the performance of a full-scale sewer system and connected remediation facility with infiltration wetland is being tested for all major motorway-derived pollutants, i.e. PAHs and heavy metals, in a point source that is normally being infiltrated into a drinking water protection zone. Another unique feature of our system was that it was instrumented with volume- and time-proportional sampling devices so that reliable estimates of average monthly concentrations and retention efficiencies could be calculated.

The system performed reasonably well hydraulically; it did detain most of the water. The average residence time of the water in the wetland system was 5 days. This was in line with the design detention capacity and with the residence time in many other vertical-flow systems [37]. There were twenty overflows at times of very exceptional rainfall during the 18-month study period. These resulted in more than 10% of the annual water loading to be bypassing the wetland infiltration basin through an overflow at the end of the wetland. This has resulted in the discharge of polluted water in the final groundwater infiltration device beyond the wetland. Unfortunately, there are no separate measurements from the overflowing water. However, because of the still rather high residence time of the water in the system (minimum 24 h), the overflowing water will have been substantially cleaner than the wetland

influent. Still, it is advisable to increase the size of the storm water detention basin to diminish the frequency of overflows.

There was also an exceptionally long period of dry weather in the summer of 2003, resulting in 6 weeks without any water input into the system. Although the water level in the wetland dropped to several cm below the root cloth for at least four weeks, the *Phragmites* vegetation survived this period well, indicating that roots had penetrated through the cloth and were able to take up water. All in all, the system performed in a robust way.

It is clear from the comparison of concentrations and standards that most PAHs and heavy metals had concentrations far above environmental standards in the road water, except for anthracene and chromium. The sewer systems removed substantial amounts of both types of pollutants, but copper, zinc and cadmium still showed averages beyond the standards, as well as two of the PAHs. At the end of the system the PAHs were all below or at the standard, but copper and zinc were still much too high. Because this is mostly due to the high peaks during periods of de-icing, the best practice would be to bypass the wetland influent directly to the groundwater infiltration area during winter periods with de-icing. A gully or tube should be constructed to bring the water directly from the detention basin to the end of the system. The wetland can then accumulate the heavy metals during the rest of the year and the average values for concentrations of infiltrating water can be assumed to drop below the environmental standards. Regular removal of sludge from gully pots in the sewer system and road sweeping are also important road management measures. Although the latter did not show direct relationships with road water concentrations, one can assume major problems when these measures would be abandoned.

The remediation facility studied has been designed for a lifetime of 25 years. In the course of time, heavy metals and PAHs will gradually accumulate on the bottom of the detention basin and in the soil and vegetation of the vertical-flow wetland. No data are available at this moment on concentrations of pollutants in plant and soil material. Recently published studies have shown that wetland plants in remediation systems mostly store heavy metals in their below-ground organs [38,39]. Metals also accumulate in the filling medium and during the generation of soil organic matter as plant litter is decomposed [40]. The facility studied by us is isolated from the environment through the plastic lining underneath it, so that no vertical flow towards the groundwater is possible. However, the prolonged loading of the facility with road water will eventually lead to a hazardous, polluted sediment and root mat [40]. The agency managing the road will monitor vegetation and filling medium near the end of the life time of the facility. It is foreseen that the contaminated sediment in the detention basin and the vegetation, soil and subsoil of the wetland will be removed after 25 years and further handled as hazardous material, depending on the actual concentrations detected at the time.

The construction of this engineered facility is an example of good collaboration between the legislative provincial authority and the national agency responsible for road maintenance. It is advisable that such plans are developed in a formalized way including the use of a contract to arrange the mutual responsibilities [11].

5. Conclusions

Overall, the remediation facility has performed well and in a robust way. It retained the PAHs very well, with retention efficiencies of 90–95%. While environmental standards for these substances were surpassed in the road water, this was never the case after passage through the system. However, although most metal concentrations had concentrations lower than the standards after passing through the system, Cu, Zn, Cd and Ni showed a dramatic increase during applications of de-icing salts. For Cu,

the concentrations even became higher than they had ever been in the road water. It is recommended to modify the hydraulic management of the system in order to let the road water bypass it during such periods; the net retention of PAHs as well as metals by the system during the rest of the year will then lead to an effective reduction of the pollution caused by this point source. It is expected that the sediment and root mat of the facility will have to be treated as hazardous waste at the end of its life time of 25 years.

Acknowledgements

References

[1] D. Purchase, L.N.L. Scholes, D.M. Revitt, R.B.E. Shutes, Effects of temperature on metal tolerance and the accumulation of Zn and Pb by metal-tolerant fungi isolated from urban runoff treatment wetlands, Journal of Applied Microbiology 106 (2009) 1163–1174.

[2] R.M. Harrison, R. Tilling, M.S.C. Romero, S. Harrad, K. Jarvis, A study of trace metals and polycyclic aromatic hydrocarbons in the roadside environment, Atmospheric Environment 37 (2003) 2391–2402.

[3] J.A. Smith, M. Sievers, S. Huang, S.L. Yu, Occurrence and phase distribution of polycyclic aromatic hydrocarbons in urban storm-water runoff, Water Science and Technology 42 (2000) 383–388.

[4] C. Dierkes, W.F. Geiger, Pollution retention capabilities of roadside soils, Water Science and Technology 39 (1999) 201–208.

[5] K. Sriyaraj, R.B.E. Shutes, An assessment of the impact of motorway runoff on a pond, wetland and stream, Environment International 26 (2001) 433–439.

[6] R.J. Hares, N.I. Ward, Comparison of the heavy metal content of motorway stormwater following discharge into wet biofiltration and dry detention ponds along the London Orbital (M25) motorway, Science of the Total Environment 235 (1999) 169–178.

[7] J.L. Bertrand-Krajewski, G. Chebbo, A. Saget, Distribution of pollutant mass vs volume in stormwater discharges and the first flush phenomenon, Water Research 32 (1998) 2341–2356.

[8] M. Scholz, Treatment of gully pot effluent containing nickel and copper with constructed wetlands in a cold climate, Journal of Chemical Technology and Biotechnology 79 (2004) 153–162.

[9] M. Backstrom, S. Karlsson, L. Backman, L. Folkeson, B. Lind, Mobilisation of heavy metals by deicing salts in a roadside environment, Water Research 38 (2004) 720–732.

[10] A.C. Norrstrom, G. Jacks, Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts, Science of the Total Environment 218 (1998) 161–174.

[11] C. Faith-Ell, B. Balfors, L. Folkeson, The application of environmental requirements in Swedish road maintenance contracts, Journal of Cleaner Production 14 (2006) 163–171.

[12] A.C. Dietz, J.L. Schnoor, Advances in phytoremediation, Environmental Health Perspectives 109 (2001) 163–168.

[13] J.L. Schnoor, L.A. Licht, S.C. McCutcheon, N.L. Wolfe, L.H. Carreira, Phytoremediation of organic and nutrient contaminants, Environmental Science & Technology 29 (1995) A318–A323.

[14] R.E. Shutes, D.M. Revitt, L.N.L. Scholes, M. Forshaw, B. Winter, An experimental constructed wetland system for the treatment of highway runoff in the UK, Water Science and Technology 44 (2001) 571–578.

[15] L. Scholes, R.B.E. Shutes, D.M. Revitt, M. Forshaw, D. Purchase, The treatment of metals in urban runoff by constructed wetlands, Science of the Total Environment 214 (1998) 211–219.

[16] R.J. Hares, N.I. Ward, Sediment accumulation in newly constructed vegetative treatment facilities along a new major road, Science of the Total Environment 334 (2004) 473–479.

[17] D.M. Revitt, R.B.E. Shutes, R.H. Jones, M. Forshaw, B. Winter, The performances of vegetative treatment systems for highway runoff during dry and wet conditions, Science of the Total Environment 334 (2004) 261–270.

[18] P.K. Lee, J.C. Touray, Characteristics of a polluted artificial soil located along a motorway and effects of acidification on the leaching behavior of heavy metals (Pb, Zn, Cd), Water Research 32 (1998) 3425–3435.

[19] C. Amrhein, P.A. Mosher, J.E. Strong, P.G. Pacheco, Heavy-metals in the environment—trace-metal solubility in soils and waters receiving deicing salts, Journal of Environment Quality 23 (1994) 219–227.

[20] C. Amrhein, J.E. Strong, P.A. Mosher, Effect of deicing salts on metal and organic-matter mobilization in roadside soils, Environmental Science & Technology 26 (1992) 703–709.

[21] A.K. Haritash, C.P. Kaushik, Biodegradation aspects of Polycyclic Aromatic Hydrocarbons (PAHs): a review, Journal of Hazardous Materials 169 (2009) 1–15.

[22] Z. Zang, Z. Rengel, K. Meney, Polynuclear aromatic hydrocarbons (PAHs) differentially influence growth of various emergent wetland species, Journal of Hazardous Materials 182 (2010) 689–695.

[23] G.F. Hua, Z. Zhu, L.F. Zhao, J.Y. Huang, Clogging pattern in vertical-flow constructed wetlands: insight from a laboratory study, Journal of Hazardous Materials 180 (2010) 668–674.

[24] J. Liu, Y. Dong, H. Xu, D. Wang, J. Xu, Accumulation of Cd, Pb and Zn by 19 wetland plant species in constructed wetland, Journal of Hazardous Materials 147 (2007) 947–953.

[25] A.C.M. Bourg, Speciation of heavy metals in soils and groundwater and implications for their natural and provoked mobility, in: W. Salomons (Ed.), Heavy metals. Problems and Solutions, Springer, Berlin, 1995, pp. 19–31.

[26] B.H. Lee, M. Scholz, What is the role of Phragmites australis in experimental constructed wetland filters treating urban runoff? Ecological Engineering 29 (2007) 87–95.

[27] B.H. Lee, M. Scholz, Application of the self-organizing map (SOM) to assess the heavy metal removal performance in experimental constructed wetlands, Water Research 40 (2006) 3367–3374.

[28] L. Scholes, R.B.E. Shutes, D.M. Revitt, M. Forshaw, D. Purchase, The treatment of metals by urban runoff by constructed wetlands, The Science of the Total Environment 214 (1998) 211–219.

[29] R.B.E. Shutes, J.B. Ellis, D.M. Revitt, M. Forshaw, B. Winter, Urban and highway runoff treatment by constructed wetlands, Wetlands Ecosystems in Asia: Function and Management 1 (2004) 361–382.

[30] A.C. Norrstrom, Metal mobility by de-icing salt from an infiltration trench for highway runoff, Applied Geochemistry 20 (2005) 1907–1919.

[31] S.M. Green, R. Machin, M.S. Cresser, Long-term road salting effects on dispersion of organic matter from roadside soils into drainage water, Chemistry and Ecology 24 (2008) 221–231.

[32] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace-metals, Analytical Chemistry 51 (1979) 844–851.

[33] G. Sposito, The Chemistry of Soils, Oxford University Press, New York, 2008.

[34] J.K. Keller, P.B. Weisenhorn, J.P. Megonigal, Humic acids as electron acceptors in wetland decomposition, Soil Biology & Biochemistry 41 (2009) 1518–1522.

[35] C. Paludan, H.S. Jensen, Sequential extraction of phosphorus in freshwater wetland and lake sediment: significance of humic acids, Wetlands 15 (1995) 365–373.

[36] T. Larm, Stormwater quantity and quality in a multiple pond-wetland system: Flemingsbergsviken case study, Ecological Engineering 15 (2000) 57–75.

[37] J. Vymazal, Constructed wetlands for wastewater treatment in Europe, Backhuys, Leiden, 1998.

[38] E. Lesage, D.P.L. Rousseau, E. Meers, F.M.G. Tack, N. De Pauw, Accumulation of metals in a horizontal subsurface flow constructed wetland treating domestic wastewater in Flanders, Belgium, Science of the Total Environment 380 (2007) 102–115.

[39] J.S. Weis, P. Weis, Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration, Environment International 30 (2004) 685–700.

[40] A. Galletti, P. Verlicchi, E. Ranieri, Removal and accumulation of Cu, Ni and Zn in horizontal subsurface flow constructed wetlands: contribution of vegetation and filling medium, Science of the Total Environment 408 (2010) 5097–5105.