Distribution and mobilisation of pollutants in the sediment of a constructed floating wetland used for treatment of combined sewer overflow events

Date revised: 13 August 2010

Annelies M.K. Van de Moortel\(^1\)*, Gijs Du Laing\(^1\), Niels De Pauw\(^2\), Filip M.G. Tack\(^1\)

\(^1\) Department of Applied Analytical and Physical Chemistry, Laboratory of Analytical Chemistry and Applied Ecochemistry, Ghent University, Coupure Links 653, 9000 Gent, Belgium; email: Annelies.Vandemoortel@UGent.be; anneliesvandemoortel@hotmail.com; Gijs.Dulaing@UGent.be; Filip.Tack@UGent.be

\(^2\) Department of Applied Ecology and Environmental Biology, Laboratory of Environmental Toxicology and Aquatic Ecology, Ghent University, J. Plateaustraat 22, 9000 Gent, Belgium; email: Niels.Depauw@UGent.be

* Corresponding author
ABSTRACT

Sediments in combined sewer overflow treatment systems may exhibit elevated pollutant concentrations. Concentrations measured in the sediment of a floating treatment wetland ranged between 0.17–1.6 (Cd), 28–142 (Cu), 10–33 (Cr), 50–141 (Mn), 5–20 (Ni), 50–203 (Pb) and 185–804 (Zn) mg kg\(^{-1}\) DM and 7.4–17 (Fe), 2–8 (total nitrogen) and 1.3–4.4 (total phosphorus) g kg\(^{-1}\) DM. During overflow events the entering water volumes can disturb the sediments. A greenhouse experiment was set up to evaluate the possible mobilisation of pollutants through disturbance. The disturbance did not result in an increased mobilisation of Cd, Cu, Cr, Ni, Pb, Zn, N, P and organic carbon towards the pore and surface water. Calcium concentrations in the surface water increased for all sediments due to release from the exchangeable sediment pool, and dissolution of carbonates. Geochemical speciation modelling indicated that in the pore water the free ion form was the most abundant for Ca, Fe, Mn, Cd and Ni, with its fraction increasing with time.

Keywords: stormwater, wastewater treatment, Visual MINTEQ, mobility, metals, nitrogen, phosphorus,
The use of combined sewer systems has lead to uncontrolled discharges of (diluted) wastewater during rain periods. When overflow events occur large volumes of water, charged with high concentrations of sediments, suspended solids and dissolved and particulate-associated contaminants such as metals, pesticides, polycyclic aromatic hydrocarbons and nutrients, are released from the sewer system into the receiving water (Karouna-Renier and Sparling, 2001; Pontier et al., 2001). Both pond systems and constructed wetlands have been used to store and treat these discharges. In Flanders, Belgium, a constructed floating wetland (CFW), consisting of a sedimentation compartment and a compartment with floating macrophyte mats, was installed for storage and treatment of combined sewer overflow water in Bornem. In contrast with other surface and subsurface flow constructed wetlands, vegetation in CFWs is not rooting in a bottom substrate but growing in a matrix floating on the water surface. In addition, CFWs allow the treatment of highly variable volumes of overflow water, and less surface area is needed as higher water levels can be maintained.

Suspended solids present in stormwater and overflow water will be retained within the treatment system together with their associated pollutants, as flow velocity decreases. The size of the solids determines the ease of entrainment and transportation in the system. The <63 µm grain size fraction is the most easily transported by runoff and is associated with higher pollutant concentrations than larger grain sizes (Luker and Montague, 1994). The major retention mechanism for metals was reported to be adsorption to particles that subsequently settle down (Harlin et al., 1982; Carpenter and Lodge, 1986; Stevenson et al., 1988; Kadlec, 2000). Adequate removal of heavy metals in vegetated stormwater systems is due to the presence of the vegetation, which can reduce hydraulic flow and thus increases the residence
time in which sedimentation, filtration and bioaccumulation processes can occur (Hares and Ward, 2004). In ponds, sedimentation rates are the highest in deeper-water areas because wind- and wave induced resuspension is reduced (Bloesch, 1982; Dillon and Evans, 1982). The floating vegetation mats in CFWs will act as a cover, screening off the water surface and enhancing sedimentation. Also the collision of particles with the roots followed by root slough enhances removal of particulate-associated pollutants. Next to sedimentation, sorption of pollutants onto the settling particles results in increased concentrations of many pollutants within the sediments and demonstrates its sink-function (Weiss et al., 2006). Moreover, the water depth influences the retention and distribution of pollutants within constructed wetlands as it can affect organic matter content, pH and redox potential of the sediments (Goulet and Pick, 2001).

Next to the above mentioned parameters, also physical disturbances may affect metal mobility. When overflow water enters the system, the sediment layer can be turned over, especially near the inlet. On a smaller scale, sediments can also be mixed due to bioturbation by macro-invertebrates. This may result in migration and mobilisation of the pollutants present in the sediment towards the pore water and water column.

The aim of this study was twofold. The distribution of heavy metals and nutrients within a constructed floating wetland was studied by sampling five sediments along the flow path of the water entering the system. Furthermore, a greenhouse experiment including the sediments of Bornem was set up (i) to evaluate the potential mobilisation of pollutants and (ii) to monitor the effect of disturbances on mobilisation of pollutants.
MATERIAL AND METHODS

Description of the CFW site and sediment sampling

Sediment was collected from a full scale treatment system installed at Bornem, Flanders, Belgium, consisting of a sedimentation compartment followed by a constructed floating wetland (Figure 1) used for treatment of combined sewer overflow water. The floating macrophyte mats were mainly planted with *Iris pseudacorus*, *Carex* spp., *Typha latifolia* and *Scirpus lacustris*. This system was in use since 2001 and was designed to store a 2-yearly rain event, corresponding with the storage of 2309 m³ at a flow rate of 0.17 m³ s⁻¹. The constructed floating wetland was sealed with a HDPE-sheet to ensure its storage capacity and to prevent groundwater seepage. A concrete shoulder was constructed to separate partly the sedimentation compartment from the floating macrophyte mats. Initially the wetland was subdivided in three sub-compartments by stiffened cloths to provide proper guidance of the incoming water towards the outlet but over time rents appeared in the cloths. This may have resulted in altered flow conditions as water could go more easily from one sub-compartment to another without following the intended flow path. As such, plug flow conditions will probably be less pronounced with ageing of the system. Furthermore, during large overflow events water would flow over the concrete shoulder directly into the floating wetland compartment.

Sediment samples were taken during a cleaning of the operational system in October 2005. For this purpose the water was pumped out of the system. When all water was removed, sediment was collected from 5 to 20 cm below the sediment surface at 5 different sampling locations, two in the sedimentation compartment and three locations in the wetland compartment with the floating mats. The upper sediment layer (to about 5 cm below the surface) was removed with a spade to ensure that the samples only contained sediment that
was not yet oxidised through contact with air. Subsequently, a 250 mL airtight PE bottle was filled with the sediment. The recipient was filled completely to prevent subsequent oxidation. This sample was used for determination of the acid volatile sulphide content. Furthermore, enough sediment at each location was sampled and put in a plastic bag and transported for use in the greenhouse experiment.

Experimental set-up
The fresh sediment samples were sieved wet over a 5 mm mesh sieve and the fraction larger than 5 mm removed. After homogenisation, the five sediments were distributed over 2 replicate polyethylene boxes (32 x 24 x 20 cm). The boxes were placed randomly in a greenhouse located at the faculty campus in Gent. Each box was filled up with a sediment layer of 4 cm. Deionised water was added up to 14 cm from the bottom of the box. Evaporation was compensated for by regularly adding deionised water. The experiment ran from October 25, 2005 till January 17, 2006. Combined platina and gel reference electrodes (HI 3090 B/5; HI 9025, Hanna Instruments, Ann Arbor, USA) were permanently installed at a depth of 2 cm for in situ measurement of the redoxpotential in each box. The measured value was converted with reference to the Standard Hydrogen Electrode by adding the difference between the redox potential measured in a ZoBells solution (0.033 M K₃Fe(CN)₆ and 0.033 M K₄Fe(CN)₆ in 0.1 M KCl) and the theoretical value of +428 mV. Average difference was 240 ± 14 mV. Each box was fitted with 2 Rhizon soil moisture samplers (type MOM, Rhizosphere Research Products, Wageningen, The Netherlands) to sample the pore water in the sediment. These samplers filter the water over a filter membrane with a pore diameter of 0.2 µm by using a vacuum tube as driving force. The samplers were installed horizontally in the sediment on both sides of the boxes at a depth of 2 cm. To install them, holes were made into the wall of the recipient. Silicone was used to make all connections water tight. Samples
of the surface water were taken at 3 different depths (1, 5 and 8 cm below the water surface) by means of a syringe and plastic sample collection tube. Sampling was done at day 1, 8, 23, 29, 36, 43, 50, 57, 64, 71, 78, and 85 between October 25, 2005 and January 17, 2006. Samples of pore water collected by both Rhizon samplers of each treatment were pooled into one composite sample. The same was done for the three surface water samples collected at different sampling depths. Sediment samples were taken from each replicate at the beginning (day 1) and end (day 85) of the experiment by means of a plastic core sampler. For determination of the acid volatile sulphide content at the end, a 50 mL PE-bottle was filled with sediment and analyses started within 15 minutes after sampling.

The five collected sediment batches were subjected to two treatments. Treatment A comprised the undisrupted sediment whereas the sediment in Treatment B was turned over fortnightly, simulating the disturbance of the sediment during overflow events. To achieve this, the redox electrode was temporally removed and the sediment was stirred during 4 minutes with a rod, at a speed of approximately 100-120 rpm, bringing all the sediment into suspension. The total duration of the experiment was 85 days, but the disturbance only started after an initial stabilisation period of 24 days. Disturbation of the sediment was done on day 24, 38, 52, 66 and 80. Accordingly, sampling occurred only 5 days after disturbance of the sediment and short term mobilisation effects were not taken into consideration.

**Sediment analysis**

All sediment analyses were done in triplicate, except for the acid volatile sulphide (AVS) measurements that were performed in duplicate. AVS contents were determined on fresh sediment samples by transformation of sulphide to \( \text{H}_2\text{S} \) and absorption in a Zn-acetate solution, followed by a iodometric back-titration (Tack et al., 1997). Dry weight of the
sediment was determined after drying at 105°C until constant weight. Sediment for all other analyses was sieved wet over a 5 mm mesh, dried at 60°C and ground. Measurements included pH, organic matter content (OM), pseudo-total and exchangeable heavy metal and Ca contents, total nitrogen content (Ntot) and total phosphorous content (TP).

For determination of the pH an extract with water (pH (H$_2$O)) and KCl (pH (KCl)) was prepared. The pH (H$_2$O) of the sediment was measured in a 1/5 soil/demineralised water suspension after equilibration during 18 h (Van Ranst et al., 1999). For determination of pH (KCl), 10 g of soil was added to 25 mL 1M KCl. After 10 minutes of equilibration pH (KCl) was measured with a pH electrode (Orion 520 A) (Van Ranst et al., 1999). The organic matter content was determined by measuring the weight loss after incineration of oven-dried samples (2 h at 550 °C). Pseudo-total Ca and heavy metal contents in the sediments were measured after destruction of 1 g sediment with aqua regia (2.5 mL HNO$_3$ and 7.5 mL HCl). After 16 h at room temperature, the suspensions were heated to 150°C during 2 h. Filtered samples were analysed for Ca, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn by ICP-OES (Varian Vista MPX, Varian, Palo Alto, CA). For the determination of the exchangeable Ca and metal contents, 5 g of sediment was percolated with 150 ml NH$_4$OAc (Van Ranst et al., 1999). Exchangeable Ca, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn in the percolate was determined by GF-AAS (Varian SpectraAA-800/GTA-100, Varian, Palo Alto, CA) and ICP-OES. Standards were inserted for quality control at the end of each analysed batch or after every 20 samples. Results were only accepted when the concentrations measured in a control standard did not deviate more than 5% from the reference standard concentration. Total nitrogen (Ntot) content was determined after destruction with a mixture of H$_2$SO$_4$ and salicylic acid, Na$_2$S$_2$O$_3$, H$_2$SO$_4$ and a selenium mixture, at 380°C followed by steam distillation (Kjeltec System 1002 Destilling Unit). The formed NH$_3$ was absorbed in a boric...
acid solution and back titrated with 0.01 M HCl (Van Ranst et al., 1999). Total phosphorus (TP) content of the sediment was determined by colorimetry (Jenway 6500 spectrophotometer, Jenway, Essex, UK) using the method of Scheel after a destruction with HClO₄ (Van Ranst et al., 1999).

Water analysis

The pH of the pore and surface water was determined on day 50. As mentioned previously, pore water was filtered over a mesh size of 0.2 µm during sampling. Samples of the surface water were filtered over a 0.45 µm mesh size (type CM membrane filter, Macherey-Nagel, Düren, Germany) for analyses of heavy metals, Ca, K, Na, Mg, NO₃⁻, Cl⁻ and SO₄²⁻, inorganic (IC) and organic carbon (OC). Preceding analyses of Ca, Cd, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, Pb and Zn by GF-AAS and ICP-OES, water samples were acidified with a few drops of concentrated HNO₃. Total organic carbon (TOC), inorganic carbon, NO₃⁻, Cl⁻ and SO₄²⁻ contents were determined on non-acidified samples. Total organic carbon and IC-contents were measured with a TOC-analyser (TOC-5000, Shimadzu, Tokyo Japan). A Metrohm configuration consisting of a 761 Compact Ion Chromatograph equipped with a 788 IC Filtration Sample Processor and an anion exchange column (IC-AN-Column Metrosep A supp 4, Metrohm Ion Analysis, Switzerland) was used for determination of NO₃⁻, Cl⁻ and SO₄²⁻. Determination of total nitrogen (Ntot) and orthophosphate (P) contents (expressed as P) was carried out on the surface water samples only. The same procedure for total nitrogen analysis was used as described for the sediment. Orthophosphate concentrations in the water were determined according to the colorimetric method of Scheel (Van Ranst et al., 1999).
Statistical analyses

The presence of equal sediment characteristics in both replicates at the start of the experiment was tested by a non-parametric Wilcoxon test. The significance of differences between the compositions of the different sediments at the beginning of the experiment was assessed by means of a one-way ANOVA analysis of variance. Homogeneous subgroups were determined with a Tuckey post-hoc test.

Wilcoxon tests were also used to evaluate the effect of disrupting the sediment by comparing the concentrations present in the disrupted and undisrupted sediments at the end of the experiment. In order to assess the effect of time on the mobilisation, initial and final sediment conditions were compared by Wilcoxon tests. Pearson correlation coefficients were calculated for the sediments at the beginning of the experiment to evaluate the existence and significance of correlations between measured parameters. All statistical analyses were conducted by means of the statistical package SPSS 15.0 (SPSS, Chicago, IL, USA). A confidence level of 5% was adopted in all applied tests.

Geochemical modelling

The speciation of metals in the pore water was assessed using the geochemical speciation programme Visual MINTEQ 2.61 (Gustafsson, 2009). Concentrations of the anions (Cl\(^-\), NO\(_3^-\), PO\(_4^{3-}\), and CO\(_3^{2-}\)) and cations (Ca\(^{2+}\), K\(^+\), Mg\(^{2+}\), Na\(^+\), Cd\(^{2+}\), Cr\(^{2+}\), Cu\(^{2+}\), Fe\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\), Pb\(^{2+}\), and Zn\(^{2+}\)) were used as input. Because of the small volumes of pore water that were sampled, K\(^+\), Mg\(^{2+}\), Na\(^+\) and PO\(_4^{3-}\) measurements were not available. Data from the surface water was used for these components. Other input parameters considered were the pH of the pore water, measured after 50 days for each sediment treatment, the respective
redoxpotentials and a temperature of 15°C. Conductivity was calculated by the model.

Speciation was assessed for all 5 sediments and treatments on day 8, 29, 50 and 85.

RESULTS

Sediment analyses

Initial characteristics of the sediment were determined at day 1 (Table 1). Analyses of these characteristics did not reveal any significant difference between both replicates at the start of the experiment. Homogeneous subgroups were assessed and presented in Table 1. Sediment 4 contained significantly higher amounts of organic matter, Ntot, Cd, Cu, Mn, Ni, Pb and Zn in comparison with the other sediment samples. Elevated concentrations of sulphides, TP, Cr, Fe and Mn were detected in both sediments 4 and 5. The amount of organic matter was positively correlated with the amount of total nitrogen (R = 0.965; p = 0.008) and total phosphorus (R = 0.958; p = 0.01). Significant correlations were also observed for pH (H₂O) and pH (KCl) (R = 0.993; p< 0.01), pH (H₂O) and Ca (R = 0.754; p= 0.001), pH (KCl) and Ca (R=0.803; p> 0.01), and Ca and S (R=0.891; p<0.01). All heavy metals were significantly inter-correlated with R values ranging from 0.589 to 0.995 and p-values <0.05.

Comparison of treatment A and B at the end of the experiment indicated no significant effect of the fortnightly disturbance of the sediment. However, the disturbance generally resulted in lower concentrations at the end of the experiment, except for sediment 4 for the considered heavy metals, sediment 1 for TP, Ntot and S and sediment 2 for Ntot and S. A significant effect of time on the sediment characteristics was only observed for pH (H₂O) (p = 0.043), pH (KCl) (p = 0.038) and the sulphide content (p = 0.025) with lower pH-values and sulphide-content (except for sediment 2) at the end of the experiment for both treatments. Furthermore, at the end of the experiment the detected homogenous subgroups contained fewer elements compared to the composition of the subgroups at the beginning (Table 1),
indicating that the difference between the individual sediments increased during the experiment.

The redox potential declined during the first 11 days of the experiment for all sediments, from -160 to -220 mV to -220 to -260 mV. Between 36 and 72 days the difference in redox potential between the different sediments increased as could be deduced from the greater divergence between the sediments. Sediment 5 showed on day 57 a sharp increase of redox potential up to -119 mV. For all other sediments redoxpotentials stabilised between -246 and -226 mV. A significant difference between the disrupted and undisrupted sediment was only observed for sediment 1 (p = 0.012) with lower potentials in the disrupted sediment.

Ratios of the exchangeable metal fraction to the (pseudo-)total amount of metals and the exchangeable metal concentrations are presented in Table 2, both as absolute concentrations and relative to the total metal content. The disturbance did not result in a significant increase of the exchangeable metal fraction. The elements Cr and Ni were not included because their concentrations in the exchangeable fraction were below the detection limits of 0.30 mg kg\(^{-1}\) and 0.15 mg kg\(^{-1}\), respectively. The percentage of Ca present in the exchangeable fraction in sediment 5 (34.2 ± 2.1 %) was significantly lower compared to the other sediments (73.4 ± 13.4 %) although both sediment 4 and 5 were characterised by similar elevated Ca-contents (7.1 ± 1.8 g kg\(^{-1}\)) in comparison with the other sediments (2.6 ± 0.2 g kg\(^{-1}\)). Elevated concentrations and percentages of exchangeable Cu, Fe, Mn and Pb were found in sediment 4. Although differences between the beginning and the end of the experiment were not significant, an increase was observed for the elements Cd, Cu Fe and Zn whereas Ca decreased.

Water analyses
The pH of the surface water measured at day 50 was 8.3 ± 0.3 for the sediments 1-3 and 5, but lower for sediment 4 (7.1 ± 0.1). The same difference in pH was reflected in the pore water (1-3 and 5: 8.3 ± 0.5; 4: 7.0 ± 0.1). Disturbance of the sediment did not result in a significant mobilisation of N, P and metals towards the pore and surface water, except for the element Ca in all sediments, and Fe and Mn in sediment 5. Calcium concentrations in the pore water were characterized by an initial decrease, followed by an increase after 29 days. In the surface water, they started to increase from the beginning of the experiment. This was especially observed in sediment 5 (Figure 2). Mobilisation of the heavy metals towards the surface water could not be detected for Cd, Cu, Cr, Ni, Pb, and Zn as the measured concentrations were often lower than the detection limits. Average concentrations measured during the experiment in the pore and surface water, respectively, were for Cd: 2 and < 2 µg L\(^{-1}\); Cr: 5 and < 4 µg L\(^{-1}\); Cu: 9 and 8 µg L\(^{-1}\); Ni: 9 and 8 µg L\(^{-1}\); Pb: 14 and 9 µg L\(^{-1}\); Zn: 31 and 63 µg L\(^{-1}\); Fe: 11.5 and 0.1 mg L\(^{-1}\); Mn: 0.37 and 0.04 mg L\(^{-1}\). In general, concentrations in the pore water were slightly higher or equal to concentrations in the surface water, except for Fe, Mn and Ca which had much higher concentrations in the pore water and Zn, which was present in lower concentrations in the pore water. The ratio of Fe in the pore water to Fe in the surface water was 100 whereas for Mn this ratio was only 10. Transport of Mn from the pore water towards the surface water seemed to be higher in comparison to Fe. For Fe and Mn an increase with time was observed in the pore water of sediment 5 (Figure 2). This increase coincided with the evolution of redoxpotential in sediment 5. However, it did not result in elevated Fe and Mn concentrations in the surface water. The mobilisation of Ca from the pore water towards the surface water differed clearly for sediment 5, compared to the other sediments and compared to the increase of Ca in the surface water. A sharp increase after 58 days was observed for the pore water of sediment 5 whereas the mobilisation of Ca in the surface water kept for sediment 5 pace with the other sediments.
Chloride, NO$_3^-$, and SO$_4^{2-}$ concentrations in the surface water were generally higher above the undisrupted sediments, although the difference was only significant for sediments 3, 4 and 5 for NO$_3^-$, for sediments 1 and 3 for SO$_4^{2-}$, and for sediments 2, 4 and 5 for Cl$^-$. Average concentrations of Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ throughout the entire 85 days were 6.9 ± 2.4, 3.3 ± 6.4, and 82.2 ± 39.2 mg L$^{-1}$, respectively. The surface water of sediment 1 was characterised by high SO$_4^{2-}$ concentrations from the start onwards (Figure 2). For the other sediments, initial SO$_4^{2-}$ concentrations were lower but they increased during the experiment. Although sediment 4 and 5 had comparable S-contents (Table 1), sulphate concentrations were much higher in the surface water above sediment 5 (127 ± 6 mg L$^{-1}$) in comparison to sediment 4 (78 ± 3 mg L$^{-1}$) at the end of the experiment. The concentrations of P in the surface water on day 1 were very high (25 ± 6 mg P L$^{-1}$) in comparison with the concentrations determined from day 8 onwards (0.4 ± 0.3 mg P L$^{-1}$) (data not shown). Phosphorus removal was characterized by a fast decrease within the first week and this was observed for all sediments. Also Ntot concentrations decreased during the 85 days experimental period, however more slowly in comparison to P (Figure 2). The higher Ntot and TP concentrations in sediment 4 resulted in higher initial N concentrations in the surface water (day 1: 40 ± 3 mg N L$^{-1}$) compared to the other sediments (day 1: 17 ± 4 mg N L$^{-1}$) but not in higher concentrations of P. Nitrogen concentrations dropped below 10 mg L$^{-1}$ from day 29 for sediments 1-3 and 5, whereas this was only reached from day 43 for sediment 4. At the beginning of the experiment NO$_3$-N concentrations in the surface water were low (< 1 mg L$^{-1}$). Peak concentrations between 1.5 and 7.5 mg L$^{-1}$ NO$_3$-N however, occurred (data not shown) after 23 to 36 days for sediments 1-3 and 5 and around day 57 for sediment 4.
Average concentrations of OC in the pore and surface water were 17 and 8 mg L\(^{-1}\), respectively (Figure 3). Elevated concentrations of OC were observed on day 1 in the pore water (40 ± 20 mg L\(^{-1}\)) and the surface water (22 ± 2 mg L\(^{-1}\)) of sediment 4. An initial increase of OC concentrations in the surface water of all sediments (until day 22) was followed by a decrease. As such, OC concentrations were below 10 mg L\(^{-1}\) (surface water) and 25 mg L\(^{-1}\) (pore water) for all sediments after 43 days. Organic carbon concentrations in the surface water were not influenced by disturbance of the sediment, except for sediment 4. For sediment 4, disturbance resulted in lower OC concentrations in the surface water (\(p = 0.003\)). However, no difference between the different sediments and treatments was observed for OC concentrations in the pore water. Inorganic carbon concentrations were higher in the pore water than in the surface water. Especially, peak concentrations of IC were observed in sediment 4A and 2B. However, similar to the OC-profiles, concentrations of IC dropped below 20 mg L\(^{-1}\) (surface water) and 50 mg L\(^{-1}\) (pore water) after 50 days.

**Geochemical speciation**

Metals present in water can occur in the form of free metal ions, complexed by organic and inorganic ligands, and adsorbed or bound to organic and inorganic particulate matter. The chemical composition of the water, especially pH, hardness and dissolved organic matter concentrations, strongly influences metal speciation (Sriyaraj and Shutes, 2001).

Assessment of the geochemical speciation was done with Visual MINTEQ. Only the data obtained for Ca, Fe and Mn are included in Table 3 as for the other elements the measured concentrations were generally low and data should be interpreted with caution. Data for all sediments were pooled because no significant difference could be observed between the individual sediments and treatments. The different composition of sediment 4 in comparison
to the other sediments (higher concentrations of organic matter and heavy metal content) did not influence the speciation. For Ca, Fe and Mn, the ionic form was the most dominant one (Table 3). Through time, the contribution of the ionic fraction increased. The binding with carbonates was especially important for Mn, but decreased in time. The formation of some species was totally absent, e.g. Ca(OH)⁺, Mn(OH)⁺ and complexes of DOM with Fe or Mn. Only Ca showed a high initial affinity for DOM. Cadmium and Ni mainly occurred as free ions. The free ionic forms of those two metals also increased as a function of time, from 68 to 91% for Cd and from 61 to 88% for Ni. Chromium was almost exclusively present in its hydroxide form (> 99%). Carbonate complexes played an important role in the speciation of Cu (day 8: 76%, day 85: 59%) and Pb (day 8: 58%, day 85: 48%). Zinc was mostly associated with hydroxides (day 8: 46%, day 85: 55%) and present in its free ionic form (day 8: 30%, day 85: 40%). Complexation of Cd, Cu, Cr, Ni, Pb and Zn by DOM varied between 9 and 29%. Formation of chloride and phosphate complexes could be neglected for all metals. Their contribution to the overall speciation was less than 1%.

DISCUSSION

The pollutant concentrations in the sediments of the CFW in Bornem were compared with those found in the literature for systems receiving different types of runoff (Table 4). Also sediment concentrations monitored in a surface flow constructed wetland used for treatment of combined sewer overflows in Herent (Flanders, Belgium) were included. Although metal concentrations in sediments are widely documented, there is a lack of information on Fe, Mn, N and P contents. Terms used for specifying the influent source are mostly very general, e.g. ‘residential runoff’ and ‘urban runoff’. It was suspected that runoff originating from roads would result in elevated metal concentrations in the sediment. However, this was only observed for Pb in one study (Legret et al., 1995). A difference based on the type of treatment
system was also not observed. Both systems monitored in Belgium and used for CSO treatment showed moderate to high pollutant concentrations in the sediment.

Deposition of contaminants may depend on the flow pattern, flow velocity and characteristics of the sediment. In the surface flow system in Herent, higher concentrations of Ntot, P, organic matter, sulphides, Cd, Cr, Cu, Pb and Zn were present near the inlet compared to the outlet (data not published). In Bornem, no significant difference was observed between the samples taken near the inlet (sediment 1-3) and the outlet (sediment 5). Only the composition of sediment 4 clearly differed from the other sediments in the higher concentrations of metals, organic matter, sulphides and nutrients (N and P). The sediment originating from the sedimentation compartment (sediment 1-2) contained lower concentrations of nutrients and heavy metals. Although both the system in Herent and Bornem were used for treatment of combined sewer overflows, and as such received pulse loadings, their design differed. The flow path of the system in Herent was much longer, as the system had a much higher L/W ratio. Furthermore, flow velocity was probably much quicker reduced as *Phragmites australis* covered the inlet area. Therefore, metals present in the influent could penetrate to a much lower extent into the system. Elevated concentrations were present near the inlet and decreased with distance. At the site of Bornem the flow was much less retarded and water entered further along the flow path into the system. Also the wilting of the stiffened cloths and accidental water passage over the shoulder may have resulted in a deeper penetration of the metals into the system.

Location 5 was situated near the end of the S-shaped flow path that was constructed in the CFW-area. As the water entered the system and followed the S-shaped flow path, electron acceptors such as dissolved oxygen, nitrates, Fe(III) and Mn(IV) were successively consumed. When all these electron acceptors were exhausted, sulphates were reduced to
sulphides, which precipitated with heavy metals present in solution. Chromium and Ni were documented not to react with sulphides (Salomons et al., 1987). Furthermore, co-precipitation of other metals together with the sulphide precipitates occurred (Billon et al., 2001). This caused an enrichment of heavy metals in the sediment. As most of the metals were removed when the water passed at location 4 due to reaction with sulphides, no further metal enrichment at location 5 was observed, except for Fe and Mn.

Iron and Mn were present in higher concentrations in the water compared to the other metals. The concentrations of Fe and Mn present in the pore water were lower than the concentrations reported by Mayer et al. (2008). They found up to 50-100 mg L$^{-1}$ Fe and 1.5–4 mg L$^{-1}$ Mn in the pore water of sediments originating from a detention pond receiving urban stormwater. Furthermore, because the solubility of FeS and MnS is higher compared to other metal-sulphide precipitates (Zumdahl, 1992), enrichment further along the flow path of Fe and Mn can occur due to reaction with sulphides. Iron and Mn concentrations measured at both location 4 and 5 were indeed higher. For the other metals, only sediment 4 contained elevated concentrations. Next to reaction with sulphides also the presence of organic matter enhanced the retention of heavy metals. This was especially apparent for location 4, which was also characterized by elevated organic matter contents. Sediments 3, 4 and 5 originated from the CFW-area but only for sediment 4 the organic matter content was clearly higher as the other two sampling locations (3 and 5) were situated near the border of the CFW-area. Due to wind dragging, the floating macrophyte mats could be moved 1-2 m, although they were anchored to the side. This may have resulted in the presence of lower organic matter contents near the borders of the CFW.
Increasing Fe and Mn concentrations in the pore water of sediment coincided with an increase of redoxpotential in that particular sediment. As a result of increasing redoxpotentials, FeS and MnS will become oxidised. However, as the redoxpotential increase was not strong enough to promote the formation of Fe and Mn-oxyhydroxide precipitates, the concentration of Fe(II) and Mn(II) in the pore water will increase. Gambrell et al. (1991) reported that the oxidation of Fe(II) and Mn(II) occurred at respectively +100mV and +200mV. Furthermore, also small pH-variations can affect the concentrations of Fe and Mn in the pore water.

The effect of vegetation on the retention of heavy metals has been extensively discussed in the literature. Some authors have reported no effect (Otte et al., 1995; Caçador et al., 1996; Kahkonen et al., 1997; Mitsch and Wise, 1998 and Goulet and Pick, 2001) while others mentioned a positive correlation between the presence of the vegetation and the heavy metal retention (Kostka and Luther III, 1995; Doyle and Otte, 1997). The emergent vegetation in CFWs is not rooted in the substrate, but grows in a floating matrix on the water surface. Therefore, there will be no direct effects of the plants, e.g. associated with root oxygen release (Wigand et al., 1997), on the biogeochemistry of metals in the sediment. Current data suggest that the distribution of heavy metals in the system of Bornem was mainly influenced by the sediment composition, in particular the sulphide and organic matter contents.

In general, only a low percentage of the metals was easily exchangeable. Only Cd and Mn were for more than 10% present in this fraction. Also Du Laing et al. (2008), Mayer et al. (2008) and Hnatukova et al. (2009) found the exchangeable fraction to be up to 10% of total Cd amounts. The source of the influent may influence the fractionation of metals in sediments. Hnatuva et al. (2009) found a shift for Cu and Zn towards more easily available
fractions in sediments affected by the occurrence of combined sewer overflows. Stead-Dexter and Ward (2004) reported for all heavy metals except Pb, an increase towards more easily available fractions when sediments were influenced by drainage systems and stormwater. The effect of the vegetation on the fractionation of heavy metals in a surface flow wetland was assessed by Goulet and Pick (2001). They found that *Typha latifolia* did not affect the metal distribution over the different fractions.

For young systems (<10 years) sorption plays a significant role in the removal of contaminants, and is especially influenced by organic substrates (Machemer and Wildeman, 1992; Weiss et al., 2006). Elevated concentrations and percentages of exchangeable metals were found in sediment 4 for the elements Cu, Fe, Mn and Pb in comparison with the other ones, probably due to the elevated organic matter content. With ageing of the system, sorption sites become saturated and sulphate reduction will gain in importance (Machemer and Wildeman, 1992). During the experiment a constant increase of sulphate concentrations in the surface water was noted, probably originating from oxidation of the sulphides that were initially present (Table 1). Apparently, oxidation of sulphides occurred although redox potentials were in general lower than -200 mV, a redox value at which Gambrell et al. (1991) observed sulphate reduction.

Discrepancies between the sulphide content measured and sulphides actually present in the sediment can occur due to partial oxidation between sampling and analysis (Du Laing et al., 2008). However, analyses were done as quickly as possible and contact between the air and the sediment was as limited as possible. Therefore, the difference in sulphide content between beginning and end of the experiment can not be explained by partial oxidation solely as sufficient precautionary measures were taken. The pH of the sediments also decreased (Table
1), probably as the result of the acidification due to sulphide oxidation. Although no significant sulphide oxidation was observed in sediment 2 (Table 1), sulphate concentrations in the surface water increased (Figure 2) and pH of the soil decreased (Table 1). This indicates that, next to the oxidation of sulphides, also other sulphate sources should be present within the sediment. Sulphates can indeed also be released from decomposing organic matter and/or other mineral phases, such as pyrite, which are not determined in the AVS-procedure (Tack et al., 1997; Du Laing et al., 2008). Although metal sulphide precipitation is seen as a long-term immobilization process, changing redox conditions can remobilize the associated heavy metals afterwards. The increase in redox potential for sediment 5 from -220 mV to -120 mV resulted in elevated Fe and Mn concentrations in the pore water (Figure 2).

Filling the recipients with the respective sediments initially caused elevated concentrations of both Ntot and P in the water column. However, P was quickly removed from the water as removal occurs mainly through adsorption and precipitation reactions which involve Ca, Mg, Al and Fe present in the sediment (Arias et al., 2001). However, increasing levels of Fe, Mn and Ca in the surface water did not result in an increase of P in the surface water. Removal of nitrogen can occur through adsorption of NH$_4^+$-N, algae uptake and microbial removal reactions. The contribution of microbial removal pathways is supported by the observation of peak concentrations of NO$_3^-$-N in the surface water. Microbial removal may occur more slowly compared to sorption and precipitation reactions. Furthermore, the addition of demineralised water could have slowed down microbial colonisation of the water column.

Increasing Ca-concentrations, as was observed clearly in the pore water of sediment 5 and the surface water for all sediments, can originate from the pool of exchangeable cations as Ca is replaced by other cations. This is suggested by the decrease of the exchangeable Ca-pool with
time (Table 2). A decrease of exchangeable Ca will also enhance the sorption of other metals.

Sulphide oxidation and the associated acid production will also promote Ca release from CaCO$_3$. Furthermore, CO$_2$ produced upon decomposition of organic matter will result in a solubilisation of CaCO$_3$ according to the following reaction: CaCO$_3$ + CO$_2$ + H$_2$O $\rightarrow$ Ca(HCO$_3$)$_2$ (van Den Berg and Loch, 2000). This results in an increase of IC as was seen in sediment 4. This sediment had peak concentrations of IC in the pore water as high as 307 mg L$^{-1}$. Increased IC concentrations can also result from decomposition of organic matter. Inorganic carbon concentrations up to 307 mg L$^{-1}$ corresponded with an OM decrease of less than 1%. This amount of OM can not be detected as it is masked by sediment heterogeneity. However, metal chemistry in the pore water can be highly affected by changing OC concentrations.

The disturbance of the sediments during the greenhouse experiment did not result in a significant mobilisation of heavy metals or nutrients towards the pore and surface water. As such, entering water volumes during overflow events will not cause a faster retention or release of pollutants from the sediment. The mobilisation observed during the greenhouse experiment was due to ageing of the sediment, independent of the disruptions. Changing redox conditions can result in a mobilisation of heavy metals due to sulphide oxidation. However, reducing conditions in the sediment of CFWs are promoted by its continuously flooding. Furthermore, the floating macrophyte mats present in CFWs promote reducing conditions of the water column and the underlying sediment as they hamper oxygen diffusion from the air to the water column. Probably the presence of the vegetation will also promote sulphide formation as the decomposing plant material can deliver the necessary electron acceptors. This was reflected by the elevated OM content of sediment 4 compared to the OM contents of the sediments originating from the sedimentation compartment.
CONCLUSIONS

Within the sediments of a constructed floating treatment wetland, concentrations of heavy metals and nutrients varied. Higher nutrient concentrations coincided with higher organic matter contents. Elevated metal concentrations on the other hand were associated with higher sulphide and organic matter contents. The highest metal retention occurred at location 4 (all metals) and 5 (Fe and Mn) due to sulphide formation as other electron acceptors became depleted. The higher solubility of FeS and MnS resulted in an enrichment of Fe and Mn further along the flow path, opposite to the retention of other heavy metals. The release of heavy metals from the sediment towards the pore water and surface water was very limited. It was not affected by disturbance of the sediment at regular intervals. After 7 weeks an increase in redoxpotential was observed for the sediment closest to the outlet together with increasing Ca, Fe and Mn concentrations in the pore water. Calcium concentrations measured in the surface water increased for all tested sediments and was attributed to the release of Ca from the exchangeable pool and to decalcification due to organic matter decomposition and sulphide oxidation. The free ion form in the pore water was the most abundant one for Ca, Fe, Mn, Cd and Ni, and its presence increased through time. Initially high concentrations of P were quickly reduced (within 8 days) by sorption to the sediment, which was in contrast with the removal of N which took around 41 days.

ACKNOWLEDGMENTS

The authors want to acknowledge Aquafin NV for its co-operation during sampling of the sediment and for putting the constructed floating treatment wetland at our disposal. Furthermore Hannelore Six is gratefully thanked for her help during the greenhouse experiment.
REFERENCES


Table 1 Characteristics of the different sediments (1-5) at the beginning and end of the greenhouse experiment for treatment A (no disruption) and B (fortnightly disruption of the sediment). Small letters (a-e) denote homogeneous subsets.

<table>
<thead>
<tr>
<th></th>
<th>pH ($H_2O$) (-)*</th>
<th>pH (KCl) (-)*</th>
<th>AVS (mg S kg$^{-1}$ DM)</th>
<th>Organic matter (%)</th>
<th>TP (g kg$^{-1}$ DM)</th>
<th>Ntot (g kg$^{-1}$ DM)</th>
<th>Ca (g kg$^{-1}$ DM)</th>
<th>Cd (mg kg$^{-1}$)</th>
<th>Cr (mg kg$^{-1}$ DM)</th>
<th>Cu (mg kg$^{-1}$ DM)</th>
<th>Fe (g kg$^{-1}$ DM)</th>
<th>Mn (mg kg$^{-1}$ DM)</th>
<th>Ni (mg kg$^{-1}$ DM)</th>
<th>Pb (mg kg$^{-1}$ DM)</th>
<th>Zn (mg kg$^{-1}$ DM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>A</td>
<td>B</td>
<td>Initial</td>
<td>A</td>
<td>B</td>
<td>Initial</td>
<td>A</td>
<td>B</td>
<td>Initial</td>
<td>A</td>
<td>B</td>
<td>Initial</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>1</td>
<td>6.91 ± 0.17 a</td>
<td>5.82 ± 0.34 a</td>
<td>5.93 ± 0.26 a</td>
<td>6.67 ± 0.11 a</td>
<td>5.72 ± 0.15 a</td>
<td>5.59 ± 0.12 a</td>
<td>2386 ± 176 a</td>
<td>283 ± 34 a</td>
<td>521 ± 61 a</td>
<td>2.58 ± 0.23 a</td>
<td>1.30 ± 0.21 a</td>
<td>1.09 ± 0.22 a</td>
<td>1.57 ± 0.43 a</td>
<td>11.7 ± 1.3 a</td>
<td>11.1 ± 1.2 a</td>
</tr>
<tr>
<td>2</td>
<td>7.01 ± 0.05 a</td>
<td>6.90 ± 0.29 a</td>
<td>6.88 ± 0.23 a</td>
<td>5.54 ± 0.12 a</td>
<td>5.57 ± 0.09 a</td>
<td>5.71 ± 23 b</td>
<td>655 ± 59 b</td>
<td>826 ± 78 b</td>
<td>8.14 ± 1.12 b</td>
<td>10.45 ± 0.45 c</td>
<td>4.11 ± 0.24 d</td>
<td>2.44 ± 0.41 a</td>
<td>2.94 ± 0.68 a</td>
<td>2.73 ± 0.47 a</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.11 ± 0.23 a</td>
<td>6.72 ± 0.14 b</td>
<td>6.86 ± 0.04 a</td>
<td>5.94 ± 0.18 a,b</td>
<td>5.8 ± 0.15 b</td>
<td>712 ± 54 b</td>
<td>672 ± 47 b</td>
<td>712 ± 54 b</td>
<td>8.07 ± 0.76 b</td>
<td>7.28 ± 0.13 e</td>
<td>3.65 ± 0.65 b</td>
<td>2.79 ± 0.92 a</td>
<td>2.57 ± 0.38 a</td>
<td>2.57 ± 0.38 a</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.99 ± 0.19 a</td>
<td>6.71 ± 0.13 b</td>
<td>6.86 ± 0.16 b</td>
<td>6.28 ± 0.23 b</td>
<td>6.32 ± 0.07 c</td>
<td>826 ± 78 d</td>
<td>2252 ± 97 d</td>
<td>2390 ± 154 c</td>
<td>8.07 ± 0.76 b</td>
<td>7.28 ± 0.13 e</td>
<td>3.65 ± 0.65 b</td>
<td>2.79 ± 0.92 a</td>
<td>2.57 ± 0.38 a</td>
<td>2.57 ± 0.38 a</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>7.42 ± 0.35 a</td>
<td>7.02 ± 0.26 c</td>
<td>7.25 ± 0.21 b</td>
<td>7.19 ± 0.09 a</td>
<td>6.87 ± 0.08 c</td>
<td>6874 ± 167 e</td>
<td>672 ± 47 b</td>
<td>712 ± 54 b</td>
<td>8.07 ± 0.76 b</td>
<td>7.28 ± 0.13 e</td>
<td>3.65 ± 0.65 b</td>
<td>2.79 ± 0.92 a</td>
<td>2.57 ± 0.38 a</td>
<td>2.57 ± 0.38 a</td>
<td></td>
</tr>
</tbody>
</table>
|          | pH determination with $H_2O$ (pH ($H_2O$)) and KCl (pH (KCl)) as an extracting agent

*B}:
Table 2 Exchangeable metal concentrations and ratio (%) of exchangeable metals to (pseudo-) total metal concentrations for the sediments at the beginning and the end of the greenhouse experiment

<table>
<thead>
<tr>
<th></th>
<th>Exchangeable metal concentration (mg kg⁻¹)</th>
<th></th>
<th>% of total metal concentration</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean ± SD</td>
<td>Range</td>
<td>Mean ± SD</td>
<td>Range</td>
</tr>
<tr>
<td>Ca</td>
<td>Before 4394 ± 2640</td>
<td>2463 - 8360</td>
<td>65.6 ± 20.8</td>
<td>34.6 - 88</td>
</tr>
<tr>
<td></td>
<td>After 3641 ± 2318</td>
<td>1544 - 7632</td>
<td>50.8 ± 12.4</td>
<td>31.4 - 72.2</td>
</tr>
<tr>
<td>Cd</td>
<td>Before 0.04 ± 0.01</td>
<td>0.02 - 0.05</td>
<td>17.6 ± 15.0</td>
<td>3.30 - 38.0</td>
</tr>
<tr>
<td></td>
<td>After 0.15 ± 0.03</td>
<td>0.12 - 0.22</td>
<td>42.5 ± 31.2</td>
<td>8.53 - 83.3</td>
</tr>
<tr>
<td>Cu</td>
<td>Before 0.76 ± 0.64</td>
<td>0.30 - 1.48</td>
<td>1.1 ± 0.1</td>
<td>1.04 - 1.23</td>
</tr>
<tr>
<td></td>
<td>After 1.09 ± 0.74</td>
<td>0.27 - 2.03</td>
<td>2.3 ± 2.3</td>
<td>0.33 - 7.44</td>
</tr>
<tr>
<td>Fe</td>
<td>Before 2.56 ± 3.64</td>
<td>0.73 - 9.07</td>
<td>0.02 ± 0.02</td>
<td>0.01 - 0.05</td>
</tr>
<tr>
<td></td>
<td>After 3.33 ± 4.57</td>
<td>0.82 - 12.9</td>
<td>0.02 ± 0.02</td>
<td>0.01 - 0.07</td>
</tr>
<tr>
<td>Mn</td>
<td>Before 15.1 ± 9.1</td>
<td>7.91 - 29.7</td>
<td>17.4 ± 2.6</td>
<td>14.2 - 21.0</td>
</tr>
<tr>
<td></td>
<td>After 14.7 ± 7.3</td>
<td>8.97 - 29.8</td>
<td>18.9 ± 6.5</td>
<td>11.8 - 34.8</td>
</tr>
<tr>
<td>Pb</td>
<td>Before 86.7 ± 65.5</td>
<td>49.9 - 203</td>
<td>1.3 ± 0.4</td>
<td>0.84 - 1.77</td>
</tr>
<tr>
<td></td>
<td>After 85.7 ± 53.0</td>
<td>36.1 - 219</td>
<td>1.9 ± 1.0</td>
<td>0.24 - 3.26</td>
</tr>
<tr>
<td>Zn</td>
<td>Before 13.9 ± 6.1</td>
<td>7.51 - 23.8</td>
<td>4.9 ± 1.7</td>
<td>2.96 - 6.82</td>
</tr>
<tr>
<td></td>
<td>After 29.9 ± 19.3</td>
<td>10.9 - 74.2</td>
<td>8.9 ± 2.5</td>
<td>5.46 - 12.9</td>
</tr>
</tbody>
</table>
Table 3 Geochemically modelled speciation of Ca, Fe and Mn present in the pore water of the sediments (1-5)

<table>
<thead>
<tr>
<th>Species</th>
<th>Day</th>
<th>Mean ± SD</th>
<th>Range</th>
<th>Mean ± SD</th>
<th>Range</th>
<th>Mean ± SD</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me⁺</td>
<td>8</td>
<td>83 ± 9</td>
<td>71 - 96</td>
<td>94 ± 5</td>
<td>83 - 97</td>
<td>70 ± 22</td>
<td>24 - 94</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>98 ± 2</td>
<td>92 - 99</td>
<td>95 ± 5</td>
<td>83 - 99</td>
<td>92 ± 8</td>
<td>73 - 97</td>
</tr>
<tr>
<td>carbonate</td>
<td>8</td>
<td>2.6 ± 2.7</td>
<td>0.37 - 8.9</td>
<td>1.2 ± 0.8</td>
<td>0.20 - 2.6</td>
<td>29 ± 22</td>
<td>5.6 - 76</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>0.45 ± 0.29</td>
<td>0.17 - 1.1</td>
<td>0.19 ± 0.11</td>
<td>0.11 - 0.44</td>
<td>7.6 ± 7.4</td>
<td>2.2 - 25</td>
</tr>
<tr>
<td>hydroxy</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>4.3 ± 4.7</td>
<td>0.50 - 15</td>
<td>0.16 ± 0.11</td>
<td>0.026 - 0.37</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>-</td>
<td>-</td>
<td>4.1 ± 4.9</td>
<td>0.50 - 16</td>
<td>0.38 ± 0.62</td>
<td>0.029 - 1.9</td>
</tr>
<tr>
<td>DOM</td>
<td>8</td>
<td>14 ± 10</td>
<td>3.1 - 27</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>1.8 ± 2.3</td>
<td>0.45 - 7.37</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 4 Total Cd, Cu, Cr, Mn, Ni, Pb, Zn (mg kg\(^{-1}\)DM), Fe, total Kjeldahl nitrogen (TKN), Ntot and P (g kg\(^{-1}\)) concentrations in the sediment of the CFW in Bornem, Flanders, compared with literature data

<table>
<thead>
<tr>
<th>Ref n°</th>
<th>Type of water</th>
<th>Type of treatment system</th>
<th>Cd mg kg(^{-1})</th>
<th>Cu mg kg(^{-1})</th>
<th>Cr mg kg(^{-1})</th>
<th>Mn mg kg(^{-1})</th>
<th>Ni mg kg(^{-1})</th>
<th>Pb mg kg(^{-1})</th>
<th>Zn mg kg(^{-1})</th>
<th>Fe g kg(^{-1})</th>
<th>TKN g kg(^{-1})</th>
<th>Ntot g kg(^{-1})</th>
<th>P g kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CSO</td>
<td>CFW</td>
<td>0.17-1.6</td>
<td>28-142</td>
<td>10-33</td>
<td>50-141</td>
<td>5.1-20</td>
<td>50-203</td>
<td>185-804</td>
<td>7.4-17</td>
<td>0.83-7.1</td>
<td>2.1-8.1</td>
<td>1.3-4.4</td>
</tr>
<tr>
<td>2</td>
<td>stormwater</td>
<td>SFCW</td>
<td>0.10-1.5</td>
<td>11-146</td>
<td>17-33</td>
<td>187-282</td>
<td>12-20</td>
<td>12-107</td>
<td>49-681</td>
<td>12-28</td>
<td>0.97-7.0</td>
<td>0.46-3.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>road runoff</td>
<td>SFCW + pond</td>
<td></td>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>232-252</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>urban runoff</td>
<td>SFCW</td>
<td>3-10</td>
<td>17-178</td>
<td>3-169</td>
<td>17-319</td>
<td>33-392</td>
<td>31-1035</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>urban stormwater</td>
<td>detention pond</td>
<td>4.1</td>
<td>107</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>91</td>
<td>465</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>stormwater</td>
<td>detention pond</td>
<td>&lt;5</td>
<td>18-341</td>
<td>18-252</td>
<td>19-267</td>
<td>9-116</td>
<td>53-1155</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>urban runoff</td>
<td>detention pond</td>
<td>0.05-0.10</td>
<td>0.45-0.78</td>
<td>0.97-1.01</td>
<td>0.21-0.53</td>
<td>1.5</td>
<td>3.71-3.81</td>
<td>0.2-0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>urban runoff</td>
<td>detention pond</td>
<td>0.08-0.39</td>
<td>0.54-12.6</td>
<td>1.2-3.7</td>
<td>0.30-1.9</td>
<td>1.6-8.9</td>
<td>1.69-93.4</td>
<td>0.2-49.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>urban runoff</td>
<td>detention pond</td>
<td>0.08-0.60</td>
<td>0.94-14.3</td>
<td>0.80-6.6</td>
<td>0.37-1.8</td>
<td>2.1-7.3</td>
<td>16.7-21.3</td>
<td>0.48-4.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>road and agricultural runoff</td>
<td>pond</td>
<td>1.1-44</td>
<td>5.8-41</td>
<td>9.7-95</td>
<td>48.46-239</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>road runoff</td>
<td>pond</td>
<td>7.9-56</td>
<td>76-286</td>
<td>23-112</td>
<td>256-888</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>residential runoff</td>
<td>pond</td>
<td>28-68</td>
<td>147-426</td>
<td>65-160</td>
<td>320-1337</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>residential runoff</td>
<td>natural surface flow wetland</td>
<td>0.7</td>
<td>39</td>
<td>16</td>
<td>11</td>
<td>45</td>
<td>397</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>residential runoff</td>
<td>SFCW</td>
<td>1.02</td>
<td>21</td>
<td>18</td>
<td>12</td>
<td>31</td>
<td>286</td>
<td>1.4</td>
<td>0.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>residential runoff</td>
<td>SFCW</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.8</td>
<td>0.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) data not published, site of Herent, Belgium; (2) Goulet and Pick (2001); (3) Pontier et al. (2001); (4) Scholes et al. (1999); (5) Mayer et al. (2008); (6) Casey et al. (2005); (7) Mallin et al. (2002); (8) Sriyaraj and Shutes (2001); (9) Hares and Ward (2004); (10) Legret et al (1995); (11) Marsalek et al (2006); (12) Bishop et al (2000); (13) this study.
CAPTIONS

Figure 1 Lay-out of the combined sewer overflow treatment system in Bornem, Flanders. Codes 1 to 5 indicate the location of the 5 sediment sampling sites.

Figure 2 Evolution of concentrations of Fe, Mn, Ca, Ntot and SO$_4^{2-}$ in the sediment pore water and/or surface water for the different sediments (1-5), with (B, dotted line) and without (A, full line) disruption during the greenhouse experiment.

Figure 3 Evolution of concentrations of OC and IC in the pore water and surface water for the different sediments (1-5) with (B, dotted line) and without (A, full line) disruption during the greenhouse experiment.
Figure 1

- Sedimentation compartment
- Constructed floating wetland (CFW) compartment

Dimensions:
- 50m (vertical)
- 55m (vertical)
- 15m (vertical)
- 20m (horizontal)
- 15m (vertical)
- 5m (vertical)
- 1m (vertical)
Figure 3