1	Effects of vegetation, season and temperature on removal of pollutants in
2	experimental floating treatment wetlands
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## 13 Abstract

14 The research and interest towards the use of constructed floating wetlands for (waste)water 15 treatment is emerging as more treatment opportunities are marked out and the technique is 16 applied more often. To evaluate the effect of a floating macrophyte mat and the influence of temperature and season on physico-chemical changes and removal, two constructed floating 17 18 wetlands (CFWs), including a floating macrophyte mat, and a control, without emergent 19 vegetation, were build. Raw domestic wastewater from a wastewater treatment plant was 20 added on day 0. Removal of total nitrogen, NH<sub>4</sub>-N, NO<sub>3</sub>-N, P, COD, TOC and heavy metals 21 (Cu, Fe, Mn, Ni, Pb and Zn) was studied during 17 batch-fed testing periods with a retention 22 time of 11 days (February-March 2007 and August 2007-September 2008). In general the 23 CFWs performed better than the control. Average removal efficiencies for NH<sub>4</sub>-N, total nitrogen, P and COD were respectively 35%, 42%, 22% and 53% for the CFWs, and 3%, 24 25 15%, 6% and 33% for the control. The pH was significantly lower in the CFWs (7.08  $\pm$  0.21) 26 than in the control (7.48  $\pm$  0.26) after 11 days. The removal efficiencies of NH<sub>4</sub>-N, total 27 nitrogen and COD were significantly higher in the CFWs as the presence of the floating 28 macrophyte mat influenced positively their removal. Total nitrogen, NH<sub>4</sub>-N and P-removal 29 was significantly influenced by temperature with the highest removal between 5 and 15°C. At 30 lower and higher temperatures, removal relapsed. In general, temperature seemed to be the 31 steering factor rather than season. The presence of the floating macrophyte mat restrained the 32 increase of the water temperature when air temperature was >15°C. Although the mat 33 hampered oxygen diffusion from the air towards the water column, the redox potential 34 measured in the rootmat was higher than the value obtained in the control at the same depth, 35 indicating that the release of oxygen from the roots could stimulate oxygen consuming reactions within the root mat and root oxygen release was higher than oxygen diffusion from 36 37 the air.

- 38 Keywords: wastewater treatment, combined sewer overflow, nitrogen, phosphorous, COD,
- 39 heavy metals

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42 Constructed floating treatment wetlands (CFWs) form the link between pond systems and 43 conventional substrate based systems. Similar as in constructed wetland systems, emergent plants are used, yet the presence of a free water compartment is in common with pond 44 45 systems. In contrast with classical constructed wetlands, such as surface and subsurface flow constructed wetlands, the vegetation is not rooted in a substrate or soil, but grows in a matrix 46 47 floating on the water surface. The treatment potential of this technology has been already 48 evaluated for different wastewater streams (Revitt et al., 1997; Smith and Kalin, 2000, 49 Hubbard et al., 2004, Todd et al., 2003) and CFWs seem to be a valuable alternative when 50 dealing with systems that are subject to high and/or highly variable water levels as drowning 51 of the vegetation is prevented.

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53 In recent years the main mechanisms for removal of organic matter, nitrogen, phosphorous 54 and heavy metals in constructed wetlands have been clearly identified (Kadlec & Knight, 55 1996; Sundaravadivel and Vigneswaran, 2001; Vymazal, 2007). The effect of the presence of 56 vegetation on the performance of constructed wetlands has been evaluated by different 57 authors, pointing out their added value in the removal of various pollutants (Tanner et al., 58 1995; Allen et al., 2002; Riley et al., 2005; Akratos and Tsihrintzis, 2007; Iamchaturapatr et 59 al., 2007; Headley and Tanner, 2008). Plants are able to modify the wetland environment by rhizosphere oxidation and the excretion of  $H^+$ , organic acids and  $CO_2$  (Armstrong et al., 1990, 60 61 Tanner et al., 1995, Coleman et al., 2001). Next to the effect of plant uptake, the presence of 62 the vegetation results in more stable year-round temperatures which, in turn, may promote enhanced pollutant removal in constructed wetlands (Hill and Payton, 2000). However, the 63 64 knowledge of the effect of the vegetation in CFWs on removal performance is still very 65 limited. Some have investigated for CFWs the effect of different plant species on the removal 66 of pollutants in CFWs and the effect of their presence compared to a system without vegetation. However, studies comprising a control without floating macrophyte mat were 67 68 mostly aiming at evaluating algae removal, rather than pollutant removal (Nakamura and 69 Shimatani, 1997, Oshima et al. 2001). A significant contribution to the removal of Cu from 70 stormwater by the presence of a floating mat was found by Headley and Tanner (2006, 2008). 71 Also the removal of N was positively affected by the presence of the vegetation in CFWs 72 (Oshima et al., 2001).

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74 The influence of temperature and season on the treatment performance of constructed 75 wetlands, however, remains less clear for substrate-based wetlands (Stein and Hook, 2005) 76 and very little research has been conducted towards those influencing factors for CFWs. A 77 study of the removal of ortho-phosphate from a reservoir used for drinking-water production 78 and supplied with floating macrophyte mats showed highly variable removal efficiencies 79 throughout the year (0-99.6%) with lower efficiencies during the period October-December 80 and higher efficiencies during April-August (Garbett, 2005). Similarly, Nakamura and 81 Shimatani (1997) found that with CFWs (Typha spp. and Scirpus triangulates) used for the 82 treatment of eutrophic lake water, a good removal could be obtained during summer, but not in winter. Also Wong (2000) observed seasonal variations at the study site of Witches Oak 83 84 Waters where floating Phragmites-wetlands were used. However, all the references cited 85 above concerned water with low nutrient concentrations, information on the influence of 86 season and temperature for higher loaded wastewater was not found.

87

In general, wetlands are affected by solar radiation and air temperature which both cycle on a
daily and annual basis, affecting plant activity and microbial processes (Kadlec, 1999). The

90 removal of pollutants from the water column is the end result of a combination of reactions, 91 all of which are possibly influenced by vegetation, temperature and season or a combination of these parameters. Because of interfering reactions, the effect of each individual variable is 92 93 not always readily distinguishable and the net effect of these reactions may be counter 94 intuitive (Kadlec and Reddy, 2001; Stein and Hook, 2005). Kadlec and Reddy (2001) 95 indicated that the effect of the vegetation on the treatment performance could not be based on 96 temperature only, as temperature is not unique to season. The effect of plant growth on the 97 removal of pollutants may vary over the different seasons with enhanced plant growth in 98 spring followed by senescence and plant decay in fall and winter.

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100 Nitrogen removal is more strongly influenced by season and temperature compared to 101 removal of P because it is mainly effectuated by microbial activity. For P, the physico-102 chemical process of sorption to the sediment is of main importance (Spieles and Mitsch, 103 2000). Picard et al. (2005) described that there was less variance in seasonal phosphorous 104 removal when compared to nitrogen. This difference in variance is demonstrated in many 105 treatment wetlands and may be due to the year-round sedimentary and substrate binding of 106 phosphorous (Kadlec and Knight, 1996; Wittgren and Maehlum, 1997).

107

In this article results are reported from a small-scale experiment investigating the removal of nitrogen, phosphorous, organic material and heavy metals (Cu, Fe, Mn, Ni, Pb and Zn) in constructed floating wetlands. Samples were gathered during the period February-March 2007 and August 2007- September 2008. The study aimed at the determination of factors influencing the removal of pollutants in constructed floating treatment wetlands. It was presumed that the presence of the floating macrophyte mats influenced both the physicochemical conditions and removal performance when comparing with a system without floating macrophyte mat. Furthermore, the effect of temperature was evaluated as removal processes can be influenced by temperature. Because plant growth, plant uptake and indirect plant influences may differ over the different seasons, also the evaluation of seasonal changes in removal performance was incorporated.

119

#### 120 MATERIAL AND METHODS

121 Experimental setup

122 Three outdoor test installations of 1.44 m<sup>2</sup> (length: 1.5m; width: 0.8m; height: 1.2m; water 123 level: 0.9m) were installed at the site of a wastewater treatment plant in Drongen (Belgium). 124 They consisted of 18 mm plywood panels sealed with a liner. Two were covered with a 125 floating macrophyte mat, mimicking constructed floating wetlands. The third one served as a 126 control as the water surface was uncovered. The floating mat consisted of two plastic pipes 127 filled with foam to enhance its buoyancy and covered with rough-messed wire netting. On top of the wire netting, a coconut coir was present in which the vegetation was rooted. The 128 129 dominant plant species were Carex spp. (> 95% of the surface area) (Luc Mertens Ltd, 130 Loenhout, Belgium). Less than 5% of the vegetation on both mats consisted out of Lythrum 131 salicaria, Phragmites australis and Juncus effusus. The surface area of the floating mats was 132  $0.77 \text{ m}^2$  (0.7m x 1.1m) but due to overhanging plant material, the effective area shaded by the vegetation was about 100%. Prior to the start of the experiments, the floating macrophyte 133 134 mats were grown in a greenhouse from April 2006 till January 2007 and fed with tap water, 135 containing very low nutrient concentrations. Both floating mats were treated as replicates as 136 their plant composition and plant and root development was comparable. From August 2007 137 till December 2007 and from March till September 2008 the water surface of the control was 138 spontaneously colonized by Lemna spp. During winter the Lemna evanesced from the water 139 column by sedimentation and went in hibernation at the bottom of the system.

141 The installations were batch loaded with raw domestic wastewater from the treatment plant in 142 Drongen (Belgium). The raw wastewater was taken before the coarse grids and sand catcher, 143 just after the screws that bring the water up to the wastewater treatment plant. After each testing period of 11 days, approximately half of the wastewater was discarded by lowering the 144 145 initial level to 45 cm and fresh raw wastewater was successively added up to a total level of 146 0.9 m in all three installations. This way of addition management was applied to preclude (i) 147 the addition of peak concentrations entering the treatment system of Drongen as the 148 remaining water in the system resulted in dilution of the added water and (ii) the difference in 149 concentrations of the raw wastewater during the addition time as the three test installations 150 were not fed simultaneously but successively. The overall time needed for adding the water to 151 all three installations was  $\pm$  1h.

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153 One measurement campaign was conducted in February-March 2007, a second one ran from 154 August 2007 till September 2008. A total of 17 batches were performed during the two 155 measurement campaigns. Water samples were taken across the width of the systems during 156 the first campaign, or across the width at a depth of 5 and 60 cm below the water surface 157 during the second campaign. These samples were combined into one composite sample before 158 further processing. Sampling was performed at day 0, 1 (only first campaign), 2, 4, 7 and 11. 159 In between two testing periods no fresh water was supplied to the system. Average 160 concentrations as measured on day 0 (start of the testing period) for all 17 testing periods are 161 presented in Table 1.

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163

## 165 Physico-chemical analysis

Water temperature was measured in situ at a depth of 5 and 60 cm below the water surface each time water samples were taken. Average daily air temperatures were obtained from <u>www.hydronet.be</u>, a website with validated data from the Flemish Environment Agency (VMM). The water level in the three test installations was measured each time at the moment of sampling.

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172 Redox potential was measured with combined platina/gel reference electrodes (HI 3090 B/5; 173 HI 9025, Hanna Instruments, Ann Arbor, USA) which were permanently installed at a depth 174 of 5 and 60 cm below the water surface. For the CFWs, an electrode was also installed at a 175 depth of 5 cm in the floating macrophyte mat (CFW mat). The measured value was corrected 176 with respect to the Standard Hydrogen Electrode as a reference by adding the difference 177 between the redox potential measured in a ZoBells solution (0.033 M K<sub>3</sub>Fe(CN)<sub>6</sub> and 0.033 M 178 K<sub>4</sub>Fe(CN)<sub>6</sub> in 0.1 M KCl) and the theoretical value of +428 mV.

179

180 Conductivity of the water samples was determined immediately upon arrival at the laboratory 181 using an LF 537 conductivity measuring unit and a Tetracon 96 conductivity cell with 182 integrated temperature measurement (Wissenschaftlich Technischen Werkstäten, Weilheim, 183 Germany). Conductivity was automatically compensated for temperature with respect to a 184 reference temperature of 25°C. For pH-measurements an Orion model 520 pH meter (Orion, 185 Boston, MA, USA) was used. The water samples were subsequently filtered over white band 186 filter paper (Machery-Nagel MN 640 m). Both NH<sub>4</sub>-N and total nitrogen (Ntot) were 187 determined following standard procedures (Eaton et al., 1995) by means of a steam 188 distillation (Tecator Kjeltec System 1002 Distilling Unit). Part of the wastewater was filtered 189 over 0.45µm and the remainder was acidified with H<sub>2</sub>SO<sub>4</sub> (0.3 mL per 100 mL) for 190 preservation. The 0.45 μm filtrate was analysed for nitrates, sulphates and total organic 191 carbon (TOC). Nitrates and sulphates were determined with a Metrohm configuration 192 consisting of a 761 Compact Ion Chromatograph equipped with a 788 IC Filtration Sample 193 Processor and anion exchange column (IC-AN-Column Metrosep, A supp 4, Metrohm Ion 194 Analysis, Switzerland). A Total Organic Carbon Analyser (TOC-5000, Shimadzu, Kyoto, 195 Japan) was used for the determination of TOC. The amount of organic nitrogen (Norg) was 196 calculated as the difference between Ntot, NO<sub>3</sub>-N and NH<sub>4</sub>-N.

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198 Total phosphorus content of the water was determined by colorimetry using a Jenway 6500 199 spectrophotometer (Barloworld Scientific T/As Jenway, Felsted, United Kingdom) after 200 digestion with potassiumpersulphate as described in Eaton et al. (1995). For the determination 201 of heavy metals, 40 mL of the filtered samples with 2 mL 65% HNO<sub>3</sub> and 2 mL 20% H<sub>2</sub>O<sub>2</sub> 202 was heated for 20 min at 150°C after which 1 mL 20% H<sub>2</sub>O<sub>2</sub> was added. This procedure was 203 repeated after 40 min and a total destruction time of 60 min was applied. The samples were 204 filtered and diluted with 1% HNO<sub>3</sub> to 50 mL followed by determination with ICP-OES 205 (Varian Vista MPX, Varian, Palo Alto, CA) (Fe, Mn) and ICP-MS (Cu, Ni, Pb, Zn).

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207 Chemical oxygen demand (COD) was determined using Nanocolor test kits (Machery-Nagel, 208 Düren, Germany). The COD-analyses were performed during 9 testing periods only (5/2 - 19/2 - 5/3 - 8/10 - 12/11/2007 - 7/1 - 11/2 - 10/3/2008). A fractionation of the COD was 210 performed for the first three periods. To that aim, 100 mL fresh wastewater was filtered over 211 0.45 µm and COD was determined in both the fresh wastewater and the filtrate. Distinction 212 was made between COD<sub>tot</sub> (before filtration), COD<sub>dissol</sub> (after filtration) and COD<sub>SS</sub> 213 (calculated as the difference between COD<sub>tot</sub> and COD<sub>dissol</sub>).

#### 215 *Removal efficiency*

216 Changes in water level due to evapotranspiration or precipitation were not compensated.217 Therefore removal efficiencies were calculated based on surface loadings:

218 Removal efficiency (%) = 
$$\frac{C_{a,0} - C_{a,11}}{C_{a,0}} \cdot 100 = \frac{C_{v,0} \cdot H_{eff,0} - C_{v,11} \cdot H_{eff,11}}{C_{v,0} \cdot H_{eff,0}}$$

with  $C_a$ : surface loading (g m<sup>-2</sup>),  $C_v$ : pollutant concentration (mg l<sup>-1</sup>), 0: day 0 (addition of the water), 11: day 11 (end of the experiment) and  $H_{eff}$ : the effective water level in the system.

The presence of vegetation on the floating mats increased the water level with 3.5 cm (on average). This was determined at three different dates by lifting the mats out of the water and allowing the remaining water to seep out. The water level before and after removal of the wetland was measured. H<sub>eff</sub> was calculated as follows:

226 
$$H_{eff}(m) = H_{meas} - 0.035 m$$

227 with  $H_{meas}$ : the measured water level in the system (m). For the control  $H_{eff}$  was equal to 228  $H_{meas}$ .

229

# 230 Effect of temperature and season

The testing periods (17 in total) over the two campaigns were grouped according to season to evaluate the effect of season on the removal of the pollutants. To evaluate the effect of temperature, four temperature categories were discerned as outlined in Table 2. As an important part of the removal occurred within the first 4 days after addition of the water, a distinction was made between the average air temperature measured over the first 4 days (T4d) and the average air temperature measured over the complete duration of the testing period (T11d).

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# 240 Statistical analyses

241 Statistical analyses were performed by means of the statistical package SPSS 15.0 (SPSS, 242 Chicago, USA). For examination of the normality of the distribution of the pollutant removal 243 efficiencies all removal efficiencies (independent of measuring campaign, vegetation, temperature group and season) were grouped together and tested by means of the 244 245 Kolmogorov–Smirnov test of normality. It was concluded that all removal efficiencies were 246 normally distributed. Also the pH and water temperature matched the normal distribution. 247 Homogeneity of variances was tested with a Levene test and showed that all variances were equal. The significance of differences in removal performance for the different pollutants and 248 249 pH between the CFWs and the control was evaluated using Univariate Analyses of Variance 250 including the factors vegetation (present or absent), temperature (T4d and T11d and this for all 4 considered temperature groups T<5°C; 5<T<10°C; 10<T<15°C and T>15°C) and season 251 252 (winter, spring, summer and winter). These factors were treated as fixed factors. Significant 253 differences in removal performance between the two CFWs and the effect of rain on influent 254 concentrations were assessed by means of Wilcoxon rank tests. Differences in water 255 temperature at 5 and 60 cm depth were evaluated by a paired t-test. A confidence level of 5% 256 was adopted to evaluate the significance in all different tests.

257

#### 258 RESULTS

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The buoyancy of the floating mat varied over the year. During summer time, the mat was submerged and an above standing water layer of 1-2 cm was observed. During autumn and winter the floating mat rose from the water so that the top of the floating mat, covered with litter, was approximately 2 cm above the water surface. The vegetation formed a dense root package with highly interwoven roots rather than individual roots dangling underneath the floating mat. Average depth of the root package was 12 to 15 cm at the end of the experiments whereas initial depth was only 3 to 5 cm. Shoots of *Carex spp*. had a length varying between 90 and 120cm in September 2008 with the tallest plants in the middle of the mat.

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270 Individual evaluation of the two CFWs showed no significant difference between both test 271 installations. Therefore, the data of both CFWs were combined for comparison with the 272 control. An overview of the average water and air temperature during each testing period is presented in Figure 1. There was no significant difference in water temperature between the 273 274 CFWs and the control when temperature was below 15°C. At higher temperatures the water in the control was significantly higher (p = 0.005). During one testing period (7-1-2008 – 18-1-275 276 2008) ice formation occurred. Ice was quicker formed and lasted longer in the CFWs although 277 no significant difference in water temperature for both depths was observed during this testing period when comparing with the control. Furthermore, no significant differences in 278 temperature at 5 cm and 60 cm depth were observed in the CFWs, (p=0,354) whereas 279 280 temperature differed significantly with depth for the control (p=0.001), with the lower 281 temperatures observed at 60 cm.

282

The redoxpotential (Eh) at day 0 was  $118 \pm 112$  mV. The Eh-value in the water column showed a decline during the first 2 (control -5 cm; CFW -60 cm) to 4 (control-60cm; CFW -5cm) days followed by an increase (Figure 2). The Eh in the floating mat at a depth of 5 cm declined slower followed by an increase after day 6. The average redox potential measured in the mat was higher than the redox potential in the water column of the CFWs at a depth of 5 cm and was comparable to the values of the control at the same depth (Table 3).

290 The pH decreased during the 11-day testing period for the CFWs whereas a stable pH was 291 observed in the control (Figure 3). The pH at the beginning of each 11-day testing period was 292 lower for the CFWs than for the control (p=0.03), except for the first testing period (February 293 2007). During the first period, the pH on day 1 was the same in all three installations. Average 294 influent pH-values for the CFWs and control were respectively  $7.25 \pm 0.19$  and  $7.49 \pm 0.18$ . 295 At higher temperatures, the pH of the effluent tended to be higher, compared to the effluent-296 pH during colder periods. However, this was not caused by a temperature effect, but related to 297 a higher initial pH of the influent during warmer periods. The pH at the end of each testing period was significantly lower (p< 0.001) in the CFWs (7.08  $\pm$  0.21) than in the control (7.48 298 299  $\pm$  0.26) (Table 4). The difference in pH between begin and end of each testing period was only influenced by the presence of the floating mats (p=0.036); no effect of temperature or 300 301 season was observed. Contrary to pH, the reduction in conductivity was significantly affected 302 by temperature (T4d and T11d p < 0.001) with the lowest decrease at temperatures between 303 10 and 15°C for both the CFWs and the control. The average decline of conductivity was low with respectively  $4.2 \pm 7.3$  % and  $1.6 \pm 4.6$  % for the CFWs and the control. 304

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306 Average influent characteristics were highly variable (Table 1). This is due to the cyclic 307 nature of human activities, industrial discharges and rain events when dealing with combined 308 sewer networks, etc. (Leitão et al., 2005). In three testing periods (3/12/2007; 1/1/2008 and 309 14/4/2008) water was pumped from the waste water treatment plant to the test installations during or within 24h after a heavy rain event. As both rainwater and domestic wastewater are 310 311 transported within the combined sewer system, the occurrence of heavy rain events affects the concentrations present in the influent. This resulted in a significant lower conductivity 312 313 (p=0.043) and Ntot concentration (p=0.018) of the influent at day 0. Influent values for conductivity and Ntot were  $773 \pm 81 \ \mu\text{S cm}^{-1}$  and  $16.9 \pm 3.8 \ \text{mg L}^{-1}$  for periods with rainfall, 314

and  $1102 \pm 78 \ \mu\text{S cm}^{-1}$  and  $23.1 \pm 5.0 \ \text{mg L}^{-1}$  for periods without heavy rainfall. The decrease of conductivity over the 11 day periods was apparently not affected (p=0.124) by the decrease in conductivity of the incoming water after rain events. All other pollutant concentrations, except NH<sub>4</sub>-N and NO<sub>3</sub>-N, were also lower during periods with heavy rainfall, but the diminution was not significant. Concentrations of NH<sub>4</sub>-N and NO<sub>3</sub>-N were higher after rain events.

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322 Evolution of concentrations (Ntot, NH<sub>4</sub>-N, TP and TOC) are presented in Figure 4 for the different seasons. As the influent concentrations varied over the different testing periods, 323 324 concentration results have been normalised by dividing the concentrations measured at time t (Ct) by the initial concentration of each testing period (Cin) in accordance with Headley and 325 326 Tanner (2008). The difference in removal performance between the control and the CFWs 327 was in general already apparent after 2 days (Figure 4). Overall removal efficiencies and the 328 removal efficiencies over the different seasons and temperature groups are presented in Table 329 5. To evaluate the effect of vegetation, temperature and season the p-values obtained by the 330 Univariate Analyses of Variances can be found in Table 6.

331

332 For both the control and the CFWs a net removal of Ntot was observed, except for the control 333 during the testing period of 3/12/2007 (-4.3%) (Table 5). Except for the testing periods carried 334 out during spring, increasing concentrations of NH<sub>4</sub>-N were observed (Figure 4). This resulted 335 in almost no net removal over the 11-day period for NH<sub>4</sub>-N. In the control, for 5 out of the 17 336 periods, negative removal efficiencies as low as -50.9 % were obtained for NH<sub>4</sub>-N. The 337 removal of NH<sub>4</sub>-N and Ntot was significantly affected by the presence of the floating mats (p = 0.042 and p = 0.03 respectively). There was no significant seasonal effect on the removal of 338 339  $NH_4-N$  (p=0.622) or Ntot (p = 0.792) for both the control and the blank as removal

340 performances showed a large variability over the different testing periods. In contrast with 341 NH<sub>4</sub>-N, there was a significant effect of temperature on the removal of Ntot (T4d p=0.01, 342 T11d p=0.03). Highest removal of Ntot for both the CFWs and the control was observed 343 between 5 and 15°C, but the variability in removal efficiency was quite high throughout the 344 entire year. The removal of Norg tended to vary in both the control and the CFWs with the highest removal in spring (Table 5) but none of the considered parameters had a significant 345 346 influence. Due to the low concentrations of NO<sub>3</sub>-N present in the influent  $(0.20 \pm 0.23 \text{ mg L}^{-1})$ 347 <sup>1</sup>), it was difficult to obtain a good evaluation of the removal of this pollutant.

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The average TP-concentration in the influent was  $2.16 \pm 1.04$  mg L<sup>-1</sup> (Table 1). An initial release of TP in the control during the first 2 to 4 days was observed during all seasons and temperature periods (Figure 4). Removal of P was influenced by temperature (T11d p=0.019), with the highest removal between 5 and 15°C, but not by the presence of a floating macrophyte mat (p = 0.65). The removal of P in the CFWs showed a high variability over the different testing periods (Table 5). Although no significant effect of season was found, higher removal performance was obtained during summer and autumn for the CFWs (Table 5).

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357 The profile of COD-removal shows the same pattern for both the CFWs and the control but 358 the removal in the CFWs proceeded faster during the first 2 days (data not shown). Removal 359 efficiency after 2 days was  $38.2 \pm 5.3\%$  and  $21.0\pm 7.2\%$  for the CFWs and control respectively. After 11 days the removal efficiency increased to  $52.9 \pm 11.6$  and  $32.6 \pm 15.5$  % 360 361 for the CFWs and control respectively (Table 5). The decrease of COD was significantly influenced by the floating mat (p=0.003) and the interaction between vegetation and season 362 (p=0.045). Further exploration indicated no significant seasonal influence for the control and 363 CFWs. Increasing COD removal in the control coincided with increasing temperature 364

although this was not significant (Table 5). This effect was less clear for the CFWs as
removal performance dropped at temperatures between 5 and 10°C.

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368 To evaluate the contribution of sedimentation to the overall COD removal, a fractionation of 369 the COD present in the influent was carried out during the first three testing periods (Table 7). 370 This fractionation showed no significant difference between the initial concentration of COD<sub>dissol</sub> in the influent and the concentration after 11 days. An initial average concentration 371 of 52  $\pm$  7 (CFWs) and 45  $\pm$  7 mg L<sup>-1</sup> COD<sub>SS</sub> (control) showed a decrease within the first 2 372 days to a level equal to the concentrations determined at day 11. Opposite to the concentration 373 of COD<sub>dissol</sub> the TOC-concentration (which was also filtered over 0.45 µm) showed a constant 374 375 decrease for both the control and the CFWs with a higher removal in the CFWs (Figure 4), 376 athough the effect of the presence of the floating mat was not significant.

377

Sulphate was eliminated to a higher extent in the CFWs (18.3  $\pm$  27.5 %) than in the control (10.0  $\pm$  26.6 %) (Table 5) but the difference was not significant (Table 6). Sulphate reduction was higher during spring and summer for the CFWs compared to the control.

381

382 The presence of the vegetation resulted in higher Fe and Mn concentrations after 2 to 4 days, 383 although the effect was less pronounced for Mn (data not shown). The increase in Fe and Mn 384 was followed by a decrease until the initial concentration (Mn) or lower (Fe). Iron concentrations were during all seasons and when temperature was between 5 and 15°C, higher 385 386 in the CFWs than in the control. This was also the case for Mn during spring and at temperatures higher than 15°C. It was not possible to detect a significant effect of vegetation 387 388 on the removal for the considered heavy metals. The influent concentrations of heavy metals 389 were in general low (Table 1). Overall average removal efficiencies were positive although 390 great differences could be observed for the individual periods as was reflected in the high 391 minimum and maximum removal efficiencies (Table 5). Removal varied between -67% (Zn) 392 and 98 % (Pb). The CFWs performed better for the removal of Cu, Mn, Ni and Zn whereas 393 the controls showed higher removal efficiencies for the removal of Fe and Pb although this 394 effect was for none of the considered metals significant. Both Mn and Pb were significantly 395 influenced by season (respectively p=0.025 and p=0.03) with the highest removal during 396 winter (Mn) and autumn (Pb).

397

#### 398 DISCUSSION

399 Hogg and Wein (1988a, 1988b) studied the source of buoyancy in natural floating Typha 400 wetlands and found that natural buoyancy showed a seasonal trend, mostly associated with the 401 increase of fresh biomass. Furthermore, the release of gas during anaerobic decomposition of 402 dead organic matter and the temperature-dependent gas solubility can affect the floating of the 403 mats. Although artificial buoyancy was provided in this study, biomass development 404 influenced the floating of the mats. During spring and summer, standing stock increased and 405 caused the mats to sink a few centimetres below the water surface. During autumn and winter, 406 senescence of the vegetation resulted in a rise of the mats. The effect of the vegetation is 407 expected to be more important in young CFWs whereas with ageing, the contribution of the anaerobic decomposition will increase as more dead biomass accumulates on top of the 408 409 floating wetland (Hogg and Wein, 1988b). Smith and Kalin (2000) reported that artificial 410 floating *Typha* wetlands became auto-buoyant after the third growing season.

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412 Average air temperatures were used to evaluate the effect of temperature rather than the water 413 temperatures. This was because water temperature was measured at the moment of sampling 414 and did not reflect the course of temperature during the day. Kadlec (1998) found that the

diurnal water temperature variation was approximately 5°C for surface flow constructed 415 416 wetlands. Average daily air temperature does reflect this diurnal changes. Water temperature was not higher in the CFWs during the colder periods, but did cause a cool down effect at 417 418 temperatures above 15°C. This is in contrast with substrate-based systems where the presence 419 of the vegetation acts as a buffer against colder temperatures (Brix, 1997). Tanner et al. 420 (1995) found that the water in vegetated subsurface flow constructed wetlands was up to 1°C 421 cooler in summer compared to an unvegetated wetland. The longer lasting ice period observed 422 in the CFWs was probably due to a combination of reduced impact of the wind on the water 423 surface and shading caused by the vegetation, preventing the sun from melting the ice. In full 424 scale applications rocking of the floating wetland by the wind may hamper ice-formation and 425 result in a longer ice-free period.

426

The difference in redox potential observed at 5 and 60 cm depth was due to reduced oxygen diffusion (Dusek et al., 2008). Smith and Kalin (2000) described how the presence of a floating macrophyte mat limits the diffusion of oxygen from the air to the water whereas for the control, oxygen diffusion was less influenced. Oxygen diffusion in the CFWs was hampered as the complete water surface was covered by vegetation, shielding the water surface from the wind. The presence of a *Lemna* cover in the control did not influence the redoxpotential.

434

A release of oxygen by the roots might explain the higher redox potential in the floating macrophyte mat (Table 3; Figure 2). The measurements indicated that the oxygen released by the roots was higher than the diffusion rate observed in the control. The oxygenation effect of the vegetation seemed to be limited in depth as the Eh measured at a depth of 60 cm was lower in the CFWs. As such there is a larger tendency towards reduction at greater depths 440 mediated by the higher abundance of biofilm in the CFWs favouring oxygen consuming 441 reactions. The effect of the floating macrophyte mat on the Eh was not only limited in depth 442 but also in space as the Eh measured at 5 cm depth in the CFWs was lower compared to the 443 Eh in the mat and comparable with the values measured in the control at a depth of 5 cm. Neither the CFWs nor the control revealed any temperature-driven or seasonal trend. As such, 444 445 the growth stage of the vegetation did not influence directly the Eh-value. However, the 446 existence of temperature-driven and seasonal changes in Eh have been proven in subsurface 447 flow constructed wetlands by Dusek et al. (2008). They found a decreasing Eh-value with increasing temperature due to an increased microbial activity and a decreased solubility of 448 449 oxygen. Lowest Eh-values were observed during June and July opposite to April and October, during which they recorded the highest values. The lower Eh-values observed in the CFWs 450 coincide with a higher removal of  $SO_4^{2-}$ . In more reducing conditions, sulphates are converted 451 452 to sulphides which precipitate (Stein and Hook, 2005).

453

454 The continuously lower pH in the CFWs was the result of plant activity as plants excrete by 455 their roots protons and organic acids (Coleman et al., 2001). This was already seen from the second testing period onwards. Although only half of the wastewater present at the end of the 456 457 11-day testing period was removed, the difference in pH between the CFWs and the control remained stable and did not increase during the following testing period. It seems that there 458 459 was an equilibrium between the excretion and consumption of pH-lowering substances. On 460 average, the difference in pH between the CFWs and the control at the beginning of each 461 testing period was 0.25.

462

463 Oxygen present in the water at the beginning of the testing period was rapidly consumed by464 various reactions, e.g. nitrification and aerobic decomposition of organic material. Organic

465 nitrogen was converted to NH<sub>4</sub>-N and caused during all seasons except spring an increase of 466 NH<sub>4</sub>-N in the control as the production of NH<sub>4</sub>-N was faster than its removal by nitrification. sorption.... This increase due to ammonification was not observed for the CFWs. Removal of 467 468 NH<sub>4</sub>-N in the CFWs was enhanced by the presence of the vegetation and the coconut coir 469 compared to the control. Plants can take up both  $NH_4^+$  and  $NO_3^-$  (Kadlec and Knight, 1996) but as the influent concentrations of  $NO_3^-$  were low, uptake of  $NH_4^+$  was preferred. 470 471 Furthermore, submerged plant parts and decomposing litter provide sorption and attachment 472 area for biofilm formation (Vymazal, 2007). Coconut fibres have proven to be useful in biofilters used for removal of NH<sub>3</sub> from gaseous streams by sorption (Baquerizo et al., 2009). 473 474 The coconut coir, present to enhance rooting and development of the vegetation, is expected to degrade with time and will be replaced by a matrix comprised of roots, decomposing plant 475 476 material and particulate matter originating from decomposed leaves and roots and adhering 477 suspended particles. Yet in the young floating macrophyte mat, the coconut fibres enhance the removal of NH<sub>4</sub>-N from the wastewater. 478

479

480 In Europe, typical removal efficiencies of NH<sub>4</sub>-N in long-term engineered wetland systems range between 35% and 50% (Verhoeven and Meuleman, 1999; Vymazal, 2002). More 481 482 specific for CFWs, NH<sub>4</sub>-N and Ntot removal has been reported to vary between -45 and 75% for NH<sub>4</sub>-N, and 36 and 40% for Ntot (Boutwell, 2002; Kyambadde et al., 2004; DeBusk and 483 484 Hunt, 2005; Gonzalez et al., 2005). Low removal efficiencies in the current test installations for NH<sub>4</sub>-N were attributed to reducing conditions, limiting nitrification. The obtained results 485 486 during this study were remarkably lower ( $25.5 \pm 2.9\%$ ), although the CFWs performed better than the control  $(2.9 \pm 22.0\%)$  (Table 5). Reducing conditions seemed to be the main factor 487 488 limiting N-removal. The removal of Ntot was influenced by temperature with the highest removal between 5 and 15°C. At higher temperatures N removal was limited as higher 489

490 temperatures are associated with more reducing conditions (Dusek et al., 2008). Also the 491 removal of NH<sub>4</sub>-N and TOC showed a decline when temperature rose above 15°C. Kuschk et al. (2003) found that nitrification was most restricted during summer. Consistent with a 492 493 reduced oxygen solubility, the input of oxygen into the rhizosphere by the plants can be 494 restricted during summer periods (Kuschk et al., 2003). In addition, an increase of microbial 495 activity will further favour the establishment of reducing conditions. Akratos and Tsihrintzis 496 (2007) and Kuschk et al. (2003) indicated that at temperatures below  $15^{\circ}$ C, neither the 497 bacteria responsible for N-removal, nor the vegetation functioned properly. In our situation, reducing conditions nullified this possible positive temperature effect at temperatures above 498 499 15°C. At temperatures below 5°C it has been reported that biological processes drastically slow down or cease (Mitsch and Gosselink, 1993). Nitrification rates in wetlands were 500 recorded to drop rapidly below 6°C (Werker et al., 2002). In contrast with studies indicating 501 502 an effect of temperature on N-removal, other studies pointed out only very small differences 503 in N-removal between warmer and colder periods (Maehlum and Stalnacke, 1999; Mander et 504 al., 2000).

505

506 Riley et al. (2005) concluded that, as plant uptake plays only a minor role in NH<sub>4</sub>-N removal 507 from normal wastewater, the effect of the vegetation on the seasonal variation of ammonium 508 removal will be minor. This is in correspondence with the results of this study, indicating no 509 significant seasonal effect. Also for Ntot no seasonal effect was detected although other 510 reports have demonstrated significant differences between seasons (Tanner et al., 1995; 511 Kadlec, 1999; Del Bubba et al., 2000; Spieles and Mitsch, 2000). The removal of N by the CFWs was more influenced by temperature. Furthermore, the presence of the floating mats 512 513 caused a less variable removal of Ntot and NH<sub>4</sub>-N from the water column compared to the 514 control. This can be due to a more stable temperature and the effect of biofilms associated with the floating macrophyte mat. Especially the latter can be of major importance in systems with highly variable water levels and systems subject to irregular loadings or batch-fed systems (e.g; stormwater treatment, combined sewer overflow treatment).

518

519 Phosphorous removal by floating wetlands was reported to vary between 6 (UK) and 83.2% 520 (Uganda) (Kyambadde et al., 2004; Gray, 2005). Ortho-phosphate removal in a single 521 treatment system might be highly variable. For a drinking-water basin equipped with floating 522 Phragmites mats removal varied between 0 and 96% (Garbett, 2005). Also in the current study TP removal rates were highly variable. For both the control and the CFWs, removal was 523 524 more influenced by temperature than by season. This could be due to the limited contribution of the vegetation to the removal of P as plants contain only a small amount of the 525 526 phosphorous that enters higher P-loaded wetlands. The soil/litter compartment is accepted to 527 be the major long-term P storage pool in traditional substrate based constructed wetlands. 528 Furthermore, sedimentation of P associated with particles, sorption, and microbial uptake are 529 possible removal pathways. The retention and remobilisation of phosphorus in wetlands is 530 controlled by the interaction of redox potential, pH, Fe, Ca and Al (Vymazal, 2002). As no 531 initial substrate was present in all testing installations, P-removal was poor and varied, 532 especially for the CFWs. Over time a sediment layer developed in all systems, formed by the 533 suspended particles present in the influent and, for the CFWs, decomposing plant material but 534 this building up did not result in increased P-removal. Although the presence of the floating 535 mats did not significantly affect the removal of P, removal pathways may differ. In addition, 536 the release of oxygen by plant roots may increase the adsorption capacity of wetlands for P (Walhugala et al., 1987). Phosphorus release in the control can be associated with 537 538 remobilisation due to reductive dissolution of Fe(III). Although lower redox potentials were present in the CFWs, thus enhancing P-release, more alternative removal pathways (binding 539

540 with sediments, sorption to coconut coir, plant uptake,..) of P are present in the CFWs 541 compared to the control.

542

543 From the COD fractionation it could be concluded that sedimentation played an important role in the removal of COD from the water column (Table 7). As sedimentation is a physical 544 545 process it is only slightly positively affected by increasing temperatures (Kadlec and Reddy, 546 2001). Next to sedimentation also part of the suspended solids may be captured within the 547 floating mat, including the coconut substrate and the pendulous roots (Smith and Kalin, 2000; Headley and Tanner, 2006). This evidences the importance of the presence of the floating 548 549 macrophyte mat for the removal of COD from the water column and was confirmed by the 550 significant influence of the floating mats on COD removal during this study.

551

552 In contrast with the COD-removal, which occurred mainly within the first 2 days, TOC 553 removal continued throughout the entire testing method. Although COD can be used to 554 characterize the amount of organic substances present in the water, there is no universal 555 relationship between TOC and COD. TOC-measurements are independent of the oxidation 556 state of the organic matter and other organically bound compounds are not determined. 557 Furthermore, during COD-measurements reduced inorganic species are also being oxidised 558 (Eaton et al., 1995). As more reducing conditions prevail in the test installation with time, it is 559 possible that part of the COD<sub>dissol</sub> originates from the oxidation of reduced species during the 560 COD-procedure, disguising a further removal of organic substances as can be seen from the 561 TOC-decrease. This indicates that, next to sedimentation, other removal pathways can take 562 place. Organic components can be degraded both aerobic as well as anaerobic by bacteria attached to the roots, rhizomes and substrates (Baptista, 2003). A biofilm layer present on the 563 roots hanging in the water column could be visually observed in the CFWs. The results 564

obtained by Akratos and Tsihrintzis (2007) indicated that for COD the temperaturedependence was less significant because removal was mainly the result of microbial activity of both aerobic and anaerobic bacteria which function even at temperatures as low as 5°C. This corresponded with the results gathered during the present study with removal efficiencies up to 60% at temperatures below 5°C. The removal of COD in the control seemed to be more related to temperature, with increasing removal efficiencies at higher temperatures in comparison with what was seen in the CFWs.

572

The presence of sulphate contributes to the removal of COD and TOC. Huang et al. (2005) indicated that influent sulphate was the major component contributing to the removal of organic matter. Reduction of sulphate was in general higher in the CFWs than in the control although there was for several periods no significant difference between the control and the CFWs (Table 5). Sulphate reduction was higher during spring and summer for the CFWs, but this was not reflected in an improved removal of TOC and COD.

579

580 The removal of heavy metals by constructed floating wetlands has only been limited 581 documented in literature. Headley and Tanner (2008) investigated the application of CFWs 582 for the removal of Cu and Zn from stormwater and found for Cu 65-75% and 0% removal for 583 CFWs and control respectively. Zn was removed to a smaller extent: 10-35% and less than 584 10% for the CFWs and control respectively. This is in line with the current study where Cu 585 and Zn removal was lower in the control. Revitt et al. (1997) studied the removal of metals 586 from airport runoff and found much lower removal performances for Zn (-5 - -20%) than for Cu (20-30%). Our results suggested that, at the low influent concentrations during the present 587 588 study, there was no significant contribution of the floating mat.

#### 590 Conclusions

591 Removal of pollutants was better in CFWs compared to a control without floating macrophyte 592 mat. The presence of the vegetation was the main factor contributing to the overall removal 593 performance although this effect was not significant for each parameter. Concentrations were 594 significantly lower in the CFWs for NH<sub>4</sub>-N, Ntot and COD. Also the pH was influenced, 595 resulting in lower pH-values in the CFWs. Both the effect of season and temperature were 596 evaluated. Removal of Ntot, NH<sub>4</sub>-N and P was the highest in the moderate temperature range 597 (5 - 15°C), but diminished at higher or lower temperatures. In general removal seemed to be hampered at higher (T>15°C) rather than lower temperatures (T<5°C). Seasonal changes were 598 599 detected but were not important, indicating that the growth cycle of plants did only influence 600 the performance of the CFWs to a minor extent. Measurements of redoxpotential evidenced 601 the less reductive conditions that persisted within the floating macrophyte mat, allowing a 602 faster removal compared to unplanted systems. However, more reducing conditions persisted in the CFWs at greater depths. Furthermore, removal of each pollutant occurred faster within 603 604 the CFWs (except for Fe and Mn), proving that CFWs have an added value over pond 605 systems and are effective when intermittent loadings occur.

606

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- 748 7. School of Biological Sciences, University of Birmingham, 2000.

- 1 Table 1. Average characteristics of the wastewater as measured at day 0 over the 17 different
- 2 testing periods (n = 54)

Parameter	Average ± SD	Min - Max
рН (-)	$7.35\pm0.22$	6.88 - 7.81
Conductivity (µS cm <sup>-1</sup> )	$1035\pm169$	626 - 1282
$NH_4$ -N (mg L <sup>-1</sup> )	$16.1\pm4.9$	8.23 - 25.9
$NO_{3}-N (mg L^{-1})$	$0.37\pm0.53$	< 0.1 - 2.85
Norg (mg $L^{-1}$ )	$4.31 \pm 4.65$	0 - 12.0
Ntot (mg $L^{-1}$ )	$21.8\pm5.0$	11.6 - 31.9
$P(mg L^{-1})$	$2.16 \pm 1.04$	1.42 - 3.22
$SO_4^{2-}$ (mg L <sup>-1</sup> )	$64.2\pm15.5$	20.1 - 90.1
TOC $(mg L^{-1})^*$	$27.7 \pm 11.1$	9.58 - 52.4
$COD (mg L^{-1})**$	$81.3 \pm 24.7$	43.0 - 124
$Cu (\mu g L^{-1})$	$10.0\pm4.6$	1.39 - 19.5
Fe ( $\mu$ g L <sup>-1</sup> )	$454\pm263$	72.2 - 1192
$Mn (\mu g L^{-1})$	$164 \pm 48$	88.3 - 312
Ni ( $\mu g L^{-1}$ )	$10.0\pm4.6$	2.30 - 18.4
Pb ( $\mu g L^{-1}$ )	$6.10\pm3.78$	1.19 - 19.5
$Zn (\mu g L^{-1})$	$57.5\pm35.0$	15.7 - 147
* TOC: n = 28		

5

6 Table 2. Partitioning of the testing periods over the different temperature groups and seasons.

- 7 A distinction was made between average air temperature during the first 4 days (T4d) and 11
- 8 days (T11d)

Temperature (°C)	T4d	T11d								
<5	5/2/2007; 12/11/2007; 11/2/2008	12/11/2007; 11/2/2008								
5_10	20/2/2007; 5/3/2007; 3/12/2007; 7/1/2008; 10/3/2008; 14/4/2008	5/2/2007; 20/2/2007; 5/3/2007; 3/12/2007; 7/1/2008; 10/3/2008								
10 15	10/9/2007: 8/10/2007	10/9/2007: 8/10/2007: 14/4/2008: 8/9/2008								
>15	13/8/2007; 26/5/2008; 16/6/2008; 30/6/2008;	13/8/2007; 26/5/2008; 16/6/2008; 30/6/2008;								
	18/8/2008; 8/9/2008	18/8/2008								
Season	Testing period									
Spring	14/4/2008; 26/5/2008; 16/6/2008									
Summer	13/8/2007; 10/9/2007; 30/6/2008; 18/8/2008; 8/9/2008									
Autumn	nn 8/10/2007; 12/11/2007; 3/12/2007									
Winter	7/1/2008: 11/2/2008: 10/3/2008: 5/2/2007: 20/2/2007:5/3/2007									

10 Table 3. Average redoxpotential (mV) over the 11 days testing period at a depth of 5 and 60

	Average $\pm$ SD (mV)	Min - Max (mV)
Control-5	$68 \hspace{0.1in} \pm \hspace{0.1in} 225$	-278 - 595
Control-60	$-93 \pm 226$	-303 - 513
CFW-5	$-24 \pm 145$	-221 - 362
CFW-60	-122 ± 111	-236 - 227
CFWmat	$72 \pm 478$	-162 - 501

11 cm for both the CFWs and control and within the floating macrophyte mat (CFWmat)

12

13 Table 4. Average characteristics of the water after 11 days for the CFWs (n = 25) and the

14 control (n=17) over the 17 testing periods

	CFW	Control			
Variable	Average $\pm$ SD	Min-max	Average $\pm$ SD	Min - max	
pH (-)	$7.08 \pm 0.21$	6.76 - 7.54	$7.48 \pm 0.26$	7.13 - 8.03	
Cond ( $\mu$ S cm <sup>-1</sup> )	$1017 ~\pm~ 144$	727 - 1284	$1015 ~\pm~ 135$	762 - 1222	
$NH_4-N (mg L^{-1})$	$10.8 \pm 7.0$	3.4 - 28.6	$16.5 \pm 5.1$	9.1 - 27.0	
$NO_3-N (mg L^{-1})$	$0.20 \pm 0.23$	< 0.1 - 0.83	$0.08 ~\pm~ 0.05$	< 0.1 - 0.19	
Norg (mg $L^{-1}$ )	$1.6 \pm 3.4$	0.00 - 8.28	$2.87 ~\pm~ 2.73$	0.00 - 5.91	
Ntot (mg $L^{-1}$ )	$13.1 \pm 8.5$	3.1 - 32.2	$19.5 \pm 6.6$	6.0 - 31.2	
TP (mg $L^{-1}$ )	$1.77 \pm 0.97$	0.32 - 4.72	$1.90 \pm 0.69$	0.44 - 3.86	
$SO_4^{2-}$ (mg L <sup>-1</sup> )	$49.8 ~\pm~ 16.5$	9.1 - 78.4	$53.7 \pm 18.0$	17.5 - 73.4	
TOC (mg $L^{-1}$ )*	$16.4 \pm 8.8$	5.9 - 33.9	$23.0~\pm~9.1$	10.6 - 41.6	
$COD (mg L^{-1})**$	$46.6 \pm 26.7$	17.0 - 89.0	$51.4 \pm 27.5$	33.0 - 115.0	
Cu (mg L <sup>-1</sup> )	$5.5 \pm 4.9$	1.6 - 22.7	$8.4 \pm 4.8$	2.7 - 21.4	
Fe (mg $L^{-1}$ )	$325 \pm 263$	95 - 961	$259 ~\pm~ 134$	83 - 578	
$Mn (mg L^{-1})$	$153 \pm 51$	85 - 241	$176 \pm 66$	85 - 383	
Ni (mg $L^{-1}$ )	$6.1 \pm 3.1$	0.8 - 12.6	$5.75 \pm 2.88$	2.45 - 12.9	
Pb (mg $L^{-1}$ )	$3.4 \pm 1.8$	0.1 - 7.4	$4.58 ~\pm~ 3.27$	0.08 - 11.8	
$Zn (mg L^{-1})$	$29.7 ~\pm~ 20.9$	7.2 - 76.4	$47.6~\pm~31.8$	8.8 - 130	

15 \* TOC: CFWs n = 15; control n = 10

16 \*\* COD: CFWs n = 13; control n = 9

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		Overall removal effici	ency (%)	Seasonal removal efficiency (%) Temperature depended removal efficiency				iciency (%)			
				Spring	Summer	Autumn	Winter	T <5	5 <t<10< th=""><th>10<t<15< th=""><th>T&gt;15</th></t<15<></th></t<10<>	10 <t<15< th=""><th>T&gt;15</th></t<15<>	T>15
		Average $\pm 1$ SD	Min-max								
NH <sub>4</sub> -N	CFWs	$34.9 \pm 24.5$	-17.8 - 81.4	35.5	34.5	34.3	35.1	31.2	34.5	51.0	17.3
	control	$2.9 \pm 22.0$	-50.9 - 33.4	24.7	-10.4	7.3	0.9	3.0	2.0	9.4	-1.2
Norg	CFWs	$44.5 \pm 45.4$	-46.0 - 100.0	84.7	27.1	56.4	37.2	45.6	60.1	28.2	60.9
	control	$18.0 \pm 59.4$	-116.2 - 100.0	61.8	39.3	-12.5	-2.2	34.6	-30.4	60.0	27.9
Ntot	CFWs	$42.3 ~\pm~ 27.6$	0.5 - 80.3	38.4	40.2	36.9	47.0	23.7	46.8	56.8	24.3
	control	$15.2 \pm 23.8$	-4.3 - 74.0	22.6	3.0	2.0	26.3	4.6	26.8	27.1	1.6
TP	CFWs	$22.1 ~\pm~ 23.6$	-24.0 - 78.5	-13.0	39.0	30.7	18.4	11.8	23.3	30.1	16.8
	control	$5.8 \pm 10.1$	-11.1 - 29.4	13.7	5.6	-2.7	3.6	4.1	4.1	2.6	14.0
$SO_4^{2-}$	CFWs	$18.3 \pm 27.6$	-24.5 - 86.4	21.8	37.1	-0.4	10.8	18.0	10.7	10.6	52.1
·	control	$10.0 ~\pm~ 26.6$	-43.5 - 65.6	-17.0	27.7	8.7	7.5	13.2	6.3	7.0	21.1
ТОС	CFWs	$36.3 \pm 24.1$	-0.7 - 71.2	36.0	19.9	35	49.1	48.9	22.4	49.5	9.7
	control	$12.4 ~\pm~ 32.2$	-56.5 - 71.1	18.4	10.2	19	32.0	7.3	13.9	17.7	10.2
COD	CFWs	$52.9 \pm 11.6$	25.4 - 69.7	n.d.	n.d.	62.5	42.7	60.3	50.2	69.7	n.d.
	control	$32.6 ~\pm~ 15.5$	10.0 - 53.8	n.d.	n.d.	23.3	29.3	21.6	33.1	49.0	n.d.
Cu	CFWs	$52.3 \pm 26.9$	-17.5 - 84.9	71.6	62.3	40.4	36.9	55.4	32.1	65.7	66.3
	control	$29.2 \ \pm \ 25.6$	-40.8 - 55.9	52.2	29.2	21.9	16.9	29.5	15.4	40.4	36.3
Fe	CFWs	$24.5 \pm 36.1$	-47.7 - 78.8	16.7	27.7	11.8	n.d.	65.2	18.0	-9.6	50.1
	control	$38.4 ~\pm~ 20.9$	-3.3 - 65.5	48.0	41.7	20.4	36.6	27.4	33.3	32.0	50.9
Mn	CFWs	$6.1 \pm 28.5$	-62.7 - 57.9	-7.7	-3.2	-13.9	16.9	27.4	16.6	-30.9	-11.6
	control	$-2.0 \pm 19.6$	-49.3 - 24.2	-2.2	-9.7	-12.6	9.9	15.1	11.8	-25.9	-4.9
Ni	CFWs	$16.4 \pm 34.5$	-21.8 - 90.3	-11.9	30.6	5.1	13.4	15.7	11.3	2.4	23.6
	control	$10.9 \pm 33.3$	-35.6 - 68.5	18.7	16.4	-4.9	8.1	25.3	2.7	12.2	13.8
Pb	CFWs	$33.0 ~\pm~ 38.0$	-33.9 - 97.7	61.5	25.3	80.4	20.1	16.5	29.6	27.1	53.8

22	Table 5 Overall removal efficiency, seasonal and temper	ature-depended removal efficiency for	the different parameters	
	Overall removal efficiency (%)	Seasonal removal efficiency (%)	Temperature depended removal efficiency (%)	

	control	$38.4 ~\pm~ 35.7$	-28.0 - 98.1	36.2	13.8	88.1	26.6	69.6	31.3	45.9	36.2
Zn	CFWs control	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	-66.7 - 88.9 -44.2 - 83.1	86.4 70.1	60.0 -11.6	57.1 21.1	27.5 10.5	29.1 33.3	31.5 12.9	57.2 7.6	73.6 32.0

23 n.d. not determined

Table 6 p-values obtained from the Univariate Analyses of Variance for the different factors and interactions influencing the removal performance of the different pollutants during the two measuring campaigns.

	NH <sub>4</sub> -N	NO <sub>3</sub> -N	Norg	Ntot	TP	SO4 <sup>2-</sup>	TOC	COD
Vegetation	0.042*	0.466	0.888	0.032*	0.65	0.213	0.341	0.003*
Season	0.622	0.142	0.998	0.792	0.359	0.716	0.192	0.156
T4d	0.529	0.122	0.908	0.01*	0.103	0.154		0.238
T11d	0.796	0.078	0.706	0.03*	0.019*	0.468	0.334	0.625
Vegetation x season	0.541	0.666	0.365	0.709	0.283	0.301	0.53	0.045*
Vegetation x T4d	0.521	0.425	0.523	0.736	0.833	0.896		0.199
Vegetation x T11d	0.956	0.072	0.357	0.942	0.76	0.982		0.129
	Cu	Fe	Mn	Ni	Pb	Zn	_	
Vegetation	0.291	0.991	0.156	0.799	0.775	0.484		
Season	0.99	0.835	0.025*	0.943	0.03*	0.617		
T4d	0.484	0.203	0.691	0.85	0.272	0.024*		
T11d	0.766	0.607	0.967	0.989	0.965	0.065		
Vegetation x season	0.613	0.929	0.312	0.763	0.926	0.85		
Vegetation x T4d	0.977	0.375	0.062	0.952	0.436	0.147		
Vegetation x T11d	0.636	0.595	0.847	0.611	0.708	0.623	_	
* p< 0.05								

Table 7 COD fractionation (mg  $L^{-1}$ ) for 3 testing periods at the start and end of the 11 day

testing periods

Testing period			Start (mg L <sup>-1</sup> )			End (mg $L^{-1}$ )	
1		COD <sub>tot</sub>	COD <sub>dissol</sub>	COD <sub>SS</sub>	COD <sub>tot</sub>	COD <sub>dissol</sub>	COD <sub>SS</sub>
1	CFWs	$106 \pm 6$	45 ± 4	$61 \pm 1$	$62 \pm 10$	$46 \pm 5$	$15 \pm 6$
	control	$118 \ \pm 0$	$40 \hspace{0.1in} \pm \hspace{0.1in} 1$	$56 \pm 10$	$79 \pm 1$	$36 \pm 4$	$21 \hspace{0.1in} \pm \hspace{0.1in} 6$
2	CFWs	$101 \pm 12$	51 ± 4	$86 \pm 3$	50 ± 13	67 ± 3	$19 \pm 1$
	control	92 ± 2	$50 \pm 10$	81 ± 12	42 ± 8	$68 \pm 9$	14 ± 19
3	CFWs	114 ± 13	59 ± 3	$71 \pm 6$	44 ± 15	53 ± 5	$18 \pm 8$
	control	113 ± 3	46 ± 1	$115 \pm 11$	67 ± 1	44 ± 3	$71 \hspace{.1in} \pm \hspace{.1in} 14$
Average	CFWs	$107 \pm 11$	52 ± 7	$73 \pm 12$	56 ± 13	$55 \pm 10$	17 ± 6
Ū.	control	$108 \hspace{0.1in} \pm \hspace{0.1in} 13$	$45~\pm~7$	$84~\pm~28$	$62 \ \pm 17$	$49\ \pm 16$	$35 \pm 30$

Figure 1. Average air and water temperature for the control and the CFWs during the different testing periods.



Figure 2. Evolution of the redoxpotential as a function of time over the 17 testing periods



◆ CFW -60cm ■ CFW -5cm ▲ CFW in ♦ control -60cm □ control -5cm



Figure 3. Average pH-values for the CFWs and the control over the 17 testing periods

CFWs Control

Figure 4. Evolution of concentrations for different selected pollutants for the CFWs (black symbols) and the control (white symbols) over the different seasons. The figures depict the proportion of the concentration that remains in the water at time t (Ct) since the start of the batch (Cin).

