



Constructed wetlands may lower inorganic nutrient inputs but enhance DOC loadings into a drinking water reservoir in North Wales

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37 (reservoirs, lakes and rivers) whilst one-third is taken from groundwater. Surface water can contain
38 naturally high concentrations of DOC. Its removal is often the largest water treatment issue as DOC
39 persisting until the disinfectant stage can react with the disinfectant, usually with chlorine (Cl⁻) to
40 produce carcinogenic disinfection by-products (DBPs) (Chow, et al. 2003). High DOC concentrations
41 in surface waters that feed reservoirs may be linked to catchment properties, hydrological conditions,
42 land management characteristics, or climatic conditions (Pacheco, et al. 2013). Total organic carbon
43 (TOC) is of multi-origin, and can be divided into two parts: autochthonous and allochthonous organic
44 carbon. The autochthonous organic carbon is mainly controlled by the production of the algae and
45 wetland plants; and the allochthonous one by climate and environment in the catchment area (Junlong,
46 et al. 1997). Eutrophication, which affects many reservoirs, may present a major problem as the resulting
47 enhanced algal growths may also increase the input of DOC, thereby increasing the potential risk of
48 DBP formation potential (Gough, et al. 2015). Only a few studies about C budgets of CWs exist, and
49 their results are variable but confirm that CW's often act as a net source for DOC (Kovacic, et al. 2000
50 and Kovacic, et al. 2006).

51

52 **2. Material and Methods**

53 *2.1 Site description*

54 The CW (figure 1) is located at one of the inflow streams of a drinking water reservoir in north Wales.
55 The reservoir in this study is eutrophic due to agricultural practices within the catchment and the streams
56 flowing into the reservoirs have moderate to high DOC concentrations (~10 mg/l). The area around the
57 reservoir is used for cattle and sheep farming aided by modern agro-chemicals (Hughes, et al. 2013).
58 The bedrock at the site consists dominantly of Schist, and the aquifer has a limited yield for groundwater
59 resources. The primary aim of the CW is the removal of nitrogen and phosphorus, to minimise the
60 growth of algae in the reservoir and the formation of DBPs at the treatment plant. Phosphorus and
61 nitrogen are high due to significant agricultural influence. The CW system consists of 414 m² of
62 treatment area in addition to 81 m² of open water. The nominal hydraulic retention time (nHRT) is three
63 days. Average inflow flow rate is 1.02 L/s. The length of the system is 33 m, width at the inflow is 12
64 m and 18 m at the outflow. Furthermore 1.8 m were added as open water zone, which allows
65 oxygenation, increased retention time and provides mixing, which can enhance removal processes.
66 Mean temperature over the sampling period was 13.4°C and average rainfall was 3.0 mm/day. The
67 treatment area comprises of a range of naturally occurring reeds, like phragmites. Only material from
68 the site was used for construction of the walls and a series of baffles, and a plastic outflow pipe was
69 added. In this study, we aim to investigate the time in which it takes a newly constructed wetland to
70 improve and enhance the water quality of an inflow into a eutrophic drinking water reservoir. Therefore,
71 physicochemical parameters at the inflow and outflow were measured on a weekly basis over a period
72 of six months and a C budget was calculated.

73 *2.2. Field and laboratory techniques*

74 Sampling was undertaken every week between 27/03/-24/10/2014. Sampling of the CW outflow started
 75 eleven days later from the 07/04 onwards, in situ measurements were temperature and DO (Milwaukee
 76 Instruments MW-600 Smart DO Meter). At the inflow and outflow three freshwater samples were
 77 collected using a one litre glass bottle, a 100 ml plastic bottle and a 50 ml amber glass bottle (to minimise
 78 UV influences on samples). The one litre glass bottle was used to measure particulate organic carbon
 79 (POC) by high temperature combustion (550°C for two hours) of the sample on a GF/F Whatman glass-
 80 fibre filter. The 100 ml plastic bottle were completely filled and left unfiltered to measure pH (Mettler
 81 Toledo SevenEasy pH meter), conductivity (Orion 5 probe), bicarbonate, dissolved greenhouse gas
 82 concentrations. Bicarbonate is measured by taking 10 ml of unfiltered sample and titrating the pH to 4.3
 83 with 0.1 mole HCl. Dissolved gases were determined using a similar headspace equilibrium method as
 84 that described by Dawson et al. (2002), with the gases analysed using a Varian 450 GC. The remaining
 85 sample was further filtered (0.45um Whatman Glass-fibre filters) and analysed for DOC and DIC
 86 concentrations (Thermalox TC/TN, Analytical Sciences Ltd), specific ultraviolet absorbance (SUVA)
 87 (Spectromax M2e Spectrophotometer, Molecular Devices) and nutrients (Metrohm 850 IC). The SUVA
 88 value gave information about the aromaticity of the water sample and is calculated with the DOC (mg/l)
 89 and the UV absorbance at 254 nm. The 50 ml amber bottle was incubated at room temperature for five
 90 days, so biological oxygen demand (BOD) could be calculated. With the Thermalox, DOC, DIC and
 91 total carbon (TC) concentrations were measured to calculate the C budget (slightly altered from Pacheco
 92 et al. 2013) of the wetland. To assess carbon processing, the following mass balance equation was
 93 applied:

$$\begin{aligned}
 & POC_{in} + DOC_{in} + DIC_{in} + TOC_{dep} \\
 & = \\
 & POC_{out} + DOC_{out} + DIC_{out} + OC_s + CO_2 + \Delta TC_{st}
 \end{aligned}$$

99 where TOC is total organic carbon, OC is organic carbon, the subscripted “in” signifies the inflow from
 100 the catchment, “dep” is atmospheric wet deposition, “out” is outflow from the lake, “s” is permanent
 101 burial in sediment, CO₂ is the concentration of CO₂ in the water. Additionally CH₄ was calculated as a
 102 CO₂ equivalent and added to the CO₂. ΔTC_{st} is the change in the pool of C in the lake over each sampling
 103 time period (one week). POC_{in}, DOC_{in}, DIC_{in}, POC_{out}, DOC_{out}, DIC_{out} were calculated from weekly
 104 measured concentrations in streams.

105 To assess the effectiveness of the wetland nutrient removal efficiency (R) was calculated as follow

$$R(\%) = \left(\frac{C_i - C_o}{C_i} \right) * 100$$

108 Nutrient concentration influent (C_i) was measured at the inflow and the nutrient concentration effluent
109 (C_o) was sampled at the outflow both on a weekly basis and for calculation of R the average mean value
110 was used.

111

112 **3. Results**

113 *3.1 Carbon*

114 Mean DOC concentration of the inflow was 7.22 ± 0.17 mg/l and average DIC concentration was 18.07
115 ± 0.21 mg/l. As seen in figure 2, the DOC concentration of the outflow was in general higher than the
116 inflow, but both exhibiting the same approximate seasonal trend. The carbon budget (figure 3) shows
117 that over the entire sampling period 17.2% less DIC, 11.5% more DOC and approximately twice as
118 much POC flowed into the reservoir compared to if the CW didn't exist. 7.5% of the carbon is retained
119 in the wetland through sedimentation and plant uptake. Nutrient removal efficiency is -60.7%. Mass
120 removal rate (MRR) was $-0.92 \text{ g}\cdot\text{m}^{-2} \text{ d}^{-1}$ calculated as mean average over the whole sampling period.
121 Pearson correlation factors for DIC, removal DIC, DOC, removal DOC, removal POC, SUVA and
122 removal SUVA were calculated with SPSS (table 1).

123

124 *3.2 UV₂₅₄ and SUVA*

125 Mean outflow UV₂₅₄ was 0.34 ± 0.005 nm and for the inflow 0.20 ± 0.004 nm. UV₂₅₄ concentration
126 increased and was higher than inflow concentrations, till the beginning of July, afterwards it decreased
127 and concentrations fell below inflow values. Mean SUVA value at the inflow was 3.49 ± 0.06 and for
128 the outflow 3.13 ± 0.04 . After initially high (>4) SUVA values at the outflow during start-up phase,
129 SUVA concentration stabilises to values lower than four at the end of April, with only a short rise at the
130 end of August. Outflow waters have a higher DOC concentration and higher UV254 absorbance. The
131 SUVA removal rate over the whole sampling period was 10.2%.

132

133 *3.3 Nutrients*

134 **Nitrate** concentration (figure 4) was 4.5 ± 0.15 mg/l (inflow) and 1.2 ± 0.09 mg/l (outflow). Nitrate
135 removal was effectively working two months after construction but concentration increased at the end
136 of the sampling period. Nitrate removal rates over the whole sampling period were 72%. Removal of
137 DIC and O₂ were negatively correlated with NO₃ removal rates (table 2). Nitrate removal rates decline
138 drastically in autumn, with an accumulation rate $>80\%$. Nitrate removal was positively correlated with
139 PO₄³⁻ removal rates (table 2). MMR of nitrate was $0.70 \text{ g}\cdot\text{m}^{-2}\text{d}^{-1}$.

140 **Phosphate** removal rate was 53.4% as an average over the sampling period. Phosphate concentration of
141 the outflow is in general higher than at the inflow, seeming to follow a time delayed peak pattern.
142 Phosphate MMR was $0.0043 \text{ g}\cdot\text{m}^{-2}\text{d}^{-1}$. Mean average phosphate (figure 5) concentration was 0.04
143 ± 0.0018 mg/l (inflow) and 0.02 ± 0.0021 mg/l (outflow).

144 **Bromide** concentration (figure 6) at the inflow was ~0.07 mg/l and ~0.1 mg/l at the outflow. Bromide
145 concentration at inflow and outflow are quite similar for the first three and a half months, afterwards
146 bromide concentration at the outflow rises to about one third of the concentration at the inflow. MMR
147 was calculated as $-0.0049 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. Nutrient removal efficiency was -31.5%.

148

149 *3.4 Dissolved oxygen, temperature and pH*

150 Dissolved oxygen increased by 4.5% from inflow to outflow, the average BOD₅ was reduced to 46%.
151 The average DO value at the outflow was $7.89 \pm 0.22 \text{ mg/l}$. The outflow of the wetland was by average
152 6.6 degrees warmer than the inflow. Outflow temperature was $19.5 \pm 0.2 \text{ }^\circ\text{C}$ on average. Mean inflow
153 pH was 7.7 ± 0.2 and at the outflow it was 7.6 ± 0.3 . Pearson correlation factors for DO, BOD, pH,
154 removal pH, temperature and conductivity were calculated with SPSS (table 3).

155

156 *3.5 Greenhouse Gases*

157 The concentration of greenhouse gases (GHGs), especially CH₄ rose significantly and was by average
158 over the sampling period almost ten times higher at the outflow compared to the inflow. Average CH₄
159 emission at the outflow was $20.11 \pm 0.56 \text{ } \mu\text{g/l}$ and $2.11 \pm 0.16 \text{ } \mu\text{g/l}$ at the inflow. By the end of June, CH₄
160 concentration decreased and rose again in August (figure 7). From the last September week onwards the
161 concentration of CH₄ at the outflow stopped exceeding the one at the inflow. Table 4 shows a positive
162 correlation between CH₄ and UV₂₅₄ removal rate. The CO₂ concentration was approximately twice as
163 high at the outflow $\sim 1130 \pm 25.15 \text{ mg/l}$ compared to the inflow. The outflow concentration increased
164 steadily until the end of September; afterwards it declined and dropped under the concentration of the
165 inflow (figure 8).

166

167 **4. Discussion**

168 This study aimed to investigate the nutrient removal capability of a new CW and the effect it has on
169 carbon cycling. Since only one site was monitored no general assumptions can be made but the results
170 show an unexpected trend of DOC concentration increase, which should be further investigated.
171 According to Pinney et al. (2000) and Villa et al. (2014) CW plants function as a net source of DOC.
172 While inorganic nutrients were sequestered in this CW, achieving the main aim of their installation, the
173 DOC outputs increased. DOC can be leached into water flowing through wetlands as plants, algae, and
174 bacteria grow, die and decay (Pinney, et al. 2000). According to Lin et al. (2002) macrophytes present
175 species-specific nitrate removal efficiency, depending on their ability to produce carbon for
176 denitrification. DOC and bromide accumulation increases the likelihood of DB production in the form
177 of trihalomethanes (THMs) and haloacetonitriles (HANs). Some of these DBPs are suspected to be
178 mutagens, carcinogens or developmental toxicants if ingested over extended periods of time
179 (Villanueva, et al. 2004). Bromide is a major inorganic DBP precursor that results in formation of

180 brominated DBPs, which are generally more toxic than chlorinated DBPs (Richardson, et al. 2007).
181 According to Ingersoll & Baker (1998) when nitrate removal efficiencies increase, dissolved organic
182 carbon in the effluent also increases, as does chloroform formation potential. Bacterial decomposition
183 of plant detritus has been shown to convert POC into dissolved form and cause the release of humic
184 substances into the bulk DOC pool (Moran & Hodson 1994). Particulate organic carbon causes the
185 formation of anaerobic microsites, supporting simultaneous nitrification and denitrification. Therefore
186 it may play a dual role in denitrification, since it supports the heterotrophic metabolism of denitrifying
187 bacteria as well as the O₂ consumption which creates anaerobic microsites necessary for denitrification
188 (Hamersley & Howes 2002). The accumulation of twice as much POC in the constructed wetland
189 enhances denitrification processes. Bioavailable POC acts not only as a C substrate for denitrifiers, but
190 also depletes DO levels within particles via aerobic respiration, supporting denitrification within aerobic
191 wastewaters. According to Moran & Hodson (1994) higher POC additions results in higher respiration
192 rates, and the faster creation of anaerobic microsite volume to support denitrification.

193 SUVA is a reliable indicator of the aromaticity and liability of natural organic matter (NOM) to
194 coagulation and it is known that the NOM in high-SUVA waters tends to have lower alkalinities and
195 hardness and higher TOC concentrations and is therefore more amenable to removal by coagulation at
196 the treatment works (Archer & Singer 2006). Results show that despite the rise in DOC concentration
197 at the outflow, SUVA values decrease. This means that the added DOC will be easier to treat and has
198 most likely less potential to form THMs.

199 Initial phosphate concentration at the inflow most likely originates from PO₄³⁻ in the soil, which was
200 released during construction work. Later increasing phosphate concentration were properly due to
201 agricultural nutrients leaching into the surface water, which is beneficial for plants growths. According
202 to Verhoeven & Meuleman (1999) in most CWs, phosphate removal does not exceed more than 50%.
203 Dissolved oxygen increased due to the growing vegetation in the start-up phase. A survey conducted by
204 Puigagut et al. (2007) stated that BOD₅ removal generally ranged from 80-95%. For denitrification,
205 DOC is a key factor as well as DO, as an anaerobic environment is needed. As in previous research
206 conducted, denitrification rates are mainly constrained by environmental conditions such as temperature,
207 pH and carbon availability (Song, et al. 2011 and Bachand & Horne, 2000).

208 The concentration pattern of GHGs can be explained by vegetation growth phases over the sampling
209 period. Plants are the main source of carbon for microorganisms in CWs. This carbon is further
210 transformed to gaseous forms and increases the loading of CO₂ and CH₄ into the wetland. Furthermore
211 plants increase the efficiency of nitrogen removal by supporting denitrifying microorganisms with easily
212 decomposable organic matter (Picek, et al. 2007). In a study conducted by Liikanen et al. (2006) it was
213 estimated that even if all global wastewaters were treated in constructed wetlands, their share in
214 atmospheric liability would be less than 1% in total.

215

216

217 **5. Conclusion**

218 Because newly CWs have not been previously monitored during start-up phase, weekly monitoring over
219 a six months period was meant to give insight into the early stage functionality. From this study it can
220 be seen that newly constructed wetlands contribute to water quality improvement within a few weeks
221 after construction. Nitrate and BOD₅ removal started showing an effect from the end of April onwards,
222 within four weeks after construction. Nitrate removal was the fastest and most efficient process,
223 probably boosted by the very rapidly establishing vegetation around the CW. The plants leached organic
224 matter into the wetland, which increased DOC concentration, nevertheless the DOC built up, is less
225 likely to form THMs. By the beginning of September nitrate was accumulated in the CW, possibly due
226 to the fact that vegetation started to decrease and could not take up nitrate as over the spring/summer
227 months. Evergreen plants for vegetation might be a valid solution to produce less organic matter and
228 take up nitrate all year around.

229

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233

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