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Abstract

The objective of this study was to monitor a newly constructed wetland (CW) in north Wales, UK, to assess whether it contributes to an improvement in water quality (nutrient removal) of a nearby drinking water reservoir. Inflow and outflow of the Free Water Surface (FWS) CW were monitored on a weekly basis and over a period of six months. Physicochemical parameters including pH, conductivity and dissolved oxygen (DO) were measured, as well as nutrients and dissolved organic and inorganic carbon (DOC, DIC) concentration. The CW was seen to contribute to water quality improvement; results show that nutrient removal took place within weeks after construction. It was found that 72% of initial nitrate ($N0_3^-$), 53% of initial phosphate (PO_4^{3-}) and 35% of initial biological oxygen demand (BOD) were removed, calculated as a total over the whole sampling period. From our study it can be concluded that while inorganic nutrients do decline in CWs, the DOC outputs increases. This may suggest that CWs represent a source for DOC. To assess the carbon in- and output a C budget was calculated.

Keywords: nutrient removal; carbon budget; constructed free water surface wetland

1. Introduction

Wetlands function as sinks for nutrients, and are often used for water quality amelioration. This nutrient retention effect is due to the accumulation of organic matter, which is based on two processes: firstly, the uptake and immobilisation of nutrients by plant, microorganisms, and soil matrix (Corbitt & Bowen, 1994) and secondly, decomposition of organic matter, which is generally low in wetland sediments (Clymo & Reddaway, 1971). Therefore, CWs offer a natural solution for removing nutrient pollution in aquatic ecosystems. Such low-tech treatment systems are often more economically favourable than energy-intensive engineered treatment plants, easier to operate, and provide numerous secondary benefits and are increasingly used to reduce concentrations of nitrate and phosphate in surface waters (Kadlec 2012). In England and Wales, two-thirds of drinking water comes from surface water

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

2. Material and Methods

2.1 Site description

The CW (figure 1) is located at one of the inflow streams of a drinking water reservoir in north Wales. The reservoir in this study is eutrophic due to agricultural practices within the catchment and the streams flowing into the reservoirs have moderate to high DOC concentrations (~10 mg/l). The area around the reservoir is used for cattle and sheep farming aided by modern agro-chemicals (Hughes, et al. 2013). The bedrock at the site consists dominantly of Schist, and the aquifer has a limited yield for groundwater resources. The primary aim of the CW is the removal of nitrogen and phosphorus, to minimise the growth of algae in the reservoir and the formation of DBPs at the treatment plant. Phosphorus and nitrogen are high due to significant agricultural influence. The CW system consists of 414 m^2 of treatment area in addition to 81 m^2 of open water. The nominal hydraulic retention time (nHRT) is three days. Average inflow flow rate is 1.02 L/s. The length of the system is 33 m, width at the inflow is 12 m and 18 m at the outflow. Furthermore 1.8 m were added as open water zone, which allows oxygenation, increased retention time and provides mixing, which can enhance removal processes. Mean temperature over the sampling period was 13.4°C and average rainfall was 3.0 mm/day. The treatment area comprises of a range of naturally occurring reeds, like phragmites. Only material from the site was used for construction of the walls and a series of baffles, and a plastic outflow pipe was added. In this study, we aim to investigate the time in which it takes a newly constructed wetland to improve and enhance the water quality of an inflow into a eutrophic drinking water reservoir. Therefore, physicochemical parameters at the inflow and outflow were measured on a weekly basis over a period of six months and a C budget was calculated.

2.2. Field and laboratory techniques

Sampling was undertaken every week between 27/03/-24/10/2014. Sampling of the CW outflow started eleven days later from the 07/04 onwards, in situ measurements were temperature and DO (Milwaukee Instruments MW-600 Smart DO Meter). At the inflow and outflow three freshwater samples were collected using a one litre glass bottle, a 100 ml plastic bottle and a 50 ml amber glass bottle (to minimise UV influences on samples). The one litre glass bottle was used to measure particulate organic carbon (POC) by high temperature combustion (550°C for two hours) of the sample on a GF/F Whatman glass-fibre filter. The 100 ml plastic bottle were completely filled and left unfiltered to measure pH (Mettler Toledo SevenEasy pH meter), conductivity (Orion 5 probe), bicarbonate, dissolved greenhouse gas concentrations. Bicarbonate is measured by taking 10 ml of unfiltered sample and titrating the pH to 4.3 with 0.1 mole HCl. Dissolved gases were determined using a similar headspace equilibrium method as that described by Dawson et al. (2002), with the gases analysed using a Varian 450 GC. They remaining sample was further filtered (0.45um Whatman Glass-fibre filters) and analysed for DOC and DIC concentrations (Thermalox TC/TN, Analytical Sciences Ltd), specific ultraviolet absorbance (SUVA) (Spectromax M2*e* Spectrophotometer, Molecular Devices) and nutrients (Metrohm 850 IC). The SUVA value gave information about the aromaticity of the water sample and is calculated with the DOC (mg/l) and the UV absorbance at 254 nm. The 50 ml amber bottle was incubated at room temperature for five days, so biological oxygen demand (BOD) could be calculated. With the Thermalox, DOC, DIC and total carbon (TC) concentrations were measured to calculate the C budget (slighlty altered from Pacheco et al. 2013) of the wetland. To assess carbon processing, the following mass balance equation was applied:

$$POCin + DOCin + DICin + TOCdep$$
$$=$$
$$POCout + DOCout + DICout + OCs + CO2 + \Delta TCst$$

where TOC is total organic carbon, OC is organic carbon, the subscripted "in" signifies the inflow from the catchment, "dep" is atmospheric wet deposition, "out" is outflow from the lake, "s" is permanent burial in sediment, CO_2 is the concentration of CO_2 in the water. Additionally CH_4 was calculated as a CO_2 equivalent and added to the CO_2. ΔTC_{st} is the change in the pool of C in the lake over each sampling time period (one week). POC_{in}, DOC_{in}, DIC_{in}, POC_{out}t, DOC_{out}, DIC_{out} were calculated from weekly measured concentrations in streams.

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

$$R(\%) = \left(\frac{Ci - Co}{Ci}\right) * 100$$

Nutrient concentration influent (*Ci*) was measured at the inflow and the nutrient concentration effluent (*Co*) was sampled at the outflow both on a weekly basis and for calculation of R the average mean value was used.

3. Results

3.1 Carbon

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

3.2 UV_{254} and SUVA

Mean outflow UV_{254} was 0.34 ±0.005 nm and for the inflow 0.20 ±0.004 nm. UV_{254} concentration increased and was higher than inflow concentrations, till the beginning of July, afterwards it decreased and concentrations fell below inflow values. Mean SUVA value at the inflow was 3.49 ±0.06 and for the outflow 3.13 ±0.04. After initially high (>4) SUVA values at the outflow during start-up phase, SUVA concentration stabilises to values lower than four at the end of April, with only a short rise at the end of August. Outflow waters have a higher DOC concentration and higher UV254 absorbance. The SUVA removal rate over the whole sampling period was 10.2%.

3.3 Nutrients

Nitrate concentration (figure 4) was 4.5 ±0.15 mg/l (inflow) and 1.2 ±0.09 mg/l (outflow). Nitrate removal was effectively working two months after construction but concentration increased at the end of the sampling period. Nitrate removal rates over the whole sampling period were 72%. Removal of DIC and O_2 were negatively correlated with NO_3 removal rates (table 2). Nitrate removal rates decline drastically in autumn, with an acculumulation rate >80%. Nitrate removal was positively correlated with PO_4^{3-} removal rates (table 2). MMR of nitrate was 0.70 $g \cdot m^{-2} d^{-1}$.

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

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

3.4 Dissolved oxygen, temperature and pH

Dissolved oxygen increased by 4.5% from inflow to outflow, the average BOD_5 was reduced to 46%. The average DO value at the outflow was 7.89 ±0.22 mg/l. The outflow of the wetland was by average 6.6 degrees warmer than the inflow. Outflow temperature was 19.5 ±0.2 °C on average. Mean inflow pH was 7.7 ±0.2 and at the outflow it was 7.6 ±0.3. Pearson correlation factors for DO, BOD, pH, removal pH, temperature and conducitivity were calculated with SPSS (table 3).

3.5 Greenhouse Gases

The concentration of greenhouse gases (GHGs), especially CH_4 rose significantly and was by average over the sampling period almost ten times higher at the outflow compared to the inflow. Average CH_4 emission at the outflow was 20.11 ±0.56 µg/l and 2.11 ±0.16 µg/l at the inflow. By the end of June, CH_4 concentration decreased and rose again in August (figure 7). From the last September week onwards the concentration of CH_4 at the outflow stopped exceeding the one at the inflow. Table 4 shows a positive correlation between CH_4 and UV_{254} removal rate. The CO_2 concentration was approximately twice as high at the outflow ~1130 ±25.15 mg/l compared to the inflow. The outflow concentration increased steadily until the end of September; afterwards it declined and dropped under the concentration of the inflow (figure 8).

4. Discussion

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

brominated DBPs, which are generally more toxic than chlorinated DBPs (Richardson, et al. 2007). According to Ingersoll & Baker (1998) when nitrate removal efficiencies increase, dissolved organic carbon in the effluent also increases, as does chloroform formation potential. Bacterial decomposition of plant detritus has been shown to convert POC into dissolved form and cause the release of humic substances into the bulk DOC pool (Moran & Hodson 1994). Particulate organic carbon causes the formation of anaerobic microsites, supporting simultaneous nitrification and denitrification. Therefore it may play a dual role in denitrification, since it supports the heterotrophic metabolism of denitrifying bacteria as well as the O_2 consumption which creates anaerobic microsites necessary for denitrification (Hamersley & Howes 2002). The accumulation of twice as much POC in the constructed wetland enhances denitrification processes. Bioavailable POC acts not only as a C substrate for denitrifiers, but also depletes DO levels within particles via aerobic respiration, supporting denitrification within aerobic wastewaters. According to Moran & Hodson (1994) higher POC additions results in higher respiration rates, and the faster creation of anaerobic microsite volume to support denitrification.

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

Initial phosphate concentration at the inflow most likely originates from PO_4^{3-} in the soil, which was released during construction work. Later increasing phopshate concentration were proberly due to agricultural nutrients leaching into the surface water, which is benefical for plants growths. According to Verhoeven & Meuleman (1999) in most CWs, phosphate removal does not exceed more than 50%. Dissolved oxygen increased due to the growing vegetation in the start-up phase. A survey conducted by Puigagut et al. (2007) stated that BOD_5 removal generally ranged from 80-95%. For denitrification, DOC is a key factor as well as DO, as an anaerobic environment is needed. As in previous research conducted, denitrification rates are mainly constrained by environemntal conditions such as temperature, pH and carbon availabiliy (Song, et al. 2011 and Bachand & Horne, 2000).

The concentration pattern of GHGs can be explained by vegetation growth phases over the sampling period. Plants are the main source of carbon for microorganisms in CWs. This carbon is further transformed to gaseous forms and increases the loading of CO_2 and CH_4 into the wetland. Furthermore plants increase the efficiency of nitrogen removal by supporting denitrifying microorganisms with easily decomposable organic matter (Picek, et al. 2007). In a study conducted by Liikanen et al. (2006) it was estimated that even if all global wastewaters were treated in constructed wetlands, their share in atmospheric liability would be less than 1% in total.

5. Conclusion

Because newly CWs have not been previously monitored during start-up phase, weekly monitoring over a six months period was meant to give insight into the early stage functionality. From this study it can be seen that newly constructed wetlands contribute to water quality improvement within a few weeks after construction. Nitrate and BOD_5 removal started showing an effect from the end of April onwards, within four weeks after construction. Nitrate removal was the fastest and most efficient process, probably boosted by the very rapidly establishing vegetation around the CW. The plants leached organic matter into the wetland, which increased DOC concentration, nevertheless the DOC built up, is less likely to form THMs. By the beginning of September nitrate was accumulated in the CW, possibly due to the fact that vegetation started to decrease and could not take up nitrate as over the spring/summer months. Evergreen plants for vegetation might be a valid solution to produce less organic matter and take up nitrate all year around.

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