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The greenhouse gas (GHG) emissions associated with aquatic carbon removal during drinking water treatment

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Abstract

Peatlands and other terrestrial ecosystems export large amounts of dissolved organic carbon (DOC) to freshwater ecosystems. In catchments used for supplying drinking water, water treatment works (WTWs) can remove large quantities of this organic matter, and can therefore play a unique modifying role in DOC processing and associated greenhouse gas (GHG) emissions within the fluvial system. During this study we quantified the GHG emissions due to processes associated with carbon (C) removal during water treatment at four contrasting WTWs in the UK. Our results demonstrate that the removal of DOC from raw water supplies via coagulation, leading to the formation of sludge, usually makes it less susceptible to short-term oxidation when compared to DOC remaining in the fluvial system. Although this could be considered a means of reducing CO₂ emissions from waterborne carbon, the current practise of land spreading of sludge is unlikely to represent a long-term C sink and therefore water treatment probably only delays the rate at which fluvial C re-enters the atmosphere. Furthermore, we estimate that indirect CO₂ emissions resulting from electricity use during water treatment, together with the use of chemicals and CO₂ degassing from the water during treatment, far outweigh any potential CO₂ reductions associated with DOC removal. Thus, the post-treatment handling of sludge has the potential to mitigate, but not to negate, GHG emissions associated with water treatment processes.

Keywords: DOC, POC, carbon dioxide, methane, drinking water, greenhouse gases

Introduction

The abstraction of freshwater by water companies for the production of clean, safe drinking water represents a small but significant alteration to the natural movement of water from the uplands to the sea. In the UK and many other temperate and boreal regions, upland freshwater environments contribute significantly as sources of drinking water due to the reliability of their supply. Such waters can contain high concentrations of organic carbon (C), principally DOC, due to the prevalence of peat soils in their catchments (Dawson et al. 2008). Water treatment usually results in the removal of 50-90% of the C from the water, therefore water treatment works (WTWs) can be considered as anthropogenically-created hotspots of C processing in the fluvial system. The fate of the C removed from the water in terms of greenhouse gas (GHG) emissions is likely to be different than if it moved through the natural drainage system, therefore the role of WTWs in overall fluvial DOC processing needs to be considered alongside other 'natural' processes.

Water treatment removes organic matter to improve the aesthetics, taste and odour of the water and microorganisms that would be harmful to human health. Most WTWs in the UK employ the same basic treatment processes involving three main stages; coagulation, filtration and disinfection. Raw water is continuously abstracted from a reservoir or river and fed to the WTW. The pH of the water is then adjusted (usually raised using lime) to optimise conditions for the main C removal stage, coagulation, which is achieved using a chemical such as aluminium or ferric sulphate. This binds organic compounds together to form flocs, which are physically removed. The water then passes through a set of filters or clarifiers to remove some of the remaining organic matter and residues of coagulant before being treated with a disinfectant, usually chlorine.

The production of clean drinking water requires the movement of extremely large volumes of water within a WTW and out to distribution. In the USA, for example, 196.8 billion litres (based on data from the year 2000) are supplied to the public every day (Griffiths-Sattenspiel and Wilson 2009). In the UK, the figure is 16.3 billion litres (DWI 2014; Northern Ireland Water 2014; Scottish Water 2014), which is equivalent to approximately 2% of the average daily rainfall received in the UK. Although WTWs have traditionally been sited at a lower altitude than the raw water source, to allow for gravity feeding of raw water to the works, the demand for electricity is very high in order to pump water around the various stages of treatment and out to consumers. As the removal of organic matter (principally DOC) could be regarded as the greatest alteration to the characteristics of the water, it is probably the most energy intensive aspect of water treatment. A WTW may therefore be a significant 'hotspot' of indirect greenhouse gas (GHG) emissions related to DOC processing, and water treatment may be the most significant anthropogenic modification of carbon processing in fluvial systems.

The environmental impact of drinking water treatment, particularly from a carbon footprint/GHG perspective, had received relatively little attention in scientific literature until recent years. In the last decade, energy use by the water industry has been considered within life-cycle assessments (LCAs) (Rothausen and Conway 2011), with the general consensus being that the impact of energy production, as

the demand for electricity is high at WTWs for pumping water, represents the greatest environmental burden of the water industry (Friedrich et al. 2007). For example, for several WTWs in California that abstract from surface waters, LCA analysis demonstrated that the operation, rather than construction or maintenance, of a WTW accounted for approximately 80-90% of energy use during their lifetime, and that treatment processes, rather than supply and distribution, accounted for the majority of these operational costs (Stokes and Horvath 2009; Stokes and Horvath 2011). Similarly, Racoviceanu et al. (2007) calculated that 94% of total energy use of a WTW in the City of Toronto was for the operation of the WTW. Friedrich (2002) reported that the greatest energy use and therefore GHG emissions resulting from the production of drinking water are due to the treatment processes themselves, whilst Tarantini & Ferri (2001) state that the majority of energy requirements during treatment are for pumping water. To our knowledge, only one peer-reviewed study has addressed the impact of water quality on energy consumption. Santana et al. (2014) reported that influent water quality was responsible for 14.5% of overall energy consumption, with variations in Total Organic Carbon (TOC) concentrations accounting for the greatest variation in consumption. Therefore, this anthropogenic form of carbon processing within the fluvial system does have a significant GHG legacy. Furthermore, rising concentrations of DOC in freshwaters, which have been observed in the UK (Freeman et al. 2001a) and many other parts of the northern hemisphere (Monteith et al. 2007) are likely to have significantly increased energy demand and therefore GHG emissions from WTWs over the last two decades and this trend may continue at sites still recovering from acidification and at risk from the effects of climate and land use change.

The processes involved in the production of clean drinking water yield a variety of residuals or waste products. Within the water industry, the waste material produced at the works is usually termed “sludge”. In the UK, the total annual quantity of sludge produced by the water industry is around 200,000 t yr⁻¹ (Babatunde and Zhao 2007). This sludge is comprised principally of the organic (i.e. DOC and POC) and mineral matter removed from the raw water and the chemical coagulants added to aid their removal. The removal of DOC and POC from the water during treatment is effectively taking the C out of an environment where it is highly susceptible to degradation to CO₂ (Cory et al. 2014) and (temporarily) storing it as a concentrated solid or liquid. In the UK, the favoured method of sludge disposal is currently spreading on agricultural land. Although the agronomic benefit of this practise is minimal in terms of the supply of nutrients there are benefits to soil structure and conditioning resulting from the application of organic matter. Some of the C will be processed by soil heterotrophs to form soil organic matter, while some will be mineralised back to CO₂. Therefore it is important to understand the fate of sludge in terms of GHG emissions as a component of DOC processing in the fluvial system. The potential GHG feedback resulting from the re-use of sludge derived from drinking water production has, to our knowledge, not been investigated and there may be potential for C from sludge to re-enter freshwater ecosystems after land spreading.

In the UK, approximately 3% of all generated electricity is used by the water industry (Rothausen and Conway 2011) and increasing recognition is being made of the need to reduce emissions from this sector (DEFRA 2008; Helm et al. 2009; UKWIR 2010). Our overall aim was to investigate the GHG emissions associated with the production of drinking water within the context of emissions derived from the processing of DOC within the fluvial system, as this has not been addressed so far in peer-reviewed literature. Specifically, in this study we aimed to i) quantify the importance of water treatment as a factor influencing the fate of terrestrially-derived carbon in aquatic ecosystems, and ii) determine the extent to which DOC removal during water treatment can be considered as a sink for aquatic carbon, with the potential to mitigate overall GHG emissions associated with activities including land-use, and water treatment processes themselves. To achieve this, we calculated the GHG emissions resulting from the processes associated with DOC removal for four WTWs in the UK, via an integrated assessment of i) the removal of the principal forms of C at each treatment stage; ii) the electricity used to operate each WTW; iii) the carbon footprint of the chemicals used during treatment; and iv) post-treatment GHG emissions from the sludge.

Materials and Methods

Site information and raw water characteristics

Four WTWs in northern England and North Wales which draw water from reservoirs containing peat within their catchments were chosen for this study. Due to company policies regarding data sensitivity we have not stated the names of these WTWs, but instead describe the basic characteristics of each. Table 1 shows the raw water characteristics and Figure 1 the percentage contribution of each of the five components of DOC, particulate organic carbon (POC), dissolved inorganic carbon (DIC), dissolved CO₂ and dissolved methane (CH₄) to the total C input to each site. Sites A and B are large, high-throughput works which abstract water from reservoirs with catchments containing significant peat deposits. Raw water DOC concentrations are relatively high and vary seasonally (4-13 mg l⁻¹). Site C is the only lowland site selected for the study. It receives water from a catchment containing both farmland and fen peatland and is influenced by marine inputs and groundwater, so it has a higher conductivity than the other sites. The character of the DOC in this reservoir is different from the other sites, with significant within-lake production (and modification) of DOC by microbes and algae. Raw water DOC is high and variable (6-13 mg l⁻¹), and DIC is high due to the influence of carbonate-rich groundwater. There are also relatively high concentrations of dissolved CH₄ in the lake, particularly during the summer when algal bloom formations reduce oxygen levels in the water and promote anaerobic decomposition. Site D receives water from a reservoir whose catchment is comprised almost entirely of blanket peat. Raw water DOC is low (3-5 mg l⁻¹) and shows little seasonal variation, because the lake area is large relative to its catchment, leading to a large direct rainfall input and a long water residence time, which is likely to increase mixing and in-lake removal. All four WTWs employ the same basic treatment

process of coagulation, filtration and chlorination. Sites A and C employ an additional dissolved air flotation (DAF) process immediately after coagulation to aid the formation of flocs. At site C this was installed because of the significant presence of organic material derived from algae, which is more difficult to remove by conventional coagulation than terrestrially-derived C. At site A this process was installed in 2010 to cope with deteriorating raw water quality (i.e. rising DOC levels).

C removal during water treatment

All four WTWs were sampled on four occasions (April, June/July, November/December 2012 and April/May 2013). At each WTW, water samples were collected at four stages of treatment in triplicate in 500 ml acid-washed bottles: raw water and post coagulation, filtration and chlorination. Bottles were completely filled so there was no headspace and stored in a cool box, to ensure the samples remained as stable as possible during transportation back to the laboratory.

Fate of sludge

The DOC and POC removed during water treatment are coagulated to form a sludge which is pumped to separate tanks, where it may undergo further treatment before either being sent to a sewage treatment plant or spread on agricultural fields. Each of the four WTWs studied employs somewhat different methods of dealing with the sludge, but all currently send the sludge they produce to arable fields. Sites A and B produce such large quantities that they employ dewatering processes to reduce the volumes that need to be taken away, although site B does this much more effectively. The sludge is transported to fields on a daily basis and stockpiled, sometimes for months at a time, before being spread. At site C the sludge is pumped to outdoor lagoons, where it is left to dry for several months before being taken away and stockpiled for several weeks before being spread. Lagoons are employed at site D and the sludge is transported away periodically as a liquid. To examine the initial reactivity of treatment sludge, we performed a consistent set of analyses across all four WTWs.

Sludge was sampled at each site in March 2013 and transported back to the laboratory for determination of its propensity to release gaseous and aquatic C under controlled conditions. At sites A and B, sludge was taken at the WTW after the dewatering phase and at two field stockpiles. At site A both stockpiles were several weeks old and are referred to as stockpile 1 and 2. At site B one of these stockpiles was only a few days old (herein referred to as 'new stockpile') and the other was several months old (herein referred to as 'old stockpile'). At site C the sludge was taken from a three day old stockpile and at site D liquid sludge was taken from one of the lagoons. In all cases five 15cm³ blocks of sludge were taken from 10cm below the surface, sealed in a plastic bag and stored at 5°C until analysis. Although it was impossible to collect sludge that had been exposed to similar conditions across all four WTW, our aim was to assess the GHG impact of the sludge under realistic storage conditions rather than take a more standardised approach. This will also be of benefit when assessing the overall GHG impact on a case-by-case basis.

Analytical techniques

For the water samples, analyses of pH, conductivity and dissolved CO₂ and CH₄ were conducted within 24 hours of sample collection. Dissolved gases were extracted from the water using a similar headspace equilibrium method to that described by Dawson et al. (2002); 40 ml of sample and 20 ml of oxygen-free nitrogen gas were taken up into 60ml syringes which were then capped and shaken for 2 minutes. The same procedure was undertaken for ultra-pure water samples. The headspace was analysed for CO₂ and CH₄ on a Varian 450 gas chromatograph (GC) using methods similar to those described by von Arnold et al. (2005). A three point calibration curve was used for each gas and all three standards were analysed after every 10 samples. The mean concentration for all the blank samples was subtracted from the sample concentrations. The remaining sample was then filtered within 48 hours of collection. Filtration was first performed through pre-washed and pre-combusted Whatman GF/F filter papers (pore size 0.7 µm) to determine POC using standard methods; we assumed POC to be half of POM (Hope et al. 1994). Blank samples, i.e. ultra-pure water were run periodically to check for contamination from the equipment. Although previous studies have demonstrated that the pore size of GF/F filters decreases to approximately 0.3 µm during combustion and may therefore be suitable for removing particulate material from water samples (Nayar and Chou 2003), all samples were filtered again through 0.45 µm cellulose nitrate filters and stored at 4 °C until analysis. Total Carbon (TC) and DIC concentrations were determined using a Thermalox TC/TN analyser (Analytical Sciences Ltd, Cambridge, UK), with DOC calculated by subtracting DIC from TC. A six point calibration was used for both TC and DIC and three standards were analysed after every 20 samples. Concentrations for ultrapure water samples were subtracted from sample concentrations. For CO₂, CH₄ and DOC analysis, data were drift corrected if measured values of standards were more than 5% outside the actual value. The limit of detection for the instrumental analyses are 0.4 mg/L for DOC, 2.1 ppm for CO₂ and 23 ppb CH₄.

The GHG emissions of the sludge were determined using a modified version of the method published by Dunn et al. (2014). Sludge samples were homogenised by hand and 10g was placed in a 50ml centrifuge tube, which was then capped and a sample of the headspace taken to provide a background reading. Three blank tubes were also used, to check for contamination from the equipment. The vials were stored in the dark at 5°C for two hours and then another sample of the headspace was taken. All vials were measured for CH₄ and CO₂ concentrations, as described previously, and a flux calculated for each GHG. Fluxes were corrected for the mass of C in the 10 g of sludge, assuming a 50% C content of organic matter (Hope et al. 1994). These fluxes were converted to 100 year global warming potential (GWP) CO₂-equivalents (for CH₄ we used a factor of 25) to allow comparison with the rest of the data from this study. The same sludge and vials were then used to determine the amount of carbon available for export as DOC, by performing the water extractable organic C (WEOC) procedure detailed in Chantigny (2003), which we assume determines the total pool of C available for export in freshwaters. 35ml of ultrapure water was added to the vials and they were placed on an orbital shaker for 24 hours. The solution was then filtered through 0.45 µm filters and analysed for DOC (TC – DIC). The procedure was also repeated for a fresh 10g of sludge at 15°C. 5 and 15°C

temperatures were selected as they represent approximate mean winter and summer water temperatures across the four sites, whilst the average of these temperature is the approximate annual average temperature for the UK. For all sites 5 sub-samples were analysed. Separate sub-samples of sludge were heated at 105° and 550°C to determine their water and organic matter contents respectively.

Indirect GHG emissions – energy and chemical usage

The production of drinking water will result in GHG emissions from a number of indirect sources, such as the energy needed to run each WTW, the production of chemicals used to treat the water, the construction of the WTW, and transport of chemicals and sludge to and from the WTW. We calculated the GHG emissions derived from on-site energy use and chemical production, given that these are likely to be the largest sources of indirect C emissions associated with C removal at the works, and the fate of sludge once it leaves the works, as it will contain the DOC/POC removed from the water. We have not included in our assessment the emissions from WTW construction, reservoir creation/modification, transportation or heating and lighting, as they would not be defined by the magnitude of C removal and therefore not directly related to C removal in the fluvial system. Furthermore, the contributions from these sources are considered minor in comparison to the operation of a WTW (Racoviceanu et al. 2007).

Electricity consumption data were compiled for the four WTWs for the period 2008-2012 and annual average figures calculated. These data were converted into CO₂ emissions (t CO₂ yr⁻¹) using an emissions factor of 0.537 kg CO₂/kWh of electricity (Defra 2012).

Lime and coagulant are the main chemicals added to the water during treatment, to adjust pH and enhance DOC removal respectively, both of which have CO₂ emissions associated with their manufacture. The quantities of both chemicals used by the four WTWs were compiled and converted to CO₂ emissions using emissions factors of 1065 kg CO₂-eq t⁻¹ for lime, 29 kg CO₂-eq t⁻¹ for the coagulant ferric sulphate (used at site B) and 145 kg CO₂-eq t⁻¹ for the coagulant aluminium sulphate, which is used at the other three sites. These emission factors were provided by the manufacturers of the chemicals.

Data analysis

For the experimental work involving laboratory analyses, which involved the collection of replicates, significant differences between sites/treatments were determined by one-way ANOVA and Tukey's HSD post-hoc test in R v2.15.1 Prior to running ANOVA analyses, all data distributions were tested for normality using the Shapiro-Wilk test and for variance heteroscedasticity using the Bartlett test. Data that did not conform to the assumptions of ANOVA were log transformed (excluding pH as it is already on a log scale).

Results

Carbon removal during treatment

Coagulation resulted in significant DOC reductions at all sites (46-67% lower than raw water concentrations; $p < 0.05$). Based on the annual average values there were no further significant reductions in DOC following filtration or chlorination for any of the WTWs. POC declined progressively throughout the treatment process, with the final water value being significantly lower than raw water for all 4 sites (68-88%; $p < 0.05$).

Concentrations of DIC remained unchanged for sites A and B, but at site C the (initially higher) DIC concentration decreased significantly following coagulation (50%, $p < 0.05$) and increased following filtration and chlorination to a concentration comparable to the raw water. The initial decrease in DIC is most likely due to the decrease in pH and subsequent degassing of CO_2 induced by the addition of the coagulant (lime is not added at this stage). We measured an increase in the concentration of dissolved CO_2 in the water following coagulation, but the difference was much less than the loss of DIC, reflecting the rapid degassing of CO_2 prior to the post-coagulation sampling point. We have therefore used the figure of the loss of DIC to calculate the CO_2 emitted by this process, rather than changes in dissolved CO_2 . The increase in DIC following filtration and chlorination may be attributed to the addition of lime and/or by the filter media. Given that the pH of the water did not decrease further during treatment, and would be unlikely to decrease during distribution, we assumed that this extra carbonate would not be eventually released as CO_2 . For site D, the raw DIC concentration averaged just 0.23 mg l^{-1} but increased to 6.4 mg l^{-1} after coagulation and remained unchanged throughout the rest of treatment. This is likely to be due to the addition of large quantities of lime prior to coagulation, which is used to raise pH and make flocculation of DOC more efficient. Again, we assumed this DIC would not subsequently be emitted as CO_2 due to the high pH of the treated water.

Dissolved CO_2 concentrations declined significantly with treatment for all WTWs except site D. For sites A and B the loss from raw to final was 53-78% ($p < 0.05$). For site C the concentration increased from 0.18 mg l^{-1} in the raw water to 2.29 mg l^{-1} after coagulation (for reasons discussed above) and reduced back to comparable levels as the raw water after chlorination. Dissolved CH_4 concentrations remained unchanged at sites A and reduced by an average of 68% from raw to final at site B and by 96% at site C (both $p < 0.05$). The greater removal rate of the latter is attributable to the higher initial concentrations.

Using these data, and annual average intake volumes for each WTW, we calculated the total amount of C removed from the abstracted water due to treatment per year (Table 2). DOC and POC are both removed as a 'sludge' solid (see later) whilst dissolved gases are lost directly to the atmosphere. DOC removal dominates at sites A, B and D but at site C the loss of carbonates as CO_2 represents the greatest C flux.

Calculation of GHG emissions from treatment sludge

Figure 2 shows CO_2 and CH_4 emissions derived from the sludge at each of the studied sites. For CO_2 , emissions were highest for site C, and greater at 15°C compared to 5°C for all sites. The old stockpile at site B

exhibited net CO₂ uptake; the sludge at this stockpile was several months old, and this could indicate reduced decomposition rates in older (and dryer) material, together with the emergence of autotrophic microorganisms within the sludge. For CH₄, emissions were negligible for all sites except site C, where very large emissions were observed at 5°C.

Measured emissions were averaged for the two temperatures to derive an emissions factor at 10°C for the sludge from each WTW. For site A data from all 3 sampled locations were averaged, but for site B only the data for the WTW and new stockpile were used. These factors were then multiplied by the total yearly quantities of C removed as a sludge (DOC + POC from Table 2) to calculate the annual GHG emissions due to the C removed from the water (Table 3). Total annual emissions of CO₂ from sludge are highest for site B, mainly due to the large volumes of water it processes, and therefore the DOC and POC it removes and sludge it produces. Site C has the 2nd highest emissions from sludge, which we suggest is largely due its high biodegradability and higher nutrient (N and P) content. The flux of CH₄ at this site is significant when considered as CO₂ equivalents. The calculated annual gaseous C flux from sludge at site C is actually higher than the total amount of C removed at the WTW (23.2 t C yr⁻¹ as CO₂ and CH₄ emissions vs 11.0 t C yr⁻¹ produced as sludge), suggesting that most if not all of the sludge produced here will be converted to CO₂ and CH₄ within a year. It is possible that the measured CO₂ fluxes from the sludge may not have been due only to the breakdown of organic matter and may have been elevated by the conversion of lime-derived carbonates in the sludge to CO₂. We cannot rule this out, but we would not expect this to be a significant source of CO₂ emissions because the sludge is not an acidic material and it would not be expected to undergo acidification necessary to convert the lime to CO₂.

Concentrations of water extractable C were in the range 1-20 mg DOC g⁻¹ sludge C, i.e. 0.1-2% of the total sludge C, implying that this is a relatively minor pathway of C loss from the water treatment process.

Calculation of GHG emissions due to treatment processes

Table 4 presents annual average electricity consumption data for the four WTWs, alongside the resulting CO₂ emissions. All four WTWs displayed a seasonal trend in their electricity consumption, with the lowest values in late summer and the highest in mid-winter. Figure 3 presents a sum of the mean monthly electricity consumption for all 4 WTWs, and provides evidence for a seasonal trend in consumption, with the lowest use in August (748 MWh) and the highest in January (920 MWh). This corresponds to an extra 171,996 kWh of electricity consumption in January compared to August for all four WTWs in total, equating to an extra 80.7 t CO₂ month⁻¹ and a 22% increase in CO₂ emissions.

Table 5 presents the consumption of the two main chemicals added to the water during treatment, lime and coagulant, alongside the resulting CO₂ emissions which are produced during their manufacture. Site B, which is by far the largest WTW, uses the most lime but site D, despite being the smallest WTW and processing the least amount of water, uses the second greatest quantity of lime. The quantity of coagulant used at the four WTWs is generally greater the more water it processes, with site B having the greatest and site D the lowest.

Overall water treatment C and GHG budgets

An overall GHG budget due to processes associated with organic C removal for each of the four WTWs is shown in Table 6. Electricity consumed during the treatment process is the dominant source of GHG emissions for three of the four sites, with the exception being site D where lime use is relatively high. Net CO₂ emissions are particularly high for site B the highest throughput WTW receiving water from a blanket peat catchment. At such sites a high proportion of the emissions resulting from electricity consumption and use of chemicals will be associated with DOC and POC removal, and could thus be considered an indirect GHG emission associated with fluxes of these substances from peatlands.

Table 7 shows rates of DOC and POC removal by each of the WTWs, expressed per unit area of their supply catchments. These calculations demonstrate that the amount of C removed is fairly small, but not trivial in terms of the overall C budget of peatlands.

Discussion

The data generated in this study have allowed us to determine the GHG emissions resulting from the removal of DOC and POC from freshwater reservoirs used to produce drinking water at four WTWs in the UK. Although several previous studies have investigated the carbon footprint of drinking water production (e.g. Friedrich et al. 2007; Racoviceanu et al. 2007; Stokes and Horvath 2011), and one study has examined the influence of raw water quality on electricity consumption at a WTW (Santana et al. 2014), as far as we are aware this is the first to produce carbon budgets for several WTWs that are focussed on the emissions derived from water treatment processes for the purposes of C removal. The calculated carbon emissions are therefore those resulting from the anthropogenic processing of natural C within the fluvial system. It is important to note that we have not undertaken complete carbon budgets for all processes involved in producing drinking water, as we have not considered the GHG emissions derived from construction of the WTW, physical creation of or modifications to the reservoir or transport, for example. Although our assessment of the GHG emissions derived from C removal processes at the four WTWs has been comprehensive, the overall findings of the study cannot be applied directly to other WTWs without prior knowledge of certain characteristics of the WTW, such as the chemical characteristics of the raw water, the nature of the treatment processes, intake volumes, etc. This is because our data demonstrate that a single factor can have a large influence on the overall GHG emissions of a WTW, such as whether the WTW is located below the reservoir and can therefore use gravity feeding rather than pumping, the pH of the water for determining whether lime needs to be added and the choice of coagulant type. We discuss the major influences on GHG emissions from water treatment below and the findings should be of relevance for those developing strategies to reduce the GHG emissions from the water industry (Helm et al. 2009).

On average the 4 WTWs removed 62% and 86% of the DOC and POC respectively from the raw water. This DOC removal rate is identical to that reported by Allpike et al. (2005) for a WTW using similar treatment processes. The total quantity of C removed ranged from 2 to 155 tonnes per year across the 4 WTWs, with the intake volume being the most important determinant of this figure. If we estimate fairly conservatively that across the UK an average of 3 mg l⁻¹ DOC and 1 mg l⁻¹ POC are removed at all WTWs and taking into account the volume of water treated by the water industry, this equates to 1.17 kT C of freshwater DOC and POC is removed by the UK water industry during water treatment every year.

Basal respiration analyses of the sludge waste material, which contains the DOC and POC removed during the treatment processes, demonstrated rates comparable to previously published studies which have reported such measurements of unmodified peat (e.g. Kechavarzi et al. 2010; Dunn et al. 2014), therefore providing evidence that some of the organic C removed during water treatment is emitted to the atmosphere as a GHG. Sludge from site C produced CO₂ at a significantly higher rate than the other three sites and it also had high CH₄ emissions at 5°C. This is likely to be due to the organic matter being less recalcitrant and more biodegradable, because it is not from a peat-dominated source, and because of the higher nutrient levels at this lowland mixed fen and agricultural catchment. There is no clear explanation as to why CH₄ emissions were higher at 5°C than 15°C, given that methogenesis normally responds positively to temperature (Westermann 1993).

The loss of C from sludge to the atmosphere, although comparable to natural peat and therefore to the form in which the C existed before being leached to freshwaters, represents a much slower rate of loss to the atmosphere compared to C moving through the fluvial system. Therefore by removing C from an environment where it is likely to undergo significant processing resulting in GHG emissions, the conversion of C to a more stable form during water treatment represents a significant opportunity for mitigating GHG emissions from fluvial C processing. The current standard practise of land application, surface spreading, is unlikely to provide a large carbon sink however, since much of the organic matter would be expected to eventually be mineralised to CO₂. Similarly, although our laboratory tests showed that only a small fraction of sludge was converted back to DOC, this fraction is likely to increase following land spreading as decomposition is likely to change the characteristics of the sludge C to a form more susceptible to leaching to freshwaters. Long-term sequestration of sludge organic matter would require protecting it from physical and biological degradation. Keeping the sludge saturated would help with this so it may be feasible to lock up sludge organic matter in a peatland environment, where the natural waterlogged conditions allow peat to accumulate due to the enzymic latch (Freeman et al. 2001b) and the same processes could stabilise sludge organic matter. Water treatment sludge may even be suitable for restoring areas of eroded peat or filling in peatland drainage ditches, if it can be demonstrated that vegetation can colonise the sludge and the sludge does not leach any contaminants such as metals. In upland areas, this could be a strategy for putting carbon

back into the environment from where it was derived, as peat is often the dominant source of DOC to freshwaters in the uplands.

Water treatment not only has an effect on the organic C component of the water but also the inorganic species, which affects the net carbon budget. At site C, which has a high raw water DIC concentration, some of this DIC degassed to CO₂ following acidification by the coagulant. This loss of DIC is a direct CO₂ emission to the atmosphere and at site C was over twice as great as the quantity of organic C removed from the water (which in any case is unlikely to be a permanent sink, as discussed below). As bicarbonates and carbonates, rather than dissolved CO₂, are likely to be the dominant constituents of the DIC at this site due to the influence of groundwater, the DIC in the fluvial system not abstracted by the WTW at this site would be unlikely to eventually degas to CO₂ as it would almost certainly not be exposed to any changes in pH comparable in magnitude to that taking place at the WTW. As coagulation is principally undertaken for organic matter removal, this process represents a significant GHG emission that can be attributed indirectly to DOC processing.

Regarding electricity consumption, for sites A, B and D there was an approximate linear trend with the volume of water processed at the works, but site C stands out as having a high electricity use for its size i.e. it uses 35% more electricity than site A, despite processing only 25% of the volume of water. This may be due to the WTW at site C being located at a higher altitude than the reservoir, therefore raw water has to be pumped to the works rather than gravity fed as it is for the other three WTWs. This may result in the greatest use of electricity at this works being from raw water pumping, rather than the treatment process itself. The clear seasonal trend in electricity consumption in the winter will partly be due to increased use of lighting and heating in the WTW buildings that are staffed, but a significant proportion may be attributed to a deterioration in raw water quality in autumn and winter. Concentrations of DOC and POC in freshwaters generally increase during late summer and peak in late autumn or early winter (Dawson et al. 2011). Raw water TOC concentrations, for site B only, are also present in Figure 3. The data show the typical seasonal cycle of this parameter in freshwaters and there appears to be a two-month lag between the maximum and minimum raw water TOC concentrations and corresponding maximum and minimum electricity usages. Poorer water quality will increase electricity demand during processing for chemical pumping (lime, coagulant, etc.), sludge removal and filter washing, with the latter two processes peaking in the days and weeks after the peak in raw water DOC concentration, possibly explaining the lag in electricity consumption. The 22% increase in emissions is comparable to the 14.5% increase in energy consumption observed by Santana et al. (2014) for a WTW in Florida due to elevated raw water TOC concentrations during the wet season.

The pattern of chemical use across the sites revealed some interesting implications of DOC removal for GHG emissions. Site D, despite being the smallest WTW and processing the least amount of water, uses the second greatest quantity of lime of all four WTWs. This is due to the raw water's low and sub-optimal pH for the coagulation process (mean 5.38), so a large quantity of lime is required to raise the pH. This increases the indirect CO₂ emissions of water production appreciably at this site, a finding also reported by Vince et al. (2008) following a review of LCA impacts of drinking water production. Site B has the highest CO₂ emissions resulting from coagulant use of all the WTWs, but the figure is only 1.7 and 2.5 times greater than sites D and C respectively, despite processing 25 and 8.5 times as much water as these WTWs. This is partly due to the works at site B using ferric sulphate coagulant, which has a much lower CO₂ footprint than the aluminium sulphate used at the other three sites. This suggests that the use of alternative coagulants is a viable option for reducing the carbon footprint of a WTW.

Overall water treatment C and GHG budgets

Electricity consumption dominates the overall GHG emissions of water treatment for three of the four studied WTWs, which agrees with a number of previous studies (Friedrich et al. 2007; Racoviceanu et al. 2007; Vince et al. 2008; Stokes and Horvath 2009; Stokes and Horvath 2011). Therefore, if water companies want to make significant reductions in the carbon burdens of their WTWs, they need to reduce their reliance on the national grid, which for most countries generates electricity using fossil fuels (Griffiths-Sattenspiel and Wilson 2009). The use of chemicals has a greater impact on CO₂ emissions than electricity at site D, due to the need to raise the low pH of the raw water using lime, which has a high CO₂ footprint during manufacture. At WTWs dealing with peaty raw waters, the magnitude of C removed from the raw water in sludge may be large, as it was at the two high-throughput WTWs receiving water from blanket peat catchments in this study. At such sites a high proportion of the emissions resulting from electricity consumption and use of chemicals will be associated with DOC and POC removal, and could thus be considered an indirect GHG emission associated with fluxes of these substances from peatlands. As most DOC and POC exported from peatlands to freshwaters will eventually be decomposed and emitted to the atmosphere as CO₂ (Moody et al. 2013), the removal of this C from the drainage system and its stabilisation in sludge offers some potential for mitigation of CO₂ emissions from energy and chemical use during water treatment (up to 32% at site A and 17% at site B). However, this flux will only become a CO₂ sink if the material removed remains in a stable form, which is by no means certain. At site C, for example, our measurements suggest that all sludge is likely to be converted to CO₂ (and some to CH₄) within a year. At other sites, our measured emissions from the sludge lagoons/stockpiles were smaller, but if sludge is then applied to agricultural land a far higher proportion may eventually be converted to CO₂. Further work is therefore required to identify uses for treatment sludge that could provide effective long-term mitigation potential, however it is important to understand that indirect CO₂ emissions resulting from electricity use during water treatment, together with the use of chemicals and CO₂ degassing from the water during treatment, far outweigh any potential C mitigation associated with DOC removal.

The catchment scale C removal calculations demonstrate that the amount of C removed is not trivial in terms of the overall C budget of peatlands, e.g. $12.7 \text{ g C m}^{-2} \text{ yr}^{-1}$ for site B. As a comparison, the net ecosystem carbon balance of two healthy peatland catchments in the UK are -56 and $-72 \text{ g C m}^{-2} \text{ yr}^{-1}$ (i.e. net CO_2 uptake) (Billett et al. 2010). Since the DOC+POC removal rate is averaged across the catchment, and in most cases (most notably at site C) the WTWs are also receiving water from non-peat areas of their catchments, the effective removal rate per m^2 of peat within the catchment may actually be even higher than that shown in Table 7.

Conclusions

The treatment of DOC and POC rich peat-draining waters by water companies is associated with a high level of energy and chemical use, and associated CO_2 emissions. This effectively ‘amplifies’ the indirect CO_2 emissions associated with fluvial organic carbon loss from peatlands, where this water is subsequently used in drinking water supplies. On the other hand, the conversion of DOC and POC to stabilised solid organic matter (i.e. treatment sludge) removes a substantial component of the POC and DOC exported from peatlands within the catchment, and could provide an effective carbon sink (mitigating at least a proportion of the energy costs from water treatment) if this sludge is managed in such a way that it remains stable in the long term.

CO_2 and CH_4 emissions during the treatment process itself, and from sludge during the immediate post-treatment period (i.e. while the sludge is still held at the treatment works) are relatively small, but appear larger where peat-derived DOC and POC are either inherently more reactive (e.g. if derived from more nutrient-rich fens) or are mixed with high-nutrient water from agricultural land prior to treatment.

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Figure 1. Annual mean contribution of the five main C components to the total aquatic C pool in each of the four studied reservoirs (n=4), sampled on four occasions from May 2012 to May 2013.

Figure 2. Mean gaseous fluxes of a) CO₂ and b) CH₄ from sludge sampled from each of the 4 WTWs, measured at two temperatures (n=5, bars represent standard error of the mean).

Figure 3. Mean monthly electricity consumption summed for all four WTWs, for the period 2006-2012, alongside the mean monthly raw water TOC concentration for weekly samples at site B, for the period 2009-2012.

Table 1. Annual average raw water pH, conductivity and concentrations of major carbon components (concentrations in mg l⁻¹ unless stated otherwise) for each of the four WTWs

Site	pH	Conductivity ($\mu\text{S cm}^{-1}$)	DOC	POC	DIC	CO ₂ -C	CH ₄ -C ($\mu\text{g l}^{-1}$)
A	5.95 (5.84-6.06)	63.3 (56.7-70.7)	10.5 (8.98-13.1)	1.75 (0.46-2.89)	0.49 (0.05-1.12)	0.17 (0.13-0.24)	0.20 (0.15-0.25)
B	6.74 (6.58-6.89)	81.5 (68.0-90.3)	8.74 (7.15-10.6)	0.58 (0.39-0.85)	1.20 (0.04-3.35)	0.14 (0.11-0.18)	0.39 (0.21-0.61)
C	7.69 (7.41-7.82)	305 (227-346)	7.12 (6.12-9.17)	0.77 (0.62-1.00)	17.93 (13.7-23.6)	0.18 (0.16-0.19)	4.22 (2.29-7.80)
D	5.38 (5.36-5.41)	30.6 (29.0-33.3)	4.56 (3.88-5.94)	0.72 (0.53-1.03)	0.23 (<0.03-0.91)	0.17 (0.12-0.29)	0.28 (0.10-0.66)

Table 2. Total quantities of each of the five components of the C pool removed/lost annually from the raw water at each of the four WTWs (blank entries indicate that the concentration of the C parameter did not decrease significantly from raw to final water).

Total quantity removed (t CO ₂ -eq yr ⁻¹)								
Site	Annual average intake volume (x1000 ML)	DOC	POC	Removed as sludge (DOC + POC)	CO ₂ -C	CH ₄ -C	DIC (as CO ₂)	Degassed (CH ₄ + CO ₂)
A	12.0	325.1	72.4	397.6	4.3			4.3
B	23.8	568.2	37.0	605.2	9.5	0.22		9.7
C	2.8	33.8	6.5	40.3	1.0	0.38	92.1	93.5
D	0.9	6.8	2.1	8.9				

Table 3. Sludge GHG emission rates and annual quantities of emissions derived from sludge (values are absent for CH₄ for sites A and D as the mean flux derived from laboratory tests was negative).

Site	Sludge emission rates		Total sludge GHG emissions			
	(µg C g ⁻² h ⁻¹)		t C yr ⁻¹		t CO ₂ -eq yr ⁻¹	
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
A	18.3		17.4		63.8	
B	51.9	0.029	75.1	0.042	275.3	0.04
C	238.3	3.618	22.9	0.348	84.1	42.0
D	50.6		1.1		3.9	

Table 4. Average annual on-site electricity consumption and resulting CO₂ emissions for each of the four WTWs

Site	Annual average electricity consumption (MWh)	CO ₂ emissions due to electricity consumption (t CO ₂ yr ⁻¹)
A	1786	941.3
B	5465	2880.0
C	2404	1266.9
D	162	85.4

Table 5. CO₂ emissions (indirect) resulting from the use of chemicals during water treatment, based on the quantity of chemicals used and their CO₂ footprint during production

	Lime		Coagulant		Total CO ₂ emissions (t CO ₂ yr ⁻¹)
	Annual average use (tonnes)	CO ₂ emissions (t CO ₂ yr ⁻¹)	Annual average use (tonnes)	CO ₂ emissions (t CO ₂ yr ⁻¹)	
A	102	108.6	1100	159.5	268.1
B	333	354.4	2460	71.3	425.7
C	120	127.8	320	46.4	174.2
D	216	230.0	125	18.1	248.1

Table 6. Overall C balance (all values shown in t CO₂-eq yr⁻¹) due to processes associated with organic C removal for each of the WTWs studied, taking account of energy and chemical use, GHG emissions during water treatment and C removal in treatment sludge.

Site	Electricity consumption	Production of chemicals	CO ₂ degassed during treatment	C removed in sludge	Losses from sludge (as CO ₂ , CH ₄ and DOC)	Net CO ₂ -eq emission
A	941.3	268.1	4.3	-397.6	64.3	<u>880.4</u>
B	2880.0	425.7	9.7	-605.2	278.7	<u>2988.9</u>
C	1266.9	174.2	93.5	-40.3	126.4	<u>1620.7</u>
D	85.4	248.1	N/A	-8.9	3.9	<u>328.5</u>

Table 7. Total annual removal of raw water DOC and POC at each WTW during water treatment, also expressed as a flux per unit area of their water supply catchments

Site	Reservoir catchment area (km ²)	DOC & POC removed by WTW (t C yr ⁻¹)	Catchment C flux (g C m ⁻² yr ⁻¹)
A	24.2	108.5	-4.5
B	13.0	165.1	-12.7
C	46.9	11	-0.2
D	1.2	2.5	-2.1

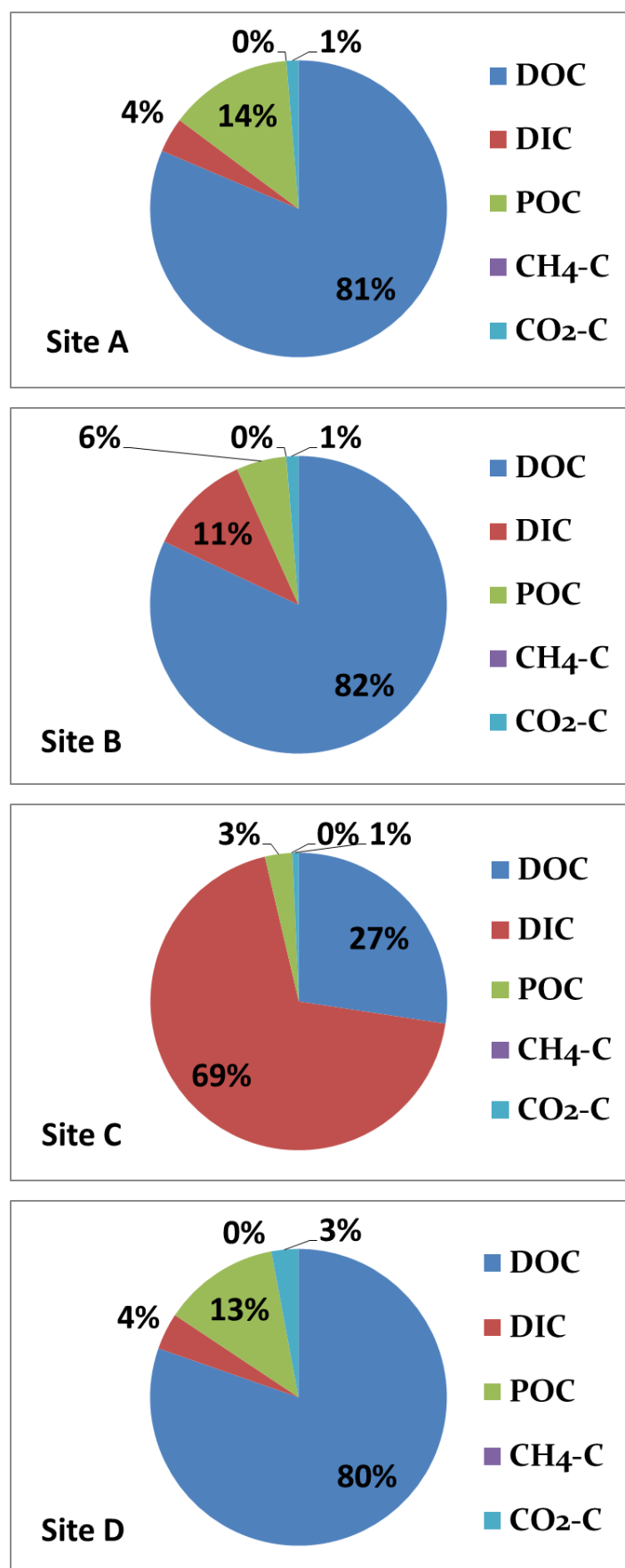


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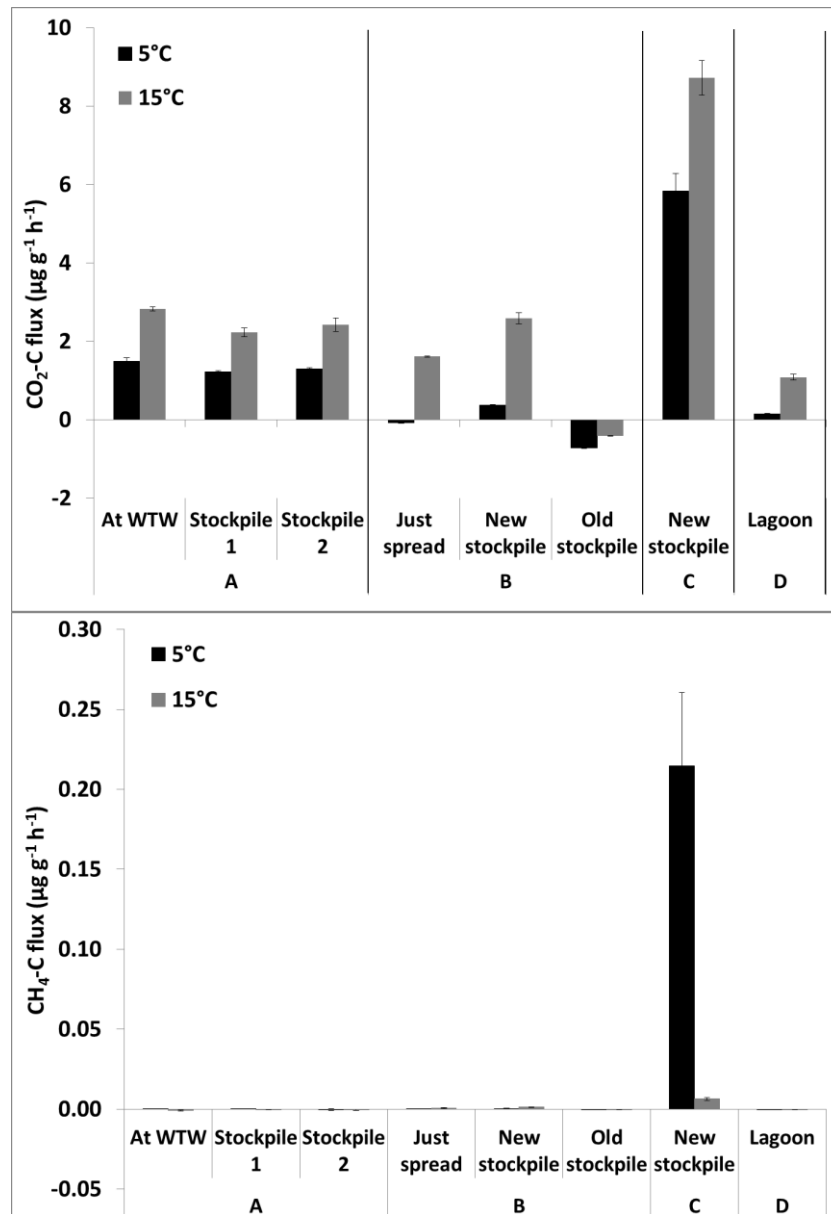


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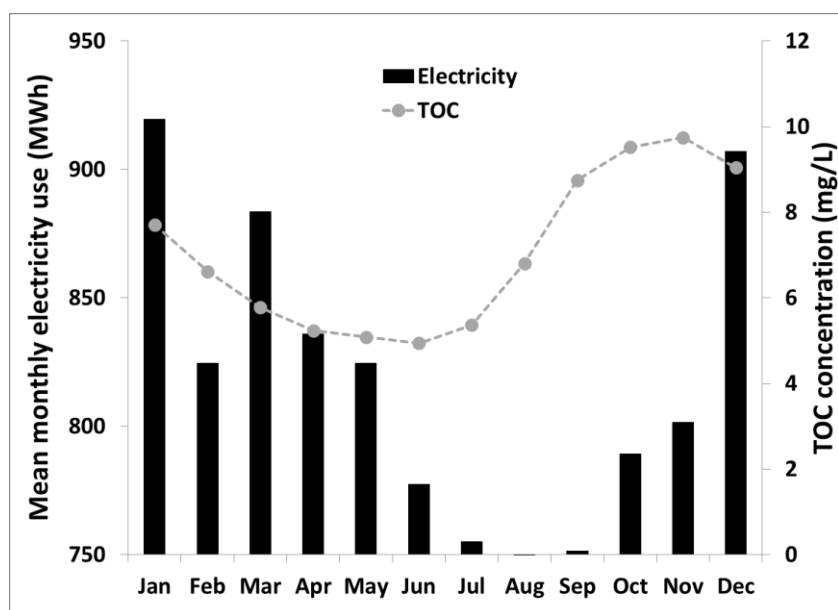


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