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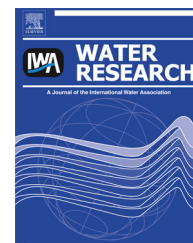
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Carbon isotopic characterisation of dissolved organic matter during water treatment

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ABSTRACT

Water treatment is a series of physio-chemical processes to aid organic matter (OM) removal, which helps to minimise the formation of potentially carcinogenic disinfection by-products and microbial regrowth. Changes in OM character through the treatment processes can provide insight into the treatment efficiency, but radiogenic isotopic characterisation techniques have yet to be applied. Here, we show for the first time that analysis of ^{13}C and ^{14}C of dissolved organic carbon (DOC) effectively characterises dissolved OM through a water treatment works. At the sites investigated: post-clarification, DOC becomes isotopically lighter, due to an increased proportion of relatively hydrophilic DOC. Filtration adds 'old' ^{14}C -DOC from abrasion of the filter media, whilst the use of activated carbon adds 'young' ^{14}C -DOC, most likely from the presence of biofilms. Overall, carbon isotopes provide clear evidence for the first time that new sources of organic carbon are added within the treatment processes, and that treated water is isotopically lighter and typically younger in ^{14}C -DOC age than untreated water. We anticipate our findings will precipitate real-time monitoring of treatment performance using stable carbon isotopes, with associated improvements in energy and carbon footprint (e.g. isotopic analysis used as triggers for filter washing and activated carbon regeneration) and public health benefits resulting from improved carbon removal.

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1. Introduction

Provision of a sufficient volume of appropriately treated water, free from potentially harmful chemical and microbiological contaminants is a fundamental requirement for human life. Treatment of surface water sources for potable supply routinely comprises a series of physical, chemical and biological processes designed to remove impurities to produce

product water in line with local legislative standards. Whilst exact design and operational details will be determined by raw water quality characteristics, a surface water treatment works (WTW) will generally involve screening of gross solids, coagulant addition to precipitate and destabilise negatively charged colloidal matter, slow mixing to encourage collision and agglomeration of destabilised particles into flocs, settlement of flocs in a clarification stage, granular media filtration,

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adsorption of pesticide, natural organic matter, and taste- and odour-causing molecules, and disinfection of residual micro-organisms. However, the use of chlorine, ozone, or chlorine dioxide as a disinfectant in water rich in organic matter (OM) can lead to the occurrence of potentially carcinogenic disinfection by-products (DBPs). Consequently, water companies must manage the competing needs of biological and chemical compliance; i.e. the risk of DBP toxicity must be weighed against the certainty that water that has not been disinfected can cause illness and even death.

Water and wastewater treatment are resource-intensive processes; latest figures suggest that the global annual treatment of $1166 \text{ km}^3 \text{ yr}^{-1}$ for domestic and industrial use (30% of total global abstraction) uses approximately $1,420,030 \text{ GWh}$ of energy and emits $1.21 \text{ Pg CO}_2\text{e yr}^{-1}$. (UNESCO, 2009; EPRI, 2002; WaterUK, 2010); see Fig. 1. This is equivalent to approximately 3.6% of annual anthropogenic carbon emissions, and is 45% of the total carbon that is transported, mineralised and buried in inland waters (Battin et al., 2009). The energy consumption of the water industry has increased significantly in the last 30 years, primarily in response to tightened legislation and regulation surrounding treatment of raw water and the discharge of final effluent from sewage treatment works to watercourses, and the corresponding increase of more energy-intensive processes (Reiling et al., 2009). Furthermore, many water companies have targeted themselves with carbon neutrality in the forthcoming 25 years. Thus, the urgent drive for more sustainable solutions and process improvements to existing solutions is clear. The use of chemicals in water treatment is widespread, being required for coagulation, as a flocculant aid, for pH correction and for disinfection (0.074 tonnes of chemical per megalitre (10^6 L) of drinking water produced (WaterUK, 2010)). This further compounds the

urgent need for identification and elimination of process inefficiencies. Carbon accounting at the unit process level can help facilitate the development of new carbon-efficient technologies.

Pressure on water resources has led to the need to utilise sources with higher organic matter concentrations. Organic matter removal at WTWs is necessary, yet complex, and occurs in the clarification, filtration and adsorption stages of treatment. There is a significant body of research characterising 'raw' water organic matter (for example, see Gjessing et al., 1999), and considering the implications for treatment and removal (Rizzo et al., 2004; Kim and Yu, 2005; Fearing et al., 2004). However, our understanding of the composition and stability of aquatic dissolved organic matter which is being removed during the water treatment process has undergone rapid revision in recent years, with our current understanding that organic carbon is processed in-stream, both by biological and physiochemical processes. Key evidence was provided by the observation that riverine DOC is relatively 'young' in radiocarbon age (Raymond and Bauer, 2001); a finding that has since been replicated in numerous rivers (Evans et al., 2007; Mayorga et al., 2005; Benner et al., 2004). Rivers are now seen as organic carbon processors, with the microbial loop utilising previously unavailable soil carbon (Ward et al., 2013). Riverine DOC is therefore repeatedly reprocessed and 'young' in radiocarbon age by the time it reaches the oceans (Battin et al., 2009), with recent evidence that bacterial and microbial processing can commence within minutes (Pollard and Ducklow, 2011). In rivers draining peatlands, observations of rising dissolved organic carbon concentrations have created concerns that those stores are beginning to destabilise, with an associated increase in DOC entering reservoirs (Freeman et al., 2001, 2004). Consequently,

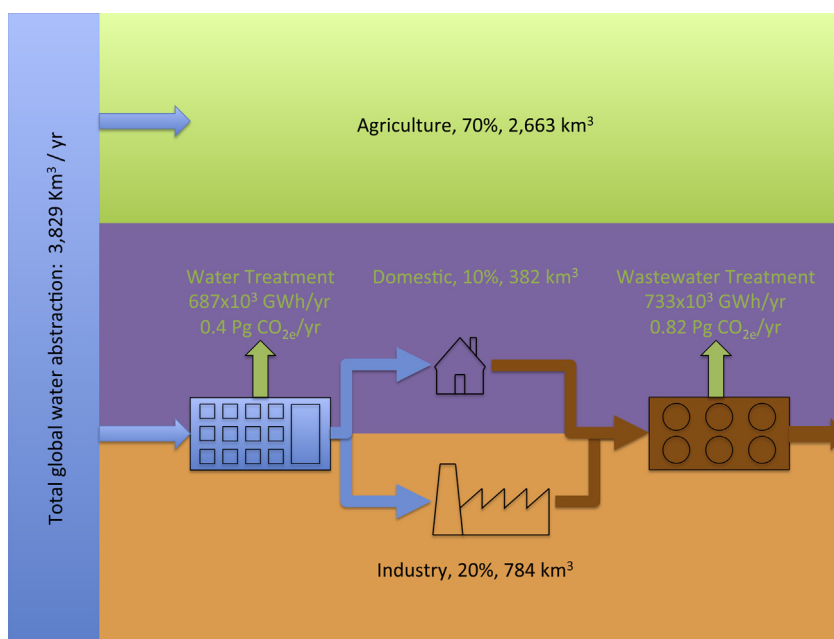


Fig. 1 – Energy consumption and CO₂e emissions associated with global water and wastewater treatment. (Abstraction figures from UNESCO (2009). Energy calculations based on 48.22% surface water at 0.371 kWh/m^3 , 48.23% groundwater at 5 kWh/m^3 and 3.55% desalination at 5 kWh/m^3 (EPRI, 2002; WaterUK, 2010). CO₂e emissions based on 0.34 and 0.7 tonnes/Ml for water and wastewater treatment respectively (WaterUK, 2010).

WTWs which were originally designed to treat what was thought to be recalcitrant organic matter, are in fact trying to remove mixtures of relatively young and labile organic matter, of varying chemical structure which influences their treatability by physiochemical processes. Despite the fact that the analysis of ^{13}C and ^{14}C of DOC has helped improve our understanding of aquatic organic matter character and processing, no studies have investigated the use of carbon isotopes to understand the water treatment process. Therefore, the aim of this study is to characterise DOC through the water treatment process using carbon isotopes for the first time.

2. Methods

We took water samples from two UK Midlands WTWs in July 2009. At both treatment works, water was stored in reservoirs with a mean residence time of ~ 3 months, and raw (treatment works intake) samples were analysed. At WTW-M, one sample was taken on one day after each of the following stages: coagulation, flocculation, clarification (using a dissolved air flotation (DAF) process), filtration, adsorption via granular activated carbon (GAC), and disinfection. At WTW-W, one sample was taken on one day after each of the following stages: coagulation, flocculation, clarification (via sedimentation), filtration, GAC and disinfection. Filter and GAC media from the relevant treatment processes at each WTW were also analysed for their carbon isotope properties. Water samples were analysed for dissolved organic carbon concentration and character, and the DOC fraction was analysed for its ^{13}C -DOC and ^{14}C -DOC.

DOC samples were filtered through a $0.45\ \mu\text{m}$ membrane and quantified using a PPM Labtroc Analyser using standard methods. UV_{254} absorbance analysis was performed using a Biochrom Libra S12 spectrophotometer and turbidity using a 2100N Hach turbidimeter. SUVA was calculated, defined as the ratio of UV absorbance at a wavelength of 254 nm to the DOC concentration in mg L^{-1} . Samples for carbon isotope analysis were filtered through pre-combusted (4 h at $400\ ^\circ\text{C}$) $0.7\ \mu\text{m}$ GF/F glass microfibre filters. GF/F filters are used as standard for ^{14}C pre-treatments at NRCF-E as they can be cleaned of contaminant carbon by heating. At the time of this study

$0.7\ \text{GF/F}$ was used as (i) a supplier of $0.45\ \text{GF/F}$ filters was not available and (ii) tests on Anodine ($0.45\ \text{GF/F}$ Ag glass) filters proved unsatisfactory as they could not be cleaned by heating due to the organic support matrix required by the filter (iii) other filters constructed of organic carbon can contribute unknown quantities of OM to a sample. Inorganic carbon was removed from the samples via the process of acidification to pH4, which moves the bicarbonate equilibrium in favour of CO_2 formation, followed by nitrogen sparging to remove dissolved CO_2 from the sample. For further methodological details see Baker et al. (2011). Samples were neutralised to approximately pH6.8 then measured volumes of filtered sample were rotary evaporated ($40\ ^\circ\text{C}$; 50 mbar) until a few ml of solution remained. This concentrate was quantitatively transferred to pre-weighed, glass beakers and freeze-dried then the resultant solid homogenised. Resultant solids were combusted and the CO_2 generated was cryogenically purified before the gas was collected in aliquots. One aliquot was converted to graphite by Fe/Zn reduction. For further methodological details see Gulliver et al. (2010). The resultant graphite analysed for ^{14}C content at the Scottish Universities Environmental Research Centre (SUERC) AMS laboratory using a NEC 5MEV accelerator mass spectrometer. ^{14}C uncertainty is calculated from a combination of (i) counting statistics during analysis of the graphite target (ii), contribution from the error associated with the ^{14}C background for the chemical process and (iii) an additional random error based on long term ^{14}C measurements of international standards processed at NRCF-E. A further aliquot was analysed for $\delta^{13}\text{C}\text{‰}_{\text{V-PDB}}$ using a dual inlet stable isotope mass spectrometer. Isotope ratios were corrected using the procedure outlined by Craig (1957) and are reported relative to the international reference standard Vienna Pee Dee Belemnite (V-PDB) (Coplen, 1994). Uncertainties on $\delta^{13}\text{C}$ are 1 standard deviation of the results from long term measurements of in-house standard material processed via the DOC method.

3. Results and discussion

Raw water DOC at WTW-M was more UV absorbent per g C than WTW-W (Table 1), indicative of a larger proportion of aromatic DOC which is typically more treatable. A slightly

Table 1 – Water quality parameters at various stages of treatment at WTW-M and WTW-W.

| Sample point | UV_{254} (Abs.m^{-1}) | Turbidity (NTU) | DOC (mg l^{-1}) | SUVA* ($\text{m}^{-1}.\text{l mg}^{-1}$) | ^{14}C (‰mc) $\pm 1\sigma$ | $\delta^{13}\text{C}$ (‰V-PDB) $\pm 0.5\text{‰}$ |
|--------------|--|--------------------|-------------------------------|---|--|---|
| WTW-M | | | | | | |
| Raw | 19.70 | 0.77 | 4.06 | 4.85 | 91.46 ± 0.42 | -22.7 |
| Clarified | 11.90 | 1.10 | 3.21 | 3.71 | 97.10 ± 0.42 | -28.9 |
| Filtered | 12.30 | 0.13 | 2.92 | 4.21 | 95.35 ± 0.44 | -28.3 |
| Post-GAC | 7.70 | 0.14 | 2.42 | 3.18 | 97.26 ± 0.43 | -28.7 |
| Final | 7.70 | 0.09 | 2.40 | 3.21 | 95.11 ± 0.44 | -29.0 |
| WTW-W | | | | | | |
| Raw | 19.70 | 1.40 | 7.17 | 2.75 | 98.10 ± 0.43 | -23.6 |
| Clarified | 10.40 | 0.36 | 6.03 | 1.72 | 96.99 ± 0.45 | -29.8 |
| Filtered | 10.20 | 0.33 | 5.27 | 1.94 | 96.21 ± 0.44 | -25.9 |
| Post-GAC | 9.30 | 0.24 | 3.61 | 2.58 | 97.14 ± 0.45 | -29.1 |
| Final | 4.10 | 0.11 | 3.66 | 1.12 | 96.27 ± 0.42 | -26.9 |

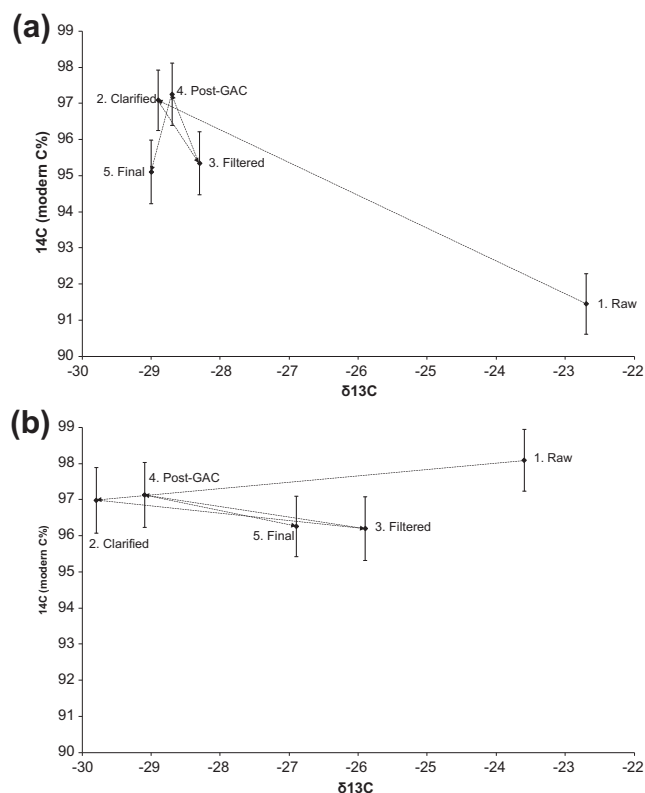


Fig. 2 – ^{13}C vs. ^{14}C isotopic composition of DOC at WTW-M (a) and WTW-W (b).

greater DOC removal was observed at WTW-W (49%) compared to WTW-M (41%). The majority of chromophoric organic matter was removed during clarification at WTW-M and by GAC at WTW-W. Treated water carbon isotopic composition is very different from raw water at both sites (Table 1 and Fig. 2). The largest single change in carbon isotopic composition occurs during clarification. At both WTWs, clarified DOC has lighter ^{13}C -DOC than the raw water. Raw water ^{13}C -DOC is typical of UK and NW European rivers (Tipping et al., 2010; Pierson-Wickmann et al., 2011) where the

carbon isotope signature is dominated by DOC from reprocessed C3 vegetation as well as in-stream algal communities. Several studies have demonstrated that algal ^{13}C -DOC is lighter than C3 vegetation, although with a large variability depending on the in-stream ^{13}C - CO_2 composition, algal growth phase, etc. (Chanton and Lewis, 1999). Within the engineered environment of the clarification stage, much of this variability is controlled and it appears that ^{13}C -DOC is tracking the efficiency of the removal of the chromophoric and relatively hydrophobic DOC fraction, comprising reprocessed terrestrial C3 plant DOC, with the algogenic and relatively hydrophilic DOC surviving this treatment process. In contrast to ^{13}C -DOC, clarification had differing effects on the ^{14}C -DOC composition between the two WTWs, reflecting the different extents of DOC processing within the two catchments. At WTW-M, ^{14}C -DOC becomes significantly 'younger', whereas at WTW-W, the DOC is already 'young' and no further change in ^{14}C -DOC is possible.

Filtration is designed to remove suspended matter and any unsettled flocs from the clarification process; however, our carbon isotope data demonstrate that at both works the DOC gets 'older' and ^{13}C -DOC heavier although this is only greater than analytical uncertainty at WTW-W. This demonstrates that there is a source of older DOC from the filter media, and this possibility is confirmed by ^{14}C analysis of the filter media (Table 2), which also has isotopically heavier ^{13}C signature than the clarified water. Sand filters are washed by backwashing every ~24 h, and mechanical abrasion of the filter material into the dissolved ($<0.7\ \mu\text{m}$) fraction would add old carbon to the water. In contrast to filtration, during GAC treatment, ^{14}C -DOC gets 'younger' and ^{13}C -DOC lighter. GAC beds are typically regenerated every 1–2 yrs, and therefore develop active biological communities when in use, although addition of biologically produced OM is not factored into the treatment processes at the majority of WTWs. The change in isotopic composition is therefore consistent with either the increased contribution of DOC from biofilms within the GAC beds or removal of 'older' carbon that was introduced by mechanical abrasion during filtration/backwashing. Our analysis of GAC material of different ages since regeneration suggests the former hypothesis is more likely at our treatment works (Table 2).

Table 2 – Analysis of filter media at WTW-M and WTW-W.

| Site | Sample | Sample description | ^{14}C (%mc) $\pm 1\sigma$ | Conventional radiocarbon age (years) | $\delta^{13}\text{C}$ (‰V-PDB) $\pm 0.5\text{‰}$ |
|-------|--------------|------------------------------|-------------------------------------|--------------------------------------|--|
| WTW-M | GAC Media | 3 months since regeneration | 9.34 ± 0.11 | $19,040 \pm 102$ | -23.27 |
| | GAC Media | 9 months since regeneration | 13.37 ± 0.12 | $16,159 \pm 73$ | -22.77 |
| | Filter media | Anthracite grade 2 | 1.41 ± 0.11 | $34,181 \pm 677$ | -24.45 |
| | Filter media | Sand 450 mm | 1.86 ± 0.11 | $31,971 \pm 512$ | -24.50 |
| | Filter media | Garnett | 1.71 ± 0.11 | $32,678 \pm 559$ | -24.14 |
| WTW-W | GAC Media | GAC virgin coal | 6.46 ± 0.12 | $22,004 \pm 147$ | -22.8 |
| | GAC Media | 11 months since regeneration | 15.09 ± 0.13 | $15,189 \pm 71$ | -23.2 |
| | GAC Media | Coconut trial media | 98.61 ± 0.43 | 112 ± 35 | -23.9 |
| | GAC Media | 2 weeks since regeneration | 25.80 ± 0.15 | $10,884 \pm 47$ | -23.3 |
| | Filter media | Anthracite grade 2 | 0.07 ± 0.12 | Background | -23.9 |
| | Filter media | Sand 450 mm | 2.61 ± 0.12 | $29,297 \pm 365$ | -23.4 |
| | Filter media | Gravel filter media | 3.73 ± 0.12 | $26,416 \pm 256$ | -24.6 |
| | | | | | |

A mass balance approach was used (See [Supplementary Information 1](#)) to determine whether a simple 2-component model could be used to determine ^{14}C and ^{13}C signatures of organic carbon removed at each step of the water treatment process. This gives results which fit with natural variations in published distributions for ^{14}C and ^{13}C signatures only for the Filtered to Post-GAC step at both sites ([Mook, 2006](#)). This supports the suggestion that, contrary to our current understanding of water treatment, the processes are not simply removing organic carbon in a step-wise manner at each stage of the process. Additional ^{14}C and ^{13}C values for unfiltered Post-GAC water, collected and processed at the same time as other samples ([Roe, 2011](#)) (See [Supplementary Information Table 2a](#)) show that there is a significant difference between ^{14}C and ^{13}C values between filtered and unfiltered Post-GAC waters WTW-M which again cannot be accounted for using 2-component mass balance calculations ([Supplementary Information Table 2b](#)). This supports the hypothesis of organic carbon addition or cycling within conventional WTWs which reduce the effectiveness of conventional treatment methods.

Disinfection via chlorination is the final treatment stage, and the effect of chlorination is that ^{14}C -DOC becomes older, significantly at WTW-M, and ^{13}C -DOC becomes heavier. Combined, the ^{13}C -DOC and ^{14}C -DOC evidence demonstrates that chlorination is preferentially oxidising the younger DOC fraction, likely to be sourced from either algogenic or microbial organic carbon that survived clarification, or from within the WTW on GAC beds. This is significant as, whilst previous research has demonstrated that the rate of DBP formation (and trihalomethane (THM) formation, in particular) is greatest upon initial chlorine dosing ([Brown et al., 2010](#)), the literature has simply classed organics as ‘fast’ or ‘slow’ reacting ([Sohn et al., 2004](#)). In terms of THM formation, however, this work provides the first evidence that it is the younger fraction that is responsible for this elevated rate of formation.

Our results from two WTWs show that, although the treatment process does decrease dissolved organic matter concentration at each treatment stage, there are changes in isotopic composition demonstrating that DOM is both added and removed. Recent research suggests that by 2030 we will face 50% increases in the demand for food and energy and a 30% increase in water demand ([World Bank, 2008](#); [IEA, 2008](#); [Shen et al., 2008](#)). Agriculture (i.e. food production) and

energy already account for 15% and 63% of all greenhouse gas emissions. An increase in water demand of 30% alone would generate an additional $0.36 \text{ Pg CO}_2\text{e yr}^{-1}$, bringing total water and wastewater treatment CO_2e emissions to $1.58 \text{ Pg CO}_2\text{e yr}^{-1}$ ([Table 3](#)), which is equivalent to 58% of the terrestrial carbon sink for anthropogenic emissions of 2.8 Pg C yr^{-1} ([Battin et al., 2009](#)). Thus, opportunities to address energy consumption and the carbon footprint of treatment processes are vitally important to the water industry. In addition, the improvements in characterisation of DBP precursors offer water utilities the opportunity to improve DOC removal and secure additional public health improvements whilst minimising environmental impact. Our results show that the addition of algogenic and microbial organic matter leads to drinking water that is ‘younger’ than the raw water and with a ^{13}C -DOC composition that is lighter. With rapid analysis of ^{13}C -DOC now possible using cavity ringdown mass spectrometry, routine analysis of ^{13}C -DOC to improve drinking water performance is now possible ([Hartland et al., 2012](#)). Rapid analysis and characterisation of DOC at WTWs will enable utilities to optimise treatment and to tailor energy and chemical usage in real time. On the basis of results presented here, isotopic analysis now offers the opportunity to optimise filter backwashing and activated carbon regeneration frequencies. The former will potentially offer cost savings, whilst the latter will do the same as well as providing a novel means to manage DBP formation via control of ‘young’ organic matter.

4. Conclusions

- The carbon isotopic composition of OM is demonstrated to characterise OM through the water treatment process for the first time. With the recent development of laser based carbon isotope analysers (e.g. cavity ringdown mass spectrometry; [Hartland et al., 2012](#)), analyses of ^{13}C -DOC can now be incorporated into routine on-line DOC measurements within works and can be routinely used in organic matter characterisation.
- Isotope analysis demonstrates that, at our two water treatment plants, OM is both removed and added in the water treatment process. The addition of algogenic and microbially derived OM from within the treatment process leads

Table 3 – Energy consumption and CO_2e emissions associated with global water and wastewater treatment.

| | Abstraction | | Water treatment | | Wastewater treatment | |
|-----------------------------------|-------------------------|----|-----------------|-------------------------|----------------------|-------------------------|
| | km^3/yr | % | Energy, GWh/yr | PgCO_2e | Energy, GWh/yr | PgCO_2e |
| <i>Business as usual scenario</i> | | | | | | |
| Drinking water | 382 | 10 | 225 | 0.13 | 240 | 0.27 |
| Industry | 784 | 20 | 462 | 0.27 | 493 | 0.55 |
| Agriculture | 2663 | 70 | | | | |
| <i>‘Perfect Storm’ scenario</i> | | | | | | |
| Drinking water | 497 | 10 | 292 | 0.17 | 312 | 0.35 |
| Industry | 1019 | 20 | 600 | 0.35 | 641 | 0.71 |
| Agriculture | 3462 | 70 | | | | |

to drinking water containing OM which is radiocarbon 'younger' and stable isotopically lighter than raw water.

- The demonstrated addition of OM within the water treatment process has implications for energy use and the carbon footprint of water treatment plants. This is especially significant given that we estimate the global water treatment CO₂e emissions to be $\sim 1.3 \text{ Pg CO}_2\text{e yr}^{-1}$ (Table 3), which is substantial when compared to the total terrestrial carbon sink for anthropogenic emissions of 2.8 Pg C yr^{-1} and the total carbon that is transported, mineralised and buried in inland waters (2.8 Pg C yr^{-1} ; Battin et al., 2009).
- Future research should investigate the carbon isotopic characterisation of organic matter as it varies seasonally, and temporal trends in the relationship between carbon isotope composition, organic matter character and drinking water treatability.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2013.09.025>.

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