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Tracing sources of natural organic matter, trihalomethanes and metals in groundwater from a karst region

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Abstract

Groundwater offers an important source for drinking water around the world; however, groundwater quality is under increasing pressure and is particularly vulnerable in karst areas. Total organic carbon (TOC) is significantly related to groundwater quality and when not removed by water treatment processes can give rise to the formation of disinfection by-products trihalomethanes (THMs) above the level of compliance. This study investigated the source of organic matter giving rise to the THM exceedances in a groundwater supply in a karst area. Results highlighted that source water for this groundwater supply was prone to surface water infiltration linked to rainfall events; was not accurately captured in the zone of contribution (ZoC); had inadequate treatment of natural organic matter (NOM) and suffered THM exceedances in 45% of sampling events. THMs were mostly represented by chloroform and caused by terrestrial delivered reprocessed organic matter. This work will support water managers tasked with decision-making.

Keywords Trihalomethanes · Groundwater · Karst · Source protection zones · Drinking water · Granular activated carbon

Introduction

More than 2 billion people depend on groundwater for their daily water use (75%, 51% and 25% of Europe, the USA and Ireland, respectively, McGrory et al. 2017, 2018), and in many parts of the world, groundwater bodies are considered the most important and safest sources of drinking water (Menichini et al. 2015). However, groundwater quality is

under increasing pressure due to point and non-point source pollution (Pavlis and Cummins 2014a) and is particularly vulnerable in areas with underlying geology composed of carbonate rocks, i.e. karst areas. Human activity in karst regions threatens to contaminate groundwater resources far more easily than is the case for other aquifers types. Groundwater vulnerability, the likelihood of contaminants reaching the groundwater system after introduction at some location above the

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aquifer through topsoil and subsoil or via surface karst features (e.g. dolines, swallow holes), cracks and fissures of bedrock, can be investigated by establishing hydrogeological conditions such as water transit time and dissolved elements (Pavlis and Cummins 2014a).

Presence of natural organic matter (NOM), for which total organic carbon (TOC) is a surrogate, in raw drinking water poses one of the greatest challenges for water treatment owing to the spectrum of problems associated with it (i.e. membrane fouling, coagulant dose, pH adjustments, higher disinfectant dose, energy consumption, transport of contaminants). NOM refers to a broad range of carbon-based compounds originating from living and dead plants, animals and microorganisms and from the degradation products of these sources (Chow et al. 1999). Understanding catchment processes including land use offers the potential to reduce ‘end of pipe’ treatment costs and will form part of the solution to addressing the problem of NOM (Brooks et al. 2015). TOC concentration is significantly related to groundwater vulnerability and land use is considered to be a driving factor of TOC concentration in groundwater (Pavlis and Cummins 2014a).

Both quantity and quality of NOM affect the efficiency of its removal, and so adequate information about concentration and composition is required at both the design and operation stage. Owing to the complexity of NOM characterisation, routine monitoring of NOM fractions poses a challenge. Fluorescence excitation-emission matrix (F-EEM) spectroscopy has been used to distinguish different types and sources of dissolved organic carbon (DOC) in natural waters and has gained popularity in recent years as a simple, relatively inexpensive yet sensitive approach (Baghoth et al. 2011). F-EEM spectroscopy has been used to characterise DOC and identify humic- and protein-like fluorescent signals in water samples from different aquatic environments (Coble 1996). F-EEMs coupled with PARAFAC (multiway data analysis using parallel factor analysis (Stedmon et al. 2003)) can provide even more detailed information about NOM character. PARAFAC has been employed successfully to track the fate of problematic NOM fractions and to optimize the design and operation of drinking water treatment processes for their removal (Shutova et al. 2014) as well as to infer DOC source (Kraus et al. 2010).

The delineation of catchment areas is crucial in terms of protecting groundwater drinking supplies. A zone of contribution (ZoC) is the area surrounding a pumped well that encompasses all areas or features that supply groundwater recharge to the well. The determination of a rigorous and scientific methodology for all types of aquifer systems is very difficult in practicality (Menichini et al. 2015). Zone of contribution's (ZoCs) are commonly delineated as a ‘rapid assessment’ desk study using information on the groundwater recharge rates and groundwater flow direction (Irish EPA 2011a) which is then made available to water managers. Caveats are typically

applied citing ‘extent and geometry of the associated ZoC is highly uncertain due to the karstic nature of the limestone aquifer’. Alternatively, hydrochemical site-specific investigations coupled with statistical techniques have been successfully applied to reveal relationships among potential indicators of groundwater vulnerability, including principal components analysis (PCA) (Pavlis and Cummins 2014a).

The presence of NOM in groundwater can affect a number of geochemical processes including the transport and mobility of metal contaminants and their interaction (dissolution and precipitation reactions) with oxides and minerals (Redman et al. 2002; Weng et al. 2009). Metals in groundwater pose a potential threat to human health worldwide (Mitchell et al. 2011; Lipczynska-Kochany 2018). Furthermore, NOM gives rise to disinfection by-product formation (DBPs) when not adequately removed. DBPs are formed when natural water is disinfected to control microbial contaminants during the treatment of drinking water. DBPs may comprise halogenated and nonhalogenated compounds, depending on the nature of disinfectants used and precursors present (Krasner 2009). Trihalomethanes (THMs) are the most prominent class of halogenated DBPs in treated water (Krasner et al. 1989) and the only one regulated by European Union Drinking Water Regulations (EU 2014); albeit the proposed new Drinking Water Directive is set to include haloacetic acids (HAAs) (European Commission 2018).

THMs are used as a surrogate for DBPs in many countries but do not give a true representation of the extent of DBPs present in drinking water (Krasner 2009). It has been estimated that prominent identifiable DBPs only constitute 30% of the total organic halogens formed during chlorination (Li and Mitch 2018). THMs have been shown to have both genotoxic and carcinogenic effects particularly in the liver and kidney in laboratory experimental studies (WHO 2011). Carcinogens differ from toxic compounds in that there is no threshold limit for the existence of risk. However, a parametric limit of $100 \mu\text{g L}^{-1}$ has been adopted in Europe and $80 \mu\text{g L}^{-1}$ in the USA. Ireland has the highest reported non-compliance for THM exceedances in drinking water across the 27 EU Member States (EC 2014), and in August 2018, the EC opened an infringement case against Ireland for failure to ensure drinking water for over 500,000 consumers is safe from THMs.

The high non-compliance has been attributed to high percentage cover of organic soils, a heavy reliance on surface water (~75%) coupled with a historical lack of understanding of NOM and treatability (O’Driscoll et al. 2018). In Ireland, half of the land area of the country is considered to be underlain by limestone, and the majority of this is considered karstified to some degree (Naughton et al. 2012). Therefore, the objectives of this study were to trace the sources of NOM and investigate the presence of THMs and priority metal pollutants in a drinking water supply abstracting water from a groundwater spring in a vulnerable karst region.

Materials and methods

Study site

Williamstown Public Water Supply (WPWS) was chosen for this study as it represents a spring source located in a vulnerable karst area with a history of THM exceedances (Fig. 1). The ZoC for WPWS was previously mapped as part of a desk study and the catchment area estimated at 1.41 km² (Irish EPA 2011b). However, the report highlighted that this source was part of a much larger spring system and several important karst features in the area, including turloughs and swallow holes, were excluded from the ZOC of the WPWS but acknowledged as important for the catchment area of the much larger spring system to the immediate west of WPWS source. In consideration of this potentially larger ZoC, a greater area was considered as part of this study, and water samples were collected at five locations within a 4-km radius of WPWS spring (hereafter referred to as the catchment sites) and incorporating (1) a wetland, (2) a turlough, (3) a small tributary, (4) a series of sister springs (SisterSpring) adjacent to the raw water abstraction and (5) the outlet of a wastewater treatment plant (WWTP). Water samples were also collected from different points along the treatment process train of the WPWS and at eleven points along the distribution network (raw, post-ozone, post-granular activated carbon (GAC), before and after two reservoirs (Reservoir 1 and Reservoir 2, located at 1.8 km and 3.3 km from the treatment plant, respectively), a public water tap (located at 2.7 km from the treatment plant) and at four of the network extremities (NS8, NS9, NS10 and NS11 located at 6.7 km, 7.5 km, 7.7 km and 8.1 km from the treatment plant, respectively) (Fig. 1). The

treatment train at WPWS consists of ozonation, GAC filtration (CARBSORB®) and UV disinfection followed by chlorine-based final disinfection. WPWS supplies 558 m³ d⁻¹ to a population of approximately 180 persons.

Water quantity and quality

In order to estimate a potential ZoC, a staff gauge was installed at the SisterSpring (01/12/2014). A rating curve was developed using spot flow measurements at a range of flows which established that while the WPWS spring had a daily discharge of ~600 m³ d⁻¹, the adjacent SisterSpring had a daily discharge of ~19,000 m³ d⁻¹. Using topography, known tracers and the integration of recharge coefficients, a reasonable and justifiable catchment size for the combined WPWS spring and SisterSpring was estimated to be ~24 km², 16-fold greater than the ZoC report for the WPWS (Irish EPA 2011b). Monthly water samples (08/2014–04/2016; 16 sampling occasions) were collected at each of the 17 sampling locations. Water samples were collected in pre-labelled, sterilized, polypropylene bottles and kept cold in the dark during transport to the laboratory, where they were analysed within 72 h.

Each water sample was analysed for coloured dissolved organic matter (CDOM) fluorescence, ultraviolet absorbance (UVA₂₅₄) and DOC analysis as follows: DOC and TN concentrations were determined using a TOC Analyser (BioTector Analytical Systems Ltd., Cork, Ireland). UV absorption data was obtained with a UV-visible spectrophotometer (Cary 50, Agilent Technologies), using a quartz sample cell with a path length of 10 mm. Fluorescence excitation emission matrices (EEMs) were obtained using a 1-cm path length quartz cuvette

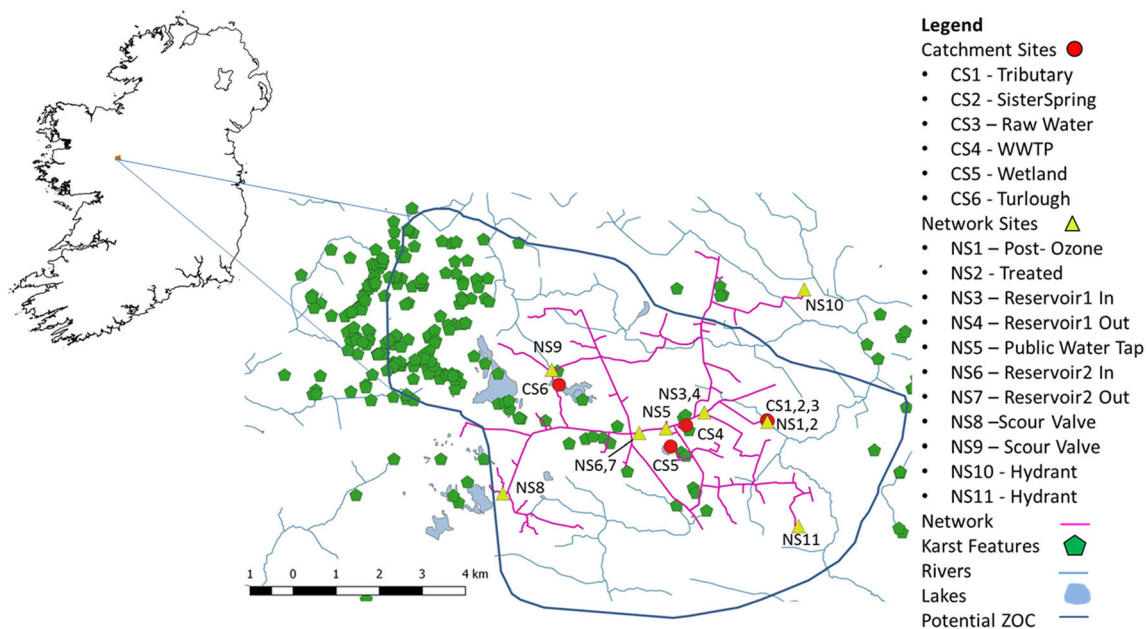


Fig. 1 Geographical location of the study site in Ireland (left) and of the 17 sampling sites in the potential zone of contribution and along the water supply distribution network

(Starna, Australia) on a Horiba Aqualog (Kyoto, Japan). A 0.1-s integration time was used during measurement of emission from 200 to 625 nm and excitation from 240 to 600 nm. Charge-coupled device (CCD) gain, i.e. the conversion between the number of electrons recorded by the CCD and the number of digital units contained in the CCD image, was set to medium. Inner filter effects and first- and second-order Rayleigh scattering were removed using the included Aqualog (v3.6.10) software. The area of the Raman peak (350 nm excitation) was used to normalize the fluorescence intensity of all spectra, which are expressed in Raman units (RU) (Lawaetz and Stedmon 2009; Murphy et al. 2010). The slope ratio or SR was calculated as the ratio of S275–295 to S350–400. The E2/E3 ratios were calculated using absorption coefficients at the appropriate wavelengths. $SUVA_{254}$, defined as the UV absorbance of a water sample at a given wavelength normalized for DOC concentration, was calculated by dividing a_{254} (m^{-1}) by the DOC concentration ($mg\ L^{-1}$) as in Weishaar et al. (2003).

In addition, water samples were collected for the determination of metals from the catchment sites ($n = 6$, including raw water) and at the post-ozone and treated water sites ($n = 8$), filtered (0.45 μm sterile syringe filter, Sarstedt Ltd.), acidified to 1% using nitric acid (HNO_3) (ROMIL UpA™ Nitric Acid) and stored in trace metal-free, polyethylene bottles for the determination of the following elements (magnesium (Mg), silica (Si), calcium (Ca), sodium (Na), strontium (Sr), potassium (K), chromium (Cr), iron (Fe), zinc (Zn), selenium (Se)) and trace elements (aluminium (Al), arsenic (As), boron (B), barium (Ba), cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), titanium (Ti), vanadium (V)). Analyses were performed using inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer ELAN DRCE, Waltham, USA) (Li et al. 2013; Brennan et al. 2017; Pathak et al. 2017; Peyton et al. 2017) in a class 1000 (ISO class 6) cleanroom at the Chemical Monitoring Facility at NUI, Galway.

Furthermore, water samples were taken for THM analysis at six locations, immediately after treatment (NS2), at the public water tap (NS5) and at each of the network extremities (NS8, NS9, NS10, NS11 (Fig. 1)). Samples were taken in glass vials (prepared with sodium thiosulfate and septa lids) and were sent to an external accredited laboratory (CLS Connemara, Galway, Ireland) for analysis of THMs (chloroform, bromoform, dibromochloromethane and bromodichloromethane).

Analysis of the fluorescence EEMs was carried out using the drEEM toolbox (Murphy et al. 2013) for MATLAB (MathWorks) for implementing parallel factors analysis (PARAFAC). The methodology presented by Murphy et al. (2013) was followed to determine an adequate PARAFAC model. The processed data (blank subtraction, Rayleigh and Raman scatter regions removed, Raman normalization and IFE corrections) was imported into MATLAB. Regions were smoothed using the drEEM interpolation functions. The fluorescence signals were then normalized to reduce the leverage of extreme values for the purposes of developing a PARAFAC model, and the normalization processes were reversed after validation. To establish a robust PARAFAC model, several samples were identified as outliers through observation of sample leverages on the model. The validity of the PARAFAC model was established through several ways. Spectral loadings of the components were observed to conform to general guidelines of how organic fluorophores signals appear (e.g. only one emission peak, no abrupt changes in loadings with wavelength). Residuals calculated as the difference between the modelled and measured spectra were generally random with few minor peaks. Split-half validation was also carried out based on a randomized split of the dataset into 6 equal parts to form 3 unique comparisons of dataset halves. For each unique half (combination of two splits), an independent PARAFAC model was developed, and the components were found to be identical for all combinations as well as to the overall model. Finally, comparison of the resulting PARAFAC components with the OpenFluor database

Fig. 2 Monthly total precipitation on the y-axis recorded at the Met Éireann weather station (circa 12 km south of the study site) and average monthly temperature on the z-axis

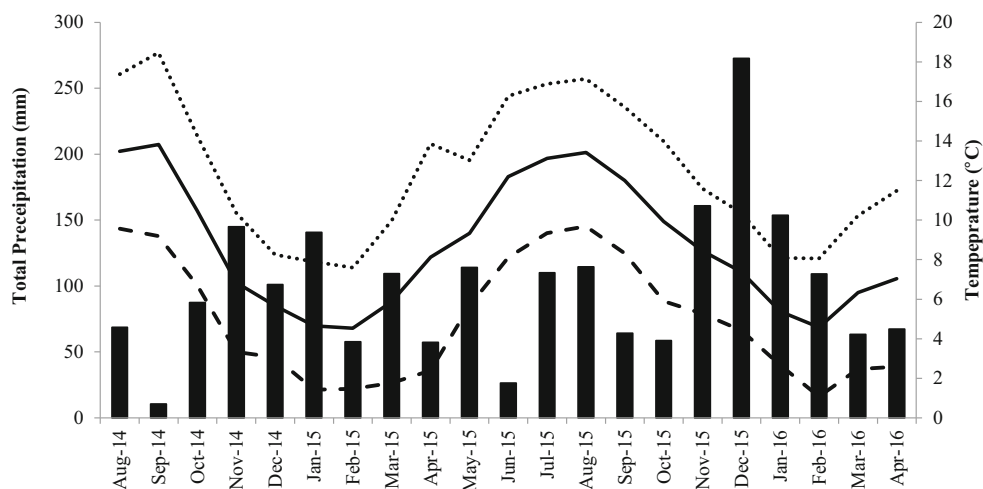
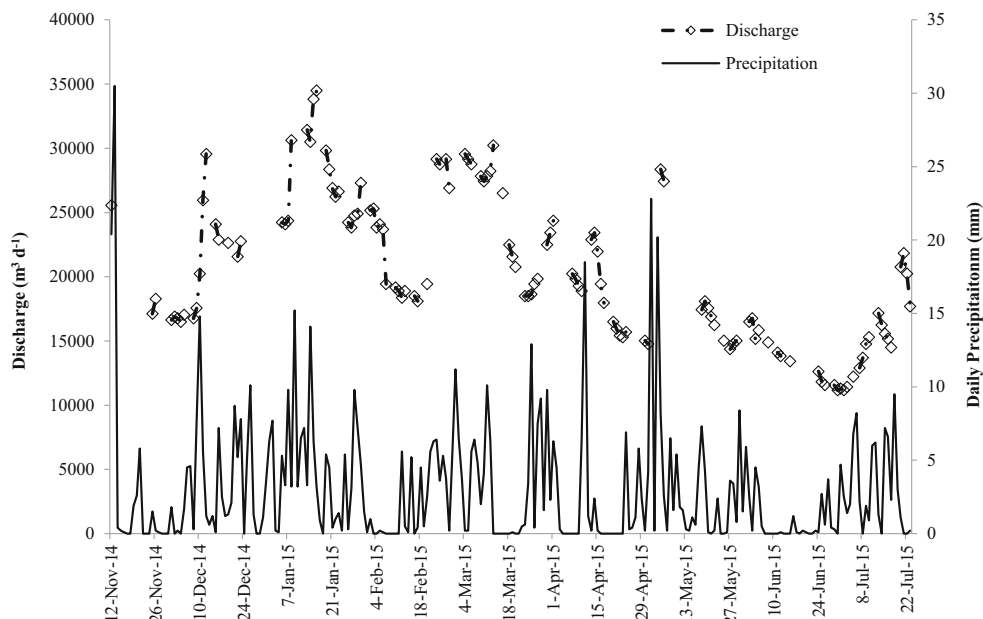


Fig. 3 Mean estimated stream discharge ($\text{m}^3 \text{d}^{-1}$), from the SisterSpring over the observation period (12/11/2014–22/07/2015), with corresponding daily total precipitation (mm)



(Murphy et al. 2014) also provide some indication of model validity. After reversal of the fluorescence normalization, results from the model were reported as Fmax values in RU.

Principal component analysis

PCA was used to investigate the relationships between the hydrochemical indicators in the database. PCA is a method of data reduction. It attempts to replace the original variables (typically standardized, see Reimann et al. 2008) by a smaller set of principal components (PCs), each of which is a linear combination of the original variables. These PCs are constructed to have decreasing variance, to be mutually orthogonal and to be such that the sum of their variances is equal to the sum of the variances of the original variables. The sample PCs extracted are estimates of the corresponding population PCs. The relationship of the variables with a given direction of maximum variance (i.e. a principal component) can be visualized with a biplot. The length of the arrows represents the variability

explained in two principal components, and the angle between two arrays indicates their correlation (Reimann et al. 2008). Principal component analysis was conducted with IBM SPSS 22.0 (IBM Corp 2013), and graphical representation was performed using CANOCO version 4.1 (ter Braak and Šmilauer 1998).

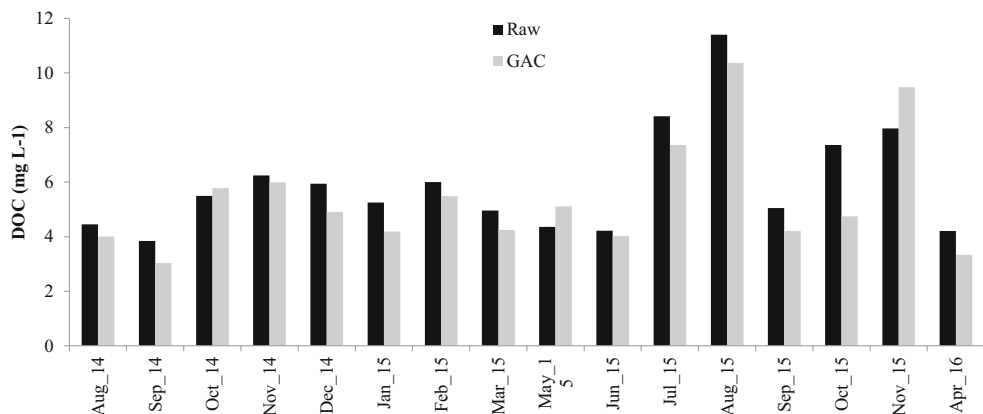
Results and discussion

Catchment sites water quality and quantity

Mean air temperature (Met Éireann) was 8.7 °C during the study period (1.08–18.5 °C, daily minimum and maximum, respectively). Average monthly precipitation was 100 mm with two extremely dry months observed (09/2014 and 06/2015) and one extremely wet month (12/2015) (Fig. 2).

Mean estimated stream discharge from the SisterSpring over the observation period (12/11/2014–22/07/2015) was

Fig. 4 Dissolved organic carbon concentrations from water samples taken at the WPWS raw water abstraction and following ozonation and granular activated carbon filtration



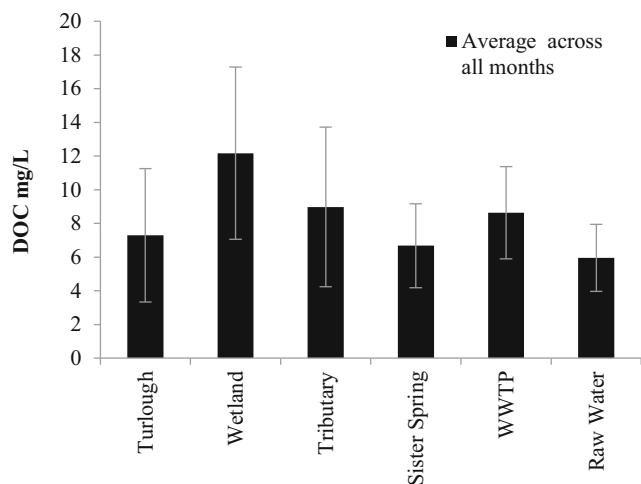


Fig. 5 Dissolved organic carbon concentrations from the five locations in a 4-km² vicinity of the WPWS spring and the WPWS spring/raw water over the duration of the study period. Error bars highlight the standard deviation

20,559 m³ d⁻¹ (11,163 m³ d⁻¹, 34,497 m³ d⁻¹ minimum and maximum, respectively, Fig. 3). Maximum change in recorded water level over the observation period was ~100 mm throughout the winter and 50 mm through the summer. Instantaneous discharge response to rainfall peaks suggests that there is no major storage deep in the groundwater/bedrock system. DOC concentrations from the WPWS Raw water varied (3.84–11.40 mg L⁻¹) with an average of 5.95 mg L⁻¹ (Fig. 4). An overall seasonal trend could be observed with DOC concentrations increasing by 2 mg L⁻¹ from summer to winter with the exception of July and August 2015. The highest DOC concentrations were observed in July and August 2015 following the drought period in June 2015. DOC concentrations plotted against temperature showed no correlation. DOC

concentrations displayed a strong positive correlation with precipitation ($R^2 = 0.7611, \rho < 0.001$).

DOC concentrations from the catchment sites varied with the wetland site showing the highest concentrations (20.46 mg L⁻¹, 09/2015) and the WPWS raw water site, the lowest (Fig. 5). DOC concentrations observed in the raw water were indicative of groundwater strongly influenced by the occurrence of surface karst features (Pronk et al. 2006). In comparison to other catchment sites, the adjacent SisterSpring and the Turlough site ~4 km away had the most similar mean DOC concentrations to the raw water. In lowland karst regions, underground water flow occurs through the epikarst and consequently discharges to springs, turloughs and streams, and as a result, surface and underground flow systems are highly connected (Pavlis and Cummins 2014b). Seasonal variation was evident; however, response to high rainfall events overrides the seasonality as can be observed in July and August 2015 (Fig. 4; Kraus et al. 2010). Temporal variation was more evident at the surface water sites, demonstrated by the high standard deviations at the wetland and tributary sites (Fig. 5).

All concentrations of major cations and trace elements in the water samples were lower than the permissible limits of the EU Drinking Water Regulations (EU 2014). PCA ordination results showed that 62.4% of water chemistry variance was explained (21.4% on axis 1, with a further 17.4% explained on axis 2, 13.8% on axis 3 and 9.8% on axis 4) (Fig. 6). There are three main groupings of samples, the first at the top of the graph (dominated by Wetland samples), the second on the left hand side (dominated by Raw water, Turlough and Sister Spring samples) and the third on the right hand side of the graph (dominated by the WWTP samples). As can be seen by the PCA biplot, the first principal component (x-axis) is determined by DOC, Ba, Mn and Mo.

Fig. 6 Biplot of the hydrochemical data produced with principal components analysis

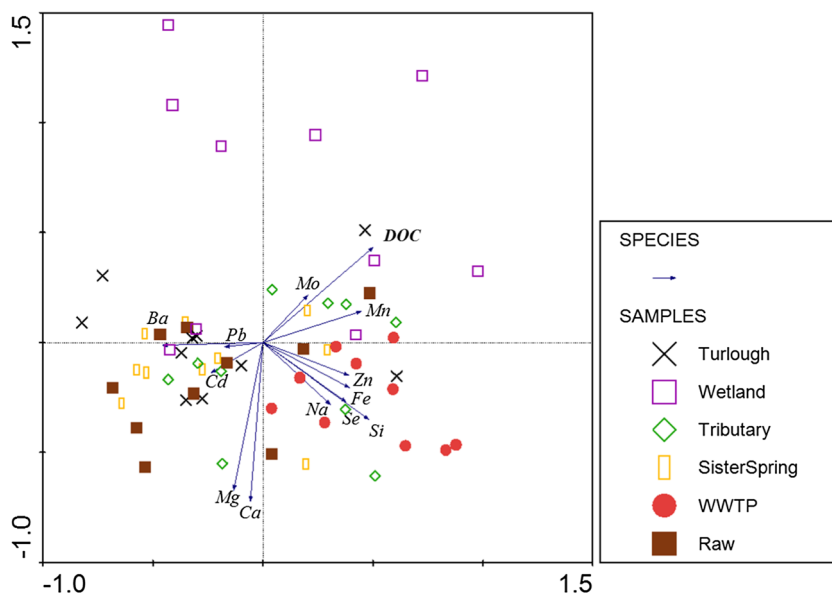


Table 1 Average concentrations of nutrients and metals analysed during the study ($n = 10$; standard deviations are denoted by italics)

	Turlough	Wetland	Tributary	SisterSpring	WWTP	Raw
DIC*	48.28 <i>7.16</i>	38.89 <i>15.17</i>	70.20 <i>13.92</i>	66.21 <i>7.09</i>	59.19 <i>8.97</i>	65.64 <i>7.49</i>
DOC*	7.03 <i>3.64</i>	13.38 <i>5.37</i>	9.68 <i>5.17</i>	6.89 <i>2.76</i>	8.92 <i>3.17</i>	6.39 <i>2.36</i>
TN*	0.78 <i>0.43</i>	0.79 <i>0.46</i>	1.37 <i>0.25</i>	1.35 <i>0.40</i>	4.49 <i>1.41</i>	1.79 <i>0.37</i>
UVA₂₅₄	0.14 <i>0.03</i>	0.42 <i>0.15</i>	0.37 <i>0.27</i>	0.23 <i>0.11</i>	0.20 <i>0.07</i>	0.22 <i>0.12</i>
Ca*	85.58 <i>15.06</i>	68.01 <i>23.13</i>	116.56 <i>19.57</i>	103.16 <i>10.07</i>	96.52 <i>12.13</i>	102.95 <i>9.52</i>
K*	2.00 <i>0.43</i>	4.07 <i>3.54</i>	2.83 <i>0.44</i>	2.40 <i>0.27</i>	9.76 <i>3.46</i>	2.42 <i>0.22</i>
Mg*	6.76 <i>1.11</i>	3.99 <i>1.62</i>	5.04 <i>1.07</i>	6.08 <i>1.13</i>	5.56 <i>1.05</i>	6.28 <i>1.53</i>
Na*	8.32 <i>1.12</i>	9.80 <i>2.69</i>	10.07 <i>1.54</i>	8.91 <i>1.20</i>	39.88 <i>9.95</i>	9.98 <i>3.28</i>
Si*	1.58 <i>0.84</i>	1.92 <i>1.35</i>	1.90 <i>0.60</i>	1.73 <i>0.45</i>	2.62 <i>0.55</i>	1.74 <i>0.42</i>
Sr*	0.35 <i>0.46</i>	0.44 <i>0.71</i>	0.44 <i>0.74</i>	0.40 <i>0.65</i>	0.51 <i>0.84</i>	0.40 <i>0.66</i>
Al**	6.11 <i>3.78</i>	8.74 <i>3.40</i>	20.10 <i>15.76</i>	7.29 <i>4.95</i>	8.86 <i>3.52</i>	8.71 <i>6.13</i>
As**	0.61 <i>0.33</i>	0.60 <i>0.17</i>	0.85 <i>0.33</i>	0.69 <i>0.10</i>	0.97 <i>0.21</i>	0.72 <i>0.09</i>
B**	10.16 <i>2.09</i>	9.78 <i>1.44</i>	12.14 <i>1.91</i>	11.42 <i>1.57</i>	25.14 <i>4.55</i>	11.52 <i>1.76</i>
Ba**	11.49 <i>10.06</i>	9.03 <i>11.11</i>	9.03 <i>8.36</i>	9.75 <i>8.82</i>	6.89 <i>6.15</i>	9.62 <i>8.65</i>
Cd**	0.04 <i>0.03</i>	0.03 <i>0.02</i>	0.04 <i>0.03</i>	0.03 <i>0.02</i>	0.03 <i>0.03</i>	0.04 <i>0.04</i>
Co**	0.18 <i>0.04</i>	0.18 <i>0.08</i>	0.29 <i>0.04</i>	0.19 <i>0.02</i>	0.26 <i>0.06</i>	0.20 <i>0.06</i>
Cr**	0.14 <i>0.10</i>	0.28 <i>0.22</i>	0.40 <i>0.21</i>	0.27 <i>0.14</i>	0.22 <i>0.07</i>	0.49 <i>0.64</i>
Cu**	0.99 <i>0.44</i>	1.71 <i>0.72</i>	1.14 <i>0.38</i>	1.21 <i>1.26</i>	3.16 <i>1.77</i>	1.98 <i>0.56</i>
Fe**	59.05 <i>41.71</i>	45.69 <i>31.86</i>	159.77 <i>107.60</i>	71.48 <i>44.09</i>	108.67 <i>63.18</i>	71.30 <i>39.63</i>
Mn**	41.65 <i>51.60</i>	89.22 <i>78.01</i>	33.59 <i>18.25</i>	10.12 <i>6.50</i>	48.04 <i>31.24</i>	6.67 <i>3.68</i>
Mo**	0.48 <i>0.85</i>	0.96 <i>2.25</i>	0.71 <i>1.62</i>	0.72 <i>1.61</i>	0.95 <i>2.21</i>	1.06 <i>2.09</i>
Nb**	0.03 <i>0.04</i>	0.08 <i>0.13</i>	0.06 <i>0.09</i>	0.04 <i>0.06</i>	0.09 <i>0.16</i>	0.04 <i>0.07</i>
Ni**	3.58 <i>0.73</i>	3.34 <i>1.19</i>	4.92 <i>0.52</i>	4.42 <i>0.69</i>	4.07 <i>0.56</i>	4.39 <i>0.66</i>
Pb**	0.07 <i>0.04</i>	0.08 <i>0.07</i>	0.08 <i>0.07</i>	0.11 <i>0.14</i>	0.11 <i>0.09</i>	0.16 <i>0.26</i>

Table 1 (continued)

	Turlough	Wetland	Tributary	SisterSpring	WWTP	Raw
Sb**	0.05 <i>0.05</i>	0.06 <i>0.07</i>	0.05 <i>0.05</i>	0.05 <i>0.05</i>	0.21 <i>0.18</i>	0.04 <i>0.04</i>
Se**	0.03 <i>0.03</i>	0.02 <i>0.02</i>	0.01 <i>0.01</i>	0.01 <i>0.01</i>	0.01 <i>0.01</i>	0.01 <i>0.01</i>
Sn**	1.02 <i>2.23</i>	0.86 <i>1.82</i>	0.71 <i>1.50</i>	0.58 <i>1.22</i>	0.67 <i>1.15</i>	0.53 <i>1.02</i>
Ti**	0.48 <i>0.27</i>	0.63 <i>0.40</i>	0.72 <i>0.45</i>	0.50 <i>0.28</i>	6.08 <i>3.66</i>	0.52 <i>0.28</i>
V**	0.31 <i>0.37</i>	0.40 <i>0.55</i>	0.66 <i>0.42</i>	0.36 <i>0.30</i>	0.58 <i>0.37</i>	0.36 <i>0.25</i>
Zn**	11.80 <i>9.36</i>	15.23 <i>11.65</i>	7.71 <i>5.31</i>	6.30 <i>3.44</i>	48.30 <i>27.49</i>	11.90 <i>6.59</i>

*mg L⁻¹; **µg L⁻¹

considered to be of external origin, is introduced into the aquifer system via infiltration from the surface and is related to water transit time (Pavlis and Cummins 2014a). On the other hand, the second principal component axis (y-axis) is determined by Ca and Mg, considered to be of internal origin (bedrock dissolution), and by elements related to anthropogenic pollution such as Na, and Se that mostly have external origin (Pavlis and Cummins 2014a), however, may also be of natural origin. The raw water samples were most similar to the SisterSpring and Turlough sites except for three occasions following high rainfall when all sites became quite similar as the water table rose and lands became flooded (Table 1).

A four component model (C1–C4) was established based on several diagnostic criteria and random split validation (Fig. 7). Derived fluorescing components were cross-referenced with the OpenFluor database (Murphy et al. 2014), which provided context for the similarities between these organic fluorophores to those reported globally from other studies. A total of 42 studies were found with at least one of the three derived components with a high similarity score (>0.95) (Table 2). The top 5 highest similarity scores are shown where available. According to previous classifications, C1 consisted of humic-like terrestrial organic matter, ubiquitous to freshwater, composed of high molecular weight and aromatic organic compounds; C2 consisted of humic-like, terrestrial-delivered reprocessed organic matter; C3 consisted of humic like terrestrial-derived organic matter; and C4 consisted of protein-like microbial-delivered organic matter. All four components are commonly reported in surface and treated water elsewhere (Shutova et al. 2014).

In all water samples taken from the catchment sites, C1 and C2 had higher fluorescence intensities than C3 and C4 (Fig. 8). All sites exhibited contrasting organic matter properties. Specifically, the Turlough and SisterSpring samples experienced the highest variability of C1 and C2 (0.99 ±

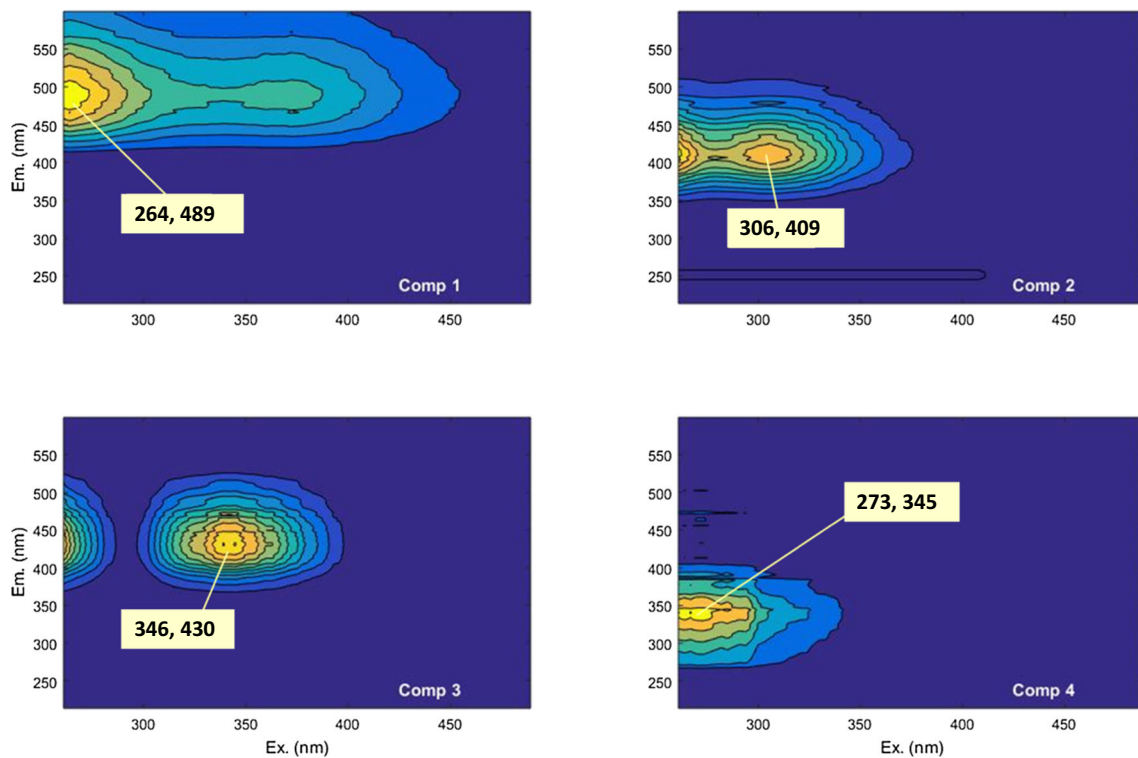


Fig. 7 Loading values for the 3 PARAFAC components with excitation (nm) on the x-axis and emission (nm) on the y-axis

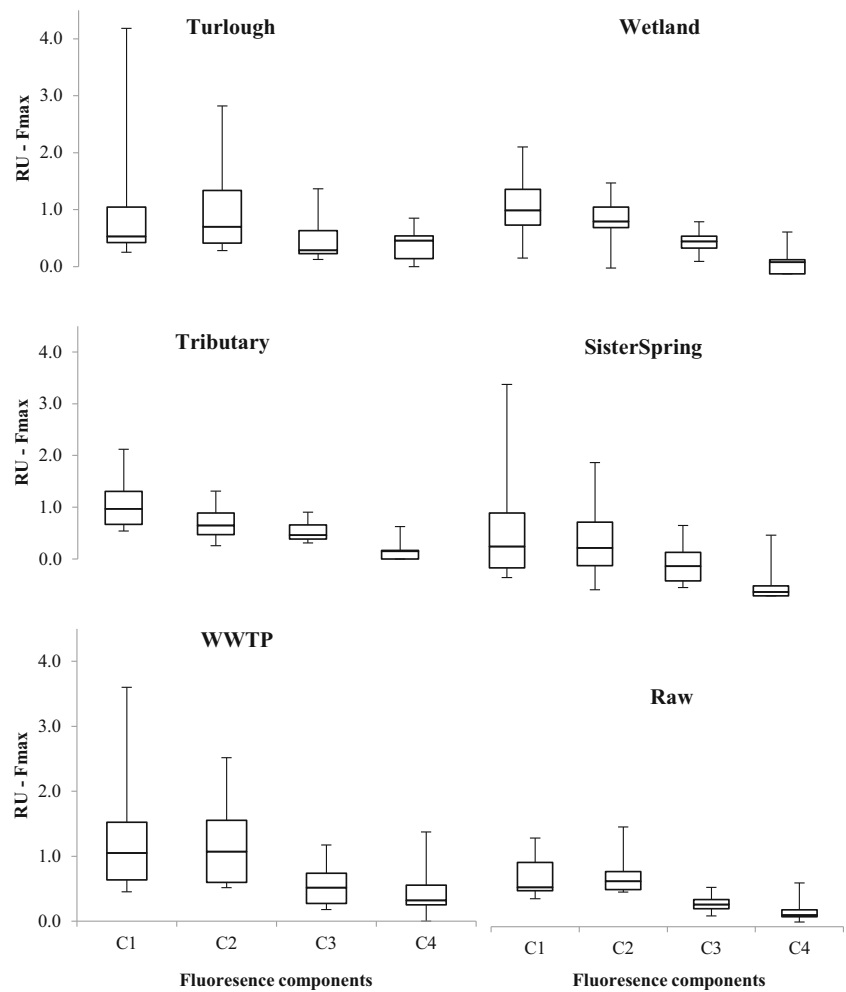
0.28 RU and 0.97 ± 0.19 RU, respectively) in contrast to the raw water samples which tended to be stable for all components (Fig. 8). The two surface water fed sources (i.e. the wetland and the tributary) had greater median values of C1 and less of C2 compared with the four groundwater sampling locations which had similar medians for C1 and C2 (Fig. 8) highlighting a lengthier residence time of the water and

perhaps prone to increased processing of OM. The WWTP has the highest range of fluorescence intensities for C4. C4 is associated with sewage-derived material presumably due to the production of NOM from microbial activity (Kraus et al. 2010). The WWTP included in this study is a constructed wetland, and catchment drainage is via a series of small streams that disappear underground via a swallow hole located

Table 2 Identities and related references for similar components using the OpenFluor database

Component	Similarity score*	Component identity	References
C1	1.00	Humic-like terrestrial-delivered OM	Shutova et al. 2014
	0.99	Terrestrial humic-like OM	Walker et al. 2009
	0.99	Humic-like fluorescence	Catala et al. 2015
	0.99	Humic-like fluorescence	Murphy et al. 2006
	0.98	Terrestrial humic-like	Lambert et al. 2016
C2	0.99	Humic-like, terrestrial-delivered reprocessed OM	Shutova et al. 2014
	0.99	Terrestrial humic-like	Stedmon et al. 2007
	0.99	Terrestrial humic-like	Lambert et al. 2016
	0.98	Terrestrial humic-like	Cawley et al. 2012
	0.98	Terrestrial humic-like	Williams et al. 2013
C3	0.95	Humic-like terrestrial delivered OM	Shutova et al. 2014
C4	0.97	Protein-like microbial delivered	Shutova et al. 2014
	0.96	Protein-like microbial delivered	Walker et al. 2013
	0.96	Protein-like	Cawley et al. 2012
	0.96	Autochthonous DOM	Kowalczyk et al. 2009
	0.96	Protein-like	Williams et al. 2013

Fig. 8 F_{max} of fluorescence components at the catchment sites



approximately 500 m east of the site. Lower efficiencies at the WWTP during the summer periods have been reported owing to the formation of algal blooms in the detention pond (Healy and Cawley 2002).

The ZoC delineated in the desktop study did not accurately capture relevant catchment information pertaining to this

supply. The application of Geographical Information Systems (GISs) in the risk assessment of drinking water for the purposes of implementing water safety plans is dependent on accurate catchment boundaries. ZoCs have recently been distinguished separate to Source Protection Areas (SPAs) and Source Protection Zones (SPZs) which have a higher degree

Fig. 9 UVA_{254} measured at the raw water, post-ozone and post-GAC sampling points

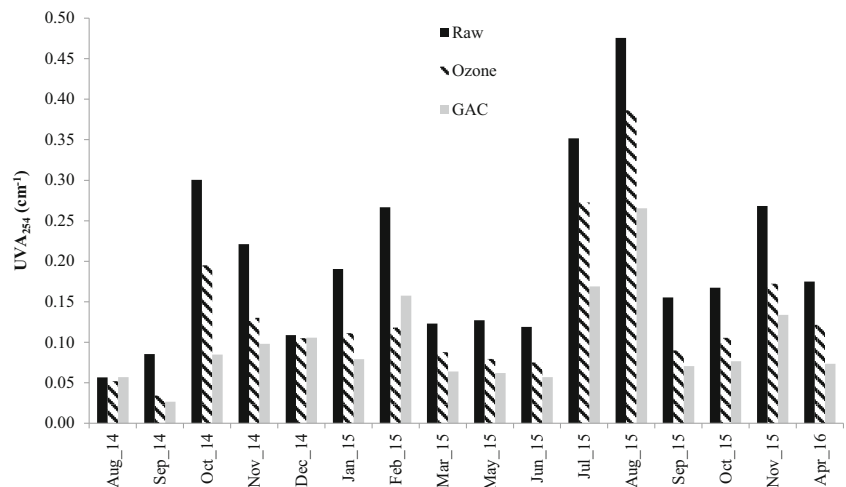
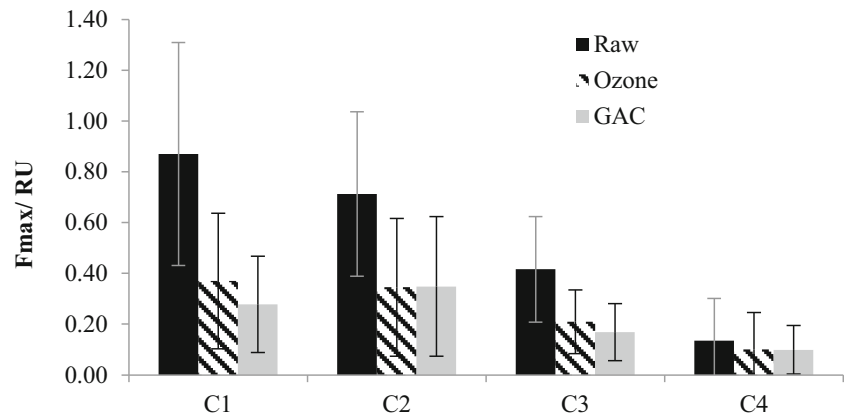


Fig. 10 F_{\max} concentrations for Components C1, C2, C3 and C4 from the raw, ozone and GAC sampling points



of certainty associated with them for protection of groundwater sources (Hunter Williams et al. 2017).

Treatment

Raw and treated water DOC concentrations had similar concentrations suggesting limited removal of NOM. The average DOC concentration in water samples taken after the GAC filter was 5.39 mg L^{-1} ($3.30\text{--}10.37 \text{ mg L}^{-1}$), and average removal percentage was 9.6% (Fig. 4). On three occasions, treated water had higher DOC concentrations than raw water samples highlighting that the GAC filter itself was a source of NOM of up to 1.51 mg L^{-1} (Fig. 4). GAC removal efficiency of NOM has been shown to be most dependent on regeneration (Matilainen et al. 2006), and the GAC filter in this study, installed in 2011, had never been regenerated. Facilities for regeneration are not in situ in Ireland and were material to be regenerated, it would have to be transported to the UK, which

would not be economically viable. Adsorption of lower molecular weight NOM has been shown to decrease after oxidation owing to polarity and formation of carbonyls and carboxyl groups upon ozonation and therefore does not absorb onto the GAC surface (Swietlik et al. 2002). The average UVA_{254} value was 0.20 cm^{-1} ($0.06\text{--}0.48 \text{ cm}^{-1}$) at the raw water, 0.13 cm^{-1} ($0.03\text{--}0.39 \text{ cm}^{-1}$) post-ozone and 0.10 cm^{-1} ($0.03\text{--}0.26 \text{ cm}^{-1}$) following GAC filtration (Fig. 9). Average reduction percentage by ozone treatment was 34%, and the GAC contributed to a further reduction percentage of 21% (except on three occasions where an increase in UVA_{254} was observed, August and December 2014 and February 2015) (Fig. 9). Ozone treatment decreases hydrophobic molecules by creating carbonyls such as formaldehyde which lowers the absorbance and the fluorescence but can create other problems in terms of taste (Sohn et al. 2007).

Average SUVA for raw water was $3.2 \text{ L mg}^{-1} \text{ m}^{-1}$, an indication of NOM of moderate aromaticity, and GAC has

Fig. 11 F_{\max} percentage reduction following ozone (hatched) and GAC (grey) treatment

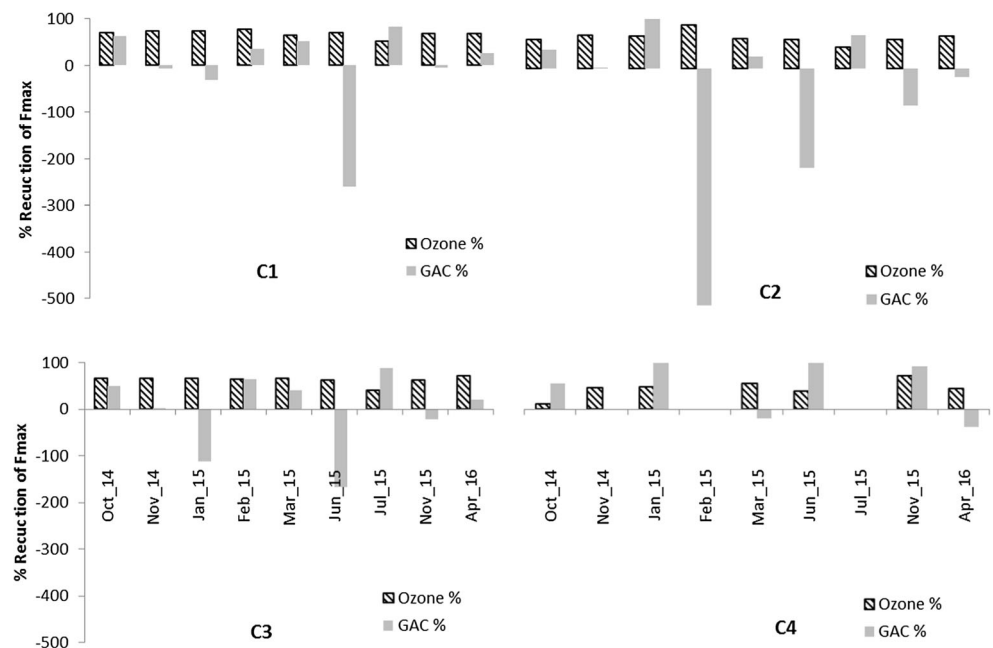


Table 3 Summary of Spearman’s rank correlation coefficients between DOC concentrations, UVA₂₅₄ absorbance, SUVA, total nitrogen, chloroform (CHCl₃), bromoform (CHBr₃), bromodichloromethane (CHBr₂Cl), dibromochloromethane (CHBrCl₂), total THMs and PARAFAC component scores

	DOC	UVA ₂₅₄	SUVA	C1	C2	C3	C4	TN	CHCl ₃	CHBr ₃	CHBr ₂ Cl	CHBrCl ₂	Total THMs
DOC	1	0.72*		0.72*	0.49*	0.67*					− 0.53*		
UVA ₂₅₄		1.00	0.62*	0.82*	0.56*	0.69*		0.52*	0.64*		− 0.52*		0.61*
SUVA			1.00						0.48*				
C1				1.00	0.56*	0.77*			0.57*		− 0.65*		0.56*
C2					1.00				0.53*		− 0.49*		0.49*
C3						1.00			0.52*		− 0.49*		
C4							1.00						
TN								1.00	0.62*				0.63*
CHCl ₃									1.00			0.62*	0.93*
CHBr ₃										1.00			
CHBr ₂ Cl											1.00		
CHBrCl ₂												1.00	0.71*
Total THMs													1.00

been shown to be most effective for removal of NOM in this range (Matilainen et al. 2006). SUVA in the finished water was 1.8 L mg^{−1} m^{−1}, which is typical of NOM with low aromaticity (SUVA < 2 L mg^{−1} m^{−1}). On five occasions, SUVA was greater than 2 L mg^{−1} m^{−1}, a parametric value specified above which THMs are likely to form (EPA 2012). E2/E3 ratios and SR revealed increases following ozonation with no further increases following GAC treatment demonstrating a decrease in molecular weight with treatment.

F_{max} was higher for terrestrial and ubiquitous humic-like component C1 in the raw water followed by C2, C3 and C4 (Fig. 10). Ozonation decreased the fluorescence intensity of all humic-like components (C1, C2 and C3). GAC marginally decreased the fluorescence intensity in the terrestrial-derived humic-like components however was ineffective for the terrestrial-delivered reprocessed organic matter (C2) and the protein-like microbial-delivered organic matter (C4). These findings are consistent with previous studies (Baghoth 2012; Shutova et al. 2014).

To evaluate the effect of water treatment on fluorescence characteristics of NOM, the percentage reduction of F_{max} across each treatment process (Fig. 11) was calculated. Ozone reduced C1 by an average of 69% (± 7%) across all sampling occasions. C2, C3 and C4 were reduced by 64% (± 11%), 64% (± 8%) and 46% (± 17%), respectively. The GAC filtered reduced C1 by an average of − 4% (± 96%), C2, − 61% (± 172%), C3, − 4% (± 80%) and C4, 41% (± 56%). Negative reductions indicate incidents where the GAC filter increased the F_{max} of C1, C2 and C3 on certain occasions in the treated water highlighting that the filter media itself was a ‘source’ of NOM.

The average total THM (TTHM) concentration measured in the treated water was 88.8 µg L^{−1} (31.8–251 µg L^{−1}). Chloroform was the most prominent THM (average ~ 72%)

across all samples taken, followed by bromodichloromethane (~ 20%), dibromochloromethane (~ 6%) and bromoform (< 1%). Average TTHMs across the distribution network displayed similar temporal changes as DOC with ambient temperature and local rainfall. Average free and total chlorine concentrations were 0.98 and 1.22 mg L^{−1}. The average DOC concentration measured from 9 locations along the distribution network was 5.59 mg L^{−1}. At DOC > 4.0 mg L^{−1}, it is likely that THM levels will exceed 100 µg L^{−1} if the residence time in the network is 2–3 days and if a free residual chlorine is to be maintained at the tap (EPA 2012). C2 had the highest fluorescence intensity in the distribution network followed by C1 and C3. THMs exceeded the parametric value in 45% of samples taken.

All samples from the post-treatment and distribution network were included in the determination of Spearman’s correlation coefficients (Table 3). There were significant correlations among DOC; UVA₂₅₄ SUVA; PARAFAC components C1, C2 and C3; TN, chloroform (CHCl₃); bromodichloromethane (CHBr₂Cl); dibromochloromethane (CHBrCl₂); and total THMs. UVA₂₅₄ and C1 had equal correlation scores (0.72) to DOC. TN was significantly correlated with UVA₂₅₄ and chloroform. It is likely that runoff from the farming activities indicated by high TN and chloroform and also the ‘terrestrial-delivered reprocessed organic matter’ is the cause for the high correlation. C1, C2 and C3 were significantly correlated with UVA₂₅₄ and chloroform. SUVA was not significantly correlated with any of the PARAFAC components.

GAC has previously been shown to act as a removal medium for metals in water streams (Dong et al. 2018; Sountharajah et al. 2016). As outlined in 2.2, the collected water samples were analysed for elemental composition prior to treatment (raw water) and also following combined ozone treatment and GAC filtration. The changes in concentrations

of the different elements following the treatment processes are presented in Table S1. As previously noted, none of the water samples analysed exceeded the permissible limits of the EU Drinking Water Regulations (EU 2014). The elemental analysis did however show that the treatment failed to consistently reduce the concentration of the elements under investigation. Total nitrogen is the only parameter that consistently showed a reduction in concentration following treatment on all sampling events. All other elemental parameters monitored showed an inconsistent concentration variation following treatment, with both decreasing and increasing concentrations evident on different sampling occasions. For example, lead concentrations were found to be well below the limit value of 10 µg/L (EU 2014), in all samples of both raw and treated water with the highest concentrations of 0.85 and 0.52 µg/L, respectively, in the raw and treated water recorded on 27/03/2015. The treatment process however did not consistently remove lead (Pb) from the water with the treated water having higher concentrations on a number of occasions (31/07/2015, 29/08/2015, 29/09/2015, 30/10/2015 and 27/11/2015) than the raw water.

As was previously observed, DOC concentrations were also found to increase following GAC filtration, on certain sampling events which highlights the potential for the GAC itself to act as a source of NOM as the GAC may become exhausted following periods of increased NOM concentrations. It is therefore possible that the GAC may also release some previously captured elemental species in a similar fashion. It has previously been noted in laboratory studies that GAC has a maximum capacity for different elemental species and that the adsorption of elements by charcoal is influenced by DOC concentrations and turbidity levels (Jusoh et al. 2007; Sounthararajah et al. 2015).

In terms of the elemental composition of the water itself, the water was found to have average concentrations for the major cations of 9.75 mg/L (Na), 2.41 mg/L (K), 103.99 mg/L (Ca) and 6.49 mg/L (Mg), and it is indicative of water sourced from a limestone region (Graham and Farmer 2007). This is as expected as the water in the WPWS is from a spring source in a karst area.

Conclusion

Groundwater, where adequate supply is available, is viewed as a preferable option to surface water in Ireland owing to the challenge posed by treating surface water (O'Dwyer et al. 2014). Online raw water UV transmission (UVT) monitors can be accurately used as indicators of the extent of surface water infiltration and potential for microbial contamination, which can inform suitable treatment options or scoping of an alternative source. UVT is related to the quantity of organic

solids and other material in the water which cause UV light to absorb and scatter as it passes through the water column. Water quality parameters, SUVA and F-EEMs, indicate that this spring source is highly comparable with surface water and E2:E3 ratios allow for targeted selection of activated carbon range, i.e. microporous or mesoporous. However, even with targeted selection, mechanisms must be put in place for replacement/regeneration of filter media once it has been shown to become exhausted to avoid repeated THM exceedances as observed in this supply. Furthermore, identification of the quality of NOM is important prior to treatment design as in this instance pre-ozonation followed by GAC was not adequate to remove the NOM indicative of lower SUVA and lower molecular weight. Additionally, SPAs and SPZs rather than ZoCs should be considered in risk assessment of raw drinking water.

As previously shown in Irish supplies, chloroform was the most prominent THM (O'Driscoll et al. 2018). C2, the terrestrial-delivered reprocessed organic matter, was responsible for majority of THM production in the distribution network. Treatment failed to consistently reduce the concentration of the elements under investigation. Total nitrogen is the only parameter that consistently showed a reduction in concentration following treatment on all sampling events. All other elemental parameters monitored showed an inconsistent concentration variation following treatment, with both decreasing and increasing concentrations evident on different sampling occasions.

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