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Relating freshwater organic matter fluorescence to organic carbon removal efficiency in drinking water treatment

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ABSTRACT

Monthly raw and clarified water samples were obtained for 16 UK surface water treatment works. The fluorescence excitation–emission matrix (EEM) technique was used for the assessment of total organic carbon (TOC) removal and organic matter (OM) characterisation. The impact of algae presence in water on TOC removal, and its relationship with fluorescence, was analysed. Fluorescence peak C intensity was found to be a sensitive and reliable measure of OM content. Fluorescence peak C emission wavelength and peak T intensity (reflecting the degree of hydrophobicity and the microbial fraction, respectively) were found to characterize the OM; the impact of both on TOC removal efficiency was apparent. OM fluorescence properties were shown to predict TOC removal, and identify spatial and temporal variations. Previous work indicates that the trihalomethane (THM) concentration of treated water can be predicted from the raw water TOC concentration. The simplicity, sensitivity, speed of analysis and low cost, combined with potential for incorporation into on-line monitoring systems, mean that fluorescence spectroscopy offers a robust analytical technique to be used in conjunction with, or in place of, other approaches to OM characterisation and THM formation prediction.

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1. Introduction

Organic matter (OM) is a complex mixture of heterogeneous chemical fractions. In drinking water treatment, the use of chlorine as a disinfectant for waters containing natural organic matter (NOM) results in the formation of carcinogenic, mutagenic and toxic compounds, which pose a potential threat to consumers of drinking water supplies (Rook, 1974; Krasner et al., 1989). The occurrence of halogenated species in drinking water post chlorination was first reported by Rook (1974) and Bellar et al. (1974). During the chlorination process, chlorine is consumed through multiple and complex reactions which give rise to undesirable reaction by-products. These harmful disinfection by-products (DBPs) include several chemical compounds, including trihalomethanes (THMs: chloroform CHCl_3 , dichlorobromomethane CHCl_2Br , dibromochloromethane CHBr_2Cl , bromoform

CHCr_3), haloacetic acids (HAAs) and haloacetonitriles (HANs) (Rook, 1974; Krasner et al., 1989; Nikolaou et al., 1999), and potential DBP formation mechanisms have been elucidated by many authors (e.g. Rook, 1974; Kavanaugh et al., 1980; Engerholm and Amy, 1983; Carlson and Hardy, 1998). Previous work indicates that the THM concentration of treated water can be predicted from the raw water TOC concentration (see, for example, Stevens et al., 1976; Singer and Chang, 1989; Singer, 1994; Chen et al., 2008) and the water industry routinely uses off-line and, more latterly, on-line TOC measurements to assess process performance and THM formation potential.

Whilst TOC is routinely measured, the results obtained are of limited value with regard to the character and composition of the OM present. However, although the structure and functionality of OM are not completely understood (Mopper and Schultz, 1993; Thacker et al., 2005), OM displays specific fluorescence properties.

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A review of the use of fluorescence spectrophotometry in water science can be found in Hudson et al. (2007); however, the key points are discussed briefly below.

When excited by UV and visible light, OM fluoresces and the characteristics and intensity of the fluorescence varies depending on the fluorophores present. The composition of aquatic OM can be visualised as a pattern of fluorescence peaks within an excitation–emission matrix (EEM). Fluorescence peaks can be attributed to both natural fluorescence (humic- and fulvic-like), defined as peaks A and C (Coble, 1996) and amino acid-like organic matter (tryptophan- and tyrosine-like fluorescence, defined as peaks T and B) at shorter emission wavelengths (Coble, 1996; Stedmon et al., 2003). Peak C fluorescence intensity has been shown to exhibit a general correlation with TOC (Smart et al., 1976; Vodacek et al., 1995; Ferrari et al., 1996), although the relationship can be weak if there are significant variations in the amount of carbon-specific fluorescence (Cumberland and Baker, 2007). Wu et al. (2003) found a significant correlation between the fulvic-like (peak C) fluorescence emission wavelength and the hydrophobicity, with higher emission for greater degree of hydrophobicity. McKnight et al. (2001) found a strong linear relationship between aromaticity and fluorescence, and concluded that microbially-derived fulvic acids have lower aromaticities and greater fluorescence indices (fluorescence index defined as the ratio of the emission intensity at a wavelength of 450 nm to that at 500 nm, obtained with an excitation of 370 nm). Stewart and Wetzel (1980) showed that larger molecular weight aquatic organic fractions had a greater absorbance but lower peak C fluorescence than smaller molecular weight fractions. Similar findings were reported by Belzile and Guo (2006). Peak T intensity (tryptophan-like fluorescence with maximum located at excitation 280 nm and emission 350 nm) is indicative of the amino acid-like fraction content and the presence of anthropogenic OM inputs. It is also known to correlate with BOD (Reynolds and Ahmad, 1997; Ahmad and Reynolds, 1999; Reynolds, 2002). The relationship between biological activity of aquatic plankton and peak T fluorescence intensity for different dissolved organic matter (DOM) has been observed (e.g. Mopper and Schultz, 1993; Ferrari and Mingazzini, 1995). More recently, Cammack et al. (2004) reported that the highest algae metabolism rates corresponded to tryptophan-like fluorescence intensities. However, they also observed correlations with other fluorescence regions (fulvic and humic-like). Additionally, the impact of algae-derived organic matter on THMs formation during treatment was investigated by Paralkar and Edzwald (1996) and Wildrig et al. (1996).

Therefore, the additional data available from fluorescence spectroscopy in real time is potentially of great process and commercial value to the water industry. This study investigates the use of fluorescence spectroscopy to provide a rapid assessment of TOC character and removal and hence a useful process assessment and optimisation tool at water treatment works. The study evaluates the use of peak C fluorescence intensity reduction between freshwater (raw) and partially-treated waters as a measure of organic matter removal, and analyses the relationship between freshwater organic matter fluorescence properties, algae numbers and TOC removal, including analyses on both seasonal and site specific data

from 16 surface water treatment works. The work focuses on the generation and analysis of additional data which are not available from the more routine TOC analyses undertaken by the water industry, and assesses the use of fluorescence spectroscopy as a complementary or replacement performance indicator.

2. Materials and methods

2.1. Sample sites

Fluorescence spectroscopy analysis was carried out on samples of raw and clarified water from 16 surface water treatment works (WTW), collected monthly between August 2006 and August 2007. The treatment works are located in the Midlands region in central UK and are owned and operated by Severn Trent Water Ltd. The works' performance did not undergo any significant changes over the study period as illustrated by only minor variations in treatment parameters (coagulant dose, clarification pH, final water chlorine residual and final water pH; see Supplementary Table 1). The treatment works extract surface water from a wide range of different sources with different factors influencing raw water quality (e.g. variation in recharge, land cover patterns, anthropogenic impacts on catchments and water sources). Therefore, the sample sites represent different organic matter properties, indicative of the prevailing environmental conditions.

Table 1 summarizes the sites that are included in this study with a description of organic matter character; specifically the land use type, mean TOC values and range of organic properties. The typical land use was calculated on the basis of the Corine Land Cover 2000 dataset obtained from the European Environment Agency (Corine Land Cover, 2007). The predominant type of catchment land use is arable land (up to 65% of the catchment for site 6 and 9) and pasture (the highest percentage value of 76% for site 16).

2.2. Analytical methods

Each month, water samples were collected from the 16 WTW over a period of two days; the samples being stored cool and in the dark until analysis, which was between three and seven days from collection. Storage test experiments were undertaken to demonstrate that degradation of water samples was insignificant for these storage conditions (typical variation, including both increase and decrease in peak C fluorescence intensity was 4.4% and for the peak T intensity 5.3%; typical change in TOC was less than 5%).

Organic matter fluorescence was measured using a Cary Eclipse Fluorescence Spectrophotometer (Varian, Surrey, UK), by scanning excitation wavelengths from 200 to 400 nm in 5 nm steps, and detecting the emitted fluorescence in 2 nm steps between 280 and 500 nm. Excitation and emission slit widths were set to 5 nm and photomultiplier tube voltage to 725v. Manufacturer provided instrument correction factors were used. In order to confirm the consistency of measurement conditions, scans of a sealed cell containing deionised

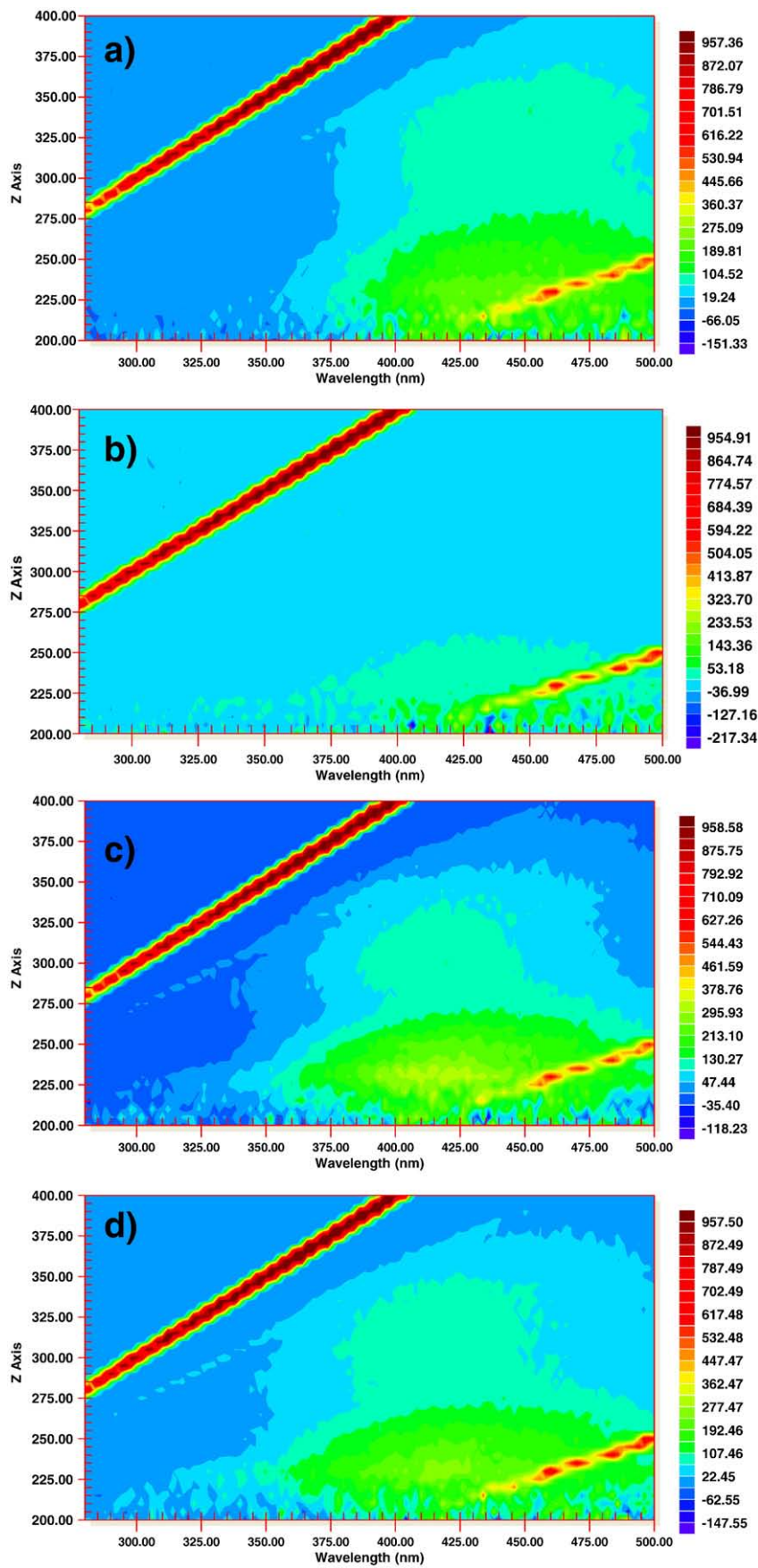


Fig. 1 – Excitation–emission matrices of waters at different water treatment stages from two contrasting sites a) site 14 raw water, b) site 14 clarified water, c) site 5 raw water d) site 5 clarified water.

Table 1 – Summary of sampling sites' catchments and organic matter characteristics (* — direct abstraction from river to WTW; Typical catchment land use types: A — non-irrigated arable land; P — pastures; C — other cultivated areas; U — urban fabric; I — industrial, transport or commercial units; G — green urban areas; F — forests; O — other areas. Mean TOC: > 6.0 mg/l indicates high TOC, Mean TOC < 3.0 mg/l indicates low TOC)

Site	Source	Typical catchment land use (main divisions)	Mean TOC	
			Mean	SD
1	River*	A 26%, U 21%, G 21%, P 21%	Low and variable	3.0 1.2
2	River*	P 30%, A 26%, C 13%, F 11%	Low and variable	3.0 1.1
3	River*	A 63%, P 24%	Intermediate	5.0 1.9
4	River*	A 38%, P 31%, C 14%	Intermediate	4.1 1.3
5	River*	A 63%, P 24%	Intermediate	5.1 2.0
6	River	A 65%, P 25%	High	6.0 1.3
7	River	P 44%, C 19%, U 11%	Intermediate	3.3 0.7
8	River	A 48%, P 24%, U 11%	High	7.0 1.1
9	River	A 65%, P 25%	High	6.8 0.6
10	River	A 43%, P 30%, U 10%	Intermediate	4.2 0.7
11	River	P 55%, C 15%, A 11%, U 11%	Intermediate	4.6 0.9
12	River	A 38%, P 31%, C 14%	Intermediate	5.2 0.9
13	River	A 55%, I 32%, F 13%	High	6.0 1.4
14	Reservoir	P 48%, O 39%	High and variable	5.6 1.6
15	Reservoir	P 45%, A 33%	Low	2.7 0.8
16	Reservoir	P 76%, F 10%	High	6.7 1.2

water were run systematically following Baker (2002) and intensity of the Raman line of water at 348 nm excitation wavelength recorded. The mean Raman value during the study period was 22.3 intensity units, 1 S.D.=0.5). All the fluorescence intensities were corrected to a Raman peak intensity of 20 units. Organic matter fluorescence was measured on unfiltered samples in 1 cm cuvettes. TOC values for raw ($4.4 \pm 1.8 \text{ mg l}^{-1}$) and clarified ($2.9 \pm 1.5 \text{ mg l}^{-1}$) were such that no inner-filter correction was applied. Arising from the fluorescence measurements, EEMs were obtained for each water sample, displaying the intensity of fluorescence within the sample against the wavelengths at which excited fluorophores emitted the light. Typical EEMs are presented in Fig. 1. Peak C fluorescence intensity was determined as the maximum intensity value in the region 300–360 nm excitation and 400–480 nm emission, and peak C emission wavelength defined as the emission wavelength of this maximum intensity. Peak T fluorescence intensity was determined as the intensity value at 280 nm excitation and 350 nm emission.

TOC was measured using a Shimadzu TOC-V-CSH analyser which uses the catalytically-aided platinum 680 °C combustion technique, with auto-sampler TOC-ASI-V. The non-purgeable organic carbon (NPOC) determination method was employed, samples were sparged with 2 M HCl to remove all inorganic carbon prior to combustion, and the resultant NPOC was calculated as a mean of the three valid measurements. The typical error of the analyses was less than 10%.

UV₂₅₄ absorbance is routinely analysed within the water industry as an OM surrogate. In order to compare our fluorescence results to this parameter, UV₂₅₄ absorbance analysis was performed using a Biochem Libra S12 Spectrophotometer, at a wavelength of 254 nm. Samples were filtered through a 0.45 µm membrane to obtain the dissolved fraction,

and analysed with a 1 cm quartz cell which was rinsed with de-ionised (DI) water prior to each analysis.

Data on algal cell counts of three groups diatoms, green, and a separate group for other algae species were also collected from raw water at WTW by Severn Trent Water. Although the algae species analyses were carried out on raw water samples taken on different dates than fluorescence samples (up to a one week difference), this ancillary dataset enabled a better insight into TOC removal efficiency and fluorescence properties relationships. Monthly algal data were provided for the period August 2006 and July 2007.

3. Results

All results are tabulated in Supplementary Table 2.

3.1. Characterising raw water DOM from fluorescence properties

The fluorescence signature of aquatic organic matter has been shown to characterize the degree of hydrophobicity and molecular size on the basis of peak C emission wavelength (Wu et al., 2003); the microbial activity on the basis of peak T intensity (Mopper and Schultz, 1993); and source variations by the ratio of peak C intensity to TOC (Cumberland and Baker, 2007). Therefore, to characterise the raw water organic matter for each site, the mean peak C emission wavelength was plotted against the mean peak T intensity (Fig. 2). Peak C emission wavelength and peak T intensity for each site are shown in Supplementary Table 2. Principal Components Analysis (PCA) results show that, peak C emission wavelength and peak T intensity (Fig. 2) provide the best discrimination of the fluorescence data (strong correlations with the both first and second principal components of opposing signs). The peak C emission wavelength and peak T intensity separate

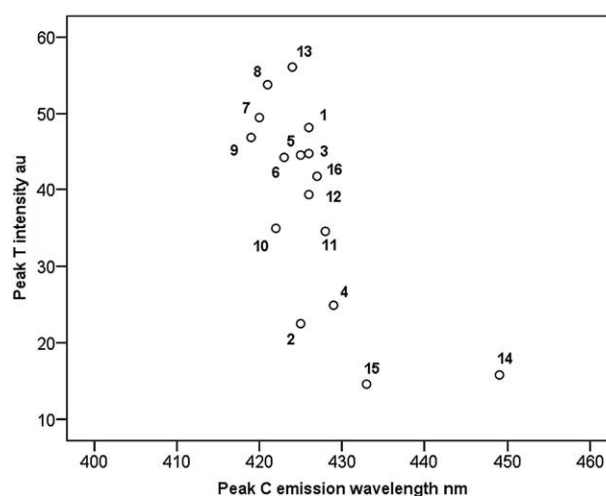


Fig. 2 – Mean peak C emission wavelength (a surrogate for hydrophobicity), vs mean peak T intensity (a surrogate for microbial organic content of raw water), for 16 WTWs.

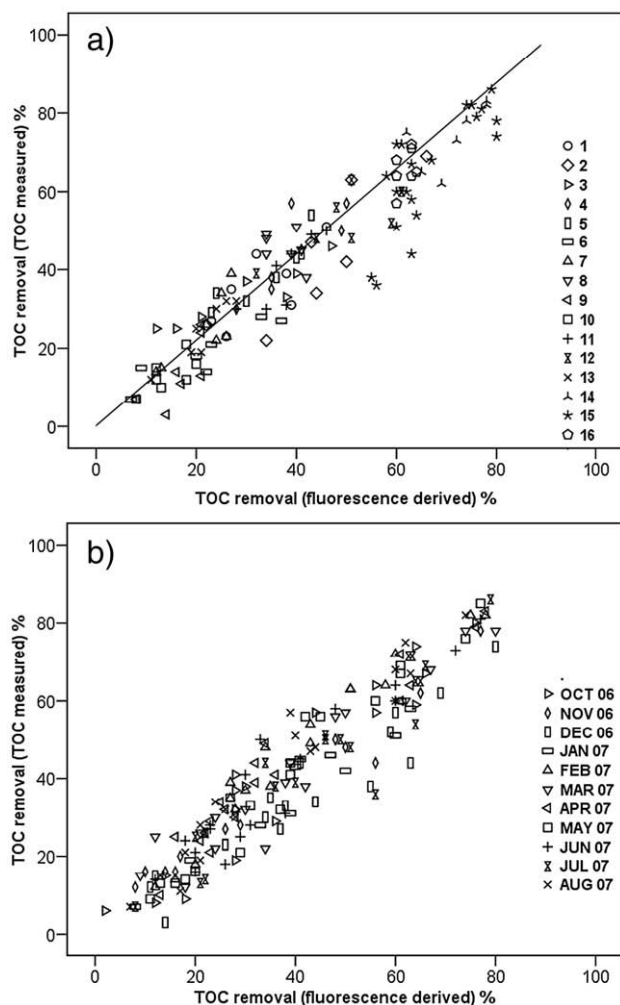


Fig. 3—The relationship between TOC removal derived from direct TOC measurements (y-axis) and from peak C fluorescence intensity (x-axis) a — labelled by site number, c — labelled by sample date.

sites 7, 8, 9, 13 (high microbial and relatively hydrophilic) and 14, 15 (low microbial and relatively hydrophobic) from the rest of the sites. Fig. 2 shows that sites 7, 8 and 13 have the highest peak T intensity; high peak T intensity is also associated with a high variability in peak T.

3.2. TOC removal

Measured TOC removal across the clarification stage (indicating organics removal efficiency) at each site was compared to fluorescence-inferred TOC removal. Fluorescence-inferred TOC removal was calculated in percentage terms from the decrease in OM (i.e. peak C) fluorescence intensity between raw and clarified samples. Fig. 3 demonstrates a strong correlation between measured TOC removal and fluorescence-inferred TOC removal, indicating that the decrease in organic matter fluorescence intensity between raw and clarified water samples can be used as an accurate, yet simple, predictor of TOC removal at WTW. However, the strength of the relationship is site-specific as a result of the different raw

water characteristics. The higher TOC removal corresponds with the predominance of hydrophobic organic matter (sites 14, 15 and 16) whereas for relatively hydrophilic waters the removal is poorer (site 9). Some underestimation of TOC removal prediction can be noticed for winter months (November, December and January), whereas in the summer months the converse effect is observed, which can be attributed to different fluorescence intensity per gramme of carbon.

We also compared fluorescence and UV₂₅₄ absorbance as predictors for TOC removal. For the whole dataset, both peak T intensity ($r=0.65$) and peak C emission wavelength ($r=0.65$) gave a better correlation with TOC removal than UV absorbance ($r=0.55$). In comparison with fluorescence spectroscopy, UV absorbance has been reported as a less selective technique (Marhaba et al., 2003), and prone to the underestimation of the OM samples where low molecular weight fraction is predominant (Matilainen et al., 2002).

4. Discussion

4.1. Comparing DOM character and TOC removal

Organic matter removal and disinfection-by products formation potential depend on the organic matter content and character (Stevens et al., 1976; Chen et al., 2008), which can be derived from fluorescence measurements and inferred from algal count data. Therefore, the relationship between TOC removal and various potential fluorescence predictors and algal counts was investigated further. Three fluorescence properties were selected on the basis of a principal components analysis (data not shown), namely, peak C intensity, peak T intensity and peak C emission wavelength, with strong positive correlation either with PC1 or PC2. Results are

Table 2 – Spatial variation in TOC removal/fluorescence and algae predictors correlation (Pearson's) coefficients (values significant at 0.05 level) (“-” indicates sites where algae species were not counted during the investigation period)

Site	Peak T intensity	Peak C emission wavelength	Peak C intensity	Total algae
1	0.02	0.04	0.41	0.17
2	0.25	0.06	0.81	-
3	0.01	0.05	0.51	-
4	0.05	0.00	0.51	0.27
5	0.53	0.18	0.41	-
6	0.17	0.17	0.37	0.08
7	0.28	0.01	0.01	0.04
8	0.53	0.01	0.56	0.74
9	0.08	0.00	0.00	0.18
10	0.37	0.00	0.11	0.19
11	0.42	0.01	0.43	0.15
12	0.23	0.26	0.39	0.01
13	0.11	0.06	0.14	0.47
14	0.05	0.09	0.86	0.15
15	0.07	0.22	0.43	0.59
16	0.00	0.33	0.06	0.00

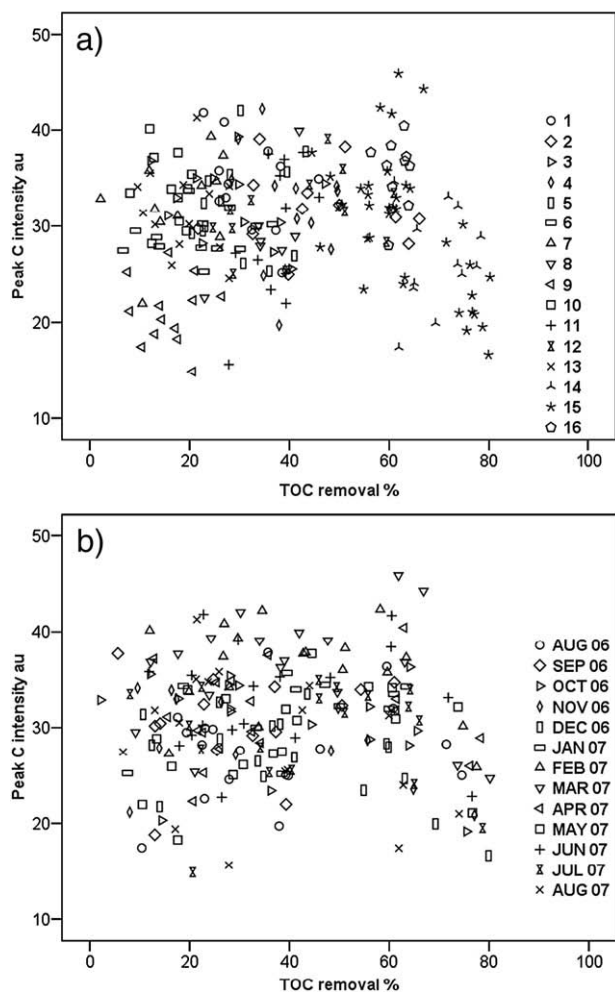


Fig. 4 – Peak C intensity (a — sites, b — months) relationships with TOC removal.

presented for each WTW in Table 2 and monthly in Table 3 (whole dataset analysed on a monthly basis). In general, we show for the first time that the best TOC removal correlation on a site-specific basis was with peak C intensity. For the peak C emission wavelength and peak T intensity, the site-specific correlations with TOC were found to be weaker. However, the monthly correlations with peak T intensity and peak C emission wavelength were significantly stronger than with peak C intensity (Table 3).

Total algae counts (diatoms, green algae and other algae group) also correlated with TOC removal (Tables 2 and 3), but the correlation was significant only for sites 8, 13 and 15 (correlation coefficients 0.74, 0.47 and 0.59), indicating the important role of algae-produced organic matter in TOC at those sites. The TOC removal relationship with particular algae groups was insignificant for most of the sites with the exception of site 8 (correlation coefficient for diatoms 0.78, green algae 0.80 and other algae groups 0.86). It is interesting to note that for these sites the total algae counts are more important TOC removal efficiency predictors than the other fluorescence properties. Nevertheless, the algal relationship

with TOC removal and fluorescence data should be analysed with caution as algal counts data were collected independently of the main fluorescence sampling.

4.1.1. Peak C intensity

Although peak C intensity was found to correlate with TOC removal on a site-specific basis (Table 2), no significant relationship was found between peak C intensity and TOC removal for the whole dataset (Fig. 4a,b). This would appear to suggest that the sites are optimised individually to TOC concentrations and that for the whole dataset the peak C intensity vs TOC removal correlation shows great variability in both TOC concentrations and OM composition between the individual sites. Furthermore, the effect of algae on peak C intensity is interesting, with the highest values of peak C intensity coincident with a summer rise in algae counts for selected sites (e.g. 8, 15).

4.1.2. Peak T intensity

Fig. 5a and b demonstrates a statistically significant linear relationship ($R^2=0.42$, $N=216$) between fluorescence-derived TOC removal and tryptophan-like (peak T) intensity. It can be seen that stable and efficient TOC removal correlates with low peak T intensity, from which we infer a low microbial activity (Cammack et al., 2004; Hudson et al., 2008); whereas low TOC removal corresponds to higher and variable microbial fraction. The outlying data for sites with lower TOC removal values can be attributed to the occurrence of algae: the outliers at lower TOC removal values with peak T intensity of approximately 80 au represent summer (especially August and September) algae peaks as suggested by ancillary data on algae counts. In particular, the extreme outlier at 100, 36 (site 1), illustrates the significant increase in peak T intensity due to high numbers of both green and blue-green algae in August 2006. A similar relationship between peak T intensity and algogenic organic matter has recently been presented by Henderson et al. (2008). The general pattern of TOC removal efficiency correlating with peak T intensity is highly temporally and spatially variable

Table 3 – Temporal variation in TOC removal/fluorescence predictors correlation coefficients (total algae not included due to data scarcity — different dates of the measurements for each site and lack of data for winter months)

Month	Peak T intensity	Peak C emission wavelength	Peak C intensity
AUG 06	0.41	0.56	0.02
SEP 06	0.53	0.29	0.05
OCT 06	0.69	0.49	0.06
NOV 06	0.62	0.47	0.00
DEC 06	0.48	0.32	0.04
JAN 07	0.73	0.09	0.36
FEB 07	0.47	0.31	0.07
MAR 07	0.36	0.44	0.01
APR 07	0.38	0.42	0.00
MAY 07	0.38	0.37	0.00
JUN 07	0.44	0.58	0.00
JUL 07	0.36	0.36	0.00
AUG 07	0.36	0.56	0.05

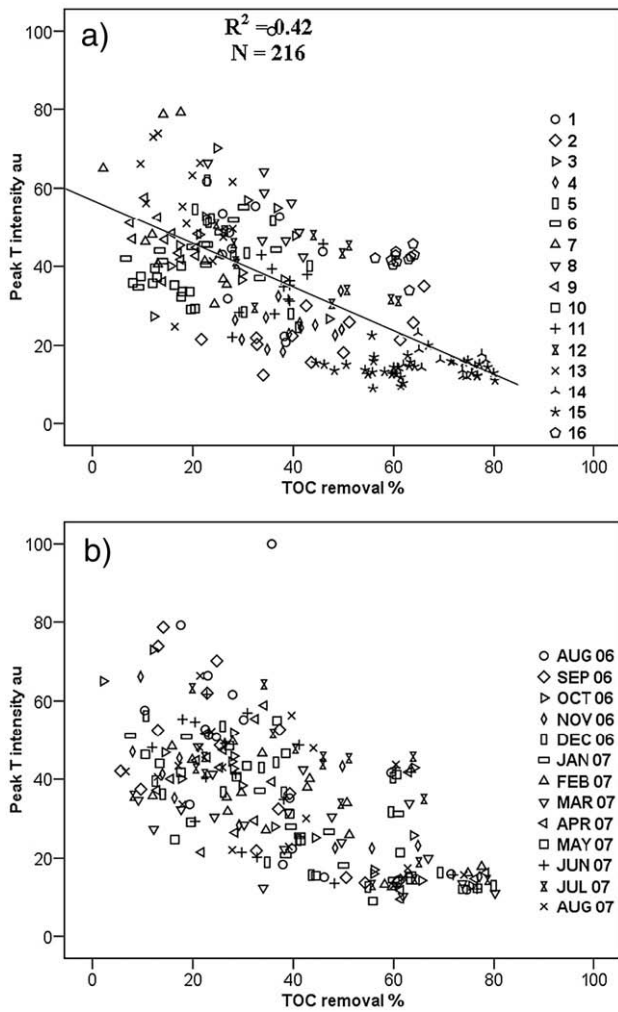


Fig. 5 – Peak T intensity (a — sites, b — months) relationships with TOC removal.

(Fig. 5a,b). A pattern of stable TOC removal and low microbial fraction content characterizes sites with water abstraction from the reservoirs (sites 14, 15, 16). However, in the case of site 15 the variation in TOC removal is higher as a result of high percentage of urban land use in the catchment.

4.1.3. Peak C emission wavelength

Peak C emission wavelength was plotted against overall TOC removal (Fig. 6a and b, $R^2=0.41$; $N=216$). A predominance of the hydrophobic fraction, indicated by higher peak C emission values (Wu et al., 2003; Baker et al., 2008), correlates with stable, high TOC removal, whereas the discernible amplitude of variation in aromaticity characterizes lower TOC removal efficiencies. The changes in the degree of hydrophobicity are greater for reservoir sites (14, 15, 16). At each WTW, the peak C emission varies significantly during the year, indicating seasonal variation in the degree of hydrophobicity. The poorer correlation of TOC removal with peak C emission wavelength during the winter months can be related to poorer optimisation of works performance, regardless of the winter predominance of more hydrophobic, easier to remove organic matter.

4.1.4. Algae

In the current study it was found that the correlations between peak C emission, peak C intensity, peak T intensity, TOC removal and total algal counts for the whole dataset are weaker when compared to site-specific correlations (Table 4). For a number of sites, a strong relationship was observed between peak T fluorescence and diatoms (sites 1, 6, 7, 10, 15), between peak T fluorescence and green algae (sites 6, 7, 8, 9), between peak T fluorescence and other algae taxa (sites 1, 4, 8), and between peak T fluorescence and total algae (sites 6, 7, 9). A significant correlation with peak C intensity existed for diatoms (sites 6, 8, 10), other algae group (sites 1, 8, 10), and total algae (sites 1, 6, 8, 9, 10, 15). The results obtained show that sites with high concentrations of green algae organic matter can significantly contribute to peak T fluorescence, in agreement with the results of Nguyen et al. (2005). However, the diatoms and the composite group of other algae species exhibit more complex fluorescence patterns, with strong correlations with peak T and peak C fluorescence intensities, showing that at some sites algae may significantly contribute to fluorescence intensities in both of these regions.

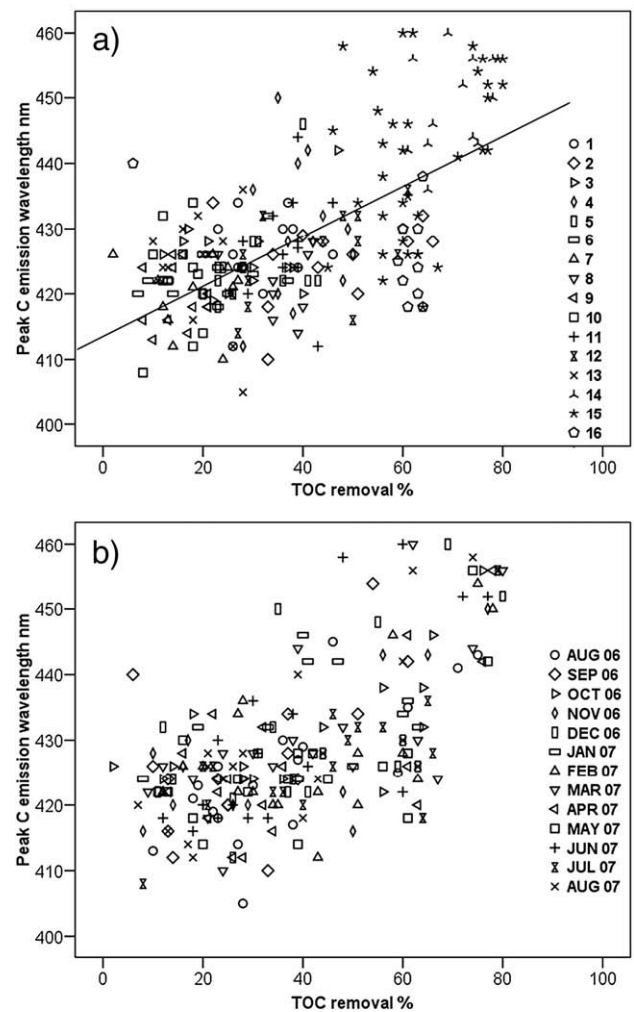


Fig. 6 – Peak C emission wavelength (a — sites, b — months) relationships with TOC removal (tabulated R^2 values are summarized in Table 2).

Table 4 – Correlation coefficients for relationships between TOC removal and fluorescence characteristics with main algae groups (algal data not available for sites 2, 3 and 5)

Site	TOC removal				Peak T intensity				Peak C emission wavelength				Peak C intensity			
	Diatoms		Other		Diatoms		Other		Diatoms		Other		Diatoms		Other	
	Green	Total	Green	Total	Green	Total	Green	Total	Green	Total	Green	Total	Green	Total	Green	Total
1	0.00	0.02	0.35	0.02	0.36	0.04	0.93	0.09	0.61	0.35	0.05	0.81	0.23	0.34	0.36	0.40
4	0.25	0.27	0.08	0.08	0.04	0.09	0.40	0.09	0.18	0.15	0.06	0.03	0.20	0.02	0.10	0.10
6	0.09	0.08	0.00	0.04	0.40	0.44	0.03	0.44	0.13	0.04	0.07	0.04	0.51	0.00	0.03	0.42
7	0.00	0.04	0.05	0.04	0.36	0.38	0.05	0.38	0.00	0.00	0.51	0.01	0.02	0.00	0.30	0.06
8	0.78	0.74	0.86	0.74	0.33	0.31	0.38	0.31	0.31	0.34	0.22	0.37	0.74	0.24	0.80	0.72
9	0.37	0.18	0.26	0.18	0.08	0.58	0.00	0.58	0.11	0.28	0.10	0.34	0.06	0.25	0.00	0.49
10	0.32	0.19	0.00	0.19	0.72	0.07	0.10	0.07	0.21	0.00	0.28	0.00	0.64	0.38	0.46	0.46
11	0.11	0.15	0.07	0.15	0.00	0.01	0.06	0.01	0.13	0.02	0.03	0.01	0.19	0.12	0.15	0.10
12	0.00	0.01	0.00	0.01	0.31	0.29	0.14	0.29	0.29	0.12	0.20	0.37	0.21	0.1	0.05	0.02
13	0.05	0.47	0.00	0.47	0.05	0.03	0.02	0.03	0.03	0.04	0.08	0.47	0.02	0.01	0.05	0.05
14	0.12	0.15	0.00	0.15	0.08	0.10	0.30	0.10	0.00	0.03	0.13	0.04	0.14	0.02	0.04	0.14
15	0.18	0.05	0.05	0.05	0.51	0.00	0.04	0.00	0.08	0.13	0.02	0.80	0.00	0.02	0.03	0.63
16	0.04	0.00	0.29	0.00	0.00	0.00	0.00	0.00	0.19	0.24	0.07	0.16	0.04	0.01	0.01	0.04

4.2. TOC removal prediction

TOC is an accepted indicator of THM precursor material. Considering the need to infer and minimise THM levels in treated water, previous work has used a variety of approaches to optimise treatment and infer TOC removal at WTW. These approaches include the standard jar test (Uyak and Toroz, 2006), ultra violet absorbance (Banks and Wilson, 2002; Iriarte-Velasco et al., 2006) and zeta potential measurements (Sharp et al., 2006). However, each of these approaches has limitations in precision or ease of use. For example, Cheng et al. (2004) showed that fluorescence is more stable than UV in detecting DOC removal from reservoir water, whilst standard jar tests such as those undertaken by Uyak and Toroz (2006), take in the region of 20 min to perform and do not, in isolation, immediately produce data from which process knowledge can be gained. Therefore, to address these limitations, work was undertaken to assess the potential for using fluorescence spectroscopy to predict TOC removal and so infer likely THM concentrations. A stepwise regression approach was employed to determine the statistically significant subset of fluorescence variables and their order of importance in predicting TOC removal efficiency. Three regression submodels were obtained for different numbers of incorporated independent variables:

$$\text{TOC removal (\%)} = 65.96 - (0.77 \times T_{\text{int}}) \quad (R = 0.64) \tag{1}$$

$$\text{TOC removal (\%)} = -244.09 - (0.50 \times T_{\text{int}}) + (0.70 \times C_{\text{em}}) \quad (R = 0.73) \tag{2}$$

$$\text{TOC removal (\%)} = -206.71 - (0.68 \times T_{\text{int}}) + (0.59 \times C_{\text{em}}) + (0.11 \times C_{\text{int}}) \quad (R = 0.77) \tag{3}$$

where

- T_{int} peak T intensity
- C_{em} peak C emission wavelength
- C_{int} peak C intensity

The results of the regression analyses were validated by conducting a 75/25% cross-validation, using the random number seed. The 75% training sample replicated the pattern of statistical significance obtained for the whole dataset. The correlation coefficient for the validation sample was slightly higher than for the training samples (0.76 compared to 0.78) indicating the models' effectiveness in TOC removal prediction based on the set of fluorescence properties.

Whilst the stepwise model presented above does not explain site-specific TOC removal, it does provide a tool for general TOC removal prediction. There exists the need for a technique which can be used accurately and quickly at a WTW and which will give a satisfactory indication of the THM concentration leaving the works (Banks and Wilson, 2002). The stepwise model is extremely useful in this regard as it allows works' managers to predict the mean works performance derived from the raw water organic matter fluorescence properties and therefore can be indicative of the THM formation potential. This is a significant advantage over

other methods which rely on lengthier, more complex analysis of treated or partially-treated water.

UV₂₅₄ ultraviolet absorbance at 254 nm
WTW water treatment works

5. Conclusions

1. The successful application of fluorescence spectroscopy to determine TOC removal at WTW has been presented.
2. For the 12 months of fluorescence data based on raw and clarified water properties from 16 surface WTWs located in the West Midlands region of the UK, the correlation between directly measured TOC removal and fluorescence-derived TOC removal was significantly high (correlation coefficient value of $R^2=0.90$), indicating a strong linear, first-order relationship between the variables.
3. The results show that measurement of fluorescence peak C intensity might be utilized for THM formation prediction, as the fluorescence property (peak C fluorescence intensity) correlates with the total amount of organic precursors.
4. Using the entire 12 month dataset, a stepwise regression model demonstrated that freshwater OM peak T intensity, peak C emission wavelength and peak C intensity can be used in combination to predict TOC removal ($r=0.77$).
5. It was apparent that the correlation coefficients between peak T intensity and peak C emission wavelength and TOC removal are less significant for the site-specific correlations than for the full dataset.
6. For several sites a significant contribution of different algae species to peak C and peak T fluorescence was found.
7. The simplicity, sensitivity, speed of analysis and low cost, combined with potential for incorporation into on-line monitoring systems mean that fluorescence spectroscopy offers a robust analytical technique to be used in conjunction with, or in place of, other approaches to OM characterisation and THM formation prediction.

5. Notation

BOD	biochemical oxygen demand
C _{em}	peak C emission wavelength (nm)
C _{int}	peak C fluorescence intensity (au)
DBPs	disinfection by-products
DOC	dissolved organic carbon
DOM	dissolved organic matter
EEM	excitation–emission matrix
HAAs	haloacetic acids
HANs	haloacetonitriles
NOM	natural organic matter
NPOC	non-purgable organic carbon
OM	organic matter
PCA	principal components analysis
PC1	first principal component
PC2	second principal component
T _{int}	peak T fluorescence intensity (au)
THM	trihalomethanes
TOC	total organic carbon

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.scitotenv.2008.11.013](https://doi.org/10.1016/j.scitotenv.2008.11.013).

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