Water and Environment Journal
Promoting Sustainable Solutions

Water and Environment Journal. Print ISSN 1747-6585

Comparison of river and canal water dissolved organic matter fluorescence within an urbanised catchment

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Keywords
canal water; dissolved organic matter; fluorescence spectroscopy; urban river.

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doi:10.1111/wej.12062

Abstract

Recently, growing interest has been shown in the study of canal water quality, yet no research using continuous fluorescence monitoring to characterise dissolved organic matter (DOM) has been performed. This paper evaluated DOM characteristics at hourly resolution. A comparison was made between canal and nearby urban river fluorescence spectra, to emphasise the specific nature of canal water DOM. Results showed that canal water had a significant proportion of microbially derived DOM, while the urban river had a greater proportion of terrestrially derived fractions. The microbial character of canal water DOM originated from the low flow of water, the nutrients predominance and continuous DOM processing. Hence, DOM fluorescence is invariant over a timescale of days, and recreational navigation and precipitation events have no major influence on DOM characteristics. Our results are expected to be applicable to future research on highly regulated freshwater systems for DOM quantity estimation or for water quality models.

Introduction

In the United Kingdom, there are over 3000 km of canals built, starting in 1757 AD, to connect urban and industrial centres with major ports (Harrison & Sutton 2003). In the last decades, canals were turned to leisure and commercial purposes (Neal *et al*. 2006; Eaton 1999). Canals are aquatic systems with special features: extremely low water flow, which under certain meteorological conditions can even change its direction, generating high susceptibility to eutrophication, increasing levels of sediments and slow diffusion of pollutants (Swanson *et al*. 2004). Some of the most important external factors that influence the canal water quality can be specified: industry, precipitation, surface runoff, stormwater drains, groundwater and navigation. Since 1990, periodic dredging of the canal bed is performed in the United Kingdom to remove the excess sediments and reduce the contamination accumulated mostly in the sediments during the industrial revolution (Bromhead & Beckwith 1994; Swanson *et al*. 2004; Bligh *et al*. 2007).

During the last decades, fluorescence spectroscopy has become a promising tool for water quality detection, by the analysis of the ubiquitous fraction, dissolved organic matter (DOM). The fluorescent fractions of DOM that can be generally identified in water systems are: humic substances, indicators of the terrestrial inputs and the amino acid fraction (represented by the fluorescent amino acids, tryptophan and tyrosine), which are indicators of microbial activity. The technique presents numerous advantages in DOM characterisation, including rapid analysis (~1 min, depending on the set up parameters), high sensitivity and selectivity, little sample pretreatment and small quantities of sample (Hudson *et al*. 2007; Huo *et al*. 2009). Furthermore, good correlation has been found between DOM fluorescence data and water quality parameters like total organic carbon (TOC) (Cumberland & Baker 2007) and biological oxygen demand (Hudson *et al*. 2008). In recent studies, fluorescence spectroscopy has been applied to real-time monitoring of river water (Spencer *et al*. 2007; Carstea *et al*. 2009, 2010; Downing *et al*. 2009). These studies have shown that DOM fluorescence exhibits rapid (hourly to diurnal) variations, depending on the river type, and that are highly influenced by river discharge, and the amount and intensity precipitation. No such studies have been made so far, with fluorescence spectroscopy, to investigate the canal water organic carbon properties at daily scale, which are important for an accurate understanding of the carbon cycle in the water system (Cole *et al*. 2007). With highly regulated flow, analysis of canal DOM properties would contrast previous studies, and be relevant to our understanding of DOM in other regulated systems. Therefore, the purpose of this study was to evaluate the properties of DOM, using fluorescence, at hourly resolution.

Canal water samples, from the Worcester and Birmingham Canal (WBC), were compared with samples from an urban river, Bourn Brook, Birmingham, UK, in order to obtain a better understanding of DOM characteristics. Furthermore, the influence of navigation on the WBC organic matter character and concentration has been assessed.

Methodology

Samples were collected from the WBC (Fig. 1), which is 48.3 km long and passes through a large variety of landscapes, from rural to urban, between Worcester (from Severn River) and Birmingham. The canal water is supplied by river-fed reservoirs, situated at regular distances.

The experiment was divided into two categories: firstly, continuous monitoring and secondly, evaluation of the impact of navigation on water quality. During the continuous monitoring period, a very limited number of boats passed on the canal, so the impact of navigation could not be assessed. Therefore, the second part of the experiment was elaborated to evaluate the changes in DOM components after the passage of boats.

Two autosamplers were set on the WBC bank to collect water from the bottom, approximately 20 cm above the canal bed, and from the top, 20 cm under the surface. Sample bottles were washed with HCl 10% and rinsed with deionised water, previous to the collection. For the first category of measurements, water sampling was performed at hourly frequency for 2 weeks, from 28 October to 11 November 2008. The second set of samples was collected over a period of 3 days, 12th–14th of November. Water was sampled every 5 min, for 1 h, starting with 5 min before the boat arrived at the point of collection. Also, for comparison, 1-h water collection was performed when no boats passed.

Bourn Brook water samples were collected, in November 2007, at hourly frequency (Carstea *et al*. 2009) using the same type of autosampler as for WBC water sampling. Bourn Brook is a small urban river, with a catchment area of 27.91 km^2, flowing within the same region as WBC (Fig. 1). The river receives water from the local urbanised catchment, which includes discharges from storm sewer systems and contained sewer overflows (Carstea *et al*. 2010). The Bourn Brook and WBC have similar cross-sectional area, differing mainly in water depth and discharge.

Fluorescence spectra, for both WBC and Bourn Brook campaigns, were recorded with a Varian Cary Eclipse spectrofluorometer (Agilent Technologies, Mulgrave, Victoria, Australia), using the following settings: excitation wavelength 200–400 nm with a step of 5 nm, emission wavelength 280–500 nm with steps of 2 nm, excitation and emission slit widths 5 nm, measurement temperature 20°C, 725 V photomultiplier tube voltage, a scan rate of 9600 nm/min and an integration time of 0.0125 s. The Varian Cary Eclipse spectrofluorometer has a wavelength accuracy of ±1.5 nm and reproducibility of ±0.2 nm. The sensitivity of the system, measured with respect to the Raman band of water, is > 750 : 1 root mean square, at 350 nm excitation wavelength. In order to check the instrument stability, the water

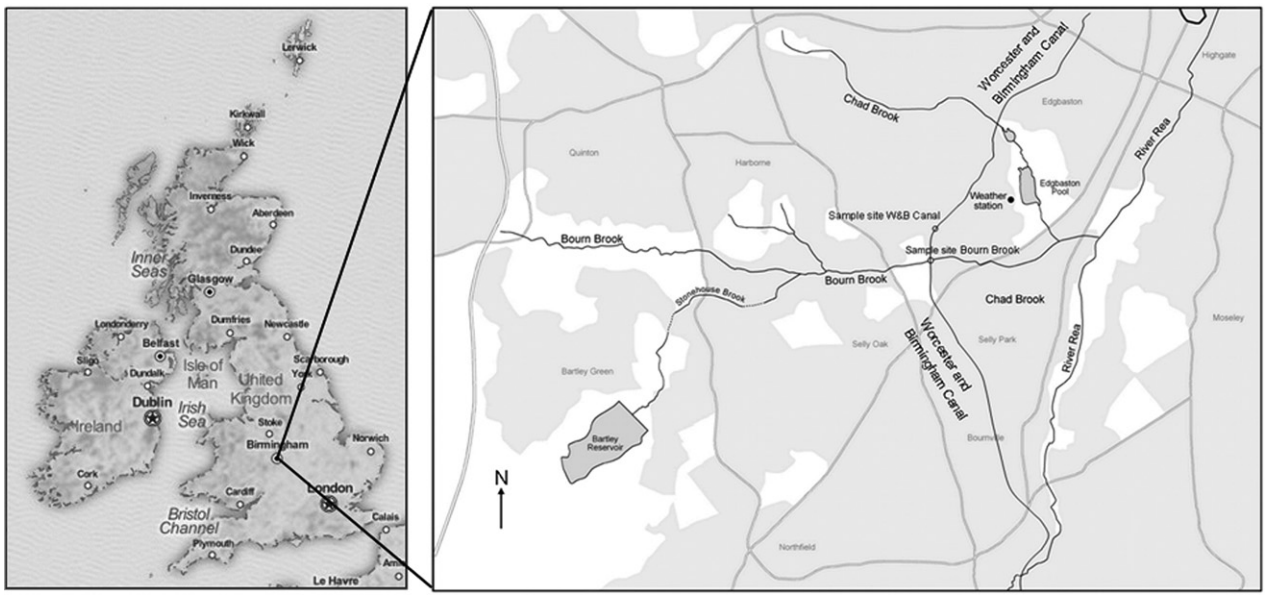

Fig. 1. Map of Worcester and Birmingham Canal and the Bourn Brook (Map of UK adapted from © OpenStreetMap contributors, CC BY-SA, Open Database License 2010). black lines – waterways, small empty circles – WBC and Bourn Brook sampling sites, grey lines – roads.

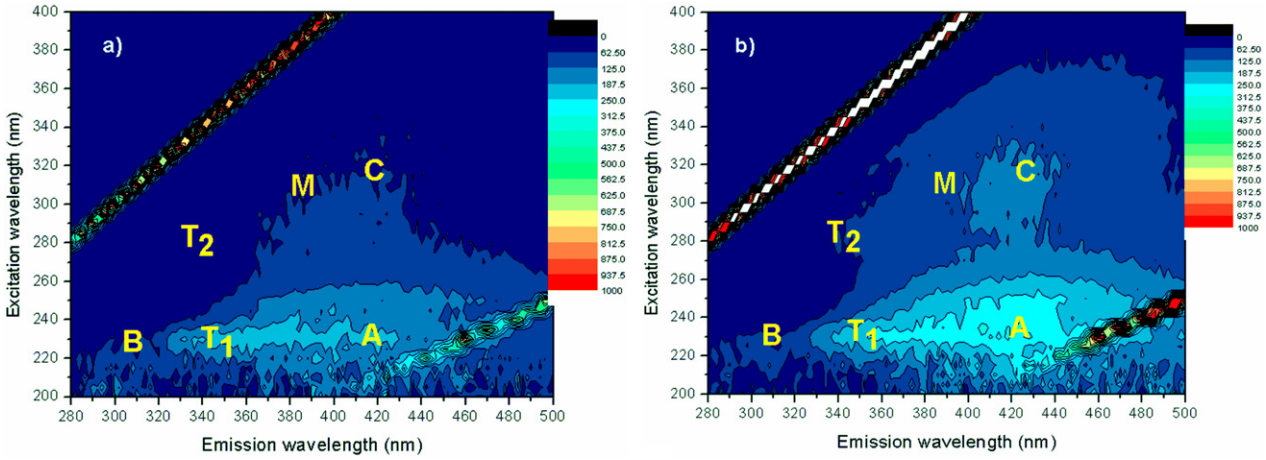

Fig. 2. Typical fluorescence excitation–emission matrix for (a) WBC water sample and (b) Bourn Brook presenting peaks T_1 and T_2 for tryptophan, peak B for tyrosine, peaks A and C for the humic substances and peak M for reprocessed DOM.

Raman peak was recorded on a daily basis, before every set of measurements. All fluorescence intensity values have been adjusted to a Raman reference value of 20 arbitrary units. TOC was measured using a Shimadzu TOC-Vcpn analyser (Shimadzu Corporation, Tokyo, Japan), and conductivity and pH were measured with an Ultrameter II (Myron L Company, Carlsbad, CA, USA).

The fluorescence of DOM is characterised by designated fluorescence peaks A, C, M, B and T (Coble 1996), and more recently by PARAFAC components (e.g. Stedmon *et al*. 2003; Murphy *et al*. 2008; Ishii & Boyer 2012). The use of this peak labelling nomenclature avoids the need to designate an individual source or process to a particular part of a fluorescence excitation–emission matrix (EEM). That being said, our current understanding is that peaks T and B relate directly to microbial biomass (Elliott *et al*. 2006; Cumberland *et al*. 2012) and correlates with biochemical oxygen demand (Hudson *et al*. 2008). Peaks C and M are increasingly attributed to microbially and chemically reprocessed DOM, whereas peak A is likely to have a primary terrestrial source (Ishii & Boyer 2012). The excitation/emission wavelength pairs are specific to each fraction and are T_1 and T_2 for tryptophan ($\lambda_{excitation}/\lambda_{emission}$ *~225/~350 nm* – T_1, $\lambda_{excitation}/\lambda_{emission}$ *~280/~350 nm* – T_2), B for tyrosine ($\lambda_{excitation}/\lambda_{emission}$ *~225/~305 nm*), A and C for humic substances ($\lambda_{excitation}/\lambda_{emission}$ *~225/400–500 nm* corresponding to peak A, $\lambda_{excitation}/\lambda_{emission}$ *300–350/400–500 nm* corresponding to peak C) and M for reprocessed DOM ($\lambda_{excitation}/\lambda_{emission}$ *310–320/380–420 nm*). An example of EEMs for WBC and Bourn Brook water samples is given in Fig. 2.

In total, 333 samples, collected from WBC, and 335 samples from Bourn Brook were measured for fluorescence, pH, conductivity and TOC. In the case of WBC water fluorescence analysis, both DOM components, protein-like (peaks B, T_1 and T_2) and humic-like (peaks A and C), were analysed. Peak T_2 was considered negligible in the Bourn Brook fluorescence spectra because of low-recorded values, relative to the other peaks (Carstea *et al*. 2009). Statistical analysis was made using the Excel tools for Student's *t*-test.

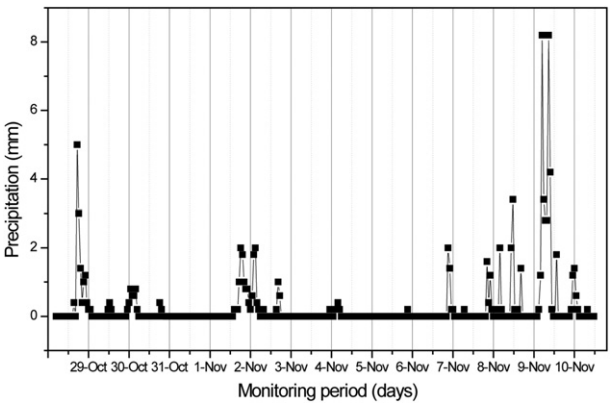

Fig. 3. Daily recordings for precipitation during the experimental period.

Results and discussion

Continuous WBC water monitoring

The experimental period was characterised by minor rain events, at almost daily basis. The highest quantity of rain did not exceed 8 mm, which was recorded on 9th of November (Fig. 3). Measurements revealed great consistency between surface and bottom samples at both water quality standard parameters and fluorescence spectroscopy. The Student's *t*-test indicated no significant differences between the two groups of samples (*P* values of 0.19 – peak T_1, 0.15 – peak T_2, 0.40 – peak A, 0.84 – peak C, 0.56 – peak B and 0.34 – TOC). Very little variation was seen at pH values, ranging from 6.7 to 8.4 in the case of surface samples, and from 7.6 to 8.2 for

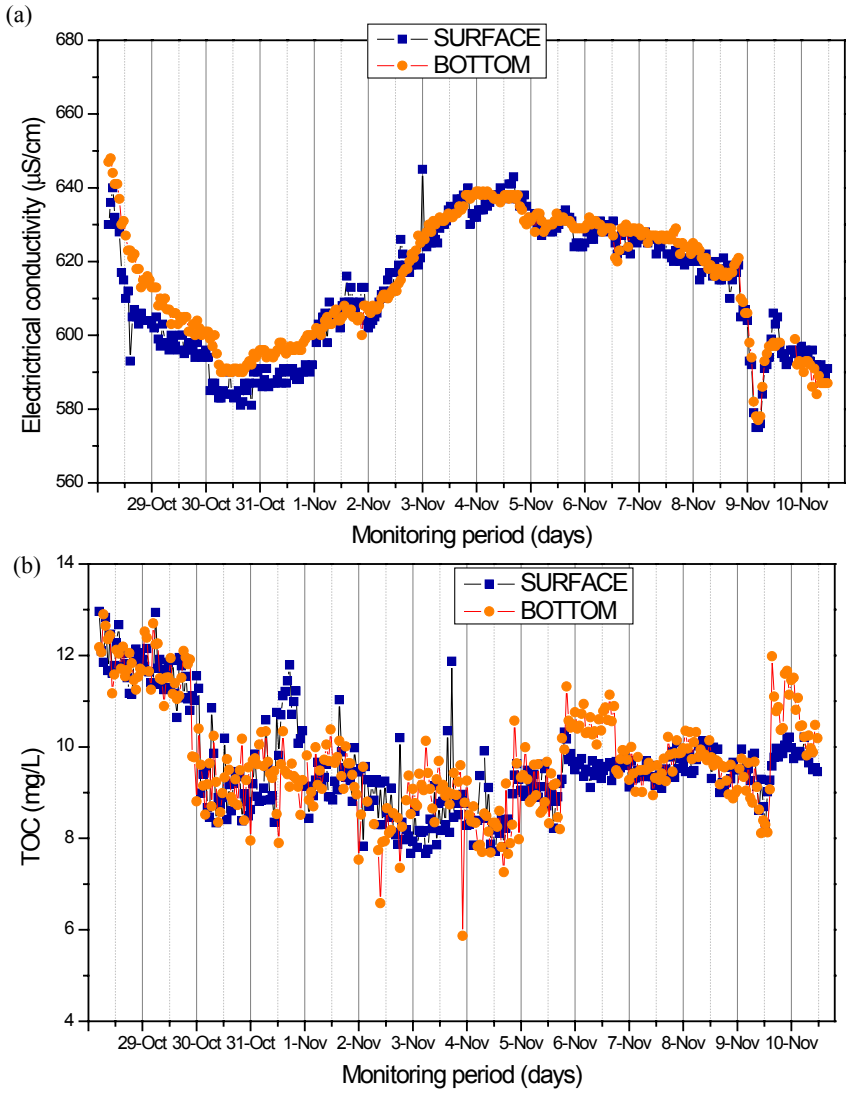

Fig. 4. Hourly monitoring of the standard parameters: (a) conductivity and (b) TOC.

bottom samples. Conductivity had relatively constant values, from 580 µS/cm to 650 µS/cm (Fig. 4a), indicative of the well-mixed and slow-moving canal water. The rain event, on 9th of November, generated a sudden drop in conductivity, followed by an increase to the initial values. TOC showed decreasing values from 13 mg/L, in the first day of sampling, to 6 mg/L on 4th of November, coinciding with the day when conductivity peak was recorded. After this day, TOC values increased to almost 12 mg/L until the last day of the experiment (Fig. 4b).

Fluorescence measurements revealed little variation, as shown in Fig. 5, for all DOM components. The slight variation of fluorescence intensity was most likely of instrumental origin. However, a slight increasing trend was noticed at DOM fluorescence peaks. Peak T_1 showed slightly increasing values between 2nd of November and 5th of November. Humic-like component, peak A, presented a small trend with a time span of 5 days. Peak C, the second humic-like component, showed a similar trend to peak A. Compared with samples collected from the surface, bottom samples showed little variation at peaks A, C, T_2 and B, peak T_1 presenting minor increasing values from 31st of October to 7th of November.

Navigation influence study

In total, 12 samples for each set of measurements were collected. As in the case of continuous monitoring, there seemed to be a certain degree of consistency in the results of the surface and bottom samples. No significant differences were observed between the values recorded after the passage of boats and the ones registered when boats passed. Student's *t*-test showed *P* values of 0.39 – peak T_1,

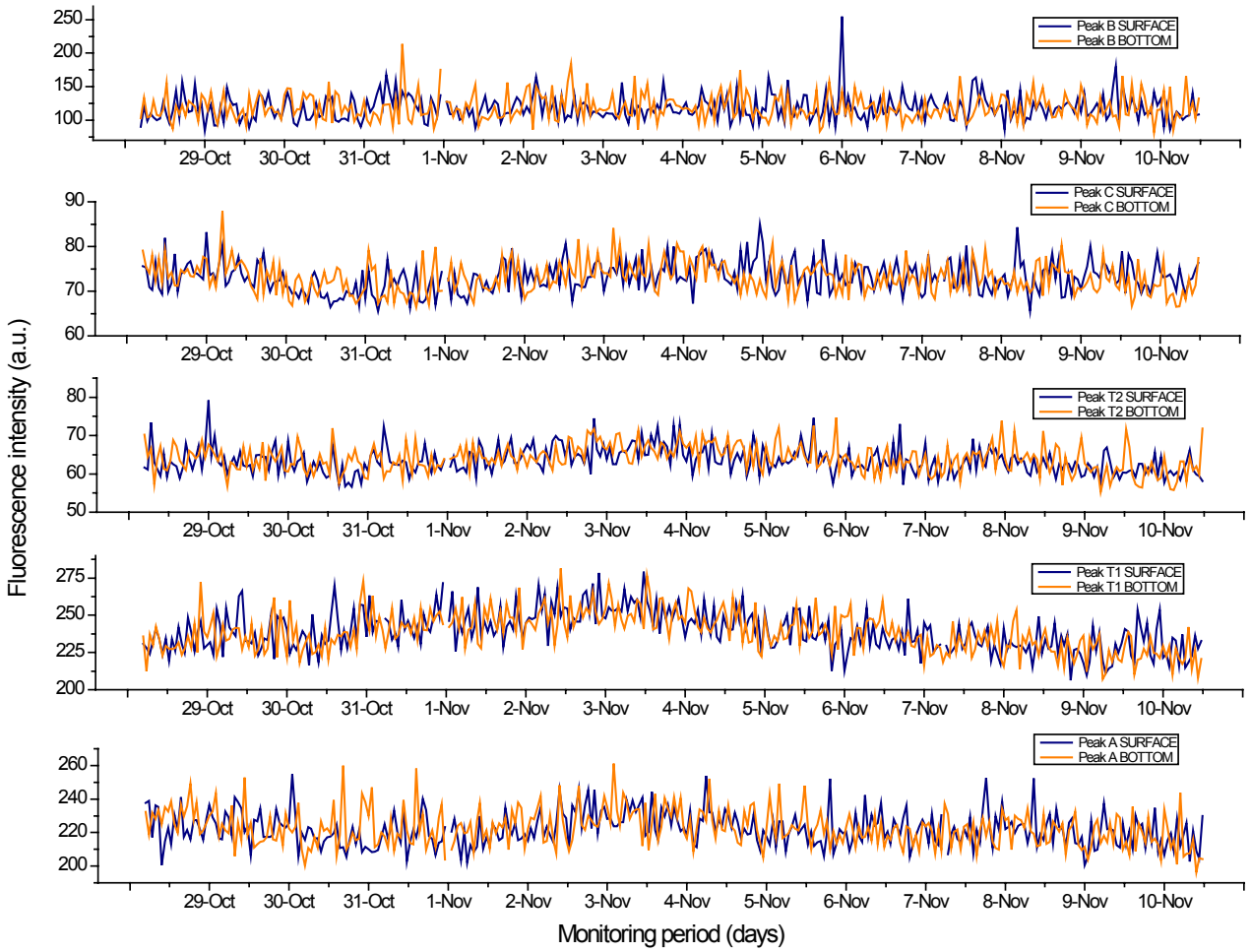

Fig. 5. Continuous monitoring of the surface and bottom WBC water quality with fluorescence spectroscopy.

0.56 – peak T_2, 0.65 – peak A, 0.32 – peak C, 0.65 – peak B, 0.27 – conductivity and 0.31 – TOC. The standard parameters, conductivity and TOC showed no influence from boats, as can be observed in Fig. 6(a) and (b).

Similar results were obtained with the fluorescence spectra, no impact being observed from boats on DOM components (Fig. 6c,d). Consequently, it was assumed that because canal water was well mixed, individual boats had a very low impact on DOM characteristics. Further studies are required in order to assess the influence of navigation on canal water quality, over a large period of time to account for seasonal variations or for periods with intense recreational navigation.

Comparison of DOM fluorescence characteristics between WBC and Bourn Brook

In order to obtain a better understanding of the peculiarities of DOM components in WBC water samples, WBC water quality data were compared with Bourn Brook data, which were recorded 1 year before the WBC experiment. Fluorescence EEMs of the Bourn Brook samples were characterised by higher quantities of terrestrial component compared with the microbial fraction (Carstea *et al*. 2009), while WBC samples presented an opposite proportion between components (Fig. 2). The fluorescence fingerprints, with regard to peak shape and location, were similar to the ones reported by Baker *et al*. (2007) and Seredynska-Sobecka *et al*. (2007). The peaks intensity was almost the same, compared with their results, taking into account the seasonal changes in DOM characteristics. The fluorescence spectra of the Bourn Brook samples showed the features of a natural urban river. Therefore, it was of particular interest to identify the dissimilarities, in the variation and characteristics of DOM components, between WBC and Bourn Brook water samples. In order to better assess the differences in variability of DOM, the mean values and standard deviations were calculated for 24 h fluorescence datasets, on WBC and Bourn Brook samples. Table 1 presents high standard deviation values at all peaks, except for peak B which presented low intensity values and was influenced by noise. The highest differences

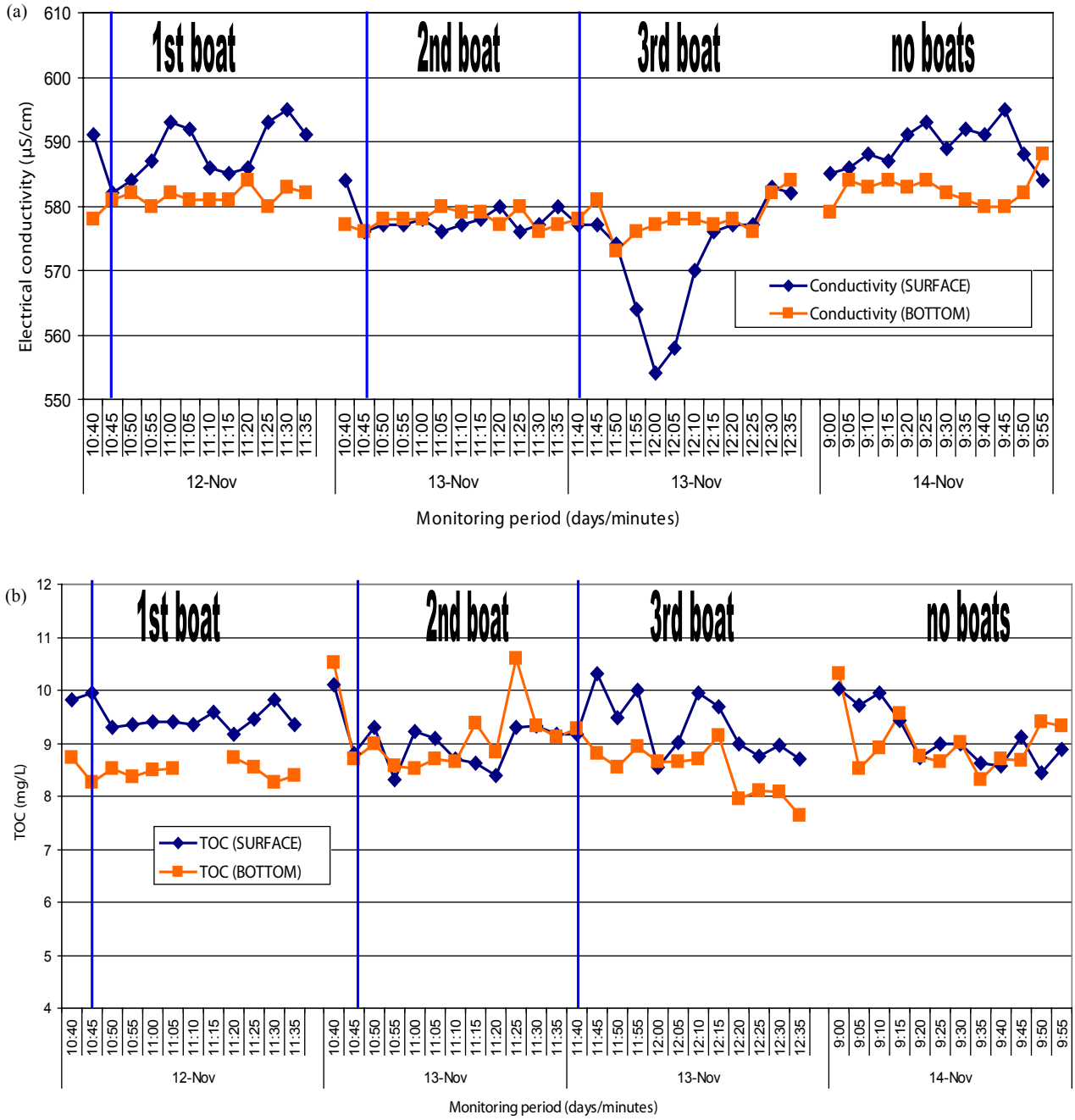

Fig. 6. Evaluation of the navigation influence on (a) conductivity, (b) TOC and DOM fluorescence for (c) surface samples and (d) bottom samples. The blue vertical lines indicate the passing of the boat.

were seen at peak C and conductivity, seeming more stable in WBC water samples compared with the Bourn Brook.

Distinction between the fluorescence fingerprints of the two water systems was also made using fluorescence indices or ratios: humification index (HIX), biological index (BIX) and T/C ratio. HIX was initiated by Zsolnay *et al*. (1999) to evaluate the humification degree of soil, but the index was later applied in water studies, as well (e.g. Ohno 2002; Huguet *et al*. 2009; Ghervase *et al*. 2010). The parameter was calculated based on Eq. (1):

$$HIX = \frac{\sum F_{300} - F_{345}}{\sum F_{435} - F_{480}} \quad (1)$$

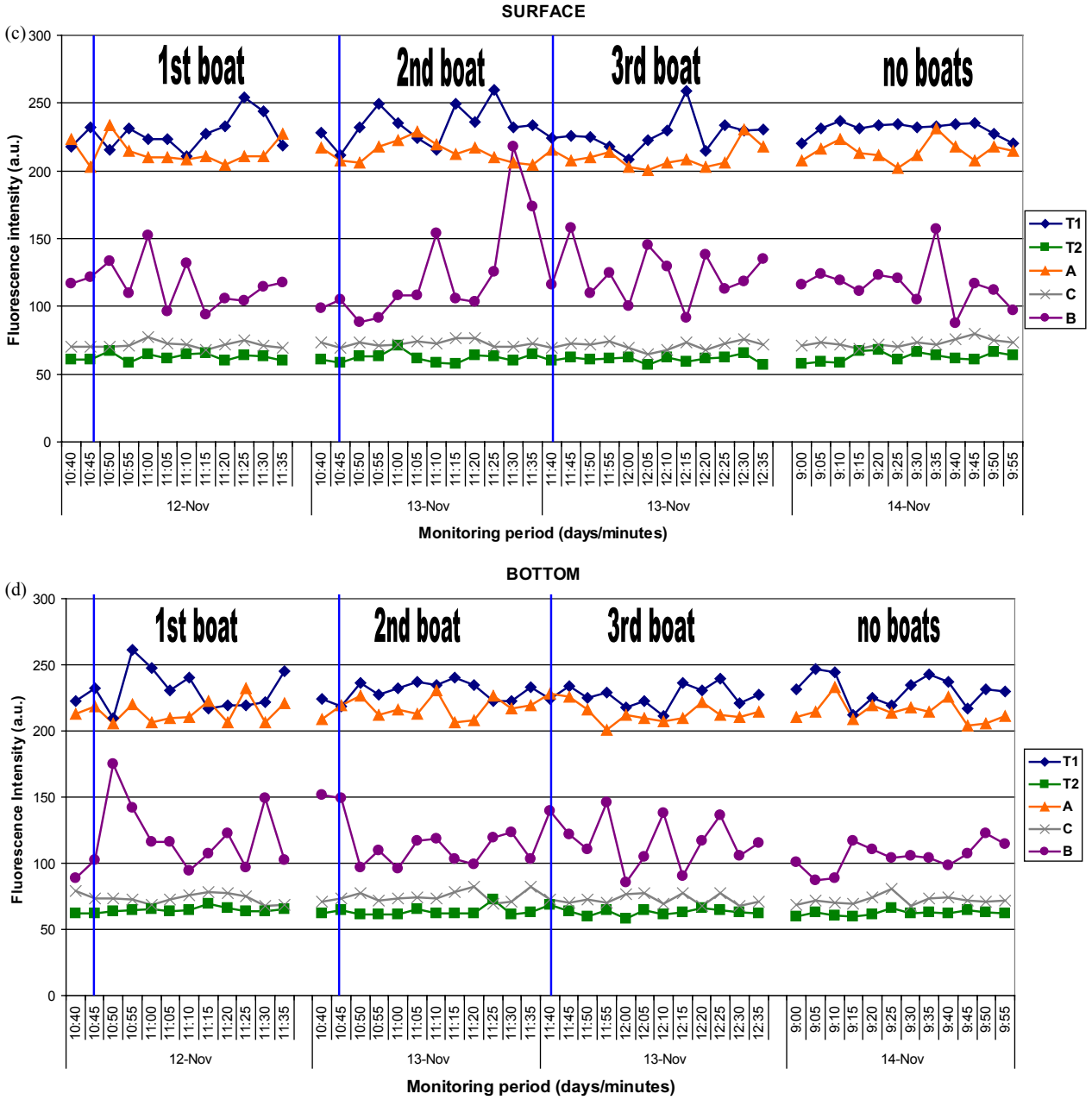

Fig. 6. Continued

where: $F_{300} - F_{345}$ and $F_{435} - F_{480}$ represent the fluorescence intensity between the specified ranges at excitation wavelength 254 nm. Based on the classification given by Huguet *et al*. (2009), Bourn Brook samples had an important terrestrial character and weak recent microbially derived component, while the WBC sample, both surface and bottom, had a weak terrestrial character, but an important microbially derived fraction (Fig. 7). BIX, developed by Huguet *et al*. (2009), focused on the recent autochthonous contribution, estimating the component strength in each fluorescence spectrum. BIX was calculated as the ratio between the fluorescence intensity at 380 nm and 430 nm with excitation wavelength at 310 nm. In the present case, a similar result, as for HIX, was obtained showing that WBC samples had a strong microbially derived component and Bourn Brook samples only an intermediate quantity of the

Table 1 Mean value and standard deviation calculated for 24 h fluorescence data sets, on WBC surface and bottom samples and Bourn Brook samples

Analysis day	Peak T1 Intensity (a.u.)	Peak A Intensity (a.u.)	Peak C Intensity (a.u.)	Peak B Intensity (a.u.)	Conductivity (μS/cm)	TOC (mg/L)
WBC surface samples						
Day 1 surface	232 ± 8	225 ± 10	74 ± 4	115 ± 19	613 ± 13	11.98 ± 0.45
Day 1 bottom	234 ± 12	231 ± 8	75 ± 2	118 ± 16	625 ± 12	11.96 ± 0.46
Day 2 surface	240 ± 13	226 ± 10	74 ± 3	115 ± 18	597 ± 2	11.47 ± 0.48
Day 2 bottom	236 ± 12	221 ± 10	74 ± 4	117 ± 16	604 ± 3	11.32 ± 0.89
Day 3 surface	238 ± 13	216 ± 6	70 ± 2	111 ± 15	585 ± 3	9.07 ± 0.62
Day 3 bottom	235 ± 12	222 ± 14	71 ± 2	121 ± 18	593 ± 3	9.14 ± 0.57
Day 4 surface	250 ± 23	219 ± 10	71 ± 3	129 ± 18	589 ± 2	10.05 ± 1.01
Day 4 bottom	244 ± 8	222 ± 13	71 ± 4	118 ± 29	597 ± 2	9.45 ± 0.57
Day 5 surface	245 ± 11	218 ± 8	72 ± 3	114 ± 12	607 ± 5	9.32 ± 0.52
Day 5 bottom	247 ± 11	223 ± 9	73 ± 3	115 ± 17	604 ± 2	9.54 ± 0.44
Day 6 surface	252 ± 11	227 ± 11	73 ± 3	120 ± 16	614 ± 7	8.80 ± 0.65
Day 6 bottom	249 ± 12	225 ± 11	73 ± 3	129 ± 24	613 ± 5	7.19 ± 1.97
Day 7 surface	256 ± 10	230 ± 8	74 ± 3	116 ± 15	631 ± 7	8.49 ± 0.92
Day 7 bottom	252 ± 11	232 ± 11	75 ± 3	120 ± 19	631 ± 3	9.09 ± 0.39
Day 8 surface	247 ± 9	226 ± 9	75 ± 3	118 ± 15	636 ± 3	7.64 ± 1.96
Day 8 bottom	248 ± 11	226 ± 10	75 ± 3	123 ± 19	638 ± 1	8.21 ± 0.75
Day 9 surface	241 ± 10	219 ± 7	74 ± 4	118 ± 20	631 ± 3	9.12 ± 0.32
Day 9 bottom	240 ± 10	225 ± 11	73 ± 3	113 ± 17	631 ± 1	9.12 ± 0.66
Day 10 surface	233 ± 10	223 ± 10	73 ± 2	121 ± 32	627 ± 3	9.59 ± 0.26
Day 10 bottom	242 ± 10	219 ± 7	73 ± 3	121 ± 16	628 ± 3	10.57 ± 0.32
Day 11 surface	234 ± 10	219 ± 8	73 ± 3	123 ± 19	624 ± 2	9.45 ± 0.19
Day 11 bottom	230 ± 8	220 ± 8	73 ± 3	111 ± 16	627 ± 1	9.50 ± 0.29
Day 12 surface	230 ± 8	226 ± 11	73 ± 4	117 ± 17	619 ± 2	9.75 ± 0.25
Day 12 bottom	232 ± 10	222 ± 8	73 ± 3	123 ± 16	621 ± 3	9.91 ± 0.24
Day 13 surface	226 ± 10	218 ± 8	74 ± 3	124 ± 19	598 ± 14	9.30 ± 0.39
Day 13 bottom	225 ± 9	218 ± 9	73 ± 3	117 ± 19	600 ± 14	9.06 ± 0.49
Day 14 surface	230 ± 12	218 ± 9	73 ± 2	113 ± 15	594 ± 2	9.84 ± 0.21
Day 14 bottom	223 ± 8	214 ± 11	71 ± 3	121 ± 22	596 ± 28	10.75 ± 0.62
Period 1–14 surface	240 ± 15	222 ± 10	73 ± 3	118 ± 19	612 ± 18	9.55 ± 1.29
Period 1–14 bottom	238	223	73	119	615	9.62 ± 1.38
Bourn Brook samples						
Day 1	279 ± 28	312 ± 27	137 ± 15	104 ± 13	413 ± 16	4.29 ± 0.35
Day 2	239 ± 22	292 ± 24	132 ± 16	105 ± 18	430 ± 39	4.20 ± 0.40
Day 3	416 ± 140	105 ± 132	202 ± 57	184 ± 72	372 ± 51	6.09 ± 1.73
Day 4	361 ± 52	399 ± 48	171 ± 27	159 ± 31	381 ± 41	3.99 ± 1.18
Day 5	365 ± 69	397 ± 64	168 ± 30	149 ± 40	402 ± 37	3.59 ± 0.88
Day 6	325 ± 31	363 ± 33	155 ± 17	136 ± 20	400 ± 31	3.66 ± 0.37
Day 7	303 ± 30	328 ± 26	143 ± 10	136 ± 19	547 ± 15	3.42 ± 0.43
Day 8	400 ± 49	421 ± 46	180 ± 20	165 ± 24	657 ± 163	4.26 ± 0.45
Day 9	289 ± 49	337 ± 44	147 ± 16	115 ± 26	479 ± 85	3.38 ± 1.41
Day 10	236 ± 17	287 ± 20	128 ± 10	104 ± 14	450 ± 23	2.93 ± 1.07
Day 11	217 ± 16	273 ± 16	121 ± 13	93 ± 11	445 ± 21	3.12 ± 0.49
Day 12	261 ± 41	320 ± 72	151 ± 49	118 ± 21	570 ± 25	3.61 ± 0.41
Day 13	326 ± 60	380 ± 49	176 ± 30	133 ± 30	690 ± 443	4.82 ± 1.28
Day 14	334 ± 24	483 ± 65	266 ± 63	102 ± 12	538 ± 464	6.99 ± 1.19
Period 1–14	311 ± 78	361 ± 80	163 ± 45	129 ± 39	484 ± 217	4.18 ± 1.39

WBC, Worcester and Birmingham Canal.

same component. In addition to these results, the ratio between peaks T_1 and C revealed the microbial nature of DOM from WBC water samples compared with DOM from Bourn Brook samples, which was mostly terrestrially derived.

The WBC and Bourn Brook (urban) samples were, further, compared with non-urban water and treated sewage samples from southwest England (Hudson *et al*. 2008), to highlight the peculiarities of the WBC samples. Non-urban and treated sewage samples were collected from several locations and measured using the same spectrofluorometer (Varian Cary Eclipse) and instrument configuration as for WBC and Bourn Brook water samples. As shown in Fig. 8, WBC had

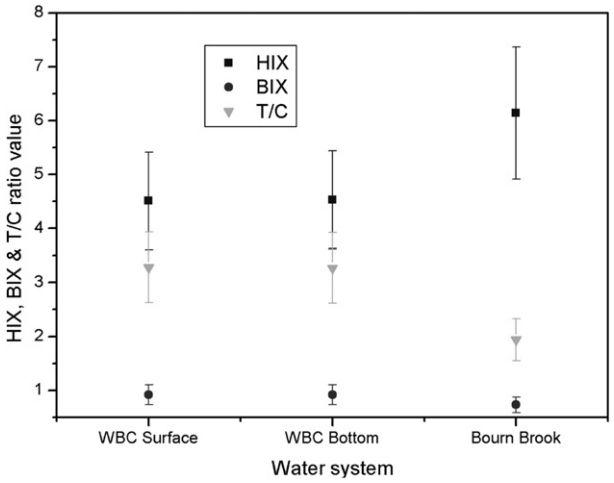

Fig. 7. Fluorescence indices of WBC and Bourn Brook samples: humification index (HIX), biological index (BIX) and T/C ratio calculated as the average value for the complete dataset.

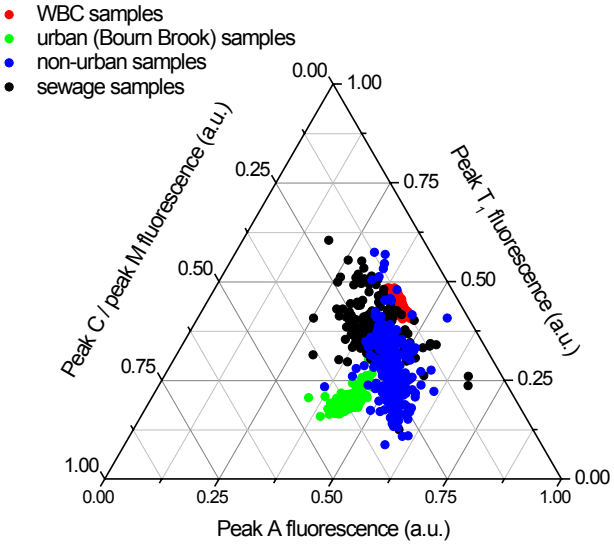

Fig. 8. Comparison between the fluorescence intensity of peaks A, T_1 and C/M for WBC, Bourn Brook (urban), non-urban and treated sewage samples.

a distinctive DOM fluorescence fingerprint and the lowest relative intensity of peak C compared with the other samples. This suggested that comparatively little reprocessed DOM remained in the system. The WBC data seemed most similar only to treated sewage, clearly distinguishing from the urban and non-urban samples. Urban samples had relatively high peak C. Non-urban samples fell in a region that had relatively high peaks A and T intensity as end-members. The fluorescence ratio A/T, in non-urban samples, therefore, likely reflected the relative amount of reprocessing. All data pointed out the specific nature of WBC water samples, with constant activity of the DOM fractions and continuous reprocessing of organic matter.

Impact of precipitation on DOM fluorescence characteristics from WBC and Bourn Brook

Bourn Brook water quality was highly influenced by precipitation, which increased the quantity of DOM components mainly by sewer release of 'old' run-off. No impact from precipitation was observed at WBC water samples, although similar quantities of rain were recorded during the WBC sampling period. According to Swanson *et al*. (2004), because of the low flows and slow dispersion processes within canals, compared with river systems, the release of surface run-off causes, generally, a predominance of nutrients – bound clay and silt sediments, providing a continuous influx of nutrients to the water column and, thus, promoting eutrophication. In these conditions, constant organic matter processing takes place, within the canal water, contrary to a river system where dissolved organic carbon is reprocessed quickly (Raymond *et al*. 2004), allowing pollutants tracing and high variations in DOM. These differences were revealed in the fluorescence spectra, as seen in Fig. 2, by the presence of more intense peak T_1 fluorescence at WBC samples, compared with Bourn Brook water samples. Constant DOM processing and increased quantities of nutrients lead to unchanging, high intensity fluorescence signal of peak T_1, in the canal spectra, while, the Bourn Brook samples exhibited high variability. Also, the constant DOM processing and lack of variability in quantity and characteristics, lead to a weak relationship between peak C and TOC, as can be seen in Fig. 9. In contrast, good correlation was obtained between TOC and peak C at Bourn Brook samples, which presented daily variability and influence from precipitation.

Precipitation also influenced the fluorescence emission wavelength of peak C, at Bourn Brook samples. Figure 10 illustrates the peak C emission wavelength and the precipitation events during the experimental period, for WBC and Bourn Brook. In the Bourn Brook case, the first four precipitation events generated a decrease of the emission wavelength towards the region of peak M. As shown by Carstea *et al*. (2009), these events provoked the flow, into the river, of urban surface run-off, which contained high quantities of organic material. The tendency to peak M suggested that this urban run-off was either previously reprocessed or was quickly reprocessed within the river; therefore, there was a significant presence of freshly reprocessed DOM. During the last rain event, less 'old' surface run-off flowed into the river so no decrease in peak emission wavelength was observed. The emission wavelength for WBC water was intermediate between peak C and peak M, showing no changes after precipitation.

Considering that, generally, canal water is well mixed and that navigation has a low impact on DOM over a short time period, it would be possible to estimate the quantity of TOC for any section of a certain canal or for the entire system of canals. Therefore, if the values recorded during the continuous monitoring of WBC were typical for UK canal water, then 1 m^3 of water contained 0.0096 kg of DOC and the total quantity of DOC for the WBC was about 9616 kg. Likewise, assuming that all canals had the same size, the quantity of DOC for the entire 3000 km of canals would have been approximately 597 312 kg.

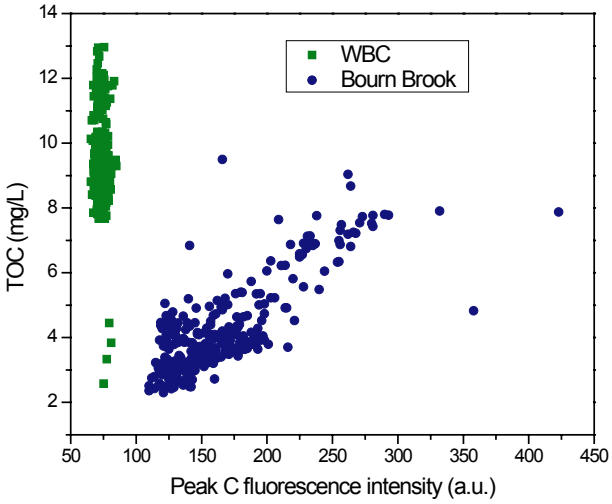

Fig. 9. Relationship between peak C fluorescence and TOC for WBC and Bourn Brook samples.

Conclusions

(1) This study presented the first continuous monitoring of water quality in a canal, using fluorescence spectroscopy and standard parameters, like pH, conductivity and TOC. The comparison between the WBC and Bourn Brook fluorescence spectra helped evidence the specific nature of DOM from canal water.

(2) The results showed that no significant variations in organic matter character occur over the timescale of days. We proposed that the slow water movement permitted the processing of a greater proportion of DOM compared with riverine systems. Also, great consistency between the samples collected from the surface and bottom of the canal was observed. This fact, together with the results from the navigation influence experiment, indicated that canal water is very well mixed. Therefore, recreational navigation and precipitation events had no major influence on DOM characteristics. The peculiarities of canal water, like regulated low flow, predominance of nutrients, continuous processing of organic carbon, suggested that canals might be characterised as a significant DOM processing system.

(3) These findings represented a first step in canal water quality evaluation at high frequency time scales, in the attempt to identify the temporal properties of DOM. The study could serve as a comparison for future research on canal water, for the estimation of canal DOM quantity or for water quality models.

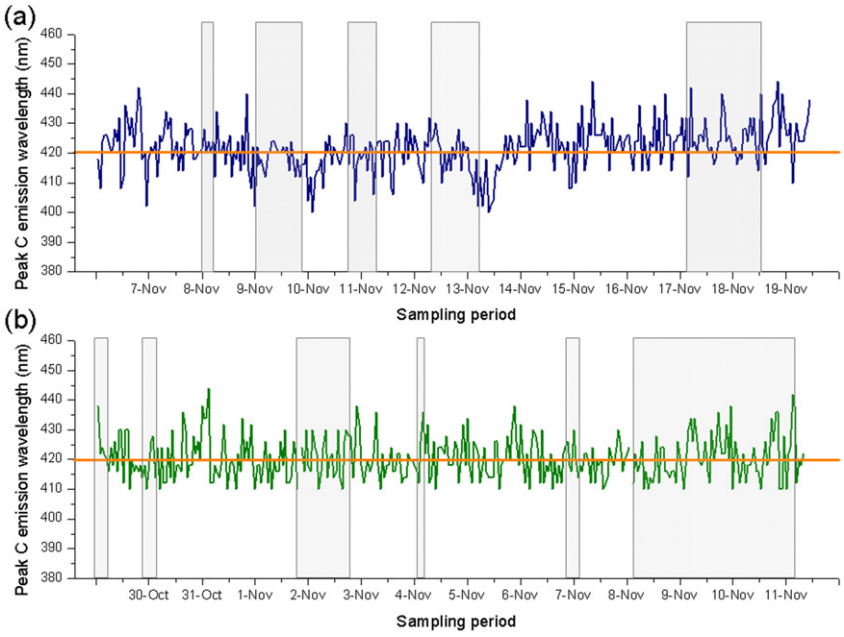

Fig. 10. Fluorescence emission wavelengths of peak C for (a) Bourn Brook and (b) WBC water samples; the orange horizontal lines indicate the border between peak C and peak M, and the grey shades show the time and length of the precipitation events.

Acknowledgements

This work of Elfrida M. Carstea was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-TE-2011-3-0077. The authors wish to thank the anonymous reviewers for the valuable comments, Richard Johnson for laboratory support and Ann Ankcorn for Fig. 1, from the University of Birmingham, UK.

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