HYDROLOGICAL PROCESSES
Hydrol. Process. **23**, 1937–1946 (2009)
Published online 13 May 2009 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/hyp.7335

Continuous fluorescence assessment of organic matter variability on the Bournbrook River, Birmingham, UK

Elfrida M. Carstea,[1]* Andy Baker,[2] Gabriela Pavelescu[1] and Ian Boomer[2]

[1] *National Institute of R&D for Optoelectronics, Magurele, Romania*
[2] *School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, UK*

Abstract:

Continuous monitoring of dissolved organic matter (DOM) character and concentration at hourly resolution is rare, despite the importance of analysing organic matter variability at high-temporal resolution to evaluate river carbon budgeting, river water health by detecting episodic pollution and to determine short-term variations in chemical and ecological function. The authors report a 2-week experiment performed on DOM sampled from Bournbrook, Birmingham, UK, an urban river for which spectrophotometric (fluorescence, absorbance), physiochemical (dissolved organic carbon [DOC], electrical conductivity, pH) and isotopic (D/H) parameters have been measured at hourly frequency. Our results show that the river had sub-daily variations in both organic matter concentration and characteristics. In particular, after relatively high-magnitude precipitation events, organic carbon concentration increased, with an associated increase in intensity of both humic-like and tryptophan-like fluorescence. D/H isotopic ratio demonstrates different hydrological responses to different rainfall events, and organic matter character reflects this difference. Events with precipitation <2 mm typically yielded isotopically heavy water with relatively hydrophilic DOM and relatively low specific absorbance. Events with precipitation >2 mm had isotopically lighter water with higher specific absorbance and a decrease in the proportion of microbially derived to humic-like fluorescence. In our heavily urbanized catchment, we interpret these signals as one where riverine DOM is dominated by storm sewer-derived 'old' organic matter at low-rainfall amounts and a mixed signal at high-precipitation amounts where 'event' surface runoff-derived organic matter dominate during storm sewer and combined sewer overflow routed DOM. Copyright © 2009 John Wiley & Sons, Ltd.

Additional Supporting information may be found in the online version of this article.

KEY WORDS dissolved organic matter; fluorescence; absorbance; isotope hydrology; urban rivers

Received 2 October 2008; Accepted 24 March 2009

INTRODUCTION

Organic matter is ubiquitous in every type of aquatic system and, due to the influence that it has on their ecological health, can be used as a useful water quality indicator. Historically, organic matter was considered rather unreactive, but recent research has shown that it is actually reactive and labile, and therefore presents both beneficial and risk effects on ecosystems (Baigorri *et al*., 2007; Hudson *et al*., 2007; Battin *et al*., 2008). Deleterious activities, especially under anthropogenic influences, lead most of the time to a perturbation in organic matter concentration and/or composition and a deterioration of aquatic ecosystems. The organic matter fraction present in natural waters (i.e. with almost no anthropogenic influence) can be autochthonous, formed *in situ* through microbial activity, algal productivity, invertebrate grazing, etc., and allochthonous, formed externally and brought into the water system through soil leaching, geological activities or degradation of terrestrial vegetation (Volk *et al*., 2002; Winter *et al*., 2007). Human influence can affect both of these fractions and in a complex manner. For example, increased algal-derived organic matter due to eutrophication, increased microbially derived organic matter from human and animal wastes and changes in allochthonous organic matter from changes in land use. Organic matter composition and concentration can therefore vary greatly from one water body to another (Coble *et al*., 1996), from source to sea (Baker and Spencer, 2004) at annual to hourly timescales (Spencer *et al*., 2007; Wu *et al*., 2007).

During the last decade, fluorescence spectroscopy has been effectively used to determine and characterize organic matter concentration and character and its link to function and chemical water quality (Coble, 1996; Thacker *et al*., 2005; Hudson *et al*., 2007; 2008). It is a quantitative and sensitive technique that requires small quantities of sample, with little or no sample preparation. Fluorescence spectroscopy can measure a sample in approximately 1 min, depending on the set-up parameters, offering the spectral fingerprint for any type of water body. The fluorescence signal can be recorded as excitation–emission matrix, generated by scanning both excitation and emission wavelengths (Coble, 1996; Hudson *et al*., 2007). Thus, the fluorescence maxima can be identified by analysing the $\lambda_{ex}/\lambda_{em}$ (excitation

* Correspondence to: Elfrida M. Carstea, National Institute for Optoelectronics, INOE 2000, 409 Atomistilor Street, P. O. Box MG-5, RO-077125 Magurele, Romania. E-mail: frida@inoe.inoe.ro

wavelength/emission wavelength) pairs. The common fluorophores detected in natural rivers are microbially and terrestrially derived. Amino acid-like components, microbial or algal derived, represent the labile fraction of organic matter showing the bacterial or algal activity in a water system (Hudson *et al*., 2008). Uncontaminated waters exhibit low amino acid-like fluorescence, but this fraction can emit high fluorescence in the case of untreated sewage and farm waste waters (Baker 2001, 2002), as well as stationary water bodies sensitive to eutrophication or algal production are analysed. The representative amino acids that fluoresce are tyrosine, which is less intense due to a lower quantum efficiency, and tryptophan with two highly fluorescent maxima. The terrestrially derived fluorescence is given by humic-like substances produced through biological and chemical degradation of plant material present in the ecosystem. Humic substances are formed of a multitude of components that are generically named humic and fulvic acids (Samios *et al*., 2007). A fraction of humic substances can be microbially derived, but having less aromatic content (12–17%) than the terrestrially derived fraction (25–30%) (McKnight *et al*., 2001).

The seasonal variation of riverine dissolved organic matter (DOM) character and concentration has been analysed at a variety of spatial scales using fluorescence spectrophotometry (for example, see, Baker *et al*., 2003; Baker and Spencer, 2004). Few studies have focused on variability at a higher temporal resolution, predominantly due to the absence of *in situ* or continuous instrumentation that can collect EEM data. For example, Spencer *et al*. (2007) used fluorescence spectroscopy and ancillary measurements to show that DOM exhibits diurnal variation in one river system, following a consistent day–night trend. However, the fluorescence characterization was limited by the use of a fixed wavelength fluorometer. Here, we continuously monitor water quality in a small urban catchment through the use of standard autosampler technology. We assess the hourly response of DOM fluorescence over five precipitation events during 2 weeks in November 2007. The fluorescence signal of all four major terestrially and microbially derived organic matter components has been measured and analysed; the first such characterization of DOM using continuous monitoring. In this study, both organic matter concentration (fluorescence intensity, ultraviolet absorbance and DOC) and character (fluorescence intensity ratios, wavelength of peak fluorescence, specific UV absorbance—SUVA), along with isotope hydrology, are continuously quantified for an urban river (Bournbrook River), and the influence of precipitation events on organic matter characteristics and concentration has been evaluated.

METHODOLOGY

Site description

Water samples were collected from the Bournbrook, a low altitude, small urban river of catchment area 27·91 km^2, that near its downstream end flows beside the University of Birmingham (52 : 26 : 51N, 1 : 55 : 49W; Figure 1). The river has no upstream wastewater treatment works, but does receive waters from both the storm sewer system and combined sewer overflows. The river has a chemical water quality classification of 'fairly good' (grade C) and biological water quality as 'fair' (grade D), as assessed by the Environment Agency. The observation of worse biological quality over chemical quality in urban rivers is a common observation where biological status is a better reflection of water quality when rivers are affected by episodic pollution events. Routine monitoring

Figure 1. The Bournbrook catchment; sampling site and weather station are shown in the picture

DOI: 10.1002/hyp

by the agency between 2004 and 2006 ($n = 36$) measured mean biochemical oxygen demand of 2·24 mg/l, ammonia 0·11 mg/l, dissolved oxygen 89%, nitrate 9·5 mg/l, phosphate 0·18 mg/l, pH 7·87, dissolved copper 89 µg/l and dissolved zinc 25 µg/l. The biological assessment was based on a 2006 invertebrate survey, where observed number of taxa was 11·0 instead of an expected 24·7 and the observed average score per taxa was 4·27 instead of an expected 5·73. Under the EU Water Framework Directive, the river has been designated to be at risk from diffuse pollution and morphological and physical alteration.

Sample collection

Water samples have been collected every hour on a daily regime for 2 weeks. The experiment started on 6 November, 2007, and lasted until 20 November, 2007, using an ISCO autosampler with 24, 1 l capacity sample bottles that had been previously washed in 10% HCl and rinsed with deionized water. Sampling began each day at 10 a.m. To reduce the quantity of particulate matter, all samples were filtered in the laboratory with Whatman (GF/C glass microfibre filter papers) 0·7 µm pore size filters before analysis. All samples were measured within 24 h from collection. The pH was not altered before absorbance, fluorescence and conductivity measurements. Samples presented variations in pH from 6·5 to 8, but did not seem to affect fluorescence characteristics.

Physical and chemical parameters

Conductivity and pH were determined by standard methods. UV absorbance measurements have been performed for all samples with a WPA Lightwave UV–VIS diode-array S2000 spectrophotometer to calculate both UV absorbance and SUVA values. Absorbance spectra were recorded between 200 nm and 700 nm for samples measured with a 10-mm path length cuvette. SUVA was calculated according to Equation (1) (EPA Method 415·3):

$$\text{SUVA (l/mg M)} = \frac{\text{UVA}(\text{cm}^{-1})}{\text{DOC}(\text{mg/l})} \times 100 \text{ cm/M}, \qquad (1)$$

where UVA is the ratio between the absorbance measured at 254 nm and the cell path length in cm.

For all samples, total organic carbon (TOC) was determined with a Shimadzu TOC-Vcpn analyser. TOC measurements were performed starting with 1 week after sampling therefore the samples were preserved by acidification to pH 2 by adding hydrochloric acid. TOC analysis has been conducted according to EPA methods 415·1 and 415·2.

Fluorescence spectroscopy

Fluorescence spectra were obtained with a Varian Cary Eclipse spectrofluorometer. Instrument settings were 725 V photomultiplier tube voltage, a scan rate of 9600 nm/min and an integration time of 0·0125 s. The sample chamber was kept at a constant temperature of 20 °C by using a Peltier temperature controller. The water Raman peak was recorded daily, before every set of measurements, to check the instrument stability. The mean value of Raman peak intensity was 25·55 arbitrary units; all fluorescence intensity values have been adjusted to a Raman reference value of 25 arbitrary units. Also, the results can be compared with a quinine sulphate standard: 32·5 intensity units are equivalent to 1 quinine sulphate unit (1 µg/l in 0·1 M H_2SO_4) (Cumberland and Baker, 2007). Water samples have been excited between 200 nm and 400 nm with a step of 5 nm, and the emitted fluorescence recorded in the range 280–500 nm, with steps of 2 nm. Excitation and emission slit widths were set to 5 nm.

Isotope hydrology

Each sample was analysed for its D/H isotopic composition to provide a continuous record of the isotope hydrology of the river. Water stable isotopes were determined using a GV Instruments Isoprime isotope ratio mass spectrometer connected to a Eurovector environmental analyser. Stable isotope values are expressed using the δ convention, with hydrogen isotopes (δD) expressed as per mil. The standard is Vienna standard mean ocean water. For hydrogen isotope analysis, approximately 0·3 µl of water was injected from sample vials on an autosampler into a column where reduction to hydrogen took place at 1050 °C over a chromium metal catalyst. At least two successive analyses were made by repeat injections from the same vial. Internal (within-run) precision is 0·4 per mil for δD and overall (external) precision estimated at 1 per mil.

Hourly rainfall data were obtained from the nearby weather station (Winterbourne climate station, 52·455 N–1·924 W, 131 m) managed by the University of Birmingham. River stage height was recorded daily by manual observations.

RESULTS AND DISCUSSIONS

Rainfall, discharge and isotope hydrology

The experimental period was characterized by a lack of precipitation in the first 3 days (6th November to 8th November), followed by 5 days of rain (Figure 2(a)). Subsequently, there were again 3 days with no precipitation. In the period from 18th November to 20th November, a heavy rain event occurred that was followed by a snow event on the last day of the experiment. This latter period was the only time that river stage height, as recorded daily at the sample site, showed a significant increase, from 15 to 45 cm (Figure 2(c)). Every precipitation event has been labelled with I, II, III, IV and V as follows: event I—9th November, event II—10th November, event III—11th November, event IV—12th and 13th November and event V—18th and 19th November.

River water D/H isotopes (Figure 2(b)) during the study period demonstrate a stable base value of ∼−40

DOI: 10.1002/hyp

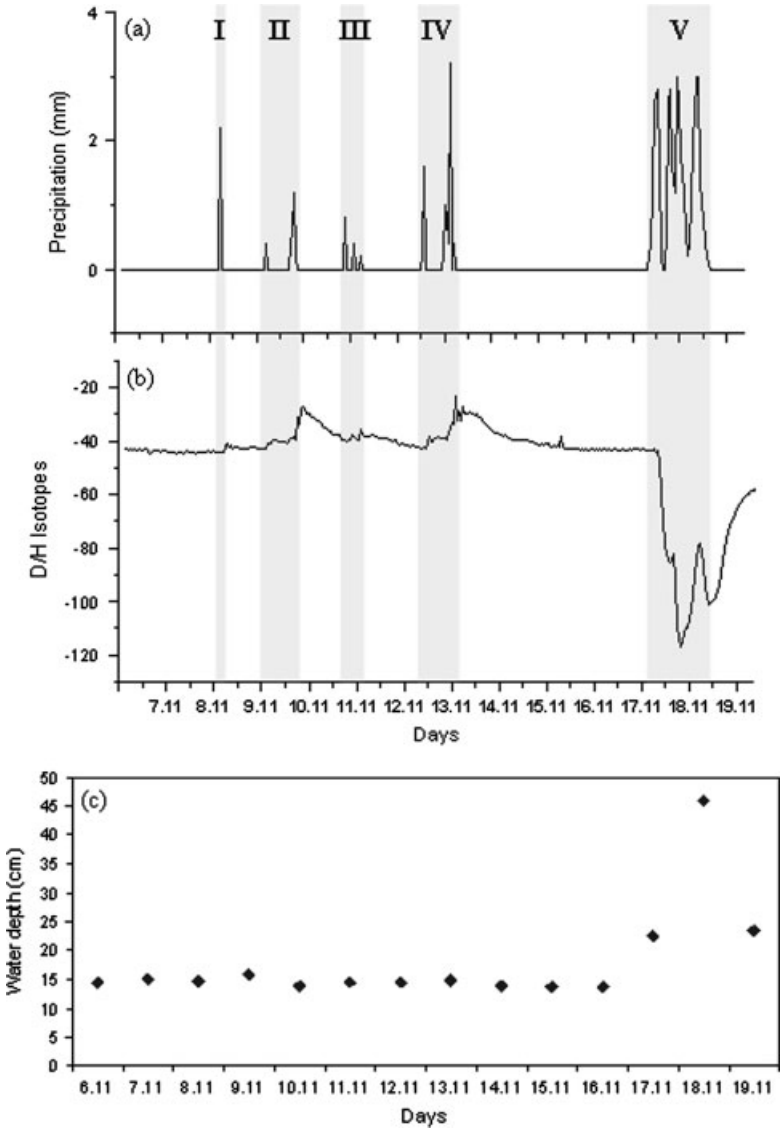

Figure 2. Continuous hydrology data: (a) precipitation, (b) D/H isotopes and (c) river water depth

to 50‰, with either positive or negative excursions in isotope ratio rapidly occurring after each of the precipitation events. For the rainfall events during the period 12–17th November, D/H ratios were heavier with shifts of between 5 and 15‰. In contrast, the final rain event led to lighter D/H with a shift of ∼70‰. Although within-event rainfall D/H was not recorded in this study, previous research has shown that negative isotopic excursions are typical during individual rainfall events (Celle-Jeanton *et al*., 2004), including rainfall at the study site (Muller, 2008). D/H isotopes, together with stage height data, therefore indicate different hydrological responses between events I to IV and event V. We hypothesize that event V could be conventionally explained by a rapid routing of 'event' water, with rain and snowfall leading to an increase in river discharge that is predominantly from isotopically light sources. In contrast, events I to IV lead to only small changes in river discharge, which comprise significant components of isotopically heavier water. This is unlikely to be sourced from rapid runoff from the preceding rainfall event, and we hypothesize that it routes from 'old' water that has been stored in storm drain and sewer networks connected to the river system.

Continuous water quality measurements

In total, 336 hourly samples were collected and analysed using fluorescence and absorbance spectroscopy and conventional chemical methods. The daily averaged results for the common fluorophores detected can be seen in Table I, along with the values for TOC, electrical conductivity, pH and absorbance at 254 nm. An example of EEM spectra for water sampled on Bournbrook River is illustrated in Figure 3. Hourly raw data are provided in Supporting Information Table I.

The four fluorescence peaks have been observed in all samples. Two peaks are associated with humic and fulvic-like substances (peak A and peak C), and other two peaks, T and B, are associated with amino acids and are typically microbially derived. The most intense fluorescence is from peak A, which has an excitation maximum between 220 and 265 nm, with emission in

DOI: 10.1002/hyp

Table I. Daily averaged results for the common analysed parameters

Date of sampling	Peak A Fluorescence intensity (a.u.)	Peak C Fluorescence intensity (a.u.)	Peak T Fluorescence intensity (a.u.)	Peak B Fluorescence intensity (a.u.)	TOC (mg/l)	pH	Electrical conductivity (μS/cm)	Absorbance at 254 nm (cm^{-1})
6th November, 2007	325	142	291	107	4·2	—	412	0·09
SD	27	15	28	13	0·3	—	16	0·02
7th November, 2007	294	133	247	103	4·3	7·5	428	0·08
SD	24	16	22	18	0·4	0·4	39	0·02
8th November, 2007	396	396	352	155	5·5	6·9	388	0·13
SD	132	57	140	72	1·7	0·3	51	0·04
9th November, 2007	406	406	366	160	4·5	6·8	383	0·11
SD	48	27	52	31	1·2	0·3	41	0·02
10th November, 2007	431	431	403	168	4	7·1	381	0·12
SD	64	30	69	40	0·9	0·3	37	0·03
11th November, 2007	365	365	329	136	3·5	7·1	404	0·10
SD	33	17	31	20	0·4	0·3	31	0·01
12th November, 2007	321	138	281	123	3·3	7	417	0·09
SD	26	10	30	19	0·4	0·3	15	0·01
13th November, 2007	409	176	395	172	4·1	6·7	724	0·12
SD	46	20	49	24	0·5	0·2	163	0·06
14th November, 2007	372	158	330	127	3·8	6·9	532	0·10
15th November, 2007	299	132	250	110	3	6·9	450	0·08
SD	44	16	49	26	1·4	0·2	85	0·02
16th November, 2007	275	125	220	94	3·1	6·8	445	0·07
SD	20	10	17	14	1·1	0·3	23	0·01
17th November, 2007	291	136	223	97	3·2	7	448	0·07
SD	16	13	16	11	0·5	0·2	21	0·01
18th November, 2007	370	169	333	150	4·4	7·2	501	0·14
SD	72	49	41	21	0·4	0·2	25	0·02
19th November, 2007	452	241	323	105	6·5	6·8	816	0·23
SD	49	31	60	30	1·3	0·4	443	0·05
20th November, 2007	483	259	337	95	7	7·7	540	0·23
SD	65	63	24	12	1·2	0·3	464	0·07

SD = standard deviation; TOC = total organic carbon.

the range 400–500 nm. Peak C shows a less intense fluorescence between 380 and 475 nm, excitation in the range 300–370 nm. Tryptophan amino acid, peak T, fluoresces in the range of 325 nm and 380 nm, excitation between 220 and 245 nm. A second tryptophan-like fluorescence peak (280/350 nm excitation/emission pair) had been frequently reported in other studies (Coble, 1996; Winter *et al*., 2007; Hudson *et al*., 2008), but it was frequently obscured by background fluorescence from the relatively blue-shifted peak C. The second microbially derived (tyrosine) fluorescence maximum, peak B, has a less intense excitation/emission pair at 220–235 nm/305–315 nm. Both the absolute and relative intensity of fluorescence peaks are comparable with previous studies of the fluorescence properties of DOM in urban rivers (for example, Baker and Spencer, 2004). Mean daily values for pH, TOC, electrical conductivity and UV absorbance are likewise typical for river water samples in the region.

The time series of all water quality parameters are presented in Figures 4 and 5. First, the hourly record for precipitation, TOC and conductivity is presented in Figure 4. The TOC (Figure 4(b)) concentration variations with time contrast with that of electrical conductivity (Figure 4(c)). The first three events generate high TOC with no response in electrical conductivity. On the contrary, event IV drives higher values in both electrical conductivity and TOC, possibly suggesting that a different source of TOC than events I to III. A more complex electrical conductivity response is observed in event V due to the higher amounts of precipitation. First, we see an increase in TOC and high electrical conductivity followed by a dramatic fall of electrical conductivity, which we presume to be a dilution effect, and finally an increase can be observed in both parameters.

Fluorescence intensity of peaks A, C, T and B has been plotted for the hourly collected samples (Figure 5(a–d)), along with UV absorbance at 254 nm (Figure 5(e)). For samples collected between 6th November, 2007, and 8th November, 2007, when there was no precipitation, a small but detectable maximum of fluorescence intensity for peaks A and C (Figure 5(a and b)) and UV absorbance (Figure 5(e)) appeared at noon and a minimum during the night. A similar trend was obtained by Spencer *et al*. (2007) but with the fluorescence maximum shifted in the morning. The cause of our diurnal variability is unknown, and it is not observed in peaks T and B. The next days, from 9th November, 2007, to 14th November, 2007, increases in fluorescence intensity of all fluorescence centers and UV absorbance occur, associated with the rainfall events and correlating with the increases in TOC observed in Figure 4. No precipitation was recorded

DOI: 10.1002/hyp

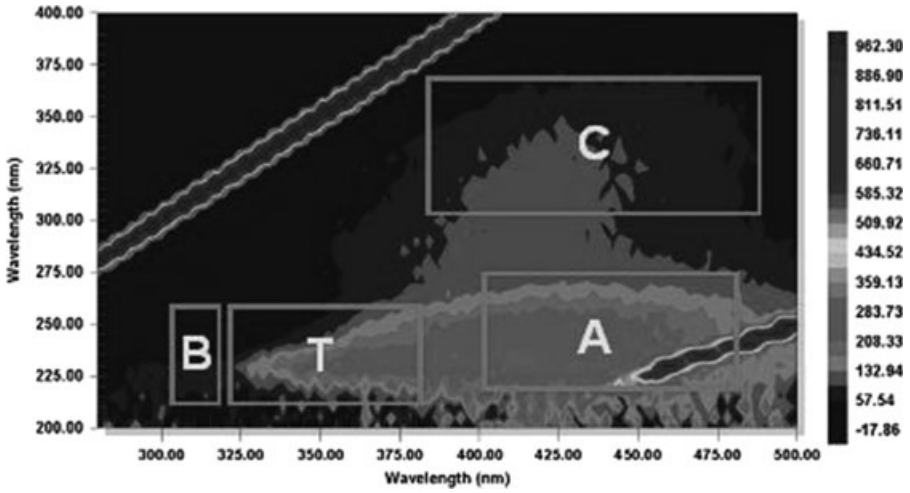

Figure 3. Excitation–emission matrix for Bournbrook river water sample. A, humic acid; C, fulvic acid; T, tryptophan; B, tyrosine

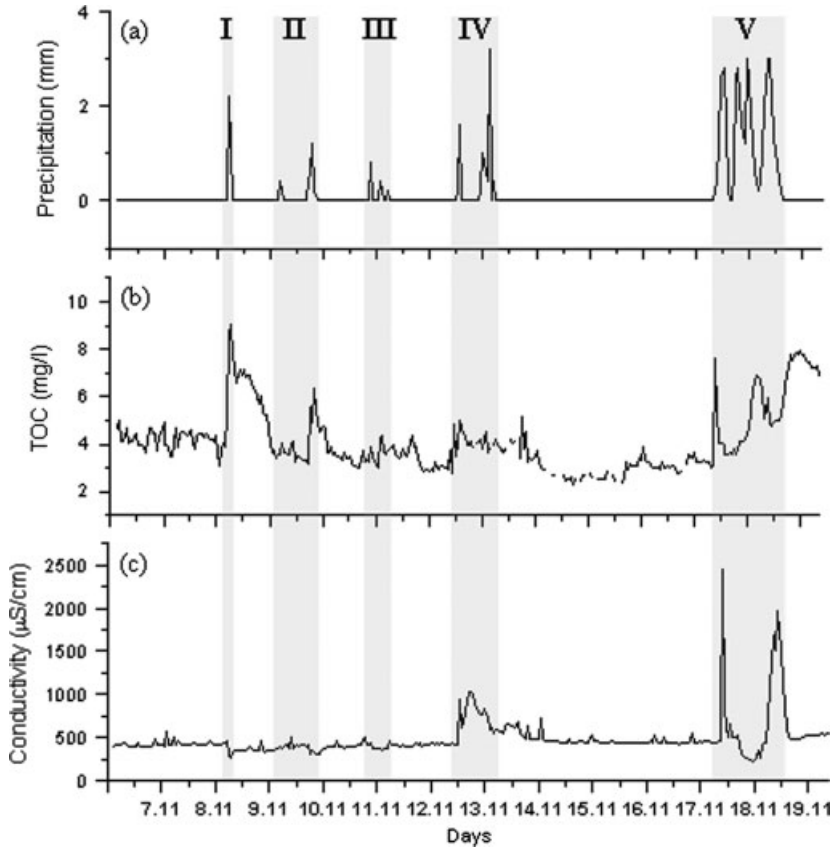

Figure 4. Continuous time series of precipitation (a), total organic carbon (b) and conductivity (c)

between 14th November, 2007, and 17th November, 2007, and a declining trend in fluorescence intensity of all peaks is observed. The high quantities of precipitation in event V generated significant inputs of natural organic matter to the river. All fluorescence peaks, and UV absorbance, increased in response to these events, again correlating with the TOC increase (Figure 4). One snow event occurred on the 19th November, 2007, which again lead to increased fluorescence intensity but relatively more peak C and A fluorescence than peaks B and T.

The good correlation obtained between TOC, UV absorbance and the fluorescence of humic and fulvic-like substances (peak C) is illustrated in Figure 6. The rank correlation coefficient ($r = 0{\cdot}84$) indicates a similar correlation of TOC with fluorescence measurements (Figure 6(a)) as with UV absorbance ($r = 0{\cdot}84$) (Figure 6(b)).

It can therefore be observed that organic matter concentration increased within approximately 1 h after each precipitation event, a rapid response typical of

DOI: 10.1002/hyp

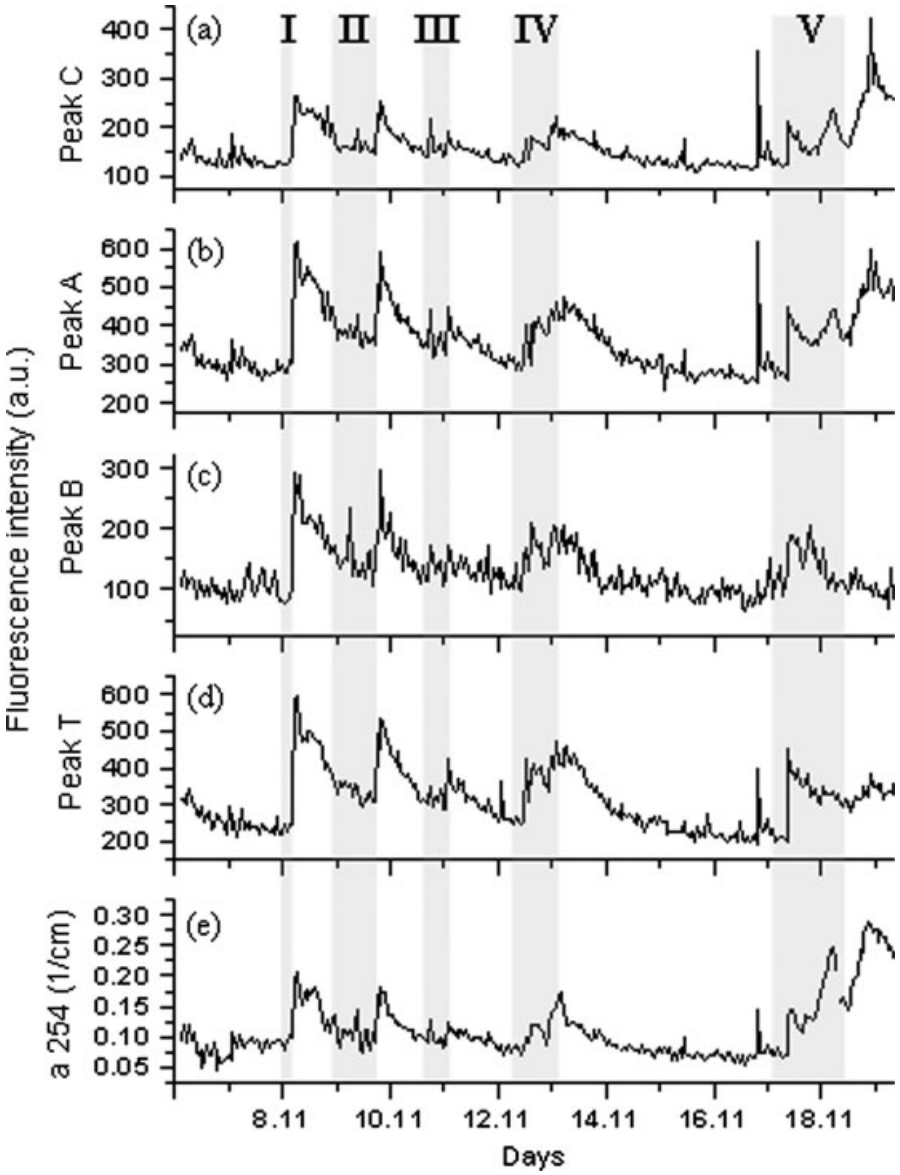

Figure 5. Continuous measurement of fluorescence and absorbance: fluorescence intensity for peaks C (a) and A (b)—humic substances; fluorescence intensity for peaks B (c) and T (d)—microbially derived; (e) absorbance data at 254 nm

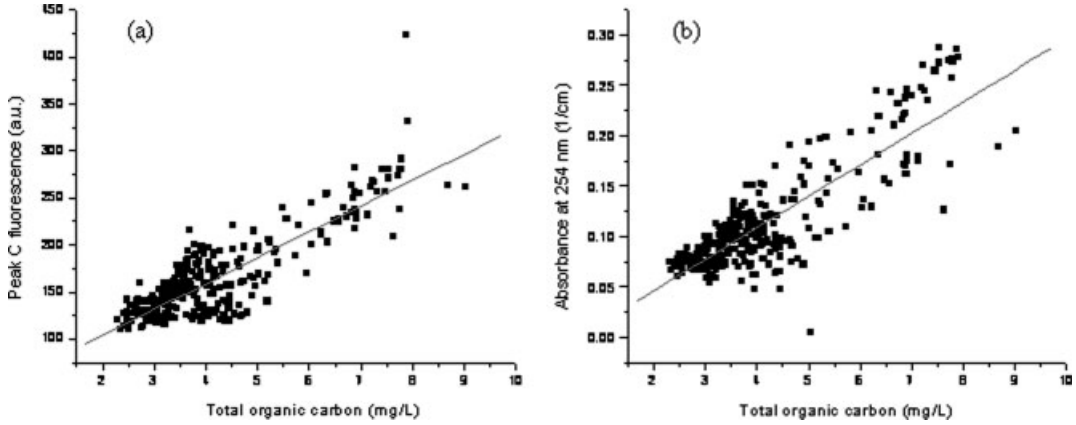

Figure 6. Correlation between TOC and (a) peak C fluorescence and (b) absorption coefficient at 254 nm

small heavily urbanized catchments. However, isotopic evidence suggests that the source of the DOM might be different between events I–IV and event V, due to the greater precipitation and discharge in

DOI: 10.1002/hyp

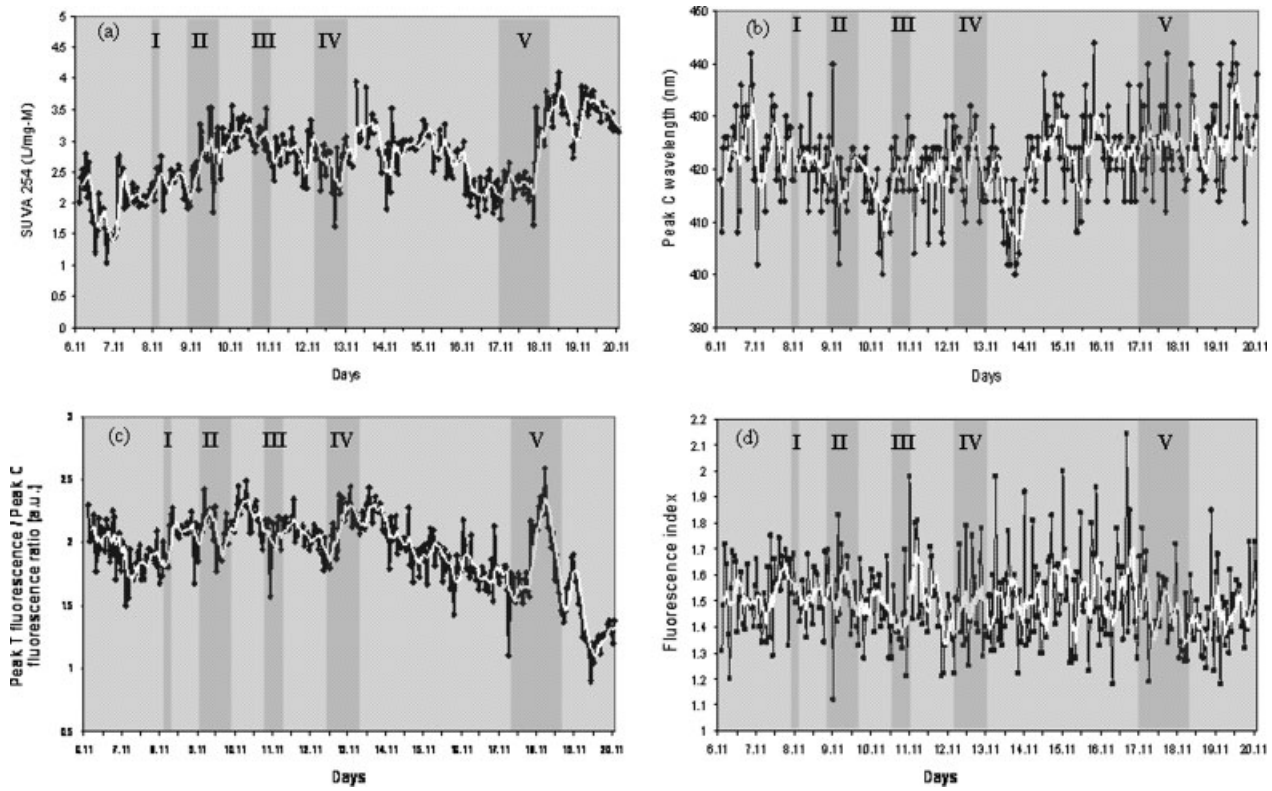

Figure 7. Continuous evolution of (a) specific UV absorbance 254 nm, (b) peak C emission wavelength, (c) peak T/peak C fluorescence intensity and (d) fluorescence index

the latter event. Whether this generated differences in organic matter character is discussed in the following section.

Continuous measurements of the organic matter character

Fluorescence spectroscopy has shown that organic matter concentration varies both with a weak diurnal trend in the absence of precipitation and a much stronger hydrological response under the influence of precipitation. The organic matter properties variations can be investigated using a variety of approaches. Using the fluorescence index (FI), the ratio of peak T to peak C fluorescence, peak C emission wavelength and SUVA (at 254 nm), this we attempt to characterize organic matter in the river water samples and to determine if organic matter character differs between events I–IV and V, using: the fluorescence index, the ratio of T / C fluorescence peaks, the peak C emission wavelength and the SUVA (specific UV absorbance at 254 nm). The water quality parameter, SUVA, has been interpreted as representing the aromatic content of natural organic matter (Edzwald and Van Benschoten, 1990; Kitis *et al*., 2004). In waters that are not dominated by humic-like substances, SUVA would be interpreted as an indicator of the relative proportions of chromophoric to non-chromophoric organic matter. It has been suggested that low-SUVA levels indicate the predominance of non-humic material (Gabelich *et al*., 2001). As can be seen in Figure 7(a), events I to IV present low-SUVA values, indicating mostly the presence of non-humic material in the water samples. In contrast, in event V, SUVA values are high, suggesting an increasing proportion of chromophoric organic matter.

Figure 7(b) presents peak C emission wavelength, which has been previously shown to be an indicator of DOM hydrophobicity, low wavelengths (400–420 nm) indicating relatively hydrophilic DOM and high wavelengths (430–450 nm) hydrophobic DOM (Baker *et al*., 2008). The lowest mean peak C emission wavelengths are observed between events II and IV. However, there are no clear trends in this DOM characteristic related to any of the precipitation events, suggesting that all DOM in the river is relatively hydrophilic, irrespective of possible source variations.

Peak T fluorescence intensity has been plotted against peak C to see which fraction, one that is predominantly microbial versus one that is predominantly derived from humic and fulvic-like material, is commonly present. From Figure 7(c), it can be noticed that the highest proportion of humic-like fluorescence is present only in event V. In the rest of the experimental period, organic matter fluorescence tends to be more microbial driven by autochthonous processes.

By analyzing the FIof peak C, calculated as a ratio between fluorescence intensity at 450/500 nm and excitation 370 nm, one should be able to identify the source and nature of humic substances. According to McKnight *et al*. (2001), microbially derived humic substances have an FI between 1·7 and 2·0 and terrestrially derived humic substances a lower one, approximately 1·3, fluorescing at longer wavelengths than microbially derived. However, the FI was formulated for algal-derived DOM in

DOI: 10.1002/hyp

Antarctic lake waters and has been rarely validated in other freshwater environments. In Figure 7(d), the continuous FI for this experiment is presented, and shows a large amount of high-frequency variability but with no apparent trends. The emission wavelengths used for the FI (450 and 500 nm) are significantly higher than the maximum fluorescence emission (410–430 nm) and therefore poorly characterize peak C fluorescence. The FI cannot further characterize the DOM.

This study has shown that short-term variations in both organic matter concentration and character can be continuously monitored using fluorescence spectroscopy. Differences in the amount of within-event precipitation change the relative importance of the different sources of organic matter, generating changes in river carbon budgeting and ultimately in chemical and ecological water quality.

CONCLUSIONS

This study presents the first continuous monitoring of organic matter character and concentration in an urban river, using fluorescence and absorbance spectroscopy to characterize DOM and TOC to quantify DOM. Our results demonstrate that variations in organic matter character occur over the timescale of hours. Evidence of diurnal variability in DOM character during periods of no precipitation is inconclusive, in contrast to the results of Spencer *et al*(2007) from a rural river. Further research is necessary, particularly at other times of the year with warmer in-stream temperatures and greater biological activity than this winter study. In contrast, observations of DOM character and concentration during precipitation events demonstrate variations in DOM character that are dependent on precipitation amount and its routing through the urban drainage system. Relatively low-precipitation events at our study site flush waters of high concentration of organic carbon that is relatively hydrophilic and relatively low in chromophoric organic matter, which we hypothesize is 'old' water flushed from the urban storm sewerage system. High amounts of precipitation also generate waters of high TOC, but of less hydrophilic character and with a greater proportion of chromophoric organic matter; more typical of 'event' water and a dominance water derived from overland flow, although still routed both directly to the river and via the storm sewer network. Fluorescence intensity, of peak C, correlates with TOC, suggesting that from a single fluorescence EEM, it is possible to both quantify and characterize DOM. The combination of *in situ* fluorescence and absorbance spectroscopy has the potential of real-time water quality monitoring. This includes both the quantification of DOC (peak C intensity) and biochemical oxygen demand (peak T intensity; Hudson *et al*., 2008) and the characterization of DOM with applications both for organic matter sourcing and pollution detection and control.

ACKNOWLEDGEMENTS

The authors would like to thank to Richard Johnson and Andy Moss for laboratory support, Ann Ankcorn for Figure 1 from the University of Birmingham and Dan Savastru from INOE 2000.

REFERENCES

Baigorri R, Fuentes M, Gonzalez-Gaitano G, Garcia-Mina JM. 2007. Simultaneous presence of diverse molecular patterns in humic substances in solution. *Journal of Physical Chemistry B* **111**: 10577–10582.

Baker A. 2001. Fluorescence excitation–emission matrix characterization of some sewage impacted rivers. *Environmental Science and Technology* **35**: 948–953.

Baker A. 2002. Fluorescence properties of some farm wastes: implications for water quality monitoring. *Water Research* **36**: 189–194.

Baker A, Inverarity R, Charlton ME, Richmond S. 2003. Detecting river pollution using fluorescence spectrophotometry: case studies from the Ouseburn, NE England. *Environmental Pollution* **124**: 57–70.

Baker A, Spencer RGM. 2004. Characterization of dissolved organic matter from source to sea using fluorescence and absorbance spectroscopy. *Science of the Total Environment* **333**: 217–232.

Baker A, Tipping E, Thacker SA, Gondar D. 2008. Relating dissolved organic matter fluorescence and functional properties. *Chemosphere* **73**: 1765–1772. DOI:10.1016/j.chemosphere.2008.09.018.

Battin TJ, Kaplan LA, Findlay S, Hopkinson CS, Marti E, Packman AI, Newbold JD, Sabater H. 2008. Biophysical controls on organic carbon fluxes in fluvial networks. *Nature Geoscience* **1**: 95–100.

Celle-Jeanton H, Gonfiantini G, Travi Y, Sol B. 2004. Oxygen-18 variations of rainwater during precipitation: application of the Rayleigh model to selected rainfalls in Southern France. *Journal of Hydrology* **289**: 165–177.

Coble PG. 1996. Characterization of marine and terrestrial DOM in seawater using excitation–emission matrix spectroscopy. *Marine Chemistry* **51**: 325–346.

Cumberland SA, Baker A. 2007. The freshwater dissolved organic matter fluorescence—total organic carbon relationship. *Hydrological Processes* **21**: 2093–2099.

Edzwald JK, Van Benschoten JE. 1990. Aluminum coagulation of natural organic matter. In *Chemical Water and Wastewater Treatment*, Hahn HH, Klute R (eds). Springer-Verlag: Berlin.

US Environmental Protection Agency. 1999. *EPA Method 415·1. Total organic carbon in water (combustion or oxidation).*

US Environmental Protection Agency. 1999. *EPA Method 415·2. Total organic carbon in water (UV Promoted, Persulfate Oxidation).*

US Environmental Protection Agency. 2005. *EPA Method 415·3. Determination of total organic carbon and specific UV absorbance at 254 nm in source water and drinking water.*

Gabelich CJ, Yun TI, Bartels CR, Green JF. 2001. *Nonthermal Technologies for Salinity Removal*. American Water Works Association: Denver; 31 p.

Hudson N, Baker A, Reynolds D. 2007. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review. *River Research and Applications* **23**: 631–649.

Hudson N, Baker A, Ward D, Reynolds DM, Brunsdon C, Carliell-Marquet C, Browning S. 2008. Can fluorescence spectrometry be used as a surrogate for the biochemical oxygen demand (BOD) test in water quality assessment? An example from South West England. *Science of the Total Environment* **391**: 149–158.

Kitis M, Karanfil T, Kilduff JE. 2004. The reactivity of dissolved organic matter for disinfection by-product formation. *Turkish Journal of Engineering and Environmental Sciences* **28**: 167–179.

McKnight DM, Boyer EW, Westerhoff PK, Doran PT, Kulbe T, Andersen DT. 2001. Spectrofluorimetric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography* **46**: 38–48.

Muller CL. 2008. A Micro-Scale Study of Clouds and Precipitation over Birmingham, UK. Unpublished PhD Thesis, University of Birmingham.

Samios S, Lekkas T, Nikolaou A, Golfinopoulos S. 2007. Structural investigations of aquatic substances from different watershed. *Desalinisation* **210**: 125–137.

Spencer RGM, Pellerin BA, Bergamaschi BA, Downing BD, Kraus TEC, Smart DR, Dahlgren RA, Hernes PJ. 2007. Diurnal variability in riverine dissolved organic matter composition determined by *in situ* optical measurement in the San Joaquin River (California, USA). *Hydrological Processes* **21**(23): 3181–3189.

Thacker SA, Tipping E, Baker A. 2005. Development and application of functional assays for freshwater dissolved organic matter. *Water Research* **39**: 4559–4573.

Volk C, Wood L, Johnson B, Robinson J, Zhu HW, Kaplan L. 2002. Monitoring dissolved organic carbon in surface and drinking waters. *Journal of Environmental Monitoring* **4**: 43–47.

Winter AR, Fish TAE, Playle RC, Smith DS, Curtis PJ. 2007. Photodegradation of natural organic matter from diverse freshwater sources. *Aquatic Toxicology* **84**: 215–222.

Wu FC, Wothawala DN, Evans RD, Dillon PJ, Cai YR. 2007. Relationships between DOC concentration, molecular size and fluorescence properties of DOM in a stream. *Applied Geochemistry* **22**: 1659–1667.

DOI: 10.1002/hyp