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Analysis of rainwater dissolved organic carbon compounds using fluorescence spectrophotometry

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ABSTRACT

Global rainwater dissolved organic carbon (DOC) flux was recently estimated as 430×10^{12} g C yr^{-1}, yet little is known about the wide range of chemical compounds present, their sources, temporal patterns of variation, and the subsequent impact on climate and the environment. Precipitation events were sampled in Birmingham, UK between April 2005 and May 2007. Rainwater DOC compounds were analysed using fluorescence spectrophotometry. Three fluorophores were identified: HUmic-LIke Substances (HULIS), TYrosine-LIke Substances (TYLIS) and TRYptophan-LIke Substances (TRYLIS). Peak fluorescence intensities and locations for each substance were examined, and their variations with various meteorological parameters were investigated. The mean HULIS fluorescence intensity from all events was 209 a.u. (with sample fluorescence ranging from 37 a.u. to 995 a.u); mean fluorescence intensity was 469 a.u. (214–988 a.u) and 265 a.u. (50–876 a.u.) for TYLIS and TRYLIS, respectively. Results indicate that highest HULIS fluorescence intensities are experienced during convective events and events of continental origin, suggesting terrestrial/anthropogenic sources. Under well-mixed conditions, HULIS fluorescence intensity decreases, whereas during low wind speed, stagnation of the atmosphere results in higher fluorescence intensities, attributed to a build up of localised sources, particularly anthropogenic. TYLIS and TRYLIS did not show any significant trends for the meteorological variables. Fluorescence spectrophotometry is a fast, non-invasive technique which is demonstrated to be a powerful means of fingerprinting rainfall DOC compounds in real time for small sample volumes.

1. Introduction

Dissolved organic carbon (DOC) refers to the hundreds of dissolved compounds found in water that derive from organic materials, and is composed of ‘organic acids’, ‘organic bases’, and ‘neutral groups’ (Seitzinger et al., 2003). The operative boundary between DOC and particulate organic carbon is set as that which will pass through a 0.45 μm filter. DOC is a mixture of simple substances such as carbohydrates, fatty acids and alkanes, and of complex polymeric molecules (aromatic and carboxylic carbon). They can be present as truly dissolved molecules, as colloids or as viruses (MacDonald et al., 2004). The amount of DOC in the hydrosphere (700 gigatons) is almost the same as the amount of carbon in the atmosphere (750 gigatons). Fully understanding the carbon cycle is of great importance to discovering the “missing sink” of CO_2 – current global carbon cycling models are unable to account for 20% of global carbon dioxide (Willey et al., 2000). Therefore both inorganic and organic carbons must be taken into consideration when clarifying the carbon cycle (Sugiyama and Kumagai, 2001). Rainwater DOC contributes significantly to the atmospheric carbon cycle – global rainwater flux was recently quantified as 430×10^{12} g C yr^{-1} (Willey et al., 2000). When this is

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considered along with the rainwater flux of $80 \times 10^{12}\,\mathrm{g\,C\,yr^{-1}}$ for dissolved inorganic carbon, it is equivalent in magnitude to approximately one-third of the missing carbon sink (Schimel, et al., 1996; Willey et al., 2000).

However, a large proportion of rainwater DOC is still uncharacterised (Sugiyama and Kumagai, 2001). Thus, little is known about the chemical compounds present (thought to be over 300, Seitzinger et al., 2003), their sources, temporal and spatial patterns of variation, and the subsequent impact on climate and the environment. DOC in the atmosphere (known as water-soluble organic carbon, WSOC) can influence cloud albedo, increase cloud condensation nuclei (CCN) concentrations – WSOC is scavenged up to three times more effectively in-cloud than below cloud (Barth et al., 2001) – contribute to rainwater pH, visibility impairment and photochemical processes, and is a nutrient input to rivers and ecosystems (Seitzinger et al., 2003). Sources of DOC compounds in rain are primary anthropogenic emissions (incomplete combustion of fossil fuels – Klouda et al., 1996; Larsen et al., 1998), photochemical transformations of precursors (in gaseous, aqueous and particulate phases) and primary biogenic emissions (Chebbi and Charlie, 1996).

A novel method for qualitatively characterising DOC compounds in rainfall is to use fluorescence. A large proportion of DOC is fluorescent and this fraction can be used to characterise DOC compounds (Baker and Spencer, 2004), yet its full potential for analysing rainwater DOC compounds has yet to be achieved. Fluorescence is the absorption of light at one wavelength and its re-emission at a longer wavelength. It can be used to fingerprint fluorophores, identify DOC compounds, and detect small concentration levels which may have otherwise gone undetected, with just 0.04 ml samples. Given the importance of better characterisation of rainwater DOC, and the presence of fluorescent DOC compounds, using fluorescence spectrophotometry, we have primarily sought to examine the fluorescent DOC compounds present in precipitation in Birmingham, UK. Furthermore, we investigate how the fluorescence of the identified DOC compounds varies with meteorological parameters, by assessing the variations with stratiform/convective storm types; examining the variations with air mass type and source area using back-trajectory analysis; and investigating variations with wind speed and wind direction.

2. Methodology

2.1. Precipitation sampling

The precipitation sampling strategy used in this study follows Sakugawa et al. (1993); Avery et al. (1991) and Talbot et al. (1988). Sequential samples from individual precipitation events (with a sampling event here defined as an individual rainfall event occurring after a dry period of more than 5 h, under which circumstances equipment was re-sterilised to minimise dry deposition and contamination) were collected from an open urban site at the University of Birmingham (52°28′N, 1°56′W, 132 m above mean sea level – Fig. 1) between the beginning of April 2005 and the end of May 2007. There is no significant agricultural activity in the local areas, since the area is primarily residential, although there is a nearby rail track, main road (A38) and steam/CO_2 emission stacks on the university campus.

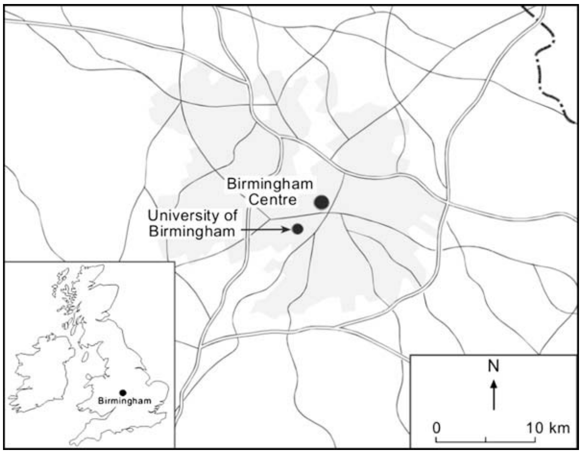

Fig. 1. Map of the location of Birmingham within West Midlands conurbation (shaded) and the UK (inset), and the location of the sampling site (University of Birmingham).

Samples were collected for different rainfall events, reflecting varying synoptic situations and meteorological conditions. Three hundred and ninety nine samples were collected from 41 precipitation events. As a result, range of storm types and storm-origins were sampled – 10 convective storms and 31 stratiform events, with 25 originating or predominantly travelling over maritime areas, 3 over continental areas, and 12 over both maritime and continental areas (1 unidentifiable). Initially (during the 2005 sampling campaign), a sterile, wide-mouthed bespoke pyrex rain collector was used, from which 1 ml samples were collected manually. During the 2006 sampling campaign, a semi-automated ‘active’ precipitation collector was developed, which involved using a 0.2 mm resolution tipping bucket rain gauge modified to sequentially collect 10 ml samples for each tip of the bucket; whilst for the 2007 campaign, a ‘passive’ precipitation collector was developed, based on a modified version of the 1978 Bourrié apparatus using a design outlined by Celle-Jeanton et al. (2004; Celle-Jeanton, personal communication, 2007). Samples were collected using a simple hydraulic system in which a 227 cm^2 surface area feeds a series of 24 30 ml bottles connected by a three-way pipe system and provided with a vertical capillary to drive the air outside. These automated instruments allowed for entire events to be sampled. The only variation between the sampling devices is the resolution at which the events were sampled, which may result in some ‘smoothing’ effects from the latter apparatus when considering intra-event trends – however, since only the mean values from the events are of interest here, this is not relevant to this study.

The sampling apparatus was exposed to the atmosphere just prior to the onset of precipitation. In order to ensure that the rain collectors were completely sterile and not pre-contaminated with any substances that may fluoresce, a specific cleaning protocol was followed whereby bleach, 10% hydrochloric acid and deionised water were used to clean the rain collector and all other equipment used (Galloway et al., 1982). Furthermore, all high-density polyethylene (HDPE) bottles, pipettes, test-tubes, tubing, funnels and quartz micro-cuvettes used to collect, store and analyse the samples, were soaked in 10% HCl for 24 h prior to use and then transferred to deionised water and re-rinsed to ensure they were sterile. Furthermore, all equipment was analysed to ensure there was no residual fluorescence prior to use. Samples were collected at varying intervals depending upon intensity of precipitation. All samples were left unfiltered, since published results indicate that there is a close correlation between DOC and TOC concentrations (Willey et al., 2000), whilst others (Likens et al., 1983; Sempere and Kawamura, 1996) have found that the majority of rainwater organic carbon is dissolved (80% and 90%, respectively). A number of filtered samples were tested against unfiltered samples and no scattering effects were observed in the optical regions examined. The analyses of the rainfall samples took place as soon as the precipitation ceased (always within 24 h, but mostly within 1–2 h of collection), since DOC compounds can be labile (Ayers et al., 2003).

2.2. Fluorescence analysis

A Varian Cary Eclipse Luminescence Spectrophotometer was used to rapidly analyse the rainwater samples – with each analysis taking ~60 s – thus limiting DOC decay. The samples were analysed in a 400 μl volume micro-cuvette. Spectrophotometer PMT voltage was set at 900 V, since it was able to detect very low concentrations of DOC compounds. For excitation wavelengths of 250–400 nm an emission scan was collected over the range of 280–500 nm, with stepwise excitation increments of 5 nm, to produce an excitation–emission matrix (EEM) (Coble et al., 1990). Once the fluorophores were detected and identified, the peak intensity for each fluorophore was located within an area covering the range of known fluorescence for each fluorophore (Section 3.1). Precision (one standard deviation) of triplicate fluorescence data sets was ±3%. The spectrophotometer was calibrated using a sealed water cell containing a pure sample and by measuring the Raman signal at excitation 348 nm (emitted between 390 and 400 nm, at 725 V). The results were standardised to 20 intensity units. Our results can be compared with a quinine sulphate standard where 80 ± 1.7 intensity units are equivalent to one quinine sulphate unit ($1\ \mu g\ l^{-1}$ in 0.1 M H_2SO_4) (see Clark et al., 2002 for method). Results are presented as fluorescence intensity units, given as arbitrary units corrected to Raman (a.u.).

2.3. Meteorological data

Personal weather logs, synoptic charts and back-trajectories were utilised to determine the storm type (stratiform/convective), origin (maritime/continental/mixed) and air mass type [polar maritime (Pm)/returning polar maritime (rPm)/tropical maritime (Tm)/tropical-continental (Tc)/polar-continental (Pc)]. The HYSPLIT 4 (Hybrid Lagrangian Integrated Trajectory) air trajectory model (Draxler and Rolph, 2003) developed at the Air Resources Laboratory of the National Oceanic and Atmospheric Administration (NOAA) was used to calculate backward trajectories from Birmingham during this study. The model is designed for use in evaluating transport on a regional, continental or global scale and the output includes a three dimensional graphical representation of the trajectory as well as meteorological conditions (relative humidity, rainfall, potential temperature, mixed depth) along the trajectory. Using manually checked gridded wind data obtained from the U.S. National Weather Service's National Centre for Environmental Prediction (NCEP) backward trajectories were calculated at 6-hourly intervals up to a period of 5 days preceding the precipitation event at 500, 1000 and 1500 m above ground level. The length of time a back-trajectory is calculated is important – if a trajectory is too long, then more than one evaporation–preciptation cycle may occur (James et al., 2004), but if it is too short, it may not represent the actual source region. Therefore, the range of horizontal and vertical scales used were due to the uncertainty involved in calculating back-trajectories, and the discrepancies within the literature for a suitable method to determine source areas and air mass types, particularly for moisture uptake regions. Precipitation from systems moving predominantly over the ocean were considered maritime in origin, those originating locally or transversing the continent were considered continental, whilst those equally moving over continental and oceanic areas were considered 'mixed' origin. Furthermore, it must be noted that storms not associated with fronts, but simply convective activity were denoted convective storms. It is acknowledged that a large number of storms associated with cold fronts also contain a large amount of convective activity, which may have an impact on the variations observed. Local wind speed was obtained from the nearby weather stations on the University of Birmingham campus for the time period each sample was collected.

3. Results and discussion

3.1. Identification of fluorophores in rainwater samples

Based on the work of Coble (1996, 2007), three fluorophores can be identified in the rainwater samples by fluorescence spectrophotometry, as discussed below. Table 1 shows the emission and excitation wavelengths observed

Table 1
Emission and excitation wavelength range observed for each fluorophore in order to extract the peak fluorescence intensity, also showing the mean and mode values for all data points

Substance		Min	Max	Mode	Mean
TYLIS	Em (nm)	295	315	302	301
	Ex (nm)	265	285	275	274
TRYLIS	Em (nm)	335	370	370	358
	Ex (nm)	260	295	275	275
HULIS	Em (nm)	390	475	413	414
	Ex (nm)	300	340	330	320

for extraction of peak fluorescence intensity for each fluorophore.

3.1.1. HULIS

HUmic-Like Substances (HULIS) (Krivácsy et al., 2000; Havers et al., 1998) in the shorter visible wavelength region of optical space represent one fluorophore (Coble, 2007) detected in the rainwater samples (Fig. 2, peak 'C'), which lies in a similar area of optical space and hence resemble terrestrial and aquatic fulvic acids, although the precise optical location of rainwater HULIS can be more blue-shifted. 'Visible' HULIS are thought to be similar to fulvic acid, which represents the fraction of humic substances that is soluble in water under all pH conditions (Weber, 1997). Fulvic acid contains all of the photochemical protective substances, amino acid peptides and nucleic acids from original plant matter, including aliphatic carbons, carbohydrates, olefinic carbons, ketonic and aldehydeic carbons, and aromatic and carboxylic carbons, with the latter two providing the fluorescence fraction (Frimmel, 1998; Sierra et al., 2005). HULIS in the UV region of optical space (or peak 'A', Coble, 1996) were not analysed in this study due to deteriorating signal-to-noise ratio at lower wavelengths.

Rainwater HULIS are thought to form from aerosols in the atmosphere and which are believed to play an important role in cloud formation processes (Kiss et al., 2003). HULIS are high molecular weight compounds, also termed 'macromolecular compounds' by some authors (Zappoli et al., 1999), 'atmospheric humic matter' by others (Gelencsér et al., 2000), whilst Varga et al., (2001) suggest polycarboxylic acids refer to the same class of WSOC. To the Authors' knowledge, few studies have specifically investigated HULIS in rainwater, however a study by Kieber et al. (2006) did analyse chromophoric dissolved organic matter (CDOM) rainwater using fluorescence spectrophotometry, finding humic-like peaks. A study by Fuzzi et al. (1997) also found that WSOC in fog water was accounted for by unidentified species derived from aerosols, with chemical characteristics similar to naturally occurring humic substances. Graber and Rudich (2006) have suggested that although atmospheric HULIS share similar features to terrestrial and aquatic humic substances, they have substantial differences, such as smaller *average* molecular weight, lower aromatic moiety content (containing a resonant, unsaturated ring of six-carbon atoms), weaker acidic nature, a higher aliphatic component (carbon atoms linked in open chains), and better surface activity and thus better droplet activation ability due to greater number of solute species in lower molecular weight HULIS. Atmospheric HULIS are thought to include – in addition to humic and fulvic acids – organic acids, mostly dicarboxylic acids, and some organic compounds that do not dissociate in solution such as sugars, organic salts and pharmaceutical compounds (Kanakidou et al., 2005). Since aerosols are scavenged both within and below clouds they are likely to be the main contributors of HULIS in rainwater (along with secondary reactions occurring within the droplets), therefore their sources are important. Approximately 20–50% of organic carbon in particulate matter can be attributed to HULIS (Havers et al., 1998; McFiggans et al., 2005). Potential sources of atmospheric HULIS include (Graber and Rudich, 2006):

- Primary anthropogenic sources – motor vehicle exhaust, tyre and asphalt wear, cooking (Dinar et al., 2006)
- Biomass burning (Mukai and Ambe, 1986; Facchini et al., 1999; Zappoli et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002) – soil-derived humic matter resulting from combustion; generation via chemical transformations during combustion and thermal breakdown of plant lignins and cellulose; recombination and condensation reactions between volatile, low molecular weight combustion products (Mayol-Bracero et al., 2002)
- Marine sources (Cini et al., 1994; Cini et al., 1996; Calace et al., 2001; Cavalli et al., 2004) – bubble bursting on ocean surfaces

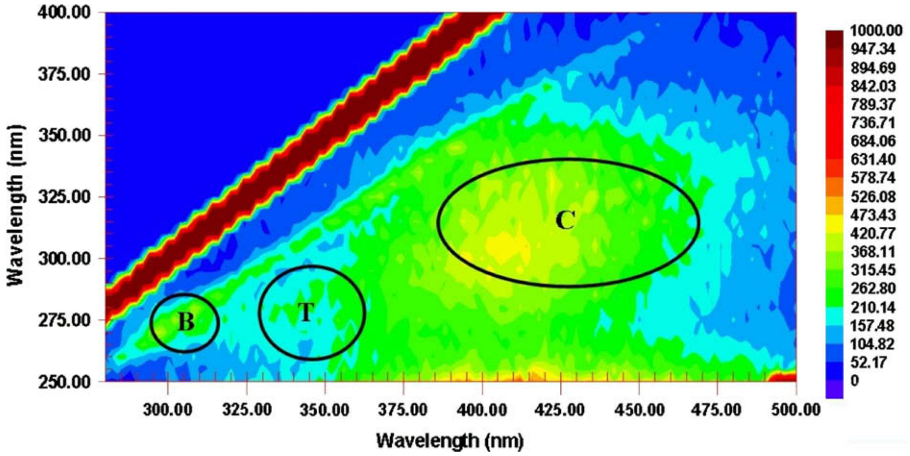

Fig. 2. An example Emission (x)–Excitation (y) Matrix (EEM) chart for a precipitation sample (from 06/07/06, a convective storm of Tm origin with the highest HULIS fluorescence) showing the approximate optical locations for (B) TYLIS, (T) TRYLIS, and (C) 'visible' HULIS (peak letters based on those designated to peaks by Coble, 1996).

- Secondary organic aerosol (SOA) formation of both higher and lower molecular weight HULIS from isoprenoid, terpenoid and α-pinene emissions, for example (Gelencsér et al., 2002; Jang et al., 2002; Jang et al., 2003; Limbeck et al., 2003; Tolocka et al., 2004; Hung et al., 2005; Kanakidou et al., 2005) – condensation, evaporation, photochemical reactions (enhanced in the presence of acidic aerosols, such as diesel soot), oligomerization and aerosol-phase polymerisation of polar, lower molecular weight degradation products of organic debris in soil and other natural and anthropogenic sources into higher molecular weight HULIS (Gelencsér et al., 2002).

3.1.2. TRYLIS and TYLIS

TRYptophan-LIke Substances (TRYLIS) and TYrosine-LIke Substances (TYLIS) were also detected in the samples (Fig. 2, peaks 'T' and 'B', respectively), which lie in similar areas of optical space as tryptophan and tyrosine, respectively. Proteins and amino acids are important components of the organic carbon pool, with total amino compounds accounting for 13% of DOC in fog waters and approximately 10% in water-soluble organic carbon in $PM_{2.5}$ (Zhang and Anastasio, 2003). They are likely to be involved in cloud formation due to the presence of biogenic and proteinaceous matter in cloud waters (Saxena, 1983; Szyrmer and Zawadzki, 1997). Tryptophan is rapidly transformed in water droplets during exposure to ozone and sunlight and such reactions are likely to influence the physical and chemical composition of the atmosphere. Tryptophan and tyrosine can directly absorb sunlight ($\lambda > 290$ nm) (Creed, 1984; Walrant and Santus, 1974; Zhang and Anastasio, 2003) and react directly with ozone to form products such as ammonium, organic acids, nitro compounds and hydroxylamines (Suzuki et al., 1985; Milne and Zika, 1993; Berger et al., 1999; McGregor and Anastasio, 2001), therefore changing the composition of condensed phase organic compounds in the atmosphere and influencing the properties of particles and water droplets. Sources of such compounds are likely to include plant matter, bacteria, yeast, spores and pollen associated with terrestrial areas (Milne and Zika, 1993), and high concentrations have also been detected in oceans (Determann et al., 1996). Therefore tryptophan and tyrosine are likely to be associated with the growth of living organisms (Coble et al., 1990). Furthermore, bacterial strains can alter the physical and chemical properties of clouds and rain via microbiological degradation and by influencing the removal of particulate and gaseous compounds (Amato et al., 2005). They can also modify other organic compounds by acting as biocatalysts and thus altering the capability of other organics, such as dicarboxylic acid, to act as ice nuclei or cloud condensation nuclei (CCN) (Ariya and Amyot, 2004).

3.2. Rainwater organic composition

In total, 399 samples were collected over 41 rainfall events covering a wide variety of meteorological conditions, seasons, source areas and storm types. Table 2 shows the mean fluorescence intensity for each event. The 06/07/07 event which contained the highest HULIS fluorescence intensity, was a convective storm associated with a tropical–continental air mass. The next highest intensities were found in 23/04/05 event, which was produced from a continental warm front, and on 28/07/05, when sampling took place during a thunderstorm which produced a destructive tornado affecting parts of Birmingham (TORRO, 2005), indicating a considerable amount of convective activity. The lowest HULIS fluorescence intensities were mainly found in maritime-sourced precipitation events. The convective event on 19/06/05 contained very high TYLIS and TRYLIS fluorescence; however, on preliminary examination of the data, there seem to be less obvious controls on TYLIS and TRYLIS in rainwater.

The mean HULIS fluorescence intensity from all events was 209 a.u., with the fluorescence of individual samples ranging from 37 a.u. to 995 a.u. Mean fluorescence intensity was 469 a.u. and 265 a.u. for TYLIS and TRYLIS, respectively. Fluorescence values for individual samples ranged from 214 a.u. to 988 a.u for TYLIS, and 50 a.u. to 876 a.u for TRYLIS. It must be noted that since different fluorophores have specific fluorescence intensity–concentration relationships, these values are not representative of concentrations of these substances *relative* to each other. However, laboratory tests have shown that fluorescence displays a simple linear relationship with dilution identical to chemical concentration (Kieber et al., 2006) – our fluorescence analyses of standard compounds of known concentrations also display this trend (data not shown). Therefore variation in concentration for a *specific* substance of interest is representative of changes in concentration, i.e. overall increasing HULIS fluorescence intensity would suggest increasing HULIS concentration.

Mean and mode peak emission and excitation locations for each fluorophore were calculated based on the 399 samples (Table 1). These can be compared with terrestrial aquatic samples previously reported: Coble (2007) identified tyrosine-like peaks and tryptophan-like peaks in natural water at 275/305 and 275/340 (Ex/Em), respectively. Coble (2007) also identified humic-like peaks at various optical locations depending upon source – a peak at 320–360 Ex/420–460 Em (defined as 'UVA humic-like', located at shorter visible wavelength bands) was associated with terrestrial, anthropogenic and agriculturally derived HULIS with more aromaticity – this peak lies in a similar area to the mode and mean optical locations for the observed rainwater HULIS, suggesting that these sources are major contributors. The precise locations of the peak excitation and emission wavelengths however, can vary between samples and events, due to ageing; the presence of different substances; or to contributions from different source areas.

3.3. Meteorological patterns

Variations in fluorescence intensities for TYLIS and TRYLIS with the meteorological parameters observed were not statistically significant (but are shown in Figs. 3 and 4 for comparison), and are therefore not discussed. The following sections will consider only the HULIS variations.

Table 2
Summary table showing the fluorescence intensity values (a.u.) for TYLIS, TRYLIS and HULIS for each rainfall event (bold values show highest fluorescence intensities)

Event	Number of samples	Storm type	Source	Air mass	TYLIS (a.u.)	TRYLIS (a.u.)	HULIS (a.u.)
23/04/05[a]	3	Stratiform	Continental	Pc	342	241	471
26/04/05[a]	40	Stratiform	Maritime	rPm	355	125	78
24/05/05[a]	19	Stratiform	Maritime	rPm	398	142	85
15/06/05[a]	4	Stratiform	Maritime	Tm	281	70	86
19/06/05[a]	1	Convective	Mixed	Tm	**956**	**876**	222
24/06/05[a]	19	Convective	Mixed	Tm	488	213	137
05/07/05[a]	18	Convective	Maritime	Tm	384	160	79
28/07/05[a]	10	Convective	Mixed	Pm	457	363	469
28/09/2005[a]	5	Stratiform	Maritime	Pm	486	159	207
24/10/2005[a]	6	Stratiform	Maritime	rPm	595	234	282
26/10/2005[a]	11	Stratiform	Maritime	Tm	477	302	102
23/02/2006[a,d]	5	Stratiform	Mixed	Pm	374	107	131
12/06/2006[b]	8	Convective	Mixed	Tm	370	192	199
13/06/2006[b]	14	Convective	Mixed	Tc	413	149	147
20/06/2006[b]	6	Stratiform	Maritime	Pm	390	192	257
06/07/2006[b]	1	Convective	Mixed	Tc	380	289	**481**
09/07/2006[b]	1	Stratiform	Maritime	rPm	431	335	411
20/07/2006[b]	5	Convective	Continental	Pc	354	248	379
22/07/2006[b]	22	Convective	Maritime	Tm	414	121	162
29/09/2006[b]	8	Stratiform	Maritime	rPm	381	124	238
05/10/2006a[b]	18	Stratiform	Maritime	rPm	389	162	182
05/10/2006b[b]	12	Stratiform	Maritime	rPm	382	136	126
06/10/2006[b]	28	Stratiform	Maritime	Pm	344	119	142
09/10/2006[b]	6	Stratiform	Maritime	Tm	411	140	143
11/10/2006[b]	16	Convective	Maritime	Tm	472	204	243
17/10/2006[b]	1	Stratiform	Continental	Tc	578	302	409
19/10/2006[b]	33	Stratiform	Maritime	Pm	359	137	142
07/12/2006[b]	12	Stratiform	Maritime	Pm	941	470	386
08/02/2007[c,d]	6	Stratiform	Mixed	Pm	462	195	217
09/02/2007[c,d]	14	Stratiform	Mixed	Pm	458	241	268
10/02/2007[c]	7	Stratiform	Maritime	rPm	528	452	173
11/02/2007[c]	2	Stratiform	Maritime	rPm	389	357	126
12/02/2007[c]	3	Stratiform	Maritime	rPm	385	181	125
13/02/2007[c]	2	Stratiform	Mixed	Pc	483	232	133
16/02/2007[c]	5	Stratiform	Mixed	Tm	487	312	141
05/03/2007[c]	5	Stratiform	[e]	[e]	564	420	174
24/04/2007[c]	4	Stratiform	Maritime	Tm	659	309	165
09/05/2007[c]	4	Stratiform	Maritime	Tm	542	314	182
10/05/2007[c]	6	Stratiform	Maritime	rPm	537	664	139
14/05/2007[c]	3	Stratiform	Mixed	Tm	594	392	175
16/05/2007[c]	6	Stratiform	Maritime	Pm	522	472	167

[a] Manual sampling.
[b] Automatic sampling using 'active' sampler.
[c] Automatic sampling using 'passive' sampler.
[d] Snow; 'Mixed' origin indicates both continental and maritime source.
[e] Data unavailable.

3.3.1. *Storm type and source area*

Fig. 3 shows the differences in the mean and standard error for HULIS fluorescence for events categorised by storm type, source area and air mass type. Table 3 shows the level of significance for the analysis of variance tests carried out. For HULIS, an ANOVA test showed that significantly higher fluorescence intensities were evident in samples from convective events. This is likely to be due to the higher contribution from localised sources. For HULIS, significantly higher fluorescence intensities were further found in continental-sourced events, with both tropical and polar–continental events favouring higher fluorescence intensities over all maritime air mass types – this suggests increasing terrestrial contributions and/or anthropogenic contributions due to trans-boundary pollution from Europe; lower fluorescence intensities were found in both mixed and purely maritime-sourced events, particularly from tropical maritime air masses.

Fig. 4 combines data from storm type and origin (resulting in 6 'types' of events). HULIS fluorescence was highest in stratiform/convective events associated with a continental source, reinforcing the idea of a larger contribution by both localised/terrestrial/anthropogenic sources. These results indicate that the highest HULIS fluorescence was evident in convective storms which originated or predominantly travelled over continental areas, whilst maritime-sourced rainfall exhibits lower HULIS fluorescence, suggesting that substances in marine storms are not heavily impacted by anthropogenic or biogenic local sources (Avery et al., 2001; Willey et al., 2000). This is further evidence of the increasing contribution of terrestrial sources to HULIS fluorescence.

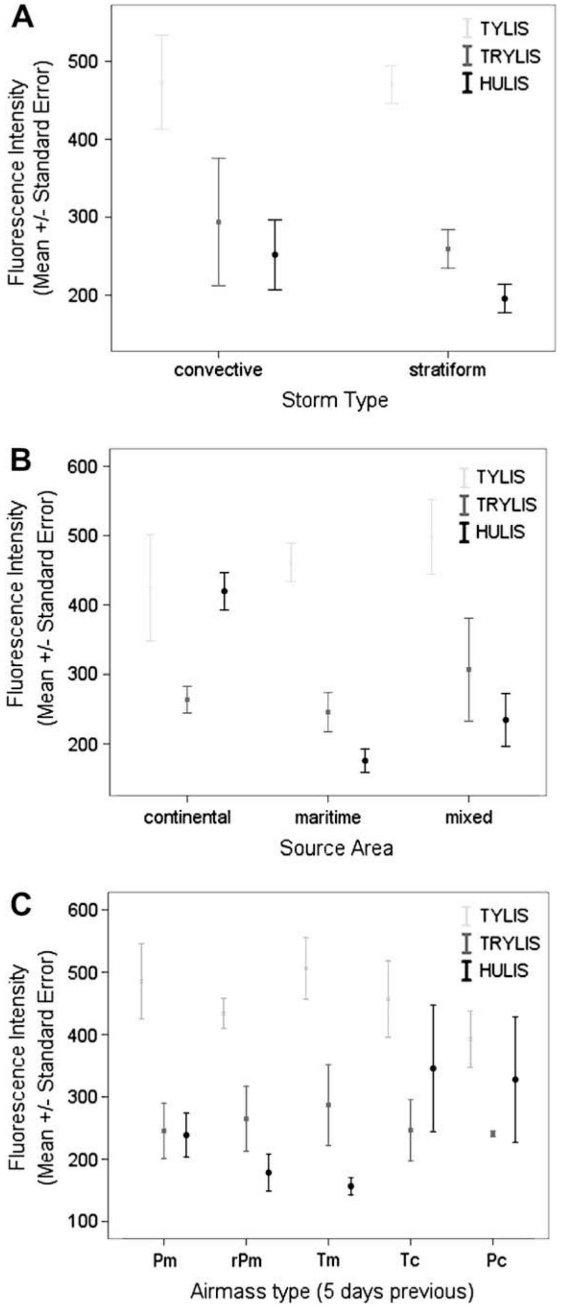

Fig. 3. Error bar charts showing the mean and standard error for HULIS*, TRYLIS and TYLIS fluorescence intensity (a.u.) for each (i) storm type, (ii) source areas, (iii) air mass type. *Only HULIS fluorescence shows statistically significant variations, as discussed in the text.

The 'continentality' of the rain producing air mass is indeed an important determinant of rainwater HULIS fluorescence intensity in Birmingham rainfall. Rainwater HULIS therefore appear to be significantly affected by storm origin.

These qualitative findings are in agreement with past quantitative results – Willey et al. (2000) found that overall DOC concentrations were highest in 'continental' rain, as a result of low-pressure systems, local thunderstorms and cold fronts, in comparison to 'marine' rain. Avery et al. (1991) also found the highest concentrations of DOC in local thunderstorms, suggesting that thunderstorms provide extensive vertical mixing in atmospheric regions with intense sunlight and high ozone, and may therefore contribute to organic acid formation. Kieber et al. (2006) anaylsed CDOM in rainwater using fluorescence analyses and found elevated levels in continentally influenced rainwater, suggesting anthropogenic/terrestrial origins. Furthermore, by examining the fluorescence emission maxima, they found a lower degree of conjugation or aromaticity in terrestrially influenced rain events compared to marine dominated events.

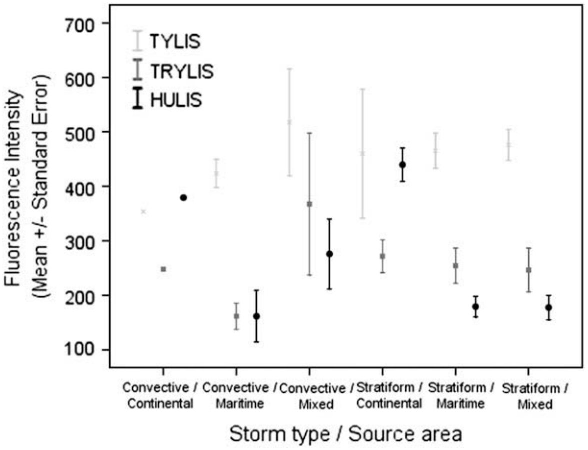

Fig. 4. Error bar charts showing the mean and standard error for HULIS*, TRYLIS and TYLIS fluorescence intensity (a.u.) for a combination of different storm types and source areas. *Only HULIS fluorescence shows statistically significant variations, as discussed in the text.

3.3.2. Wind speed

A Kendall's tau test indicated a significant negative correlation between HULIS fluorescence intensity and local wind speed ($\tau = -0.227$; $n = 41$; $p < 0.05$) indicating that the observations are likely to be discordant, and can therefore account for some of the trends observed. This suggests that calm conditions can contribute to elevated rainwater HULIS content, whilst more turbulent conditions may result in lower amounts of HULIS in rainwater. Thermal inversion and weak winds cause the stagnation of the atmosphere due to limited ventilation, transport and dispersion, and thus encourage the build up of pollutants emitted by anthropogenic or local terrestrial sources

Table 3
ANOVA output table for statistically significant results

Sub-category	Substance	N	F	*p*
Storm type	HULIS	41	3.977	0.047***
Source area	HULIS	40	9.047	0.001*
Air mass type	HULIS	40	3.694	0.013***
Storm type/source area	HULIS	40	4.131	0.005**

*$p < 0.001$, **$p < 0.01$, ***$p < 0.05$.

(Migliavacca et al., 2005). This may suggest that during weak winds, there may be a higher contribution from local sources, perhaps providing an explanation for the increasing HULIS fluorescence found in some 'marine' events. Furthermore, clear sky conditions and high amounts of solar radiation which are also associated with thermal inversions and weak winds, may influence photochemical reactions and therefore increase rainwater HULIS content.

4. Conclusions and recommendations

The fluorescence analysis of rainwater DOC in 399 samples from 41 events identified TYLIS, TRYLIS and HULIS compounds in rainwater samples in Birmingham, UK, and allowed peak fluorescence intensities, and emission and excitation locations to be extracted. Overall, fluorescence intensity averaged (extremes) 209 a.u. (37–995 a.u.), 469 a.u. (214–988 a.u), and 265 a.u. (50–876 a.u.) for HULIS, TYLIS and TRYLIS, respectively. The average HULIS peak location was found in an area of optical space previously attributed to terrestrial and anthropogenic sources. Rainfall from convective storms exhibited higher HULIS fluorescence intensities due to extensive mixing, and an increased local contribution. HULIS were also found to be strongly correlated with the 'continentality' of the rain producing air masses – air masses that had spent more time over land were associated with higher HULIS fluorescence intensities than air masses that had maritime origins. Wind speeds were found to be significantly negatively correlated with HULIS fluorescence, indicating stagnation of the atmosphere causing a build up of pollution and organic material to be important to rainwater concentrations. Overall, the fluorescence analysis results presented here are in agreement with quantitative results from previous studies which have looked at total rainwater DOC concentrations.

Our results demonstrate the utility of fluorescence analysis for identifying and characterising rainwater DOC compounds. This research has revealed information regarding fluorescent rainwater DOC compounds in Birmingham, UK and provides evidence in support of using fluorescence spectrophotometry as a means of qualitatively characterising rainfall DOC. The pioneering fluorescence technique can detect compounds which may have previously gone undetected, and, since DOC compounds can be labile (Ayers et al., 2003), provides a more accurate characterisation of rainwater DOC compounds due to the rapid analysis. It will help expand the limited pool of knowledge on the subject, assist in enhancing our understanding of the variations in rainwater DOC compounds under different conditions, and their relationships with meteorological parameters. Future work will analyse temporal trends, including intra-event data, and investigate the variation in peak emission-excitation location, since the precise location can vary between samples and events, and thus could provide further information on ageing, the presence of different substances, and/or contributions from different source areas.

Precise calibrations of TYLIS, TRYLIS and HULIS fluorescence against concentration cannot currently be quantified using fluorescence spectrophotometry. Standard compounds, such as Suwanee River Fulvic Acid (SRFA) which is chemically well characterised and widely used to calibrate humic substances'fluorescence in terrestrial waters, cannot be used since HULIS have a wide range of molecular weights, and many individual compounds are currently uncharacterised. In order to improve this powerful technique, and use it to its full potential, there is further need for in-depth research into the fluorescence properties of individual organic compounds, in order to link information regarding precise optical locations and fluorescence intensities for specific compounds, to their relative concentrations.

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