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Spatial and Seasonal Variation of Dissolved Organic Carbon (DOC) Concentrations in Irish Streams: Importance of Soil and Topography Characteristics

**Wen Liu · Xianli Xu · Nicola M. McGoff ·
James M. Eaton · Paul Leahy · Nelius Foley ·
Gerard Kiely**

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Abstract Dissolved organic carbon (DOC) concentrations have increased in many sites in Europe and North America in recent decades. High DOC concentrations can damage the structure and functions of aquatic ecosystems by influencing water chemistry. This study investigated the spatial and seasonal variation of DOC concentrations in Irish streams across 55 sites at seven time occasions over 1 year (2006/2007). The DOC concentrations ranged from 0.9 to 25.9 mg/L with a mean value of 6.8 and a median value of 5.7 mg/L and varied significantly over the course of the year. The DOC concentrations from late winter (February: 5.2 ± 3.0 mg/L across 55 sites) and early spring (April: 4.5 ± 3.5 mg/L) had significantly lower DOC concentrations than autumn (October: mean 8.3 ± 5.6 mg/L) and early winter (December: 8.3 ± 5.1 mg/L). The DOC production sources (e.g., litterfall) or the accumulation of DOC over dry periods might be the driving factor of seasonal change in Irish stream DOC concentrations. Analysis of data using stepwise multiple linear regression techniques identified the topographic index (TI, an indication of saturation-excess runoff potential) and soil conditions (organic carbon content and soil drainage characteristics) as key factors in controlling DOC spatial variation in different seasons. The TI and soil carbon content (e.g., soil organic carbon; peat occurrence) are positively related to DOC concentrations, while well-drained soils are negatively related to DOC concentrations. The knowledge of spatial and seasonal variation of DOC concentrations in streams and their drivers are essential for optimum riverine water resources management.

Keywords DOC concentrations · Riverine DOC · Stream DOC · Ireland · Water quality

Introduction

Dissolved organic carbon (DOC) is composed of a range of organic compounds, including fulvic and humic acids, and is derived from root exudates, microbial biomass, and the decomposition of plant litter and soil organic matter. Concentrations of DOC in natural waters range from <1 to >50 mg/L (Thurman 1985). DOC concentrations in riverine systems are dependent on the organic matter content of the soil, the depth of mineral soil and watershed hydrology (Dalva and Moore 1991; Hope et al. 1997; Aitkenhead et al. 1999; Ågren et al. 2008; Dawson et al. 2008; Eimers et al. 2008; Ågren et al. 2010b). Tipping et al.

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W. Liu
College of Resources and Environmental Sciences, Hunan Normal University, Changsha 410081, China
e-mail: wenwen424@gmail.com

X. Xu (✉)
Key Laboratory for Agro-Ecological Processes in Subtropical Region, Institute of Subtropical Agriculture, Chinese Academy of Sciences, Changsha 410125, China
e-mail: xuxianliww@gmail.com

X. Xu
Huanjiang Observation and Research Station for Karst Ecosystem, Chinese Academy of Sciences, Huanjiang 547100, China

N. M. McGoff · J. M. Eaton · P. Leahy · N. Foley · G. Kiely
Centre for Hydrology, Micrometeorology and Climate Change, Department of Civil and Environmental Engineering, Environmental Research Institute, University College Cork, Cork, Ireland
e-mail: g.kiely@ucc.ie

(1999) found adsorption by mineral soils to be a dominant control in the transport of DOC. Stream water DOC concentrations decrease with increased mineral soil depth due to the effect of soil water percolation and increased residence time. In addition, riverine DOC concentrations are negatively correlated with the clay content (Kalbitz et al. 2000) and to the content of iron and aluminum oxides/hydroxides in watershed soils. With decreasing soil pH, the adsorption capacity is increased as a result of increasing positive charge on the hydroxides. In general, maximum adsorption of humic substances (such as DOC) occurs near a pH of 5.0; adsorption decreases under anaerobic conditions (Kalbitz et al. 2000). Seasonal dynamics in DOC concentrations might be due to the seasonal change in DOC production (Worrall et al. 2002; Koehler et al. 2009).

Recent work in Europe and North America indicates an increase in riverine DOC concentrations due to global warming (Worrall et al. 2003; Freeman et al. 2004), to a combination of declining acid deposition and rising temperatures (Evans et al. 2005), to rising temperatures, declining sulfur deposition and changing sea-salt loading (Evans et al. 2006) or to streamflow change (Eimers et al. 2007). Increases of DOC concentrations in rivers may modify structure and functions of aquatic ecosystems, by modifying water chemistry, carrying nutrients and contaminants (Dawson et al. 2008; Eimers et al. 2008; Ågren et al. 2012). High DOC concentrations affect local water quality, discoloring drinking water and the enhanced formation of carcinogenic trihalomethanes and haloacetic acids when riverine water (high in DOC) is treated with chlorine (Fleck et al. 2004; Aitkenhead-Peterson et al. 2007). The knowledge of spatial and seasonal variation of DOC concentrations is required for effective water resources management.

The aims of this research are as follows: (1) to examine the seasonal and spatial variation of DOC concentrations in streams across Ireland; and (2) to identify the drivers in the variability of DOC concentrations.

Methods

Site Descriptions

In total, we visited 55 sites (streams) throughout the Ireland (Fig. 1), and each site is an outlet for each watershed. The selected 55 sites (watersheds) are considered to represent the most prominent combinations of land and soil in Ireland. At each of the 55 sampling points, the date, time of sample, latitude, longitude, land use, elevation, estimated stream width and depth, the current weather and a visual description of the riparian area were recorded. In addition to attribute data collected at each sampling point, ArcGIS version 9.2 (ESRI 2006) and ArcHydro version 1.2 (ESRI 2007) were used to delineate the watershed boundary and extract watershed attributes such as watershed area, precipitation, topographic conditions [slope, aspect, topographic index (TI)], land use and soil class. The TI, commonly used in the TOPMODEL rainfall-runoff framework (Beven 1997), was computed as:

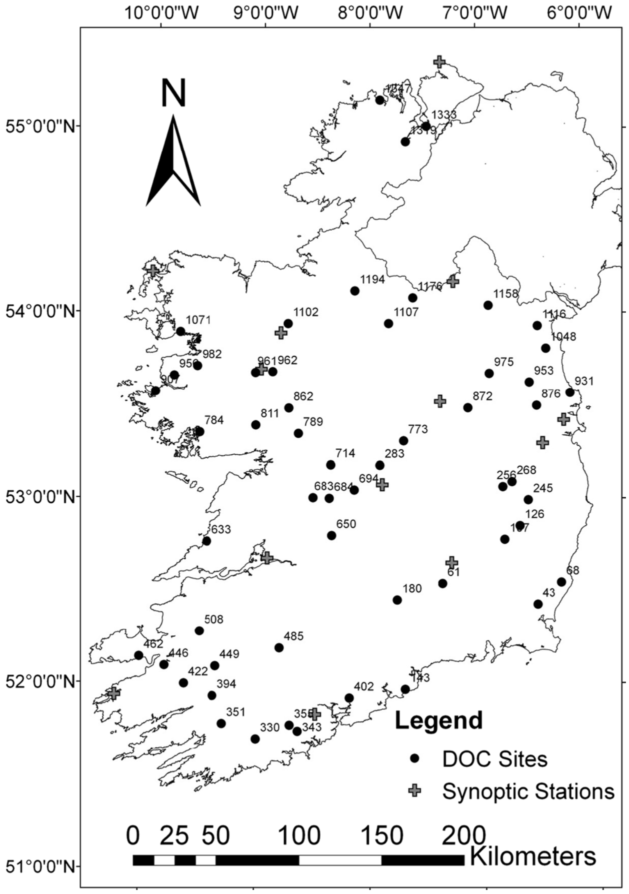

Fig. 1 Location of sampling sites and meteorological stations in Ireland

$$\mathrm{TI} = \ln(\alpha/\tan\beta) \tag{1}$$

where α is the local upslope area draining through a certain point per unit contour length and $\tan\beta$ is the local slope. The index describes the propensity for a site to saturate at the surface given its contributing area and local slope characteristics. The watersheds ranged in area from 2.2 to 7,151 ha (Table 1), and these watershed areas were verified using Ordnance Survey Ireland Discovery Series Maps (OSI 1995).

A spatially explicit (approximately 84 % coverage for all watersheds) land use map was generated, in cooperation with the Environment Protection Agency (EPA), using vector data from the Land Parcel Information Service (LPIS, Department of Agriculture, Food and Forestry (DAFF) completed 2004, pers. comm.), Forest Inventory Parcel Service (FIPS) (Bulfin 1998) and afforestation data (DAFF, completed 2004, pers. comm.). Gaps (the remaining 16 % coverage of these watersheds) in land use

Table 1 Sampling site and watershed information

Site number	Easting	Northing	Catchment area (ha)	Dominant land use	Soil class	Elevation (m)	Estimated precipitation (mm)	Closest synoptic station	TI	SOC (%)
43	301369	132736	187	Arable	DPDM	56	1,173	Kilkenny	8.7	5.7
61	244076	145096	1,946	Grassland	–	72	1,098	Kilkenny	8.4	6.4
68	315814	146090	3,104	Grassland	–	38	1,107	Kilkenny	8.5	5.2
107	281443	171638	815	Arable	SWDM	66	1,062	Kilkenny	8.5	6.1
126	290498	179850	31	Grassland	DWDM	112	1,253	Kilkenny	8.3	6.5
143	221352	081426	100	Grassland	DWDM	72	1,018	Cork Airport	7.9	5.5
180	216456	135152	356	Grassland	DWDM	94	1,135	Kilkenny	8.3	5.3
245	295546	195614	22	Forest	POD	191	1,578	Casement	6.4	9.2
256	280195	203491	1,212	Grassland	SWDM	104	1,020	Casement	8.4	5.3
268	285649	206465	1,765	Grassland	DWDM	128	1,026	Casement	8.0	6.2
283	206050	216200	122	Peatland	PEAT	58	998	Birr	8.9	20.1
330	130805	051567	119	Grassland	DWDM	96	1,736	Cork Airport	7.5	5.9
343	156036	056124	347	Grassland	DWDM	11	1,317	Cork Airport	7.3	3.7
351	110493	060929	428	Peatland	POD	95	2,352	Cork Airport	6.7	13.5
355	151187	059894	2,845	Grassland	DWDM	28	1,335	Cork Airport	7.7	4.6
394	104752	077729	117	Peatland	POD	88	3,461	Valentia	6.6	11.8
402	187641	076152	1,322	Grassland	DWDM	26	1,161	Cork Airport	7.6	3.8
422	087414	085326	245	Peatland	POD	143	2,797	Valentia	5.7	9.9
446	075683	096238	149	Grassland	DWDM	20	1,903	Valentia	8.0	9.1
449	106594	095571	230	Peatland	PEAT	156	1,468	Valentia	8.5	11.1
462	060552	101762	55	Grassland	POD	96	2,385	Valentia	6.0	9.9
485	145144	106267	1,737	Grassland	DPDM	100	1,063	Cork Airport	8.2	6.6
508	097027	116639	114	Forest	PEAT	200	1,367	Shannon	7.7	14.8
633	101600	170600	6,127	Peatland	–	12	1,094	Shannon	8.0	16.4
650	177100	173900	284	Grassland	DWDM	160	1,235	Shannon	7.4	7.4
683	165525	196800	412	Forest	PEAT	150	1,544	Birr	7.8	9.6
684	175650	196400	560	Grassland	PEAT	42	1,266	Birr	8.1	9.4
694	190600	201350	3,198	Grassland	DWDM	62	1,026	Birr	8.6	9.8
714	176500	216400	84	Grassland	DPDM	68	1,235	Birr	8.4	7.2
773	220220	230750	182	Grassland	–	49	1,068	Birr	8.3	10.4
784	097300	236300	91	Peatland	PEAT	3	1,720	Claremorris	8.3	52.6
789	156801	235229	318	Peatland	PEAT	60	1,177	Claremorris	9.0	12.0
811	131250	240350	76	Grassland	DWDM	7	1,238	Claremorris	9.1	10.3
862	151000	250500	706	Grassland	DWDM	52	1,138	Claremorris	8.7	11.8
872	259173	250598	7,151	Grassland	–	68	998	Mullingar II	8.6	12.2
876	300518	252224	961	Grassland	DPDM	96	944	Dublin Airport	8.8	4.8
907	070800	261000	19	Peatland	–	43	1,444	Claremorris	7.3	25.0
931	320784	259871	87	Arable	DWDM	79	815	Dublin Airport	8.1	3.6
953	296032	266211	34	Grassland	DWDM	75	920	Dublin Airport	7.8	4.7
956	082000	270500	124	Peatland	POD	69	2,313	Claremorris	6.1	32.2
961	131050	271900	207	Grassland	–	50	1,238	Claremorris	8.3	11.4
962	141400	272500	69	Grassland	DPDM	65	1,233	Claremorris	8.7	12.4
975	272060	271397	354	Grassland	DWDM	75	1,037	Mullingar II	8.8	5.5
982	095941	276106	39	Grassland	DWDM	107	2,589	Claremorris	7.2	15.5
1048	305899	286600	3,055	Grassland	DPDM	43	945	Dublin Airport	7.9	4.1
1071	085750	296550	897	Peatland	POD	26	2,196	Belmullet	6.9	18.8
1102	150693	301266	273	Forest	DPDM	93	1,423	Knock	7.6	13.7

Table 1 continued

Site number	Easting	Northing	Catchment area (ha)	Dominant land use	Soil class	Elevation (m)	Estimated precipitation (mm)	Closest synoptic station	TI	SOC (%)
1107	211265	301358	728	Grassland	DPDM	60	1,107	Clones	7.5	10.4
1116	300831	300082	22	Arable	DWDM	27	794	Clones	7.8	6.1
1158	271308	312304	218	Grassland	DPDM	126	1,004	Clones	7.2	9.4
1176	225706	316664	21	Peatland	DPDM	63	1,362	Clones	7.8	9.4
1194	191033	320879	28	Peatland	PEAT	62	1,370	Knock	7.0	11.8
1319	221277	410921	77	Grassland	DWDM	30	1,486	Malin Head	7.6	6.1
1333	233817	420184	692	Grassland	DPDM	10	1,429	Malin Head	7.6	6.7
1347	206018	435862	2	Grassland	DPDM	12	1,494	Malin Head	8.8	12.3

Easting and northing values are coordinates of the Irish National Grid; dominant land use and soil classes represent >50 % of the watershed area. Elevation was recorded at the DOC sampling site; estimated precipitation values were calculated as the sum P_s (see Eq. 2); synoptic stations nearest to our sampling site were used; Rosslare station was not used

DPDM deep poorly drained mineral soil, *DWDM* deep well-drained mineral soil, *SWDM* shallow well-drained mineral soil, *PEAT* peat, *POD* podzol, *TI* topographic index, *SOC* soil organic carbon content

data were filled using CORINE 2000 (O'Sullivan 1994; Bossard et al. 2000). In general, CORINE 2000 data represented <10 % of each watershed. Land use was grouped into seven classes: arable, forest, grassland, peatland, other, rough and water. For the 55 watershed areas, we ascribed a dominant land use based on 50 % or greater land use. This resulted in four land use classes: arable, forest, grassland and peatland. Knowing the bias of these data sources, the grassland and peatland classifications were adjusted using data from the Derived Irish Peat Map (DIPM) (Connolly et al. 2007). This correction generated a clearer understanding of peatland as the dominant land use of a watershed, as some peatland is reported as grasslands (after active drainage) due to their capacity for animal grazing.

Soil classes for the 55 watersheds were generated in ArcGIS by clipping the Irish Forest Soils (IFS) map (Fealy et al. 2006) with the watershed boundaries. The 26 soil classes of the IFS map were simplified by grouping the data into nine major soil categories. The 55 watersheds were again classified based on dominant (area proportion: 50 % or greater) soil class in the watershed resulting in five soil classes: deep poorly drained mineral (DPDM); deep well-drained mineral (DWDM); peats (PEAT); podzolized soils with/without peaty topsoil (POD); and shallow well-drained mineral (SWDM). Seven of the 55 sites had no dominant soil class and were thus excluded from analyses which involved soil class. The terms “peatland” and “peat soils” were used as a land use and soil class, respectively. Soil organic carbon (SOC) concentrations were extracted from a GIS map of Zhang et al. (2008).

Measurement of DOC Concentrations

Water was collected at 55 sites (Fig. 1) on seven occasions over a 12-month period. The sampling times are reported as hydrologic day with dates given in Table 2. We consider that day 1 of the hydrologic year for Ireland is October 1. Sampling began in November (day 40) and ended in October the following year (day 369). Day 369 could equally be considered day 4 of the next hydrologic year. A 500-mL grab sample was collected from each of the 55 stream sites, all within a 48-h period. The water samples were stored on ice during transport. The samples were returned to the laboratory, filtered through ashed (450 °C for 2 h) GF/C filter paper prior to analysis with a Shimadzu total organic carbon analyzer (TOC-V CPH). The data from the water samples generated DOC concentrations, in mg/L.

Climate Data

The sampling year was split into seven hydrologic periods corresponding to the seven DOC sampling times (Table 2). The start and end dates of the hydrologic periods were chosen so as to make the precipitation pattern within the hydrologic period similar to the precipitation surrounding the DOC sampling date (Fig. 2). The daily precipitation of the 13 Irish synoptic weather stations (Fig. 1) as well as the standard annual average precipitation (SAAR) was obtained from Met Éireann (MÉ 2005), the Irish National Weather Service. The daily precipitation at each site was estimated using Eq. 2.

$$P_s = P_{syn} \times \frac{\mathrm{SAAR_s}}{\mathrm{SAAR_{syn}}} \tag{2}$$

where P_s is daily precipitation for the sampled site, P_{syn} is daily precipitation for the closest synoptic weather station, $\mathrm{SAAR_S}$ is standard annual average precipitation for the sampled site and $\mathrm{SAAR_{syn}}$ is standard annual average precipitation for the closest synoptic weather station.

Table 2 Averaged temperature (°C), precipitation (mm/day) and dissolved organic carbon (DOC) concentrations (mg/L) across sampling sites per sampling period

Sampling day	Hydrologic day	Season	Mean temperature (°C)	Mean precipitation (mm/day)	Mean DOC concentration (mg/L)	Minimum DOC concentration (mg/L)	Maximum DOC concentration (mg/L)
November 9, 2006	40	Autumn	7.67 ± 0.87	1.48 ± 1.04	7.32 ± 4.87	1.2	23.3
December 12, 2006	73	Winter	6.72 ± 0.87	6.94 ± 2.97	8.33 ± 5.11	1.9	25.9
February 9, 2007	132	Winter	6.13 ± 0.87	3.75 ± 2.08	5.22 ± 3.01	1.0	12.4
April 5, 2007	187	Spring	10.75 ± 0.87	0.30 ± 0.22	4.53 ± 3.46	0.9	18.4
June 7, 2007	250	Summer	14.00 ± 0.87	3.79 ± 1.26	7.13 ± 4.77	1.3	19.4
August 3, 2007	307	Summer	14.79 ± 0.87	4.02 ± 1.04	6.90 ± 4.31	1.2	15.6
October 4, 2007	369	Autumn	11.81 ± 0.87	2.44 ± 1.33	8.27 ± 5.59	1.5	23.2

Rather than an average for all sites, temperature is the average monthly temperature at the 13 synoptic stations

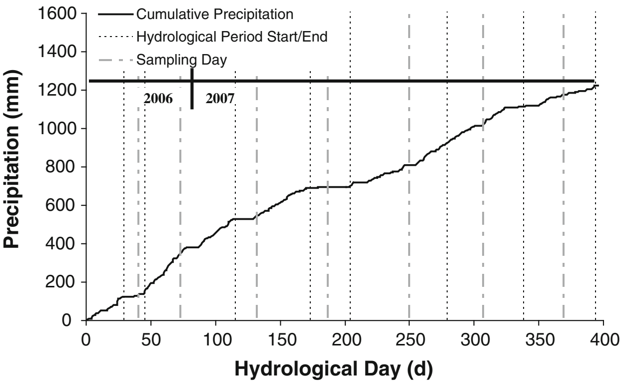

Fig. 2 Cumulative precipitation, sampling dates and hydrologic periods as a function of the hydrologic year (October 1, 2006, is hydrologic day 1). Cumulative precipitation was calculated as the accumulation of daily average of all synoptic stations

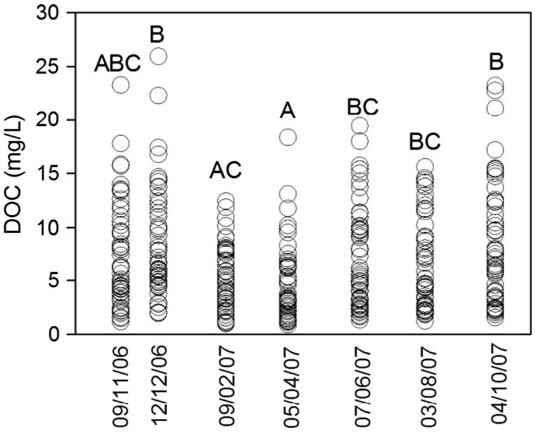

Fig. 3 DOC concentrations (mg/L) per sampling time (DD/MM/YY). Each *circle* represents DOC concentration at a site. Different letters indicate significant differences (one-way ANOVA, $P < 0.05$)

Statistical Analysis

Seasonal trends in DOC concentrations were explored using one-way ANOVAs. Differences with respect to the influence of land use and soil class on DOC concentrations were investigated using repeated-measures ANOVAs (RM-ANOVAs). Tukey's honest significant difference (Tukey's HSD) test was used to determine differences among means following a significant ANOVA. Data were log-transformed when it failed to meet the assumptions of ANOVA. Stepwise multiple linear regression (MLR) analysis was used to identify the driving factors of spatial and seasonal patterns of DOC concentrations. All statistical analyses were completed using SPSS version 12.0.1 (SPSS 2003).

Results

Characteristics of Dissolved Organic Carbon Concentrations

Over the samplings of 7 times × 55 stream sites, the DOC concentrations ranged from 0.9 to 25.9 mg/L with a mean value of 6.8 and a median value of 5.7 mg/L. DOC concentrations varied significantly over the course of the year (ANOVA, $P < 0.05$), as shown in Fig. 3. The higher DOC concentrations were found in autumn (October: mean 8.3 mg/L, day 369; November: mean 7.3 mg/L, day 40) and early winter (December: mean 8.3 mg/L, day 73). Water samples from later winter (February: mean 5.2 mg/L across 55 sites, day 132, see Table 2) and early spring (April: mean 4.5 mg/L, day 187) had significantly lower DOC concentrations than autumn (October) and early winter (December). DOC concentrations of April were also significantly lower (Table 2, $P < 0.05$) than that of summer (June: mean 7.1 mg/L, day 250; August: mean 6.9 mg/L, day 307). November (mean 7.3 mg/L, day 40) was not significantly different to any other time.

Factors Influencing DOC Concentrations

The DOC concentrations appeared to decrease in the following order (Fig. 4a): forest (mean 4.8–10.8 mg/L,

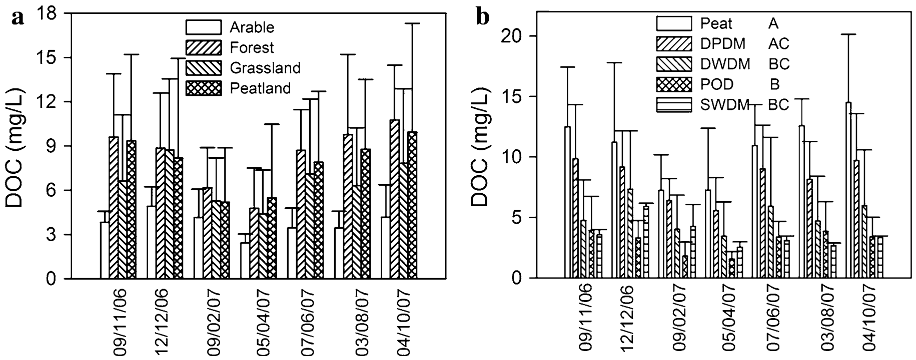

Fig. 4 Seasonal (DD/MM/YY) trend of DOC concentrations (mg/L) for several **a** land uses and **b** soil classes. *DWDM* deep well-drained mineral, *SWDM* shallow well-drained mineral, *DPDM* deep poorly drained mineral, *POD* podzol soils with and without a peaty surface, *Peat* peat. Data represent the mean DOC concentration ± SD per sampling time. *Different letters* indicate significant differences (RM-ANOVA, $P < 0.05$)

averaged across sampled sites for each of the seven sampling times) and peatland (mean 5.2–9.9 mg/L) > grassland (mean 4.4–8.7 mg/L) > arable lands (mean 2.4–4.9 mg/L) dominated watersheds, but the differences were not statistically significant.

The DOC concentrations differed significantly between soil classes (RM-ANOVA, $P < 0.05$, Fig. 4b). Watersheds dominated by peat soils had the highest mean DOC concentrations and ranged throughout the year from 7.2 to 14.5 mg/L. Stream water DOC concentrations from watersheds dominated by peat soils were significantly higher than those of the watersheds dominated by DWDM soils (mean 3.4–7.3 mg/L), podzolized (mean 1.6–3.9 mg/L) and SWDM soils (mean 2.5–5.9 mg/L). DOC concentrations from watersheds dominated by deep poorly drained mineral soils (mean 5.5–9.8 mg/L) were not significantly different from those of peat-dominated watersheds, but were significantly higher than those of podzol-dominated watersheds.

Taking all possible influencing factors into consideration, we developed different models of DOC concentrations for different seasons (Table 3). Climate variables were not important factors for all seasons except in summer; arable was the single land use variable in all the DOC models and was negatively related to DOC concentrations; more soil variables were selected than others (climate, land use, etc.) in these models, and the models in Table 3 also showed that high SOC content (SOC and Peat) increased DOC concentrations. Well-drained soils decreased DOC concentrations. The TI was included in all of the models except the summer model and showed a positive relationship with DOC concentrations. These models are different for all four seasons. For example, precipitation was included only in summer model, while geo-location (northing) only occurred in the autumn model. In the whole year, the soil and topographic variables were the determinant factors of DOC concentrations.

Discussion

Magnitudes of Irish Stream DOC Concentrations Relative to Other Studies

For the 55 sites investigated in our study, the DOC concentrations, ranging from 0.9 to 25.9 mg/L, were comparable to those reported by others in similar environments: 1.4 to 12.2 mg/L in Scotland (Aitkenhead-Peterson et al. 2007); 0 to 45 mg/L in the UK (Evans et al. 2005). In Europe, Laudon et al. (2011) found DOC concentrations ranged from 2 to 41 mg/L in a boreal watershed; the study of Ågren et al. (2010a) showed that extreme DOC concentrations and the DOC concentrations in peak flood ranged from 0.8 to 27.4 mg/L in boreal Scandinavia. In North America, Xu et al. (2012) found DOC ranged from 1.8 to 14 mg/L at event scale in a forest headwater watershed. In the study by Raymond and Saiers (2010), mean DOC concentrations, ranging from 0.9 to 4.3 mg/L across 30 USGS forest watersheds, seem to be lower than other studies. In this study, we wish to place our measured DOC values into a worldwide context to reflect the DOC level of Irish streams, noting that we did not correct for differences introduced by different sampling and analysis methods used in different studies. Koehler et al. (2009), working in a peatland watershed in Ireland, found the seasonality of DOC concentrations was strongly linked to air temperatures, with the highest value (11.5 mg/L) in summer and the lowest value (2.7 mg/L) in winter. This suggests that low temperatures suppress the biologic production of DOC, which may be a characteristic of peatland streams. However, our national data vary in space and time and do not support the result of Koehler et al. (2009) as a general conclusion. December and February, the two coldest months sampled in our study, had the highest and second lowest DOC concentrations (Fig. 3; Table 2), respectively. Our relatively higher DOC concentrations were found in autumn (October, November), early

Table 3 Models of DOC concentrations (mg/L) for different seasons

Season	Equation	R^2	p
Spring	DOC = −14.46 + 2.23TI + 0.14SOC	0.313	<0.001
Summer	DOC = 14.49 + 3.96Peat − 1.77PPTday − 4.14Arable − 2.31DWDM	0.434	<0.001
Autumn	DOC = −12.92 + 4.64Peat + 0.000016Northing + 2.26TI − 4.2Arable − 2.39DWDM	0.578	<0.001
Winter	DOC = −16.28 + 3.07TI − 2.11DWDM − 3.57Arable	0.447	<0.001
Average	DOC = −13.07 + 2.69TI − 2.93DWDM − 5.95SWDM + 2.59Peat	0.505	<0.001

Independent variables considered include: coordinates (easting, northing), area (ha), elevation (m), TI, slope (%), soil organic carbon content (SOC, %), land use classes (1, occurrence; 0, none), soil classes (1, occurrence; 0, none), daily precipitation (PPTday, mm), daily temperature (°C) and antecedent 7-day precipitation (mm)

DWDM deep well-drained mineral soils, *SWDM* shallow well-drained mineral soils

winter (December) and summer (June, August). The relatively low DOC concentrations appeared at late winter (February) and early spring (April) (Fig. 3; Table 2), the period when DOC sources (litterfall) were relatively limited. This suggests the seasonal change in DOC concentrations in Irish streams was controlled by the sources of DOC production. Worrall et al. (2002), working in the UK, found a pulse of DOC from senescing vegetation at an end of the growing season. This seems to support our results. The DOC concentrations used by Jutras et al. (2011) for southwestern Nova Scotia streams in Canada, varied across streams from about 3 to 40 mg/L, being highest during mid-summer to autumn and lowest during winter to spring. This also seems to support our study. Dalva and Moore (1991) found their lowest concentrations, <3 mg/L, were representative of groundwater DOC concentrations. Our low DOC concentrations in April (mean 4.6 mg/L) may also represent stream base flow DOC concentrations. Field notes indicated that stream flow for April 2007 was close to base flow levels.

Factors Influencing DOC Concentrations

Land use has been reported by others as an important factor in explaining DOC concentrations (Eckhardt and Moore 1990; Worrall et al. 2004), but we did not find a statistically significant difference in DOC concentrations among land uses (Fig. 4a). This might be blurred by some underlying factors. For example, forests in Ireland have often been planted on marginal lands with peat being the dominant soil type for 44 % of all state-owned forests (CT 1999). Therefore, forest and peatland dominated watersheds did not show significant difference in DOC concentrations between each other. The DOC concentrations generally decreased in the following order: peatland and forest dominated watershed > that in grassland dominated > that in arable land dominated (Fig. 4a).

As soil type and classification systems vary, it is difficult to find comparative values for soil classes in the literature. The mean DOC concentrations across all our sampling times (Fig. 4b) were highest for peat soils (10.9 mg/L) and lowest for podzols (3 mg/L). DPDM (8.3 mg/L), DWDM (5.2 mg/L) and SWDM (3.6 mg/L) soils were at intermediate DOC levels. This suggests that SOC has an influence of increasing the stream DOC concentrations. This is similar to the study by Aitkenhead et al. (1999). The DOC concentrations (10.9 mg/L) of stream waters emanating from watersheds dominated by peat soils in this study were higher than those found elsewhere in Ireland by Koehler et al. (2009), with a mean of 6.5 mg/L, but within their range of 2.7–11.5 mg/L.

Significant differences between DOC concentrations based on soil class might be explained by soil properties and soil processes, which affect DOC production and transportation. High levels of organic matter in soils raise stream water DOC concentrations. High binding capacity in soils (e.g., clay content) lowers the DOC concentrations (Tipping et al. 1999). Apparently, these processes working together have resulted in the significant differences we found between peat, DPDM soils and podzol soils. Increases in acidity have also been shown to reduce soil solution DOC (Kalbitz et al. 2000; Evans et al. 2006). Podzol soils are subject to leaching, with an organic horizon overlying an acidic surface horizon depleted of nutrients (i.e., iron and aluminum) and a B horizon accumulating these leached nutrients (Gardiner and Radford 1980). The acidic nature of the podzol surface horizon and the accumulated iron and aluminum in the B horizon appear to be reducing the DOC concentrations through an increasing binding capacity of these soils.

Considering all possible influencing factors (climate, land use, soil and topography) together, the MLR technique identified the TI (an indication of saturation-excess runoff potential) and soil conditions are the important factors influencing DOC for most seasons. It is consistent with the result of ANOVA that also showed that soil rather than land use was more important in influencing DOC concentrations. TI is positively related to DOC concentrations, while well-drained conditions are negatively related to DOC concentrations. Many other studies (Eimers et al. 2008; Ågren et al. 2010a; Raymond and Saiers 2010) related DOC concentrations to discharge. However, both TI and soil drainage conditions can reflect the hydrologic conditions in temperate maritime environments. This study confirms the importance of hydrologic conditions on DOC variation.

Conclusions

This study investigated spatial and seasonal variation of DOC concentration in Irish streams across 55 sites and on seven time occasions (over 1 year) throughout the whole country. The DOC variation in space and time is similar to findings of other studies in temperate maritime environments (e.g., the UK, Scotland). DOC production sources (litterfall) might be a driving factor of seasonal change in Irish stream DOC concentrations. Soil (e.g., organic carbon content and drainage conditions) and topography-controlled hydrologic conditions (TI) are key driving factors of the spatial variation of DOC concentrations. However, there are differences in the influencing factors in different seasons. The knowledge of spatial and seasonal variation of DOC concentrations in streams and their drivers are essential for optimum riverine water resource management and in particular water quality of potable water.

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