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Identifying DOC gains and losses during a 20-year record in the Trout Beck catchment, Moor House, UK

C.S. Moody[1*], F. Worrall[1], T.P. Burt[2]

* Corresponding author: c.s.moody@durham.ac.uk

[1] Department of Earth Sciences, University of Durham, DH1 3LE, UK.

[2] Department of Geography, University of Durham, DH1 3LE, UK.

Abstract

The turnover of organic carbon in rivers could represent a large source of greenhouse gases to the atmosphere and studies have suggested that of the order of 70% of the dissolved organic carbon exported from soils could lost in rivers before it flows to continental seas. The Environmental Change Network monitoring of the dominantly peat-covered Trout Beck catchment within the Moor House site means that it was possible to estimate the amount of dissolved organic carbon (DOC) lost within a stream over a 20-year period. The study compared DOC concentrations of precipitation, shallow and deep soil waters with those at the catchment outlet. The mass balance between source and outlet was reconstructed by two methods: a single conservative tracer; and based upon a principal component analysis (PCA) using multiple tracers. The study showed the two methods had different outcomes, with the PCA showing a DOC gain and the single tracer showing a DOC loss. The DOC gain was attributed to an unmeasured groundwater contribution that dominates when the river discharge is lower. The DOC loss was related to the in-stream residence time, the soil temperature and month of the year, with longer in-stream residence times, warmer soils and summer months having larger DOC losses. The single trace study suggest a 10 year average loss of 8.77 g C/m^2/year, which is 33.1 g CO_{2eq}/m^2/year, or 29% of the DOC flux from the source over a mean in-stream residence time of 4.33 hours.

Highlights

- Two models of DOC concentrations within an ECN catchment at Moor House NNR
- Single tracer regression model showed DOC loss between source and catchment outlet
- Longer in-stream residence time, warm soil and summer months had larger DOC losses
- PCA model showed DOC gain, attributed to an unmeasured groundwater contribution

Keywords

mass balance, dissolved organic carbon, ECN

1. Introduction

The northern peatlands are the single most important terrestrial carbon (C) store and Gorham (1991) has estimated that 20-30% of the global terrestrial carbon is held in just 3% of the land area. Complete carbon budgets of peatlands are now common (e.g. Worrall et al., 2003a; Billett et al., 2004; Roulet et al., 2007; Nilsson et al., 2008) and although all of these published budgets would see the inclusion of fluvial carbon fluxes as essential, few have considered the loss of fluvial carbon to the atmosphere and so none of these assessments can present a greenhouse gas budget of a peatland. Some have included an estimate of gaseous evasion from stream surfaces, but for a true greenhouse gas budget of a peatland the loss of DOC and POC to the atmosphere would have to be included.

Approaches to understanding the turnover of organic matter have been based upon mass balance, experimental measurement and modelling studies, with several studies measuring organic carbon losses to the atmosphere. Gennings et al. (2001) state that 40-70% of annual inputs into boreal lakes are evaded to the atmosphere, while at a global scale, Cole et al. (2007) estimated that 1.9 Pg C/year enters rivers of which 0.8 Pg C/year (42% of the input) is returned to the atmosphere. Battin et al. (2009) suggested a lower removal rate of 21%, and Raymond et al. (2013) estimated a value of CO_2 lost from global rivers of 1.8 Pg C/year and 0.32 Pg C/year from lakes and reservoirs. Worrall et al. (2012a) was able to consider directly the mass balance of DOC across UK watersheds and found a loss rate of 74% relative to the export from the terrestrial biosphere. Subsequently, Worrall et al. (2014a) extended the method to include POC fluxes and found the average loss of POC across UK rivers was 20% of which 3% was retained in long-term storage and 17% was lost to the atmosphere. Losses of approximately 50% of the organic carbon to the atmosphere have been recorded from lakes in Sweden (Jonsson et al. 2007; Humborg et al. 2010) and in the Yukon river basin (Striegl et al. 2012) where residence times would be long relative to the UK. Several of these studies have been conducted in countries with peat soils; because of their high organic carbon content, peat soils are the most important source of DOC and POC to rivers (Aitkenhead et al. 2007; Rothwell et al. 2008; Tipping et al. 2010).

The organic matter in rivers can undergo a range of processes that can increase or decrease the concentrations, including: photolysis (e.g. Graneli et al., 1996), flocculation, adsorption and desorption (e.g. McKnight et al., 1992); biodegradation (Gregorich et al., 2003); both degradation and production could occur and DOM can be produced or desorbed from POM (e.g. Lumsdon et al., 2005; Evans et al., 2012) or flocculation processes (e.g. Alperin et al., 1995). Unlike mass balance studies where the net DOM fate is measured, it is more difficult to find experimental studies that have measured net change in DOC let alone for the TOC (DOC + POC). Wickland et al. (2007) observed up to 3%/day conversion of DOC to CO_2, and del Georgio and Pace (2008) measured rates of loss as low as 0.4%/day, but both studies were samples held in the dark, and so did not consider photo-induced changes in DOC concentration. Stutter et al. (2013) found losses of DOC as low as 5% over 41 days but the experiments were performed on filtered DOC separated from its original solution, and so did not consider the impact of larger microbes or POC on the DOC concentration. Dawson et al. (2001) studied a short river reach (2 km) in a peat headwater, under ‘natural’ conditions and estimated that 12-18% of DOC was removed, showing rapid removal of DOC. Moody et al. (2013) performed experimental observations of the net fate of DOC and POC in "young", fresh, peat stream water from the River Tees, northern England, and found an average 73% loss of the DOC over 10 days, with the majority of the loss occurring in the first two days, and between 38 and 87% removal of peat-derived POC. Worrall and Moody (2014) developed a model of POC and DOC within rivers and showed turnover rates of between: 20 and 43% for POC; 63 and 75% for DOC; and 53 and 62% for TOC across a river system with an in-stream residence times between 12 and 127 hours. These studies show that DOC, POC and TOC can be lost and gained from natural water over short time scales.

The Environmental Change Network monitoring within the Moor House site provides a unique opportunity to consider DOC turnover over a 20 year period, and therefore consider the scale of this important flux. Therefore, the aim of the study was to use the measured DOC concentrations measured at Moor House to identify the main source waters for DOC in the catchment, and to quantify and model any losses that occurred between the sources and catchment outlet over the course of two decades.

2. Approach and Methodology

The approach of this study was to use long term water quality records from one set of nested catchments to construct a mass balance of DOC over time. The Trout Beck catchment within the Moor House National Nature Reserve (Figure 1) provides 20 years of stream water monitoring in the context of source water monitoring (e.g. rain and soil water), and alongside hydroclimatic variables (e.g. discharge).

2.1. Study Site and Data Collection

The water samples were collected from various sites within the Trout Beck catchment at Moor House National Nature Reserve (NNR; Figure 1) by the UK Environmental Change Network (ECN). Moor House NNR is situated in the North Pennines, and is a terrestrial and freshwater monitoring site; the Trout Beck catchment (11.4 km^2) is entirely within Moor House NNR, and is one of the main tributaries of the River Tees, which flows 132 km to the North Sea near Middlesbrough, North-East England. Blanket peat covers 90% of the catchment, and the vegetation is dominated by *Eriophorum* sp. (cotton grass), *Calluna vulgaris* (heather) and *Sphagnum* sp. (moss). An automatic weather station at the site records the hourly solar and net radiation, air temperature, wind speed and direction, rainfall, sky and ground albedo and soil temperature. From 1993 to 2013, the average air temperature was 5.9^{0}C (range -16.8 – 27.6^{0}C); the mean annual precipitation was 1930.9 mm (range 869.2 – 2763.4 mm). For the same time period, the water leaving the catchment in Trout Beck had an average conductivity of 74.3 µS/cm, an average pH of 6.8 and an average DOC concentration of 9.7 mg C/l; the average discharge was 57 m^3/day. Cottage Hill and Rough Sike are small streams that flow into Trout Beck above the gauging station (Figure 1). Cottage Hill is too small to be shown on the map in Figure 1, but the sampling sites are marked.

This study uses the 20 years of water chemistry data collected by the Environmental Change Network from Moor House National Nature Reserve. The water samples were taken from 10 sources, including precipitation, soil water from two depths (10 and 50 cm; called shallow soil and deep soil), Trout Beck (TB), two sites on Rough Sike (RS lower and RS upper), two sites on Cottage Hill Sike (CHS 1 and CHS 2), a soil pipe and Sphagnum flush site (Figure 1). The sources were sampled weekly or fortnightly, from 1993 to 2013 (CHS 1, rain, RS lower, shallow and deep soil, TB), 1993-2003 (RS upper), 1998-2011 (Sphagnum flush), 2004-2011 (soil pipe), and 2006 to 2011 (CHS 2). There were no dates on which all 10 water sources were measured, as RS upper was discontinued when the soil pipe measurements commenced, and CHS 2 was only measured for six years. With reference to this study the water was analysed according to the protocol described in Sykes and Lane (1996) for aluminium, calcium, chloride, conductivity, DOC, iron, magnesium, pH, potassium, sodium, sulphate and total nitrogen.

2.2. Modelling Methods

The DOC concentrations across the catchment were modelled and calculated based upon end-member mixing analysis (EMMA - Christophersen and Hooper, 1992) and the approach of the previous study on DOC removal within this catchment (Worrall et al., 2006), by using principal component analysis (PCA). Worrall et al. (2003b) and Worrall et al. (2006) contain further explanations as to the EMMA and PCA approach and a similar method was used in this study. A single tracer approach was also used, for comparison to the multi-tracer PCA approach. In each case, the model of the mixture of water from the different sources was used to assess the mixing of waters and the expected dilution of DOC from its sources; the respective end-member mixing model is used to predict the DOC concentration that would be expected if dilution alone were controlling concentrations; the actual measured concentration is then compared to this estimate to assess the extent of DOC addition or removal across the watershed. The two methods were used so as to compare the results of a single vs. multiple tracer approach. Worrall et al. (2003b) showed that it was possible to describe the composition of Trout Beck stream water using just three end-members based upon principal component analysis of the data available for the Trout Beck catchment. Worrall et al. (2006) used a similar data set from the same site to estimate DOC losses, but only used five water sources.

2.2.1. PCA model

The first approach used principal component analysis (PCA) to analyse the composition of the different sources of water and to identify end-members. The PCA used the aluminium, calcium, chloride, conductivity, iron, magnesium, pH, potassium, sodium, sulphate and total N variables and all data from the 10 different water sources, in total 11 variables and 5329 observations. The measured DOC concentrations were not included in the PCA, as the results of the model were used to predict DOC concentrations. Although there were no dates when all 10 source waters were sampled on the same day, the whole data set was used for this analysis, so to include all the sources and ensure a large dataset. The data were found to be normally distributed (using the Anderson-Darling test) and were not transformed prior to the PCA. Unlike previous PCA studies within this catchment (e.g. Worrall et al., 2003b; Worrall et al., 2006) this study did not utilise alkalinity data as there were over 3900 missing values. Another PCA was carried out separately, using only the 'conservative' ions, calcium, chloride, magnesium, potassium and sodium, and the same three sources were found to be the end-members, showing the analysis was robust against changes in the variables used. This PCA was not used for the DOC model analysis. In order to compare the results of the PCA using all variables and all water sources to the variation in TB water, a third PCA was carried out using all 11 variables and only the TB water. The results of this PCA showed a similar pattern to the main PCA, in as much as the end members identified were the same 'types' of water, and the variation explained by, and variables attributed to, each principal component were approximately the same.

For the main PCA used to model DOC, using all 11 variables, only principal components with an eigenvalue of more than 1, and the first with an eigenvalue of less than 1, were considered in the analysis. Using the results end-members were identified from combinations of PCs. Once end-members were identified a mixing analysis was carried out to calculate the proportion of each of the end-member waters that contributed to the TB water samples. These proportional contributions were then used to calculate the expected DOC concentrations at TB, and compared to the measured DOC concentrations so that estimates of the loss/gain of DOC could be made.

2.2.2. Single–tracer model

The second approach was to consider a single tracer assumed to be conservative (chloride). Multiple linear stepwise regression analyses were applied to the dataset to model the chloride concentrations at the catchment outlet (Trout Beck) based upon the chloride concentration of the source waters. This model was then applied to the DOC concentrations of the identified end-members to calculate DOC concentrations expected at the catchment outlet and compared to the measured DOC concentration for the catchment outlet at TB. The fluxes of DOC (g $C/m^2/year$) were calculated using the daily river discharge from TB at the catchment outlet and the daily measured and modelled DOC concentrations, and then calculated for the whole catchment area (as t C/year). No gap-filling was carried out, so this method only calculated fluxes for the days where all the required source waters were recorded.

Once the source waters that were significant to the Trout Beck model had been identified, these source waters themselves were then modelled, also using the single conservative tracer. This resulted in three models, one of Trout Beck, and two of the significant source waters, CHS and RS upper.

2.2.3. Statistical analysis of models

The values of the difference, as calculated by both approaches, between the observed and predicted DOC concentration at the Trout Beck monitoring point, were analysed by analysis of variance and covariance

(ANOVA and ANCOVA, respectively) to show any differences over time, and to find the covariates that affect the differences. For the DOC difference as calculated by both approaches the ANOVA considered were month and year as factors where the month factor had 12 levels (one for each calendar month) and the year factor had 20 levels (one for each of the years of ECN monitoring). To investigate what may explain the difference found between factors, ANCOVA was used with the same factors but with the following covariates: river discharge (mean daily flow and stage height); in-stream residence time, and the site meteorological data (air and soil temperatures, rainfall, solar radiation). In doing these statistical analyses, the factors that affected the difference between the measured and modelled DOC concentrations (i.e. any DOC loss or gain) were considered, and these were then used to model the potential losses or gains of DOC, to show what controls the magnitude of the loss or gain and therefore the DOC turnover.

When performing either ANOVA or ANCOVA the homogeneity of the variance was assessed using the Levene test and the normality was assessed using the Anderson-Darling test – if either was failed at the 95% probability the data were log-transformed and re-analysed. The results from any significant (significance is judged at 95% probability) factors were assessed as main effects plots based upon the least squares means, i.e. the marginal means of any given level of any given factor controlled for the influence of the other factors and covariates. Post-hoc Fisher's least significant difference tests were used to identify which factors were significantly different.

2.2.4. Residence time calculations

For the study catchment the in-stream residence time was calculated for the entire period of ECN sampling (1993 to 2013) using the equation of Worrall et al. (2014b):

$$\underset{(0.2)}{log_e t_r = 3.5} + \underset{(0.04)}{0.58} log_e \%P - \underset{(0.12)}{1.19} log_e S_{1085} \qquad \text{Eq. 1}$$

Where: %P = the percentile exceedance flow (%); and S_{1085} = 1085 slope (m/km – NERC, 1975) - for TB, S_{1085} = 35 m/km.

3. Results

The mean concentrations of the measured variables are shown in Table 1. The DOC concentrations varied throughout the year for each water source, between 0 and 58 mg C/l, with generally higher concentrations measured in the summer/early autumn months (all plots in Figure 2). The rain had the lowest average DOC concentration (1.62 ± 0.07 mg C/l (mean ± standard error)), followed by Trout Beck (9.73 ± 0.16 mg C/l). The highest average concentrations were recorded in the shallow soil, soil pipe and Cottage Hill Sike waters (22.75 ± 0.27, 20.75 ± 0.50 and 19.35 ± 0.63 mg C/l, respectively). There were significant differences between the DOC concentrations from the 10 different sources; all sources were significantly different to all others, except CHS 1 and CHS 2; deep soil and sphagnum flush; and RS lower and RS upper.

The in-stream residence time calculations found that the mean average in-stream residence time of Trout Beck was 4.33 ± 0.02 hours.

Table 1. The mean concentrations and standard errors of the 12 measured variables from the 10 source waters. All variables are in mg/l, except conductivity (μS/cm) and pH.

Variable	Rain	Soil			Sphag. flush	Trout Beck	Rough Sike		Cottage Hill Sike	
		Shallow	Deep	Pipe			Upper	Lower	1	2
Aluminium	0.01± 0.00	0.09± 0.00	0.03± 0.00	0.08± 0.00	0.05± 0.00	0.05± 0.00	0.10± 0.00	0.11± 0.00	0.09± 0.00	0.08± 0.00
Calcium	0.30± 0.03	0.52± 0.03	0.69± 0.03	0.64± 0.03	0.53± 0.04	11.09 ± 0.22	5.91± 0.21	4.67± 0.10	1.01± 0.03	0.74± 0.03
Chloride	2.36± 0.08	2.97± 0.04	3.77± 0.02	3.84± 0.08	3.66± 0.12	3.95± 0.05	4.15± 0.08	3.99± 0.06	3.85± 0.05	3.92± 0.13
Conductivity	19.79 ± 0.75	42.35± 0.91	32.30 ± 0.17	45.84 ± 0.61	45.41± 0.75	74.31 ± 1.33	51.86 ± 1.39	44.97 ± 2.11	43.19± 0.42	40.91± 0.72
DOC	1.62± 0.07	22.75± 0.27	17.74 ± 0.09	20.75 ± 0.50	17.07± 0.48	9.73± 0.16	12.08 ± 0.24	12.47 ± 0.18	18.87± 0.27	19.35± 0.63
Iron	0.03± 0.00	0.20± 0.00	0.22± 0.00	0.46± 0.01	0.21± 0.01	0.37± 0.01	0.53± 0.01	0.75± 0.01	0.60± 0.01	0.51± 0.02
Magnesium	0.16± 0.01	0.27± 0.01	0.46± 0.00	0.28± 0.01	0.26± 0.01	0.91± 0.02	0.72± 0.02	0.64± 0.01	0.31± 0.00	0.29± 0.01
pH	5.21± 0.02	4.27± 0.01	4.58± 0.01	4.24± 0.01	4.27± 0.02	6.79± 0.02	6.15± 0.03	5.91± 0.02	4.37± 0.01	4.36± 0.01
Potassium	0.10± 0.01	0.08± 0.01	0.05± 0.00	0.27± 0.01	0.28± 0.01	0.31± 0.00	0.29± 0.00	0.29± 0.02	0.25± 0.00	0.23± 0.01
Sodium	1.38± 0.04	2.73± 0.03	2.17± 0.01	2.54± 0.03	2.59± 0.04	2.64± 0.02	2.87± 0.03	2.69± 0.02	2.67± 0.02	2.62± 0.06
Sulphate	0.51± 0.02	0.38± 0.05	0.04± 0.00	0.35± 0.02	0.51± 0.02	1.30± 0.02	1.56± 0.05	1.10± 0.03	0.55± 0.02	0.34± 0.02
Total N	0.76± 0.05	0.52± 0.01	0.80± 0.01	0.52± 0.01	0.49± 0.01	0.34± 0.00	0.37± 0.01	0.38± 0.01	0.52± 0.01	0.59± 0.02

3.1. PCA analysis

In the PCA with all 11 variables, the first five components (four with eigenvalues over 1, and the first with an eigenvalue less than one) explained 84% of the total variance in the data (Table 2). The first component was characterised by base cations; high loadings for calcium, magnesium and sulphate, and a low loading for total N. Trout Beck had the highest average values of PC1 and Rain had the lowest, indicating that these two sites have the largest differences in base cation concentrations. The second component was characterised by acid cations: high loadings for aluminium and iron, and low loadings pH and calcium. Cottage Hill Sike had the highest average values of PC2 and Rain had the lowest, indicating that these two sites have the largest differences in acid cation concentrations. The third component was characterised by high loadings for pH, iron and aluminium, and low loadings for chloride and sodium. Rough Sike lower had the highest average values of PC3 and Sphagnum flush had the lowest, indicating that these two sites have the largest differences in pH and iron, aluminium, chloride and sodium concentrations. The fourth component was characterised by high loadings for total N and potassium, and low loadings for pH, iron and aluminium. Sphagnum flush had the highest average values of PC4 and Rough Sike lower had the lowest, the opposite of PC3, further indicating that these two sites have the largest differences in pH and iron and aluminium concentrations. The fifth component was characterised by high loadings for potassium and pH, and low loadings for conductivity. Rough Sike lower had the highest average values of PC5 and shallow soil had the lowest, indicating that these two sites have the largest differences in potassium and conductivity.

Table 2. The first five principal components of the PCA.

Variable	PC1	PC2	PC3	PC4	PC5
Aluminium	0.01	0.58	0.39	-0.11	-0.10
Calcium	0.43	-0.22	0.19	-0.02	0.05
Chloride	0.20	0.29	-0.57	-0.10	0.24
Conductivity	0.35	-0.06	-0.08	0.11	-0.66
Iron	0.12	0.51	0.45	-0.11	0.04
Magnesium	0.46	-0.09	0.09	0.00	-0.07
pH	0.32	-0.25	0.31	-0.13	0.45
Potassium	0.28	0.15	-0.09	0.47	0.49
Sodium	0.29	0.41	-0.39	-0.07	-0.07
Sulphate	0.39	-0.09	0.03	0.06	-0.20
Total N	-0.11	0.10	0.11	0.84	-0.08
Eigenvalue	4.18	1.75	1.54	1.10	0.65
Cumulative variance explained %	38.04	53.98	68.01	78.02	83.98

The end-members were identified using the comparison of PC1 and PC2 values. Of the 5329 observations on the graph, only 92 (1.7%) fell outside the area of ABC, meaning that 98.3% of the observations were within the ABC triangle. The graph of PC1 against PC2 contained 5329 observations (Figure 3; Supplementary Figure 1), which made it difficult to visually compare between the different water sources, and so the data were also plotted to show the mean average (and standard deviations) of PC1 against PC2, for the each of the 10 different water sources, thus making the end-members and relationships easier to see (Figure 4a).

Plotting the data from only one year made visual comparisons clearer, and the differences between the water sources can be seen (Figure 4b). The year 2010 was chosen for this as nine out of the 10 water sources were sampled (RS upper ceased in 2004) and 2010 was the last full year that CHS 2, soil pipe and Sphagnum flush were sampled. There were 287 water samples with all 11 variables. To show the scope of the dataset, the PCA results were also plotted for an individual day in 2010 (Figure 4c).

Table 3. Comparison of end-member compositions of the three end-members data points identified from Figure 3. These are the actual data from the three sites on three separate days that form the end-members in Figure 3.

Source, end-member Variable	Rain A	CHS 1 B	RS upper C
Aluminium (mg/l)	0.00	0.97	0.00
Calcium (mg/l)	0.09	0.26	30.70
Chloride (mg/l)	0.19	2.90	4.60
Conductivity (μS/cm)	5.10	32.30	193.50
DOC (mg C/l)	0.64	29.60	4.80
Iron (mg/l)	0.00	0.05	0.11
Magnesium (mg/l)	0.02	0.15	3.16
pH	5.20	4.28	7.07
Potassium(mg/l)	0.00	0.17	0.62
Sulphate (mg/l)	0.12	0.63	7.29
Sodium (mg/l)	0.26	1.49	3.41
Total N (mg/l)	0.22	0.20	0.31

Using the end-members A, B and C, the proportional contributions of the three water sources to the TB water were calculated for each sampling day. A one-way ANOVA on the data showed that there were significant differences between the proportional contributions from all three different waters (regardless of sampling day), with the rain having the highest contribution (end-member A), followed by "groundwater type" end-member (end-member C - Rough Sike), then the "soil water type" end-member (end-member B - Cottage Hill Sike) having the lowest contribution.

There were 901 days with data available from TB, and so a time series of the relative contributions could be plotted. Even though there is only a 10 year data record for RS upper, the sum of the relative contributions from the three sources must always equal one, and so the proportion of RS water (taken to be groundwater end-member) could be calculated for the whole 20 years, based on the other two source waters (Figure 5). The rain water generally had the highest mean contribution every year, except in 1995, 1996 and 2003 when the RS, groundwater type water had a higher contribution. End-member B (soil water type – Cottage Hill Sike) had the lowest proportional contribution to TB water every year. There were significant differences between the contributions from the rain and the other two types of water (CHS/soil water and RS/groundwater) in 1993 and 2012, with the rain water contributing significantly more to TB in both years than the other two water types. There were no significant differences in the proportional contributions of the soil water and groundwater.

The daily proportional contributions were compared to the daily discharge at the catchment outlet, at TB (Figure 6). The days where the proportional contribution of the groundwater-type RS upper water was greater than the contributions from soil water-type CHS water and rain (i.e. groundwater contributed the largest proportion to TB water) only occurred when the daily discharge was low (between 0.23 and 149 m^3/day, mean 6.56 ± 0.76 m^3/day), and occurred on 253 out of the 889 days (there were some days without discharge data). There were 410 days where the groundwater-type RS upper water contributed the smallest proportion to TB water, where the river flow ranged from 3.91 to 660 m^3/day, with a mean and standard error of 106.6 ± 4.66 m^3/day. This comparison with discharge demonstrates that end-member C is the baseflow or groundwater component.

The proportional contributions were combined with the DOC concentrations from each of the end-members to calculate a DOC concentration that would be expected at TB (Figure 7a). This was compared to the measured DOC concentration, and the difference between the two was plotted against time (Figure 8). Negative values indicate the calculated DOC concentration was larger than the measured value, suggesting DOC loss, and positive numbers occurred when the measured DOC was greater than the calculated DOC concentration, therefore DOC was gained.

The difference between the calculated and measured DOC concentrations varied from -19.86 to 28.91 mg C/l, with a mean value of 1.07 ± 0.16 mg C/l (standard error), and a median of 0.83 mg C/l. The model showed that higher concentrations of DOC were measured at TB than would be expected based on the results of the mixing analysis, suggesting DOC had been gained between the sources and TB measuring point. The difference between the measured and calculated DOC concentrations showed a seasonal cycle, and an ANOVA showed that there were significant differences between months and years. From the main effects for the month factor it is possible to observe that negative differences (DOC loss) pre-dominated in January, February, March, April and December, whereas positive differences (DOC gain) dominated in May to November. As for the differences between years, the main effects for the year factor show DOC loss in 1995, 1996 and 1999; DOC gain occurred in 1993, 1998, 2000, 2004, 2005, 2006 and 2008 to 2013. For the remaining five years the main effect plots suggests no clear dominance. There was a significant, positive trend with time, indicating that more DOC was gained with time, as the difference between the modelled and measured DOC concentrations was becoming more positive with time.

The daily proportional contributions were also compared to the differences between the measured and modelled DOC at TB (Figure 6). The days where the groundwater-type RS upper water contributed the largest proportion to TB water had an average difference of -0.49 ± 0.17 mg C/l (DOC loss), whereas the days where the contribution of the groundwater-type RS upper water was smallest had an average difference of 2.05 ± 0.27 mg C/l (DOC gain). This showed that on days where there was a low contribution of groundwater to the TB water, there was a DOC gain (measured DOC greater than modelled DOC concentration) at TB and there was higher TB river discharge. This has two possible explanations, firstly, that the DOC from the groundwater source is more-readily degraded than the DOC from other sources, or that, secondly, the groundwater source dominates at times when the discharge is lower and that therefore the in-stream residence time is longer giving more time for degradation.

The measured and PCA modelled DOC concentrations and discharge data for TB were used to calculate DOC fluxes at the catchment outlet. The measured flux over the 20 years was 21.29 g C/m^2/year, whereas the modelled flux was 18.28 g C/m^2/year, or 243 and 208 t C/year, respectively, for the catchment area. Therefore the modelled flux was 86% of the measured flux, suggesting 3.01 g C/m^2/year, or 34 t C/year, is gained across the catchment.

3.2. Single tracer approach

Using the three source waters identified as end-members by the PCA results (Figure 3), the daily chloride concentrations at TB were modelled. The resulting equation and coefficients were then applied to the DOC concentrations, resulting in a calculated TB DOC concentration for each sampling day.

$$Cl_{TB} = 0.68 + 0.02Cl_{PPT} + 0.61Cl_{RSU} + 0.22Cl_{CHS} \qquad \text{Eq. 2}$$

(0.07) (0.02) (0.05) (0.05)

N=428, r^2=0.93

where *Cl* is the chloride concentration (mg/l), *TB* is Trout Beck, *PPT* is the rain water, *RSU* is Rough Sike upper and *CHS* is Cottage Hill Sike. The bracketed numbers are the standard errors of the parameter estimates above. The error associated with the model (0.07) equates to an average DOC concentration of ± 0.71 mg C/l. All parameters were significant at $p<0.0001$ except rain, which had the p value of 0.026. Only significant parameters were included in this and all further regression models.

The difference between the calculated and measured DOC concentrations varied from -14.99 to 12.30 mg C/l, with a mean value of -2.45 ± 0.12 (standard error), and a median of -2.04 mg C/l (Figure 7b), both of these are of a larger magnitude than the error associated with the model, meaning that the differences are likely to not just be due to model error. The model showed that lower concentrations of

DOC were measured at TB than would be expected based on the results of the regression analysis, suggesting DOC had been lost between the sources and TB measuring point. The difference between the calculated and measured DOC concentrations varied over time, but there was no clear trend over the ten years (Figure 8). The parameter estimates from the three sources were used to calculate the proportional contribution of the three waters to the TB water; the largest contribution was from RS upper (72%), followed by CHS (26%), with rain contributing the smallest proportion (2%). This result, similar to the model based on the PCA results, shows that where there was a large contribution of RS upper water there was a loss of DOC (measured DOC lower than modelled DOC concentration).

An ANOVA on the difference between the calculated and measured DOC values showed that there were significant differences between months ($p<0.0001$) and years ($p=0.0193$). There is a clear pattern to the monthly averages of the DOC differences, as shown in Figure 9a, whereas the differences between the years have a less clear pattern (Figure 9b). June, July and August have significantly greater loss of DOC compared with the other months, and 1997 has the greatest loss compared with the other years. The ANCOVA was carried out using the mean daily discharge, in-stream residence time, stage height, air temperature, rainfall, solar radiation and soil temperatures (at 10, 30 and 100 cm depths). The stage height, discharge data and in-stream residence times were collinear, and so only one was included in each model. A significant model based on the log of the mean daily discharge ($p<0.0001$), year ($p=0.014$) and soil temperature at 30 cm ($p<0.0001$) was found to have the best r^2 (0.66). The discharge explained the largest proportion of the variation in the model (48% - Figure 9d), followed by the soil temperature (5%). This is interesting as it showed that the scale of the DOC loss was influenced by the soil temperature. A regression using only the soil temperature at 30 cm to model the difference between the modelled and measured DOC concentrations had an r^2 of 0.20, and showed a significant, negative relationship:

$$DOC_{TB} - DOC_{calc} = \underset{(0.22)}{-0.43} - \underset{(0.03)}{0.30}T_{30} \qquad \text{Eq. 3}$$

$N=420, r^2=0.20$

where *DOC* is the DOC concentration (mg C/l), *TB* is Trout Beck and T_{30} is soil temperature at 30cm. As soil temperature increased, the DOC difference decreased, indicating that at warmer soil temperatures, more DOC is lost. This could lead to further DOC loss from peatland catchments, as climate change is expected to cause an increase in peat soil temperatures, higher peat decomposition and higher DOC losses (Delarue et al., 2014).

An ANOVA on the discharge data, using month and year as factors, found significant differences between the months ($p=0.0004$), but not the years ($p=0.1550$), and the main effects plot of discharge per month is shown in Figure 10. There were several significant differences, with the winter months tending to be higher than the summer months: January was significantly higher than June and July;

February was significantly higher than April, May, June, July and August; March, September, October and November were significantly higher than June; December was significantly higher than April, May, June, July and August. These differences in discharge account for the difference between months in the previous model, explaining why year was still significant, but month was not, as the differences were accounted for by the discharge.

The relationship between the measured and modelled DOC concentrations to the Trout Beck in-stream residence times had an r^2 of 0.54, and showed that there was a significant, negative linear relationship (Figure 9c), with the longer in-stream residence times having negative differences (DOC loss):

$$DOC_{TB} - DOC_{calc} = \underset{(0.20)}{1.47} - \underset{(0.05)}{1.01}t_r \qquad \text{Eq. 4}$$

N=409, r^2=0.54

where *DOC* is the DOC concentration (mg C/l), *TB* is Trout Beck and t_r is the in-stream residence time in hours. Applying this equation to the average in-stream residence times of Trout Beck (4.33 ± 0.02 hours), as found by equation 1, resulted in a DOC difference of -2.90 mg C/l (standard error -2.92 to -2.88 mg C/l), between the source and catchment outlet. The implication of equation 4 is the removal of DOC in-stream is zero-order with respect to DOC predicting a constant rate of 1.47 mg C/l/hour.

The measured and modelled DOC concentrations and discharge data for TB were used to calculate DOC fluxes at the catchment outlet. The measured flux over the 10 years was 20.62 g C/m^2/year, whereas the modelled flux was 25.80 g C/m^2/year, or 235 and 294 t C/year, respectively, for the catchment area. Therefore the modelled flux was 25% larger than the measured flux, suggesting 5.18 g C/m^2/year, or 59 t C/year, is lost from the catchment.

3.2.1. Modelling the CHS water

Regression analysis showed that the best model of the mixing of source waters using ion concentrations was based on the chloride concentration of the soil pipe and sphagnum flush waters.

$$Cl_{CHS} = \underset{(0.08)}{-0.12} + \underset{(0.04)}{0.93}Cl_{SP} + \underset{(0.03)}{0.09}Cl_{SF} \qquad \text{Eq. 6}$$

N=232, r^2=0.92

where *Cl* is the chloride concentration (mg/l), *CHS* is Cottage Hill Sike, *SP* is the soil pipe water and *SF* is the Sphagnum flush water. The partial regression coefficients showed that the soil pipe explained the largest proportion of the variation; indeed a regression using only the soil pipe water had an r^2 of 0.88.

The model using soil pipe and Sphagnum flush had an r^2 of 0.92, suggesting that only 8% of the data did not fit the model, implying that the majority of the CHS water is derived from the two sources.

This model was used to calculate the expected DOC concentrations at CHS, and these calculated DOC concentrations were compared to the measured DOC concentrations. The difference between the calculated and measured DOC concentrations varied from -10.98 to 14.93 mg C/l, with a mean value of -1.70 ± 0.17 (standard error), and a median of -1.52 mg C/l (Figure 11a). Assuming that all the water leaving the catchment at TB has come from first-order streams such as CHS and that all such first-order streams are sourced as shown in equation 6 then the loss from soil water to first-order stream would be 3.59 g C/m^2/year and giving a total loss across the catchment of 8.77 g C/m^2/year – or a flux of 100 t C/year from the catchment. The model showed that lower concentrations of DOC were measured at CHS than would be expected based on the model of chloride, suggesting DOC had been lost between the sources and CHS measuring point. Plotting the difference between the calculated and measured DOC concentrations over time shows that the difference between the two has been increasing significantly (p=0.0037) over time; however, the gradient of the trend line is 0.008 and the r^2 of the trend is 0.08 suggesting only a very slow change over time (Figure 11b).

An ANOVA on the difference between the calculated and measured DOC values at CHS showed that there were significant differences between years (p=0.0002), but not months, but the interaction between month and year (p=0.0045) was significant. The interaction explained the largest proportion of the variance in the model (17.7%); year explained the smallest proportion (9.2%). The main effects plot for the differences between the years is shown in Figure 12. There were significant differences between 2005 and all other years, and 2009 was significantly different to 2004 and 2006.

ANCOVA was carried out using the mean daily air temperature, rainfall, solar radiation and soil temperatures (at 10, 30 and 100 cm depths). The stage height and discharge data were not available for CHS. A significant model based on the year (p=0.0001), the interaction of month and year (p=0.0073) and soil temperature at 10 cm (p=0.0499) was found to have the best r2 (0.49), however this was no better than the model using only the time factors, and the soil temperature explained 1.3% of the variation on the model. This result is interesting nonetheless, as it shows that the temperature had an effect on the DOC loss. As with the TB DOC concentration model, a regression was carried out using only the soil temperature at 10 cm to model the difference between the modelled and measured DOC concentrations at CHS, however the model was not significant.

3.2.2. Modelling the Rough Sike upper water

The regression analysis on RSU showed that the best model of the mixing of source waters using ion concentrations was based on the chloride concentration of the shallow soil and rain waters.

$$Cl_{RSU} = \underset{(0.35)}{1.05} + \underset{(0.10)}{0.57}Cl_{SSS} + \underset{(0.04)}{0.49}Cl_{PPT} \qquad \text{Eq. 7}$$

N=218, $r^2=0.48$

where *Cl* is the chloride concentration (mg/l), *RSU* is Rough Sike upper, *SSS* is the shallow soil water and *PPT* is the rain water. The partial regression coefficients show that the rain water accounts for a large part of the variation. A regression using only rain water had an r^2 of 0.40.

The models of the DOC concentrations at CHS and RS were combined with the model of TB DOC concentration; however there were no dates where all the necessary sites were measured (as Rough Sike Upper and Soil pipe were not measured at the same time), and so there was no data to create a model.

4. Discussion

This study used two approaches to developing a mass balance study of the fate of DOC and these two approaches give quite distinct results, with the PCA approach suggesting a net gain of DOC across the catchment while the single tracer approach suggested a net loss. Autochthonous production of DOC within streams is perfectly possible by internal spiralling of organic matters to go from particles to DOC. However, we would suggest that the evidence from the PCA approach does not support net in-stream production; net gain is greatest at the highest flows when in-stream residence times are at the their lowest and so when in-stream production would have less time to influence the DOC concentration at the catchment outlet. Alternatively, it could be that the source of DOC at low flows is particularly labile while the source of DOC at high flows is particularly refractory. Such a mechanism would explain the relatively high net loss of DOC on low flows but not the net gain on high flows. So it would suggest that on high flows an additional source is contributing DOC to the outlet and that this source has not been sampled as part of the long term monitoring with the ECN programme. This source is most important at high flows and so we would suggest that this source is shallow in the peat profile and so active when water tables are at their highest and it may well include surface runoff.

The soils, temperature, precipitation and vegetation vary across the catchment, however the end-members identified are all located relatively close to the catchment outlet, and so it is possible that the water chemistry from those sites was not representative of the wider catchment. Another limitation to the modelling was the assumption about chloride, as the concentrations varied across the catchment and over time. This was considered to be a negligible influence on the models, as the in-stream residence times of the water are so short in the catchment. As DOC is not included in the PCA it was not possible to quantify the variation in DOC with PC1 and PC2, or with the other principal components. This could lead to the hydrochemical features of water associated with DOC to not be well represented within the mixing model. However, the analysis was used to identify the water end-members, rather than DOC sources, and applied to the DOC concentrations in a way that assumed non-conservative behaviour of DOC. This limitation of the PCA method therefore did not affect the outcome of the model. The application of the chloride model to the DOC concentrations from the different sites also assumed non-conservative behaviour of the DOC.

The difference between the measured and single-tracer modelled DOC concentrations at the catchment outlet showed that there was a loss of up to 8.77 g C/m^2/year, or 100 t C/year from the catchment. This is larger than the range of the previous study on the same catchment that found a loss of between 4 and 7.4 g C/m^2/year (Worrall et al. 2006). That study compared the same two methods of calculating the DOC concentrations: principal component analysis based on several tracers, and single conservative tracer method. Like this study, Worrall et al. (2006) found the two methods gave different results, with the PCA method estimating a 32% loss, and the single-tracer method estimating 20% DOC loss – the estimate here would be 29% loss relative to the soil source.

The most up-to-date carbon and greenhouse budgets for the Trout Beck catchment (Worrall et al. 2009) suggest that the release of DOC at the soil source was between 12.5 and 85.9 g C/m^2/year based upon a flux of between 10.3 and 21.8 g C/m^2/year at the catchment outlet at TB. This study would concur with that analysis giving a 10 year average flux of 21 g C/m^2/year at the catchment outlet and 29.8 g C/m^2/year.

In considering the greenhouse gas budget of these important carbon stores it is not only important to consider the fate of the DOC but the fate of DOM. The DOC flux is actually a flux of dissolved organic matter (DOM) and this has two consequences for greenhouse gas budgets. Firstly, DOM contains nitrogen which means that as DOC is turned over in rivers then so too is DON and that could be released as N_2O – a very powerful greenhouse gas. Secondly, not only does the organic matter consist of elements other than C that play a role in its turnover, but also the form of release, or species, can vary: nitrogen could be released as N_2 or N_2O, and the carbon can be released as either CO_2 or CH_4, the latter, like N_2O, being the more powerful greenhouse gas than CO_2 (Houghton et al. 1995). Worrall et al. (2012b) showed that the C:N of the DOM in the soil water at 10 cm depth varied from 24 – 146 with an average of 64. Comparing the flux at the soil profile with that at the catchment shows that the amount of in-stream removal varied from 0.06 - 0.36 g N/m^2/year, and indeed for two of the years in that study there was a net gain in the streams across the catchment – similar to that observed in this study for DOC. Baulch et al. (2011) have considered the proportion of N lost in rivers that is released as N_2O for 75 US rivers and give a median value of 0.75%, i.e., an equivalent greenhouse gas flux of between 0.13 and 0.82 g CO_{2eq}/m^2/year. Striegl et al. (2012) found that the proportion of C released as CH_4 as 0.72%, i.e. 1.47 g CO_{2eq}/m^2/year compared to 31.2 g CO_{2eq}/m^2/year as the loss of DOC as CO_2. Therefore, the total greenhouse gas flux due to DOM turnover within this catchment would be 33.1 g CO_{2eq}/m^2/year. It should be remembered that this study could not consider the fate of POM released from peat within the catchment and POM, like DOM, would be turned over to CO_2, CH_4 and N_2O.

Equation 4 showed that the relationship between in-stream residence time and DOC loss represented a zero-order reaction. Previous studies have found the order of reaction of DOC turnover to range between zero and third order: Worrall and Moody (2014) modelled the turnover of organic matter in streams; they found that the turnover of POC was a first-order reaction, whereas the turnover of DOC varied between first, second and third order. Worrall et al. (2013) proposed a simpler model with two separate zero-order rates for DOC turnover during the day and night, and Heitmann and Blodau (2006) also used first-order reactions in their models. Experimentally, DOC production was determined to follow first-order kinetics in forest soils (Buzek et al., 2009), and DOC degradation in a peat-sourced headwater was found to be either second or third order (Moody and Worrall, in press). It should be pointed out that zero-order kinetics can be an approximation of more complex mechanisms such as Michaelis-Menten kinetics, i.e. a common enzyme limited mechanism.

Worrall et al. (2014b) found the UK rivers discharge-weighted in-stream residence time was 26.7 hours for median flow. Applying the zero-order rate found by equation 4 to this showed a DOC loss of 25.5 mg C/l between source and sea. Specifically for the River Tees, Worrall et al. (2014b) estimated the in-stream residence times from 3.8 hours (1% exceedance) to 34.9 hours (95% exceedance). This results in a DOC loss of between 2.37 and 33.78 mg C/l between the source and the sea.

5. Conclusion

This study has used two approaches to reconstruct the mass balance of DOC across the Trout Beck catchment. The study has shown that:

i) The two approaches gave very different results with the PCA model suggesting a net DOC gain across the catchment and the single-tracer model suggesting a net DOC loss.

ii) The net gain observed from the PCA is interpreted as due to an unsampled source of DOC that was most active at high flows.

iii) The single trace study suggest a 10 year average loss of 8.77 g C/m^2/year (33.1 g CO$_{2eq}$/m^2/year) which is 29% of the DOC flux from source over a mean in-stream residence time of 4.33 hours.

iv) The modelled DOC loss was related to the soil temperature, so as soil temperature increased, the DOC difference decreased, indicating that in warmer soils, more DOC would be lost to the atmosphere. Also, the DOC loss was shown to be increasing over time. These could have implications for future climate warming, carbon budgets of peatlands and positive feedback cycles.

v) The relationship between in-stream residence time and DOC loss was a zero-order reaction with a constant rate of DOC removal of 1.47 mg C/l/hour.

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