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Sources and ages of dissolved organic matter in peatland streams: evidence from chemistry mixture modelling and radiocarbon data

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Abstract Monitoring data over the period 1994–2007 were analysed for three streams (Cottage Hill Sike, CHS; Rough Sike, RS; Trout Beck, TB) draining blanket peat underlain by glacial clay and limestone-rich sub-strata at Moor House (Northern England). Dissolved organic carbon concentration, [DOC], showed complex relationships with both discharge and calcium concentration, [Ca]. A model based on [Ca] was constructed to simulate stream [DOC] by mixing dissolved organic matter (DOM) from shallow peat, quantified by measured [DOC] (15–30 mg l^{-1}) in peat porewater, with DOM assumed to be present at a constant concentration (*c*. 5 mg l^{-1}) in groundwater. A temperature-based adjustment to the measured porewater [DOC] was required to account for relatively low streamwater [DOC] during winter and spring. The fitted model reproduced short-term variation in streamwater [DOC] satisfactorily, in particular variability in RS and TB due to groundwater contributions. Streamwater DOM is largely derived from surface peat, which accounts for more than 96% of the total DOC flux in both RS and TB, and 100% in CHS. Model outputs were combined with streamwater and porewater DO^{14}C data to estimate the ^{14}C contents, and thereby the ages, of DOM from peat and groundwater. The peat-derived DOM is 5 years old on average, with most of it very recently formed. The derived age of groundwater DOM (8,500 years) is comparable to the 4,000–7,000 years estimated from the DO^{14}C of water extracts of clay underlying the peat, suggesting that the clay is the source of groundwater DOM.

Keywords Carbon isotopes · Discharge · Dissolved organic matter · Groundwater · Peat · Stream

Introduction

Dissolved organic matter (DOM) is an important component of streamwaters, as it participates in many ecological and geochemical reactions (Perdue and Gjessing 1990; Kullberg et al. 1993; Hessen and Tranvik 1998). For example, DOM influences the

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underwater light climate, controls the transport and fate of heavy metals, aluminium, radionuclides and organic pollutants, initiates photoreactions, participates in particle surface and colloid chemistry, and affects ionic balance, including pH. It also plays an important metabolic role in streams, supplying carbon and energy to heterotrophic bacteria (Meyer et al. 1988). DOM is important for human society because its required removal from water used for domestic and industrial supply entails significant plant and cost. Interest in the formation and transport of DOM has grown because of the widespread increases (65–100%) in concentrations and fluxes seen over recent years (Monteith et al. 2007), and attributed to a variety of causes including climatic warming, changes in hydrology, increased primary production and acidification reversal (Evans et al. 2006).

Peatlands are of particular interest because they produce the highest concentrations of surface-water DOM. The export flux of DOM from peatlands is a significant component of catchment carbon balance (Billett et al. 2004; Roulet et al. 2007), and is globally important in transporting labile carbon to the Arctic Ocean from boreal peatlands (Opsahl et al. 1999; Benner et al. 2004). Therefore an understanding of the processes generating DOM in peatlands, and how they will respond to changing environmental drivers, is needed. A key factor is the time that elapses between carbon fixation in photosynthesis and DOM export to streamwaters. The literature contains a variety of hypotheses, mainly prompted by the desire to explain the upward trends in DOC mentioned above. Freeman et al. (2004) and Fenner et al. (2007) emphasised the production of DOC from recent photosynthate, suggesting that increases in DOC concentration may arise from increased primary production. Formation from slightly older but still very recent material is suggested by the results of Clark et al. (2008), showing that streamwater [DOC] correlates better with [DOC] in blanket peat at 1 cm depth, rather than with concentrations in deeper, older, layers. In contrast, Worrall and Burt (2005) considered much of the DOC to be produced at the acrotelm-catotelm boundary, through the “enzymic latch” mechanism of Freeman et al. (2001a), in which the enzyme phenol oxidase is activated following droughts. Worrall et al. (2002) suggested that base flow in blanket peats is provided by slow drainage from the catotelm, which implies old sources of DOC under these conditions. Freeman et al. (2001b) considered the increase in DOC fluxes to be due to release from a store of “highly aged” organic matter.

Carbon isotopes, especially ^{14}C, can provide considerable insight into the age of DOM and the timescales of its production and transport. Dissolved organic carbon in samples from streams draining peatlands are usually enriched in ^{14}C (DO^{14}C $> 100\%$ modern absolute, or $\Delta^{14}\text{C} > 0$ ‰). For example, Schiff et al. (1997) reported values in the range 107–119% for samples taken in the early 1990s from streams draining wetlands in central Ontario, while Palmer et al. (2001) reported values in the range 102–106% for samples collected in 1998 from a stream draining a predominantly peat catchment in NE Scotland. The enrichments indicate that at least some of the material has been produced since the atmospheric weapons-testing of the 1950s and 1960s. However, in both studies either some or all of the ^{14}C values were appreciably lower than that of contemporary atmospheric ^{14}CO$_2$, which is continuing to decline from its northern hemisphere peak of *c.* 190% modern in 1964. This suggests that some of the DOC originated from carbon fixed well before the mid-1950s, to dilute the “bomb carbon” signal. Evans et al. (2007) obtained ^{14}C values of ca. 113% modern for DOC in Welsh peatland streams at high flow in autumn 2004. Since this value is greater than the contemporary atmospheric ^{14}CO$_2$ of 107%, the simplest interpretation is that the DOC was produced from carbon fixed on average about 11 years previously, when the atmospheric ^{14}CO$_2$ value was 113% modern. At summer baseflow, the same stream had DOC with $^{14}\text{C} = 105\%$ modern, which Evans et al. (2007) interpreted to indicate the presence of older DOC from deeper within the peat. However, their main conclusion was that most of the DOC flux from the peatland was derived from recent plant material. Raymond et al. (2007) found that DO^{14}C increased with discharge in major Artic rivers draining peatlands and other carbon-rich soils, and used the information to correct the result obtained under high-discharge conditions for the relatively small baseflow components, depleted in ^{14}C. This led to a similar value for three rivers of 110% modern for the soil surface-derived DOC for the years 2004–2005. Again the simplest interpretation indicates an average age of 7–8 years for the majority of the exported DOM, quite similar to the Evans et al. (2007) result.

Therefore if baseflow corrections can be applied, or if baseflow can be ignored, a consistent estimate of the age of DOM derived from surface peats at high discharge might apply. In the present study we tested this possibility in more detail with data for streams draining a catchment dominated by blanket peat (unconfined ombrotrophic mire) at Moor House in the Pennine hills of northern England. Through the monitoring activities of the UK Environmental Change Network (ECN: http://www.ecn.ac.uk), relevant chemical data covering the period 1994–2007 are available for three streams differing in order, catchment area and water composition, and also for peat porewater. Discharge and temperature data are also available. We used these data to construct a mixing model to attribute streamwater DOC to different sources (surface peat and groundwater), and then applied the parameterised model to interpret measurements of the ^{14}C contents of streamwater DOM from two of the streams.

Methods

Field sites

The Moor House National Nature Reserve, situated in the North Pennines (54°7′ N, 2°4′ W), is a terrestrial and freshwater site of the ECN. Location maps can be found in Evans et al. (1999), Worrall et al. (2002) and Clark et al. (2008). Mean annual air temperature is 5.3°C and rainfall 1,982 mm (Holden and Adamson 2001). Trout Beck (TB) drains 11.5 km^2 of the Reserve, with an altitude range of 535–848 m. The mean annual discharge is 0.57 m^3 s^{-1}, which corresponds to 1,570 mm of run-off. The catchment geology comprises mainly Carboniferous limestones with alternating bands of sandstone, shale and coal, overlain in much of the area by a grey sandy glacial boulder clay containing limestone boulders and pebbles (Johnson and Dunham 1963). A younger (7,500–10,300 BP) post glacial solifluction deposit containing sandstone clasts is present in much of the Moor House Reserve. Inter-stratified peat and clay layers beneath the blanket peat are also common reflecting the onset of soil development in the post glacial period. Over 90% of the catchment is overlain with blanket or eroded peat (Dystric Histosol) at depths of roughly 1–4 m (Heal and Smith 1978), and there are small areas of skeletal, limestone and alluvial soils. Vegetation is dominated by heather (*Calluna vulgaris*), cotton grass (*Eriophorum* spp.) and *Sphagnum* moss. Cottage Hill Sike (CHS) and Rough Sike (RS) are tributaries of TB, with catchments comprising almost entirely blanket peat. The CHS catchment has an area of 0.20 km^2 and an altitude range of 545–560 m; the corresponding figures for RS are 0.83 km^2 and 560–700 m.

Maximum peat temperatures occur in July and August, minima in January and February. In most years, the water table is at about 10–20 cm depth in summer, and within a few centimetres of the surface in winter; in drought years it has been recorded as deep as 40 cm. The peat responds quickly to rainfall events, producing “flashy” stream hydrographs, the majority of the water flux being due to short periods of high discharge. Holden and Burt (2003a, b) concluded that storm runoff production is due to saturation-excess overland flow together with near-surface throughflow in the peat acrotelm, with very little water produced from the peat matrix below 5 cm depth. However, high calcium concentrations at low flow in RS and TB attest to weathering inputs from the underlying limestone (Crisp 1966), suggesting that some of the runoff water penetrates to the underlying mineral matter before entering the stream, possibly in part via “pipes” (Holden and Burt 2003a, b).

Environmental Change Network (ECN) monitoring activities at the Moor House site have been in progress since late 1992. They include analyses of weekly streamwater grab samples from from CHS, RS and TB, and weekly or fortnightly porewater samples, collected with tension lysimeters from peat depths of 10 and 50 cm at a location near to the CHS catchment (see Clark et al. 2008). The samples are analysed for a range of chemical determinands, including pH, Ca and DOC. The discharge of TB is gauged continuously by the Environment Agency of England and Wales, while the stream stage of RS is recorded weekly and converted to discharge. Soil temperature is recorded hourly at several depths. For the purposes of the present study, soil temperature data at 10 cm were averaged over the periods of collection of peat porewater. Missing temperature data for June and July 2004 were estimated by linear interpolation. Discharge at CHS has been measured continuously since November 2007. Full details of sampling and analytical protocols are given on the ECN website (http://www.ecn.ac.uk).

Carbon isotopes

Samples of streamwater for isotope analysis were collected using 1-litre high-density polyethylene bottles at RS and acid-washed glass bottles at CHS. Separate samples were taken for the determination of DOC (TOC-VCPN/CPN analyzer, Shimadzu, Kyoto, Japan), pH (Radiometer GK2401C combination glass electrode), conductivity (Jenway 4510 meter), major cations (ICP-OES, Perkin–Elmer Optima 4300 DV), major anions (Dionex DX100) and alkalinity (Gran titration). Discharge at the time of sampling was determined and for RS the stage was converted to discharge as in the ECN programme.

Peat porewater was sampled using three tension-free lysimeters installed at depths of 10 cm at a representative location within the Rough Sike catchment (Buckingham et al. 2008). Porewater was collected for 2 weeks, and then the samples were pooled for the measurements of carbon isotopes.

Samples of the clay underlying the peat were collected from three locations in the RS catchment by forcing an Eijkelkamp corer through the peat (*c.* 2 m in each case) and into the clay, then rotating and withdrawing. Samples of the clay (330–430 g dry weight) were slurried with *c.* 650 cm^3 deionised water in 1 l polyethylene bottles, with frequent vigorous shaking over a period of 2 weeks. The slurries were transferred to 370 cm^3 capacity centrifuge bottles and centrifuged at 10,000*g* for 1 h. The brown supernatants were filtered (Whatman glass fibre GF/F), then taken for isotope analysis.

The analytical procedures for isotope determination followed those described in detail by Tipping et al. (2007). One-litre aqueous samples were passed through glass-fibre filters (Whatman GF/F 0.7 µm pore size), then the filtrates were acidified to pH 6 and sparged with nitrogen gas to ensure the removal of inorganic carbon, neutralised by dropwise addition of KOH solution until the sample pH was 7, then rotary-evaporated, and freeze-dried. The resulting solids were combusted to CO_2, aliquots of which were analysed for $\delta^{13}C$ by mass spectrometry using a dual-inlet VG OPTIMA spectrometer (Fisons, UK) and further converted to graphite for ^{14}C analysis by Accelerator Mass Spectrometry (AMS). The AMS instrument used at SUERC (publication codes SUERC-) was supplied by the National Electrostatics Corporation (NEC), Wisconsin, USA; the instrument used at the University of Arizona AMS (publication codes AA-) was manufactured by General Ionex Corporation, Massachusetts, USA with an ion source produced by NEC.

Results for ^{13}C are expressed by the delta notation, where $\delta^{13}C$ is the difference (‰) between the ^{13}C content of the sample and that of the standard (Vienna-Pee Dee Belemnite). The dual inlet mass spectrometer was calibrated with international reference materials to a precision of ±0.1 ‰. For ^{14}C, the results are reported as absolute % modern, the ^{14}C enrichment being expressed as a percentage of the ^{14}C activity relative to a modern oxalic acid standard (provided by the US National Bureau of Standards; now the National Institute of Standards & Technology), where 100% modern is defined as the value in AD 1950, in the absence of any anthropogenic influences; a mathematical adjustment is made to account for ongoing radioactive decay of the standard. Overall analytical precision in the ^{14}C data, expressed as one standard deviation, was 0.4–0.6%. Absolute % modern values are equal to $100 + 0.1 \times \Delta^{14}C$ (‰).

To interpret the isotope values, atmospheric $^{14}CO_2$ contents were required for the period leading up to the sampling dates. These were obtained from Hua and Barbetti (2004) for the period to 1998 (Northern Hemisphere zone 1), then from Levin and Kromer (2004) to 2003, and by extrapolation with a polynomial function until 2008.

Modelling

We used mixture modelling to relate the concentration of DOC in porewater, $[DOC]_{PW}$, to the streamwater concentration, $[DOC]_{SW}$. As justified under RESULTS, we attempted to account for variations in terms of two end-members, i.e. the peat porewater the composition of which varied in time and the groundwater which was assumed to be of constant composition. Thus, the concentration of Ca is used as the controlling variable. The model is developed as follows.

Dilution of peat pore water at high water flows is taken into account by multiplying the measured $[DOC]_{PW}$ by a term in [Ca];

$$[\mathrm{DOC}]_{\mathrm{PW,corr}} = [\mathrm{DOC}]_{\mathrm{PW}}\frac{[\mathrm{Ca}]}{\alpha + [\mathrm{Ca}]} \quad (1)$$

where $[\mathrm{DOC}]_{\mathrm{PW,corr}}$ is the concentration corrected for dilution. The term in [Ca] only applies at low [Ca] and potentially varies from zero to unity for positive α.

Measured $[\mathrm{DOC}]_{\mathrm{PW}}$ is further modified by the equation;

$$[\mathrm{DOC}]_{\mathrm{PW,corr}} = [\mathrm{DOC}]_{\mathrm{PW}}\frac{[\mathrm{Ca}]}{\alpha + [\mathrm{Ca}]}\beta(1+\gamma \mathrm{T}) \quad (2)$$

where the scaling parameter β permits the mean $[\mathrm{DOC}]_{\mathrm{PW}}$ to be adjusted to match the streamwater value, and $(1 + \gamma\mathrm{T})$ permits seasonality to be accounted for, through soil temperature, T. Finally, the fraction of streamwater DOC from groundwater is given by;

$$\mathrm{X}_{\mathrm{GW}} = \frac{[\mathrm{Ca}] - [\mathrm{Ca}]_{\mathrm{min}}}{[\mathrm{Ca}]_{\mathrm{GW}} - [\mathrm{Ca}]_{\mathrm{min}}} \quad (3)$$

where $[\mathrm{Ca}]_{\mathrm{GW}}$ is the calcium concentration of groundwater, assumed constant, and $[\mathrm{Ca}]_{\mathrm{min}}$ is the minimum concentration of Ca in streamwater. Thus, the full mixing model equation is;

$$[\mathrm{DOC}]_{\mathrm{SW}} = \mathrm{X}_{\mathrm{GW}}[\mathrm{DOC}]_{\mathrm{GW}} + (1-\mathrm{X}_{\mathrm{GW}})[\mathrm{DOC}]_{\mathrm{PW}}\frac{[\mathrm{Ca}]}{\alpha + [\mathrm{Ca}]}\beta(1+\gamma \mathrm{T}) \quad (4)$$

remembering that when [Ca] exceeds a certain (low) value, the term [Ca]/(α + [Ca]) is set to unity.

The ^{14}C content of streamwater DOC is calculated from the outputs of the mixing model for the sampling date in question, combined with the ^{14}C contents of DOM originating from the peat and groundwater sources;

$$\mathrm{DO^{14}C_{SW}} = \mathrm{X_{GW}DO^{14}C_{GW}} + (1-\mathrm{X_{GW}})\mathrm{DO^{14}C_{PW}} \quad (5)$$

This can be elaborated to take into account two DOM sources within the peat, “fast” and “slow” turnover carbon pools;

$$\mathrm{DO^{14}C_{SW}} = \mathrm{X_{GW}DO^{14}C_{GW}} + (1-\mathrm{X_{GW}}) \times \left\{\mathrm{f_{fast}DO^{14}C_{fast}} + (1-\mathrm{f_{fast}})\mathrm{DO^{14}C_{slow}}\right\} \quad (6)$$

Fitting was done by adjusting parameters and to minimise the sum of residuals in either $[\mathrm{DOC}]_{\mathrm{SW}}$, i.e. $\sum([\mathrm{DOC}]_{\mathrm{SW,obs}}-[\mathrm{DOC}]_{\mathrm{SW,calc}})^2$, or DO^{14}C, i.e. $\sum(\mathrm{DO^{14}C_{SW,obs}}-\mathrm{DO^{14}C_{SW,calc}})^2$, using Excel Solver. Goodness-of-fit is gauged using the root-mean-squared deviations (RMSD).

Results

Stream and pore water chemistry

Table 1 summarises means and ranges of pH, DOC and Ca for the three streams and peat porewater for the period 1993–2007. Although most monitored upland catchments in the UK have seen marked increases in [DOC] over recent decades (Freeman et al. 2001b; Worrall et al. 2004), this is not strongly evident in the records for the Moor House streams. For the period 1994–2007, neither RS nor TB showed a significant long-term trend when the data were analysed with the Seasonal Kendall test (Helsel et al. 2006) ($p > 0.1$ in each case), while the average annual increase in [DOC] at CHS was 0.29 mg l^{-1} ($p = 0.02$), which is modest in comparison with changes at other UK sites (Worrall et al. 2004). The Ca concentration is greater than the long-term

Table 1 Summary of pH and the concentrations of Ca and DOC (both mg l^{-1}) for the period 1993–2007, based on results for 761, 743, 770 and 4538 samples for Cottage Hill Sike (CHS), Rough Sike (RS), Trout Beck (TB) and peat porewater, respectively; 5% and 95% refer to the percentile ranges

	Mean	SD	5%	95%
pH				
CHS	4.34	0.32	4.01	4.74
RS	5.84	0.68	4.74	6.84
TB	6.68	0.69	5.58	7.75
Porewater	4.38	0.29	4.01	4.73
Ca				
CHS	1.1	0.9	0.4	2.0
RS	4.8	3.3	1.2	11.3
TB	11.4	7.4	2.9	26.4
Porewater	0.7	0.7	0.4	1.1
DOC				
CHS	18.8	8.7	6.6	34.2
RS	12.3	5.4	5.6	23.4
TB	9.6	4.9	4.1	20.0
Porewater	20.6	4.1	15.3	28.4

average of 0.22 mg l^{-1} in rainwater at a collector within 5 km of the study sites (Lawrence et al. 2007). Since there are no obvious weathering sources within the shallow peat, and assuming it to be genuinely ombrotrophic, the higher average values in porewater compared to rainwater are presumably due to dry deposition of Ca, and evaporative concentration.

Because each of the mean stream values exceeds the porewater pH and Ca values, it can be concluded that an additional source of relatively base-rich water is also contributing (Worrall et al. 2003; see also "Field sites" section). In the case of CHS the effect is small (mean Ca 1.1 mg/l), but for RS and TB it is clear that even the lowest 5% of the values are appreciably greater than those of the porewaters.

Logarithmic time-series plots of [Ca] (Fig. 1a) show considerable coherence among the three streams, but there are no obvious relationships to porewater [Ca]. The plots of Ca against discharge for RS and TB (Fig. 1b), show the greater relative contribution of deep groundwater at low discharge. Note that we do not have the necessary discharge data to make a comparable plot for CHS, but a small data set ($n = 21$) indicates that [Ca] is higher in this stream at low discharge. However the weathering input is very small in comparison with the other two streams (Table 1).

Logarithmic time-series plots of DOC show strong coherence between RS and TB (Fig. 2a), with frequent departures to low [DOC] that coincide with high [Ca] (Fig. 1a). The record for CHS lacks most of the departures to low [DOC] seen for RS, but there is coherence at high [DOC] (Fig. 2b). Concentrations in CHS can exceed those in the porewater particularly in summer (Fig. 2c), but for most of the time porewater [DOC] is higher than [DOC] in all three streams. Plots of [DOC] against discharge do not show any clear trends (Fig. 3), but for both RS and TB, low concentrations are seen at both the lowest discharges, due to groundwater low

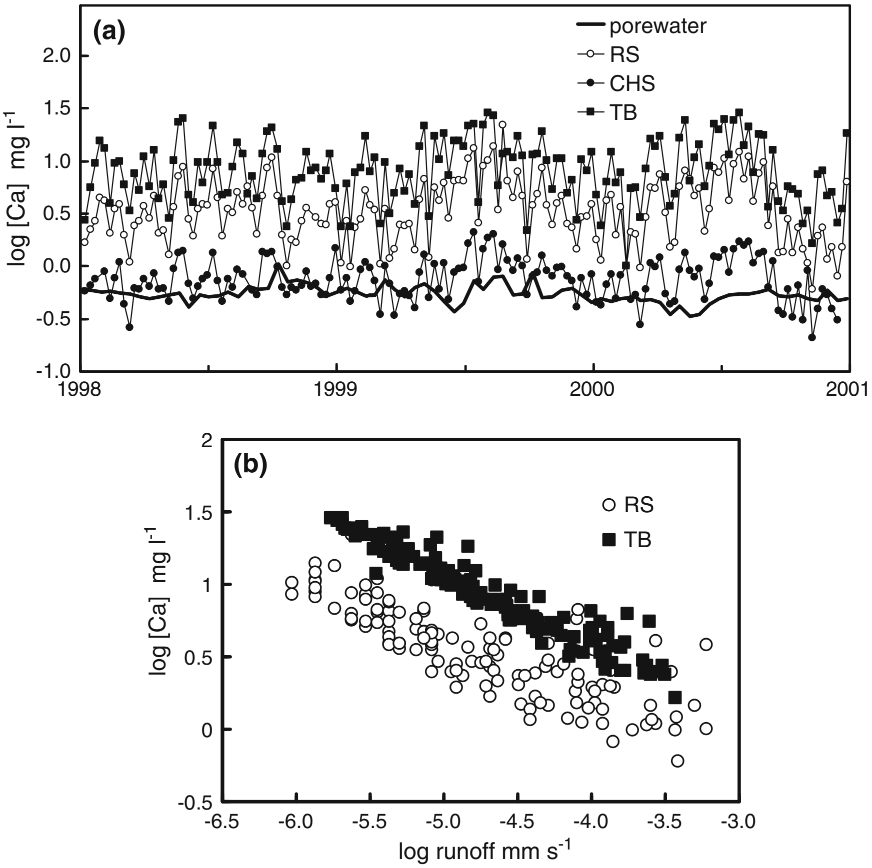


Fig. 1 Steam and pore water Ca concentrations as functions of **a** time and **b** runoff. CHS Cottage Hill Sike, RS Rough Sike, TB Trout Beck

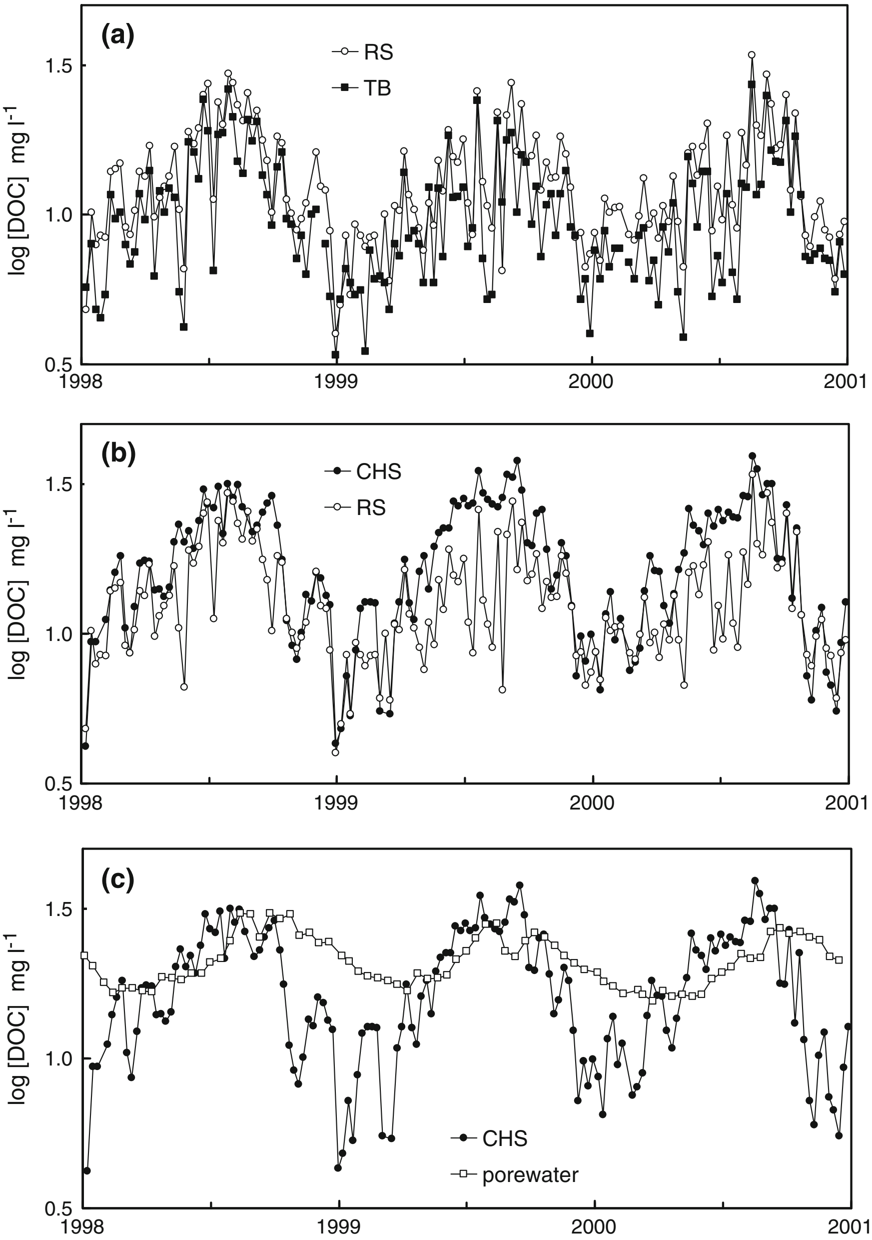


Fig. 2 Stream and pore water time-series plots for DOC concentration between 1998 and 2001. CHS Cottage Hill Sike, RS Rough Sike, TB Trout Beck

in DOC, and the highest ones, due to dilution at high rain input (Worrall et al. 2003; Clark et al. 2007).

The strong relationship of [Ca] to discharge, and the fact that it acts as a signal of water that has encountered dissolving limestone (or Ca-enriched till) make it a good variable against which to compare DOC concentrations, in order to obtain insight into sources within the catchment. The use of [Ca] has the advantage of providing an "internal" measure of the history of a water sample, thereby obviating the need to relate [DOC] to discharge history, for example. For both porewater and CHS there is a general increase in [DOC] with [Ca] (data not shown), which we attribute mainly to dilution by rainwater. The range of [DOC] values in CHS (nearly 8-fold) is considerably larger than found for the porewater (~2-fold), due to the slightly higher [DOC] in the stream than the porewater in summer, but more importantly the lower values in winter (Fig. 2b).

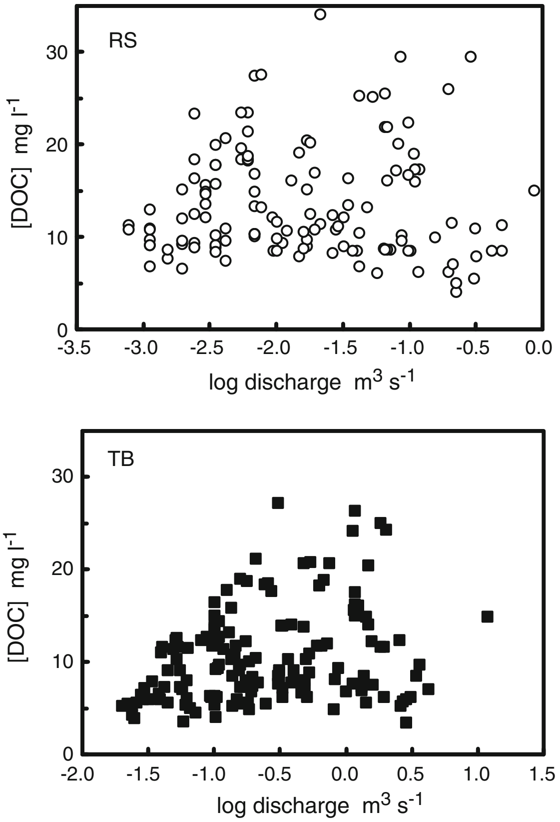


Fig. 3 Relationships of [DOC] to discharge in Rough Sike (RS) and Trout Beck (TB)

In RS and TB low concentrations of DOC occur at both low discharge, when [Ca] is high, and high discharge when [Ca] is low (Fig. 4). At intermediate [Ca] a range of [DOC] is possible, because of variations in [DOC] source with season, dilution effects, and groundwater contributions. For example, in RS, a very low [DOC] at [Ca] ~ 5 mg l^{-1} could be due to low winter porewater [DOC] combined with a significant fraction of groundwater.

Partitioning streamwaters into peat porewater (PW) and groundwater (GW)

We applied the mixing model to relate $[\mathrm{DOC}]_{\mathrm{SW}}$ to measured $[\mathrm{DOC}]_{\mathrm{PW}}$ and to an assumed constant $[\mathrm{DOC}]_{\mathrm{GW}}$, using [Ca] to take into account dilution at high discharge and to provide an estimate of the groundwater contribution. Fitting was done for the entire available dataset, covering the period 1994–2007. At the outset we set $[\mathrm{Ca}]_{\min}$ to 0.2 mg l^{-1}, the average rainwater value.

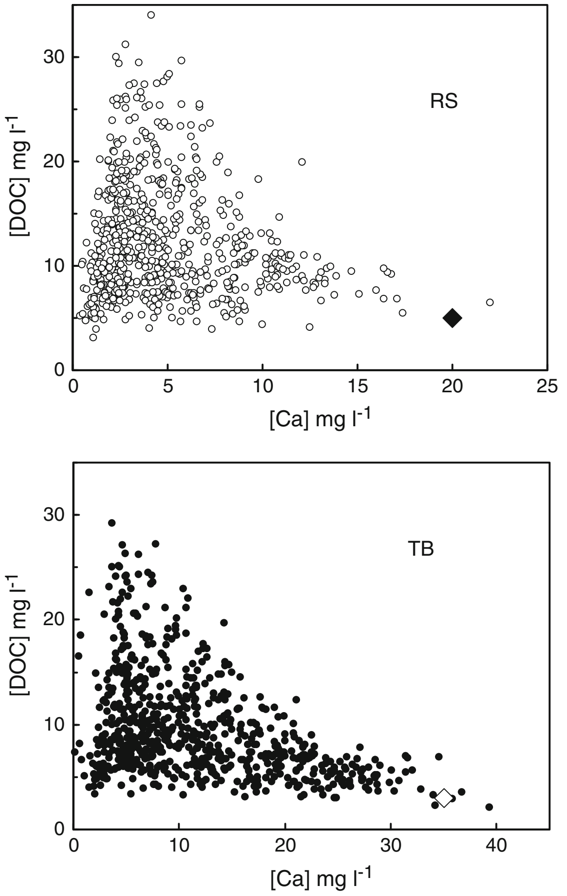


Fig. 4 Variation of [DOC] with [Ca] in Rough Sike (RS) and and Trout Beck (TB). The diamonds indicate the assumed groundwater (GW) compositions

First, consider CHS, the simplest of the three streams, for which we assume a negligible groundwater input. If α in Eq. 1 is set to zero, i.e. no dilution correction is made to $[\mathrm{DOC}]_{\mathrm{PW}}$, an RMSD in $[\mathrm{DOC}]_{\mathrm{SW}}$ of 7.2 mg l^{-1} is obtained. With an optimised α of 0.28, for $[\mathrm{Ca}] < 0.63$ mg l^{-1}, the RMSD is reduced to 6.1 mg l^{-1}. This value of α means that at the lowest [Ca] concentrations, corresponding to the highest discharges, stream $[\mathrm{DOC}]_{\mathrm{SW}}$ is 42% of $[\mathrm{DOC}]_{\mathrm{PW}}$. After making this correction, simulated $[\mathrm{DOC}]_{\mathrm{SW}}$ was too high in spring-winter and slightly too low in summer. These discrepancies could be rectified by application of Eq. 2, with $\alpha = 0.15$ ($[\mathrm{Ca}] < 0.63$ mg l^{-1}), $\beta = 0.59$ and $\gamma = 0.087$. The RMSD was thus reduced to 4.4 mg l^{-1}.

To apply the model to RS and TB, values are required for $[\mathrm{Ca}]_{\mathrm{GW}}$ and $[\mathrm{DOC}]_{\mathrm{GW}}$. The values of

$[\mathrm{Ca}]_{\mathrm{GW}}$ were set to 20 mg l^{-1} for RS and 35 mg l^{-1} for TB, and those of [DOC] to 5 and 3 mg l^{-1} respectively (Fig. 4). These choices were made on the basis that the streamwater will consist of groundwater alone only under the most extreme low flow conditions. Since these are rare and the model is a simplification, it is unreasonable to select the very highest observed concentrations. We return to the choice of groundwater composition later in this section.

We fitted the model simultaneously to all three streams using Eqs. 3 and 4. The same value of γ was assumed to apply to all three catchments, but β was optimised for each (β_{CHS}, β_{RS}, β_{TB}). High-discharge dilution was based only on the [Ca] data for CHS, but the new optimisation of α took into account the fits for the other two catchments. Thus five parameters in total were used. The optimisation was done on the entire available data set of 2,031 points (689, 657, 685 for CHS, RS, TB). The best fit parameters were as follows; $\alpha = 0.10$ ([Ca] < 0.48 mg l^{-1}), $\beta_{\mathrm{CHS}} = 0.54$, $\beta_{\mathrm{RS}} = 0.45$, $\beta_{\mathrm{TB}} = 0.41$, and $\gamma = 0.099$. The RMSDs in $[\mathrm{DOC}]_{\mathrm{SW}}$ were 4.7, 3.5 and 3.0 mg l^{-1} for CHS, RS and TB respectively, representing 25-30% of the mean values (Table 1). Illustrative results are shown in Fig. 5 for the years 1998–2000. Modelled

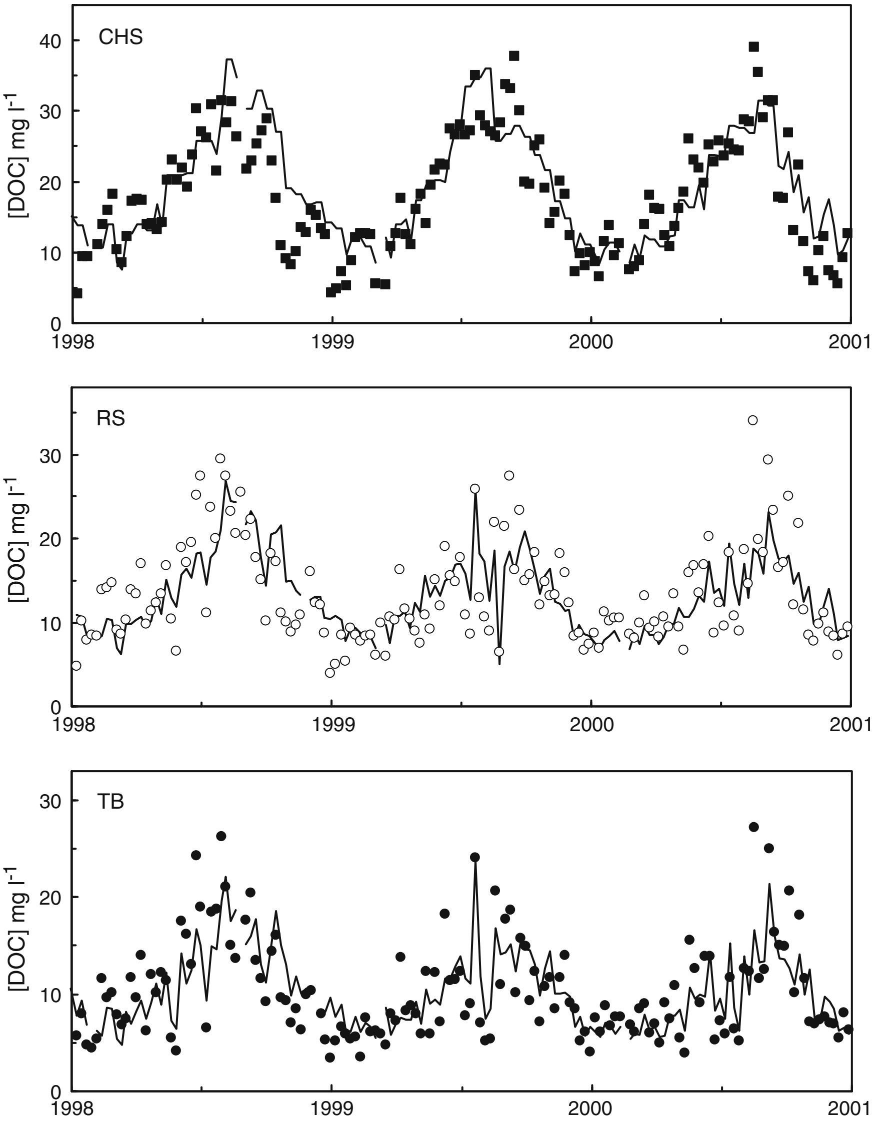


Fig. 5 Observed (points) and modelled (lines) [DOC] for Cottage Hill Sike (CHS), Rough Sike (RS) and Trout Beck (TB). The model was fitted to the entire record (1994–2007) not just the years shown

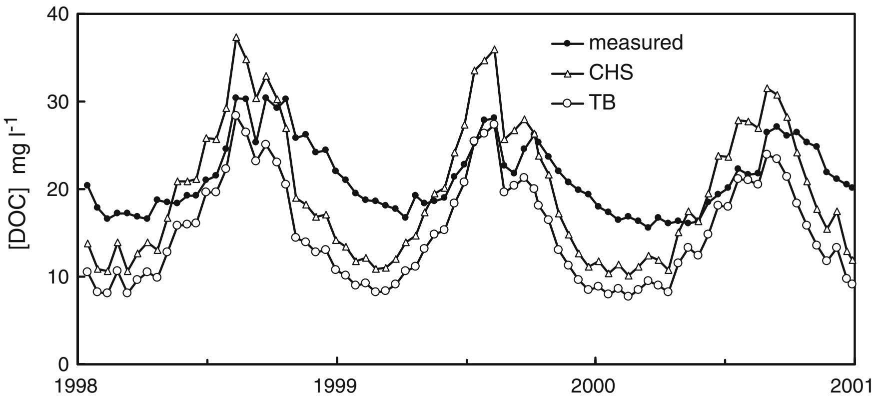


Fig. 6 Comparison of fortnightly measured $[DOC]_{PW}$ and the adjusted values for Cottage Hiill Sike (CHS) and Trout Beck (TB) from model optimisation (Eq. 2). Results for Rough Sike are omitted for clarity; they are intermediate between those for TB and CHS, although closer to those for TB

values of $[DOC]_{PW}$ (Fig. 6) reflect differences in the model parameter β, and show that $[DOC]_{PW}$ for CHS is required to be greater at all times than the values for TB (also RS).

The parameterised model provides estimates of the partitioning of both discharge and [DOC] in the stream. For RS and TB, the proportions of peat water and groundwater were calculated for each sampling date during the period 1998–2000 and multiplied by the measured total discharge (Q), to obtain Q_{PW} and Q_{GW} (Fig. 7). The results show that Q_{GW} is not constant, but increases with Q. However, the slope of the log Q_{GW} vs. log Q plot is not unity, showing that the proportion of groundwater declines with Q, from near to 100% at low Q to about 10% at the highest discharges. Overall, groundwater accounts for 9.0% of the total water flux at RS and 12.0% at TB.

Similar patterns are seen for the DOC fluxes (Fig. 7, lower panels), but with bigger differences because $[DOC]_{GW}$ is relatively low. Thus, groundwater DOM accounts for only 3.2% of the DOC flux in RS and 3.4% in TB, over the period 1998–2000. However if concentrations are considered, the groundwater assumes greater importance; in RS the average contribution of $[DOC]_{GW}$ is 7.8% of the total DOC, with a minimum of 0.9% and a maximum of 27.4% during the 3-year period analysed. The corresponding values for TB are 9.4, 1.2 and 39.2%.

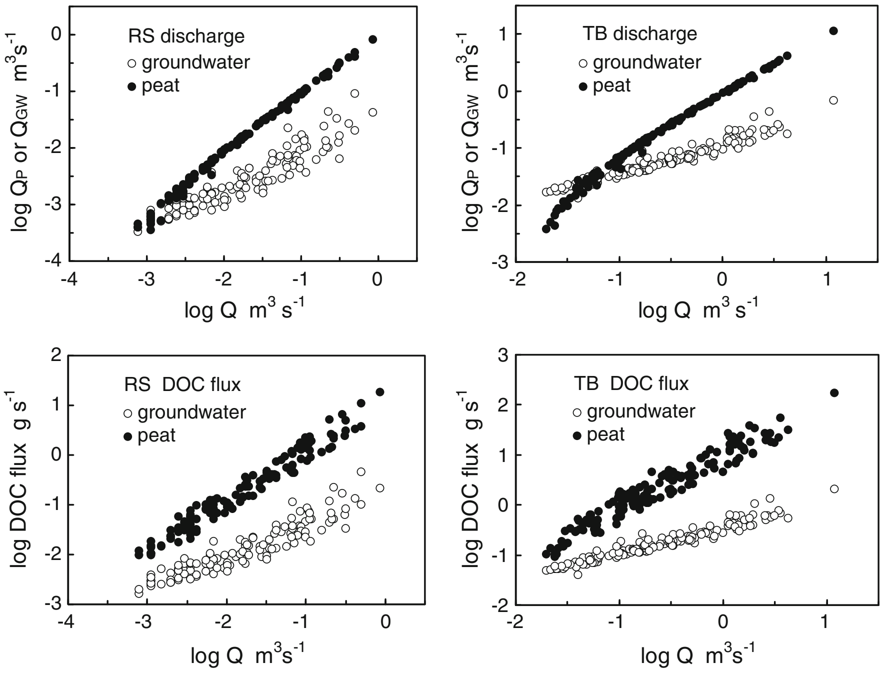


Fig. 7 Apportionment of discharge (Q) and DOC flux between peat and groundwater sources. CHS Cottage Hill Sike, RS Rough Sike, TB Trout Beck

The model fit could be improved slightly by adopting groundwater compositions with lower [Ca] and higher [DOC]. Optimisation of $[\mathrm{Ca}]_{\mathrm{GW}}$ and $[\mathrm{DOC}]_{\mathrm{GW}}$ for RS and TB reduced the RMSDs in $[\mathrm{DOC}]_{\mathrm{SW}}$ for these two streams to 3.3 and 2.6 mg l^{-1}, respectively (from 3.5 and 3.0 mg l^{-1}). However, the composition giving the best fit for RS was $[\mathrm{Ca}]_{\mathrm{GW}} = 12$ mg l^{-1} and $[\mathrm{DOC}]_{\mathrm{GW}} = 7.8$ mg l^{-1}, while the corresponding values for TB were 23 and 4.8 mg l^{-1} respectively. These were judged unrealistic because they fell well within the clouds of points shown in Fig. 4, and therefore cannot be considered end-members. Therefore we retained the original groundwater compositions (triangles in Fig. 4).

Carbon isotopes

The ^{14}C contents of DOM from CHS varied between 105 and 116% modern absolute, while those from RS ranged from 94 to 106% (Table 2). These values suggest considerable differences in the average ages of the DOM. A value of DO^{14}C less than 100% means that ^{14}C has been lost by radioactive decay since its original fixation in plant material, permitting a conventional ^{14}C age (Stuiver and Polach 1977) to be calculated. For example, the lowest value of 93.8% (Table 2) corresponds to a conventional ^{14}C age of 460 years (before 1950). It is important in the context of the present work to note that this age is an average of the DOM components, and can in principle be produced from an infinite number of mixtures.

If a sample has DO^{14}C $>$ 100% then it contains "bomb carbon", released into the atmosphere by weapons testing in the 1950s and 1960s. This feature is shown by most of the samples in Table 2. After peaking at about 190% in the northern hemisphere in 1964, the atmospheric $^{14}\mathrm{CO}_2$ signal declined, falling to *c.* 116% by 1990, then to *c.* 109% in 2000 and we estimate a value of *c.* 102% for 2010. Therefore if a carbon pool is turning over on a time scale of years to decades, its ^{14}C value will have declined by several % over recent years, as more ^{14}C-enriched carbon is replaced by carbon with less enrichment. This needs

Table 2 Chemical and carbon isotope data for filtered streamwater samples. Discharge (Q) was determined at the time of sample collection

Date	Q $\mathrm{m^3 s^{-1}}$	Ca mg l^{-1}	DOC mg l^{-1}	δ^{13}DOC ‰	DO^{14}C % modern absolute	RCL code
Cottage Hill Sike						
25/08/05	0.019	1.2	43.0	−28.1	115.6	SUERC-7814
19/04/06	0.0069	1.2	15.2	−27.9	108.2	SUERC-11402
27/07/06	0.00008	3.7	33.1	−28.0	105.8	SUERC-11715
12/09/07	nd	1.6	32.7	−28.1	105.4	SUERC-16747
07/11/07	0.00025	0.9	26.9	−28.0	111.5	SUERC-17710
21/11/07	0.00427	0.7	16.6	−28.2	111.7	SUERC-17715
05/12/07	0.06578	0.4	8.4	−28.2	109.0	SUERC-18957
Rough Sike						
10/04/02	0.0030	6.6	6.1	−27.6	93.8	SUERC-3010
22/05/02	0.0930	2.4	27.5	−28.4	105.2	AA-53481
24/07/02	0.0242	3.4	29.2	−28.3	106.1	AA-53541
28/08/02	0.0030	8.4	15.3	−27.7	98.7	SUERC-3013
06/11/02	0.1812	2.0	10.1	−28.3	106.3	AA-54795
04/12/02	0.3366	1.6	15.0	−28.3	105.9	AA-55221
12/02/03	0.0103	2.7	7.1	−27.8	102.3	SUERC-1446
11/02/06	0.1612	1.7	13.3	−28.0	103.2	SUERC-11383
21/05/06	0.6140	1.7	19.0	−28.2	104.1	SUERC-11384
05/07/06	0.0069	11.0	11.0	−26.3	97.6	SUERC-12422
15/11/06	0.0601	2.9	16.5	−27.9	103.3	SUERC-12983
12/09/07	0.0069	11.0	11.2	−27.0	96.7	SUERC-16723

to be taken into account when interpreting DO^{14}C values greater than 100%. It should also be noted that if a sample has DO^{14}C greater than 100% but significantly less than the contemporary atmospheric value, it must contain some material with ^{14}C < 100%, fixed into plant material well before 1900. This applies to most of the samples from Rough Sike (Table 2).

Table 3 shows results for DO^{14}C in samples of peat porewater (10 cm depth) and water extracts of the boulder clay layer underlying the peat. The porewater DO^{14}C values of *c.* 112% could indicate that the DOM is all quite recent, since it is greater than the atmospheric value at the time of sampling (*c.* 106%). The value of 112% corresponds to the atmospheric ^{14}CO$_2$ in 1994, 12 years before the samples were taken. In contrast water-extracted DOM from the underlying clay had low DO^{14}C values, giving conventional ages of 3,700–6,900 years. The bulk clay contained 1.2% C, and the ^{14}C contents were on average lower than those of the extracted DOC (Table 3), with conventional ages of 5,200–13,500 years.

We attempted to account for the DO^{14}C data using results from the streamwater partitioning based on [Ca] described above. Values of streamwater DO^{14}C were calculated from the Eq. 5 with DO^{14}C$_{PW}$ values set to the atmospheric ^{14}C value corresponding to the average age of the peat DOC, taking into account the year of sampling. Note that this equation was only applied to samples from RS; for those from CHS, only the time-dependence of DO^{14}C$_{PW}$ needs to be taken into account, since there is assumed to be no groundwater DOM. First, we assumed DO^{14}C$_{GW}$ to be 51.7% (the average of the values for clay extracts; Table 3), and that the peat DOM was 12 years old (see above), its DO^{14}C value decreasing over the period of sampling, from 115.5% in 2002 to 111.7% in 2007, to reflect the changes in atmospheric ^{14}CO$_2$. The simulations gave some explanation of the observations, but the calculated values of streamwater DO^{14}C were generally greater than the measured ones, by an average of 5.4%, and the RMSD between observed and calculated DO^{14}C was 6.3%. Therefore the model was optimised by adjusting both DO^{14}C$_{GW}$ and the age of the peat DOM. The best fit was obtained with 33.9% (8,630 years before 1950) and 5 years respectively, with a mean difference of −0.1% and an RMSD of 3.0% in DO^{14}C.

Table 3 Isotope results for peat porewater and water extracts of the underlying clay

Date	δ^{13}DOC ‰	DO^{14}C % modern absolute	RCL code
Peat porewater			
23/11/05	−27.6	111.8	SUERC-9570
20/02/07	−27.8	111.5	SUERC-11379
15/06/06	−28.0	112.5	SUERC-12416
Clay extracts			
05/11/08	−26.0	42.3	SUERC-23412
05/11/08	−26.2	49.6	SUERC-23413
05/11/08	−26.5	63.3	SUERC-23414
Clay solids			
05/11/08	−24.6	19.5	SUERC-23042
05/11/08	−27.7	53.1	SUERC-23043
05/11/08	−24.4	26.9	SUERC-23044

Although the results can be analysed by assuming a single average age of peat DOM, it is much more likely that the material has a range of ages. In work on SOM turnover, a common approach is to regard the SOM as comprising three pools, fast, slow and passive (e.g. Amundson 2001). These are not strictly defined, but the fast pool undergoes almost immediate decomposition, the slow pool decomposes on a timescale of decades, and the passive pool over centuries or millennia. We assumed that peat DOM is produced from fresh litter, i.e. the fast pool, and from a slow pool with a mean residence time of 20 years. The ^{14}C content of the 20-year pool was calculated using steady-state modelling, taking into account the atmospheric ^{14}C input over the last several hundred years. That of the fast pool was set equal to the atmospheric ^{14}C of the year in question. The isotope results were then fitted to Eq. 6 by adjusting the fraction of fast DOM; note that this does not increase the number of model parameters, because the average DOM age is now not fitted. The best fit was obtained with a fast fraction of 0.79 and GW DO^{14}C = 34.6%. The fit was slightly better (RMSD = 2.9%) than with the single average age version of the model, and indeed the weighted average age of the two pools is necessarily about 5 years. Table 4 shows the calculated results for each sample from the application of Eq. 5 and Fig. 8 compares observed and calculated values of DO^{14}C.

Inspection of residuals between observed and calculated DOC^{14}C revealed that the modelled values

Table 4 Model outputs for water samples subjected to isotopic analyses. Key: X_{GW}, fraction of discharge due to groundwater; $[DOC]_{GW}$, concentration of groundwater DOC; $[DOC]_{fast}$ and $[DOC]_{slow}$, concentrations of DOC derived from the fast and slow soil organic matter pools

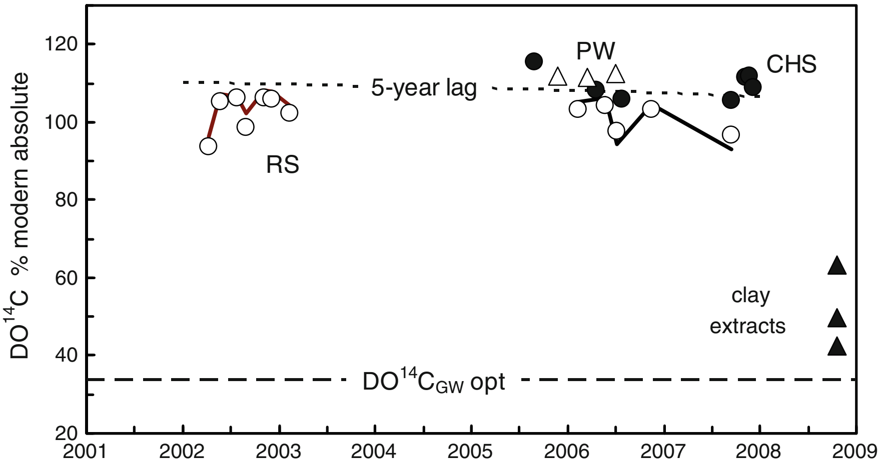
Date	X_{GW}	$[DOC]_{GW}$ mg l^{-1}	$[DOC]_{fast}$ mg l^{-1}	$[DOC]_{slow}$ mg l^{-1}	$DO^{14}C$
Cottage Hill Sike					
25/08/05	0	0	22.1	5.8	108.7
19/04/06	0	0	13.4	3.5	108.1
27/07/06	0	0	28.9	7.6	108.1
12/09/07	0	0	23.5	6.2	107.4
07/11/07	0	0	15.9	4.2	107.4
21/11/07	0	0	13.6	3.6	107.4
05/12/07	0	0	8.5	2.2	107.4
Rough Sike					
10/04/02	0.32	1.6	5.8	1.5	96.2
22/05/02	0.11	0.6	11.4	3.0	107.2
24/07/02	0.16	0.8	13.0	3.4	106.4
28/08/02	0.41	2.1	14.3	3.8	102.2
06/11/02	0.09	0.5	13.1	3.4	107.9
04/12/02	0.07	0.4	10.0	2.6	107.9
12/02/03	0.13	0.6	6.4	1.7	103.8
11/02/06	0.08	0.4	7.4	1.9	105.2
21/05/06	0.08	0.4	12.7	3.3	106.4
05/07/06	0.55	2.7	9.5	2.5	94.4
15/11/06	0.14	0.7	11.2	3.0	104.7
12/09/07	0.55	2.7	8.8	2.3	93.1

were generally too low in the summer-autumn period (June–November), and too high during winter-spring. (They were also more variable in summer-autumn.) Therefore we attempted to improve the model by assigning different values of f_{fast} for winter-spring and summer-autumn. Re-optimisation then gave f_{fast} values of 0.90 and 0.70 for these two periods respectively, and the RMSD was reduced to 2.7%. However addition of an extra parameter only produced an improvement at $p = 0.09$ (χ-squared test), and so the use of seasonal values of f_{fast} cannot be justified.

Discussion

The conceptual understanding of water flow through the RS and TB catchments used here is similar to that proposed by Worrall et al. (2003), in that the streamwater comprises a variable mixture of peat porewater, sometimes diluted by rainwater, and a base-rich groundwater component. However, we assume that groundwater has essentially bypassed the peat column and gained solutes, notably Ca and DOC, from the mineral layers beneath the peat, whereas Worrall et al. (2003), on the basis of principal components analysis of streamwater data, concluded that some of the groundwater solutes are acquired through cation-exchange reactions during percolation through the peat catotelm. In Moor House Ca-enriched groundwater could either be derived directly from the underlying limestone or from the overlying boulder clay containing weathering products derived from bedrock below. According to our analysis, groundwater accounts for 9% of the total water export from RS and 12% from TB, while not contributing at all to that from CHS. The dominance of water that has only passed through the peat surface

Fig. 8 $DO^{14}C$ values for Cottage Hill Sike (CHS), Rough Sike (RS) and peat porewater (PW). Observed $DO^{14}C$: open circles RS, closed circles CHS, open triangles PW, closed triangles clay water extracts. Modelled $DO^{14}C$: solid line RS, short dashes CHS, long dashes groundwater



accords with the findings of Holden and Burt (2003a, b), and this also fits with the young age of peat-derived DOM, as discussed below. It is also compatible with these authors' observation that flow through pipes can bypass the peat.

The expression β $(1 + \gamma T)$ in Eq. 2 has two functions in the modelling. The parameter β is an overall scaling factor. It is highest for CHS, which may arise because this catchment is at lower average altitude than the other two catchments (see "Field sites" section), and has a southerly aspect, whereas RS and TB both face to the north-east. Therefore the CHS catchment may have greater plant productivity and a higher rate of carbon cycling, including DOM production.

The term $(1 + \gamma T)$ in Eq. 2, where T is the soil temperature, modifies the measured values of $[\mathrm{DOC}]_{\mathrm{PW}}$ according to season, the main effect being to decrease the source $[\mathrm{DOC}]_{\mathrm{PW}}$ for all three streams in winter-spring. The concentrations in winter (i.e. when temperatures are low) may be too high for the model's requirements because the composition of water collected at 10 cm responds slowly to changes occurring in the shallower peat layers through which runoff water is passing (Holden and Burt 2003a). This mechanism accords with the observations of Clark et al. (2008) who showed that, over a 7-month period, the streamwater [DOC] in CHS followed [DOC] in peat porewater sampled near (1 cm depth) to the peat surface, rather than at 10 cm. In particular, their results showed a large decrease in [DOC] at 1 cm depth in autumn, consistent with the model output shown in Fig. 6. We attempted to express the required modification of $[\mathrm{DOC}]_{\mathrm{PW}}$ in terms of the position of the water table, but little explanation was achieved, because the water table can be high in summer as well as winter. Probably, temperature is a more effective guide to the relatively slow diffusional and advective processes within the peat that govern changes in the measured $[\mathrm{DOC}]_{\mathrm{PW}}$. The inclusion of temperature along with discharge has previously been found to improve the description of [DOC] in peatland streams (Dawson et al. 2002; Billett et al. 2006).

Our model assumes that within-stream processing of DOC is negligible, which contradicts the assertion of Worrall et al. (2006) that 18% of DOC entering CHS could be lost within the stream channel. Whilst Dawson et al. (2001) estimated that 12–18% of DOC was lost in a similar type of peatland stream in NE Scotland, their measurements were carried out under optimal conditions for within-stream producing of DOC, i.e. during summer daylight hours and at low flow. Under most conditions and at most times of year within-stream DOC loss in acidic organic-rich streams will be substantially lower.

By taking account of both the groundwater inputs and modifying the peat source of DOM, we have produced a model to analyse the isotope data, while also describing concentrations and fluxes of DOC. The model is not a complete description of DOM generation because it relies on the $[\mathrm{DOC}]_{\mathrm{PW}}$ values, and so avoids the need to describe the decomposition processes that generate DOM (see e.g. Tipping et al. 2007). In contrast, the modelling work of Clark et al. (2005) aimed to understand how drought-induced acidification affected streamwater [DOC], and so they were more concerned with the quantification of DOM production, and focused their work on CHS. As can be seen from Fig. 5, [DOC] in CHS varies fairly smoothly in time, the main features being high concentrations in summer-autumn and low ones in winter-spring. More important for the interpretation of isotope data is the ability of the model to describe the frequent departures from the main annual trend to lower [DOC], displayed by RS and TB at times when groundwater contributions are important. Figure 5 shows that the timings of the departures are captured well, although their magnitudes are not always properly reproduced. However, the model simulates quite well the major events seen in both RS and TB in summer 1999, in which [DOC] fluctuated from low to high values twice over a short period.

Application of the mixing model to RS provides a reasonable explanation of the variations in $\mathrm{DO}^{14}\mathrm{C}$, showing that all samples contain some of the very old groundwater DOM. When the old DOM is accounted for, and the results for CHS included, we obtain an estimate of 5 years for the average age of DOM from the surface peat. As far as we are aware, ours is the first study to quantify this in detail. The correction procedure used by Raymond et al. (2007) for DOM in rivers draining into the Arctic Ocean, mentioned in the "Introduction", was more approximate, involving the assumption that the DOC flux and $\mathrm{DO}^{14}\mathrm{C}$ content of baseflow, determined under low-discharge conditions in winter, remained the same during the high-discharge period following spring ice-melt. Other workers (Schiff et al. 1997; Palmer et al. 2001; Neff et al. 2006; Billett et al. 2007; Evans et al. 2007) have reported the presence of post-bomb carbon in surface water samples, but without estimating either average age or attempting to partition DOM sources.

The 5-year average age of surface peat-derived DOM itself probably arises from a mixture of ages. We have partitioned the material in terms of two pools of organic matter, "fast" and "slow" that are employed in soil organic matter turnover studies Amundson (2001). In this simple picture, 79% of the total is in the fast pool, i.e. produced from carbon fixed within the last year, while the rest is from a pool with a mean residence time in the soil of 20 years. A more complex description was used by Raymond et al. (2007), with a continuum of ages. They assumed surface-soil-derived DOM in Arctic rivers to be dominated by DOM from the previous year's primary production, and that contributions from preceding years decrease exponentially into the past. Application of the simplest form of this model suggested that *c.* 50% of the DOM is 1–5 years old, *c.* 25% 6–10, and *c.* 15% 11–20. The two models thus give comparable age ranges.

To account for the $DO^{14}C$ in RS while assuming the surface peat-derived DOM to have the same age and source as that in CHS, mixing with highly aged groundwater DOM is required. The best fits of the model indicate an average age of about 8,500 years, which is comparable to the range of ages (3,700–6,900 years) of DOM extracted from three samples of the clay underlying the peat (Table 3). Therefore the clay is a likely source of the groundwater DOM. It can be envisaged that water by-passing the peat by transport in natural pipes first acquires DOM from the clay then calcium from the limestone or clay derived limestone before emerging into the stream. The groundwater DOM may simply be acquired from a pool of clay-associated organic matter deposited before peat formation, which probably started at this site about 7,500 years ago (Johnson and Dunham 1963). Alternatively, it may be a mixture of the originally-deposited clay organic matter mixed with contemporarily-formed DOM carried down from the surface and then adsorbed to the clay. The second possibility is consistent with the greater age of bulk clay carbon (5,200–13,500 years), and could also explain why the concentration of groundwater DOC (estimated by modelling to be 3-6 mg l^{-1}) is relatively high compared to those encountered in soil mineral horizons.

These uncertainties are compounded by imprecision in the choice of the groundwater compositions for RS and TB used in the mixture modelling (see "Results"). Therefore our analysis and conclusions about groundwater fluxes, $[DOC]_{GW}$ and $DO^{14}C_{GW}$ must be considered only approximate. However, they are sufficient to permit the "correction" of streamwater DOM properties and thereby to elucidate DOM formation in the peat. The high average age of groundwater DOM means that only small fluxes are required to account for the considerable variations in $DO^{14}C$ observed for RS. A similar situation was identified for Siberian rivers and streams by Neff et al. (2006), who estimated groundwater DOM ages of 5,000 or even 18,000 years. The contributions of these very old organic matter fractions to surface water DOM, especially at low discharge, make it difficult to interpret $DO^{14}C$ data unless appropriate corrections can be made, as demonstrated in the present work.

The analysis presented here demonstrates rapid production of DOM at the peat surface, which must arise in the early stages of plant decomposition. Then because much of the water passes only through the upper few centimetres of the peat, and the peat solids exert only weak sorptive retention, the newly formed DOM is rapidly transferred to the streams. In contrast, in mineral soils with vertical percolation and greater sorptive capabilities, DOM is formed, retained and largely mineralised, leading to very small leaching fluxes (see e.g. Fröberg et al. 2007). The relatively high DOC export from these peatlands (15–30 gC m^{-2} a^{-1}) represents roughly 5% of the net primary productivity, which can be estimated to be about 500 gC m^{-2} a^{-1} from data reported by Jones and Gore (1978).

Conclusions

(1) Streamwater at Moor House can be considered mainly to be water that has passed only through the surface peat, with a minor contribution from groundwater, which contributes between zero and 12% to the total water export, depending upon the stream catchment.

(2) Streamwater DOM is derived from these two main sources, the surface peat supplying between 96 and 100% of the annual DOC flux.
(3) Streamwater [DOC] varies seasonally, due to variations in DOM supply from the peat, with maxima in summer-autumn. It also depends upon discharge, being reduced by dilution with rainfall at high flow, and with low-[DOC] groundwater at low flow. Under intermediate conditions, a range of [DOC] is possible, depending upon season.
(4) Dissolved organic matter derived from surface peat is from recently fixed carbon. It has an average age of 5 years, probably dominated by DOM formed within the preceding year, and including older material produced on a decadal timescale.
(5) Groundwater DOM is thousands of years old, and probably acquired by desorption from fluvioglacial clay underlying the peat. Although responsible for only a small part of the total DOC flux, its contribution to the streamwater DOM substantially modifies DO^{14}C values, especially at low discharge.

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