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The organic carbon dynamics of a moorland catchment in N. W. England

E. Tipping · E. J. Smith · C. L. Bryant · J. K. Adamson

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Abstract The carbon cycle was quantified in the catchment of Doe House Gill, which drains high-relief moorland, with thin organic-rich soils (leptosols and podzols) 10–25 cm deep, in northern England. The soil C pool of 8,300 g m^{-2} is due mainly to humic acid and older humin. If steady state is assumed, and a single soil C pool, the average ^{14}C content of the whole soil (93% modern) yields a mean carbon residence time of 800 years, although this varied from 300 to 1,600 years in the four samples studied. Stream water fluxes of dissolved and particulate organic carbon (DOC, POC) were 2.5 and 0.4 g m^{-2} a^{-1} respectively in 2002–2003, lower than values for some other upland streams in the UK. The C pool, flux, and isotope data were used, with the assumption of steady state, to calibrate DyDOC, a model that simulates the soil carbon cycle, including the generation and transport of DOC. According to DyDOC, the litter pool (ca. 100 gC m^{-2}) turns over quickly, and most (>90%) of the litter carbon is rapidly mineralised. The soil is calculated to gain only 16 gC m^{-2} a^{-1}, and to lose the same amount, about 80% as CO_2 and 20% as DOC. From the $DO^{14}C$ content of 107.5% modern (due to ''bomb carbon'') the model could be calibrated by assuming all DOC to come directly from litter, but DOC is more likely a mixture, derived from more than one soil C pool. The seasonal variability exhibited by stream water DOC concentration (maximum in September, minimum in January) is attributed mainly to variations in rainfall and evapotranspiration, rather than in the metabolic production rate of ''potential DOC''. The model predicts that, for a Q_{10} of 2, the total soil organic C pool would decrease by about 5% if subjected to warming over 200 years. DyDOC predicts higher DOC fluxes in response to increased litter inputs or warming, and can simulate changes in DOC flux due to variations in sorption to soil solids, that might occur due to acidification and its reversal.

Keywords Carbon · DOC · Isotopes · Model · Moorland · Soil

E. Tipping (✉) · E. J. Smith · J. K. Adamson
Centre for Ecology and Hydrology, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster LA1 4AP, UK
e-mail: et@ceh.ac.uk

C. L. Bryant
Natural Environment Research Council Radiocarbon Laboratory, Scottish Enterprise Technology Park, Rankine Avenue, East Kilbride G75 0QF, UK

Introduction

Soil organic matter is a major component of the carbon cycle, and is important in soil functioning, playing significant roles in water retention, and control of pH, redox status, nutrient levels, trace elements and pollutants, and being a reservoir for N, P and metal nutrients (Anderson 1995). We therefore

need to account for observed soil organic carbon pools and fluxes, and predict how they might respond to changing environmental conditions. Most of the UK's soil carbon is contained in upland soils, principally in peats, but also in thinner leptosols, gleys and podzols (Howard et al. 1995). Recent reports have raised concerns about the stability of such soils. Firstly, dissolved organic carbon (DOC) concentrations in many upland UK surface waters have risen by up to 100% during recent decades (Freeman et al. 2001; Worrall et al. 2004), which might reflect the mobilisation of stored soil carbon. Secondly, Bellamy et al. (2005) reported that the soils of England and Wales, especially organic-rich ones, have undergone substantial losses of carbon over the past 25 years, and suggested this to be a response to climatic warming. These reports emphasise the need for an appreciation of the dynamics of carbon in upland catchments, and of possible future changes.

The purpose of the present study is to characterise, in terms of composition, turnover times, and carbon fluxes, the soil and water organic matter of a small upland moorland catchment with thin organic-rich soils in the Lake District of north-west England. The catchment is located in the Duddon valley, which has featured in a number of previous studies of acidification and heavy metal behaviour (Tipping et al., 2000, 2006a, b). By characterising the present situation we can establish a reference point, against which to address the key question of the long-term stability of the soil organic matter under current or altered conditions, and also possible effects on the transfer of DOC to surface waters. We measured soil C pools, stream water concentrations of dissolved organic carbon (DOC) and particulate organic carbon (POC), together with their ^{14}C contents.

The ^{14}C data were used to obtain information about rates of carbon turnover, using both long-term radioactive decay and ''bomb carbon'' associated with the enrichment of atmospheric $^{14}CO_2$ by weapons testing in the 1950s and 1960s (Jenkinson 1963; Harkness et al. 1986; Trumbore et al. 1989). This was done in terms of simple mean residence time calculations, based on a single soil carbon pool, and by fitting a modification of the process-based model, DyDOC (Michalzik et al. 2003; Tipping et al. 2005), to describe both soil carbon cycling and the export of DOC to stream water. DyDOC is based on a series of increasingly humified organic matter fractions, and includes descriptions of DOC formation, sorption to soil solids, and transport by water percolation. DyDOC differs from DocMod (Currie and Aber 1997) in that it includes water percolation and tracks ^{14}C through different C pools, whereas DocMod confines itself to an overall annual leaching flux of DOC. It differs from the model of Neff and Asner (2001) in its use of ^{14}C, and because its parameters are estimated by fitting field data for individual sites, whereas the Neff–Asner model generalises from the results of many studies. The DOC aspects of DyDOC distinguish the model from CENTURY (Parton et al. 1987) or the Rothamsted model (Jenkinson 1990), but the use of relatively few soil C pools follows these established models.

The parameterised DyDOC model was used to explore changes in soil carbon pools and DOC fluxes due to warming and fertilisation. It was also used to explore how DOC concentrations and fluxes could be altered by acidification reversal, following the suggestion of Evans et al. (2006) that changes in soil pH, due to changes in sulphur deposition, influence the sorption of ''potential DOC'' by soil solids, and thereby DOC leaching.

Site description

Doe House Gill (DHG) is a tributary of the River Duddon, located in the north-west of England (54°20′ N 3°12′ W). The stream drains a hillside of average slope 20° (altitude range 240–730 m a.s.l.), and has an area of ca. 0.3 km^2. The average annual temperature is 6°C, the average rainfall 3,000–3,500 mm a^{-1}, and the average evapotranspiration 500 mm a^{-1}. The stream runoff is rapid and strongly dependent on previous rainfall. Hall and Folland (1970), using the England and Wales soil classification system, identified the soils as acid humic rankers (stony organic matter overlying bedrock) and peaty gleyed podzols, with a sandy loam texture. In the FAO system they are Histic Leptosols and Histic Gley Podzols respectively (FAO, 1998), and we use the shortened designations leptosol and podzol hereinafter. Chemical data for 10 similar soil samples were given by Tipping et al. (2006a). The mean pH in 1 mM NaCl was 4.5 for the leptosols, 4.2 for the podzol organic horizons, and 4.6 for the podzol mineral horizons, while mean C:N ratios were 17.9

for the leptosols, 14.3 for the podzol organic horizons, and 15.1 for the podzol mineral horizons. The soils have a total thickness between 10 cm and 40 cm, and overlie slowly weathering, metamorphosed, igneous rocks of the Borrowdale Volcanic Group. Over most of the catchment area, the soils are fairly free-draining, although lateral, rather than vertical, movement of water is predominant (Pearsall and Pennington 1989). Temporary waterlogging occurs, but permanently waterlogged soil accounts for only a small area. The vegetation comprises grasses (*Nardus, Festuca, Agrostis*), bracken (*Pteridium aquilinum*), and *Sphagnum* moss. The land is used as rough pasture for sheep. In the past, the site was probably under oak forest, which was cleared between 5,000 BP and 1,000 BP (Pearsall and Pennington 1989).

The net primary production (NPP) at DHG has not been determined, but an approximate estimate can be made from the results of Perkins et al. (1978) who performed a detailed study of production in an *Agrostis-Festuca* grassland at Lyn Llydaw (Snowdonia, N. Wales), with altitude, slope, climate and land use similar to those at DHG. They estimated NPP to be 1,450 g dry weight m^{-2} a^{-1}, taking into account both above- and below-ground growth. They also reported above-ground growth in a nearby *Nardus-Festuca-Agrostis* grassland, situated on a more acid soil, and therefore similar to the DHG system, to be c. 25% of the *Agrostis-Festuca* value, suggesting a total NPP of c. 375 g dry weight m^{-2} a^{-1}, or about 200 gC m^{-2} a^{-1}. It should be noted that NPP is generally not well estimated for grasslands, but is typically several hundred gC m^{-2} a^{-1} (Long and Hutchin 1991; Scurlock et al. 2002).

Doe House Gill is one of several streams in the upper Duddon valley that have been monitored intermittently for stream chemical variables since the 1970s (Carrick and Sutcliffe 1983; Tipping et al. 2000). Although stream pH, metal cation concentrations, and alkalinity vary appreciably among the streams, due to spatial variations in weathering rates, concentrations of acid anions and DOC are very similar, reflecting uniform deposition and soil characteristics. Thus, DOC trends from other streams in the valley can be taken to represent those at DHG, for which time series data are limited.

For modelling with DyDOC, we required daily air and soil temperatures. Air temperatures were estimated from values recorded at Ambleside (13 km E of the field site), corrected for altitude according to Manley (1989). Soil temperature was estimated from air temperature using an empirical relationship derived from data for moorland soils of similar composition to those at DHG, and situated at an altitude of 480 m in the Pennine hills (55 km north-east of the study site); soil temperature at 10 cm could be estimated as equal to 1.06 times the average air temperature for the preceding 5 days, except for average air temperatures of less than 0°C, when soil temperature was set to 0°C. This procedure fitted the daily Pennine data over 3 years with a standard deviation of 1.1°C, and no bias.

Methods

Soil sampling and analysis

Soil samples were collected by digging small pits (c. 30 cm square). Samples were placed in plastic bags for transport to the laboratory, where they were stored at 5°C. Bulk densities of leptosols were determined by cutting cuboids with a knife, determining their volumes and wet weights, and then measuring the dry masses of sub-samples after oven-drying (105°C). For soil with appreciable mineral matter, the volume of the horizon was measured in the field, the excavated soil sample was sieved (4 mm) and the total mass of moist fine earth determined. Oven-dried samples were analysed for C, H and N with a Universal CHNS-O Vario EL elemental analyser.

Soil organic matter was fractionated as recommended by the International Humic Substances Society Method (Swift 1996). Roots were removed from the sample and it was thoroughly homogenised. Sub-samples (75 g) of field-moist soil were weighed into a 375 cm^3 polycarbonate centrifuge tube and 300 cm^3 of 0.1 M HCl were added. The suspensions were shaken vigorously for two hours, then centrifuged for 45 min at 9,000 *g*. The total supernatant volume was determined, and sub-samples were taken for the determination of DOC (Dohrmann DC-190 instrument). The insoluble residue was neutralised to pH 7.0 with 1 M NaOH (previously boiled under N_2 to remove dissolved carbonate), and the pH was raised further by adding 0.1 M NaOH under a nitrogen atmosphere. The suspensions were again

shaken for two hours, and then centrifuged. The supernatant volume was measured, and samples taken for DOC determination. To obtain the soil humin, the sedimented pellets were neutralised to pH 7, rinsed with distilled water, re-centrifuged, and dried at 105°C. The material was weighed, and analysed for carbon. The supernatant was acidified to pH 1 with 6 M HCl, left to stand overnight, and then centrifuged to separate the humic acid (pellet) from fulvic acid (supernatant). The solution volume was determined and sub-samples were taken for DOC determination. The solution was then combined with the original acid extract, to form the fulvic acid extract, the DOC content of which was determined. The pellet (humic acid) was rinsed with distilled water and stored. Humic acid C was determined as the difference between total DOC in the base-extracted solution, and the DOC due to fulvic acid in the supernatant.

Stream water sampling and analysis

Stream depth was measured hourly using a pressure transducer, and was calibrated to discharge by salt dilution gauging. Samples of stream water for the determination of DOC and POC were collected in polyethylene containers that had been cleaned by rinsing with distilled water, and by pre-filling and emptying several times before taking the final sample. Up to 50 l of sample were required to provide sufficient material for isotope analysis, and in a number of cases this was still insufficient for PO^{14}C measurements. Filtration (Whatman GF/F 0.7 μm pore size) was used to separate dissolved from particulate organic carbon. Particulate organic carbon was determined by weighing the dried filters.

Isotope analysis

Bulk soil samples were oven-dried and converted to benzene for ^{14}C analysis by liquid scintillation counting using standard procedures at the NERC Radiocarbon Laboratory (RCL) (Harkness and Wilson 1972). Stable carbon isotope ratios were measured on benzene combusted to CO_2 using a dual-inlet mass spectrometer with a multiple ion beam collection facility (VG OPTIMA) in order to normalise ^{14}C data to $-25‰$ $\delta^{13}C_{VPDB}$. The delta (δ) notation expresses relative differences in stable carbon isotope ratios of sample to standard, where δ^{13}C is the parts per thousand (‰) difference between the ^{13}C content of the sample and that of the standard. By international convention δ^{13}C values are expressed relative to a defined standard Vienna-Pee Dee Belemnite (V-PDB) (Coplen 1994). The mass spectrometer was calibrated with international reference materials to a precision of ±0.1‰. Water samples were filtered (pre-combusted Whatman GF/F) and the filtrates rotary evaporated and freeze-dried. Graphite targets from all water samples, and from extracts of fulvic and humic acids, for ^{14}C analysis by Accelerator Mass Spectrometry (AMS) were prepared by quantitative recovery of carbon in sealed quartz tubes followed by cryogenic separation of CO_2 (Boutton et al. 1983). Aliquots of CO_2 were converted to an iron/graphite mix by iron/zinc reduction (Slota et al. 1987). A sub-sample of CO_2 was used to measure δ^{13}C as described above. Graphite from samples collected before 2003 were sent for AMS analysis to the NSF-AMS Facility University of Arizona, Tucson, USA (Donahue 1990). From 2003 onwards, the establishment of the SUERC AMS Laboratory, East Kilbride, UK (Xu et al. 2004), permitted AMS measurements to be performed locally. In keeping with international practice the results are reported as absolute % modern which involves a mathematical adjustment to account for ongoing radioactive decay of the international reference standard (oxalic acid) since AD 1950 (Stuiver and Polach 1977). The ^{14}C enrichment of a sample is measured as a percentage (or fraction) of the ^{14}C activity relative to a modern standard (oxalic acid provided by the US National Bureau of Standards), where 100% modern is defined as the value in AD 1950, in the absence of any anthropogenic influences. Overall analytical precision, expressed as one standard deviation, was 0.4–0.6%. Quality control ^{14}C backgrounds and standards (bituminous coal, TRI barleymash and ANU sucrose) were processed as for samples to check accuracy and precision of results, which were within acceptable analytical limits.

Calculation of mean residence times (MRT)

Values of MRT were calculated following the method of Harkness et al. (1986), assuming a single carbon pool, in steady state with respect to inputs and losses of C. The soil ^{14}C content in a given year was computed from the value in the previous year,

modified by the input of ^{14}C in fresh material and the loss of ^{14}C from the soil pool. The year-to-year variation in atmospheric ^{14}C for the study site latitude (see next paragraph) was used to drive the ^{14}C input. The flux of C to the soil was adjusted until the calculated soil ^{14}C matched the observed value. The MRT was then obtained as the ratio of the soil pool to this flux.

In the absence of anthropogenic or ^{14}C production rate influences on the atmospheric ^{14}C concentration, ^{14}C enrichment of soil organic material reflects the extent of radioactive decay of the isotope since the death of the constituent organisms (plant, soil animal etc.) into which it had been incorporated. During the late 19th and 20th centuries, the atmospheric ^{14}C concentration was diluted by the input of 'dead' carbon (containing infinitesimal amounts of ^{14}C) from the burning of fossil fuels (Suess effect). More importantly, the atmospheric ^{14}C concentration was almost doubled during testing of thermonuclear weapons in the late 1950s to early 1960s. Fossil fuel burning decreased the ^{14}C signal to c. 97% modern by AD 1950, and bomb testing increased it to c. 190% modern after which the atmospheric ^{14}C concentration steadily decreased, largely due to uptake into the oceans (Broecker and Olson 1960; Nydal et al. 1980). Changes in atmospheric ^{14}C concentrations since the bomb peak have been well documented (Walton et al. 1970; Baxter and Walton 1971; Nydal et al. 1980; Levin and Kromer 1997, 2004), and used to provide the input ^{14}C signal for both the MRT calculation, and DyDOC modelling (see below).

Dynamic DOC model (DyDOC)

DyDOC simulates the metabolic transformations and transport of organic carbon in soil profiles. When applying the model to podzolic forest soils, Michalzik et al. (2003) considered three horizons to explore the transfer of DOC from the forest floor to mineral horizons, whereas Tipping et al. (2005) dealt only with the O-horizon. In the present work, the soil is treated as a single homogeneous compartment, with a uniform temperature estimated from air temperature as described above. DyDOC is a model under development, and some modifications were made in the present study in view of the different characteristics of the moorland soils.

Water enters the soil as wet precipitation or snow. The soil pore space comprises macropores, within which water moves rapidly under gravity, and micropores, within which it is immobile. Incoming water mixes with water already present in the macropores, and macropore water and solutes can enter the micropores if they are not filled. Dissolved organic carbon exchanges between the macropores and micropores, according to a pseudo-diffusive process, governed by an exchange constant D_{exch}. Water is lost by evapotranspiration from the micropores, at a rate proportional (via the constant k_{evap}) to air temperature. Drainage loss from the base of the soil column is proportional, via a constant (k_{drain}), to the total volume of macropore solution. To relate rainfall to stream discharge, it was necessary to include a water store (volume V_S), with an associated drainage rate constant ($k_{drain,S}$) to create base flow; if this store is full, excess soil water passes directly to the stream. The hydrology sub-model runs on an hourly time step.

Organic carbon enters the soil as above-ground and root litter, treated as a single component, and undergoes metabolic transformations that convert it to other organic carbon forms, or to CO_2. The soil carbon comprises recent litter, substrate (partially decomposed litter that is the source of humified material), and humic substances (Hum1, Hum2 and Hum3). In applications of the model to spruce forests, scheme A of Fig. 1 was employed, with or without the transformation from litter directly to Hum1 and Hum2. In the present work, a simpler transformation scheme is employed (Scheme B of Fig. 1(b)). The litter and substrate pools account for part of the humin, i.e., organic matter that is insoluble in base. The humic fractions Hum1 and Hum2, when in solution, correspond to DOC; Hum1 approximates hydrophilic acids, Hum2 hydrophobic acids. In both schemes A and B, Hum3 corresponds to the sum of immobile fulvic acid, humic acid and aged humin. The different versions of the model are distinguished as DyDOC-01 (Scheme A without direct litter conversion to Hum1 and Hum2; Michalzik et al. 2003), DyDOC-02 (Scheme A with litter conversion to Hum1 and Hum2; Tipping et al. 2005), DyDOC-03 (Scheme B, present work). The metabolic transformations are assumed to be mediated principally by microorganisms, and are described with first-order rate constants and ''Q_{10}'' relationships, according to the general equation

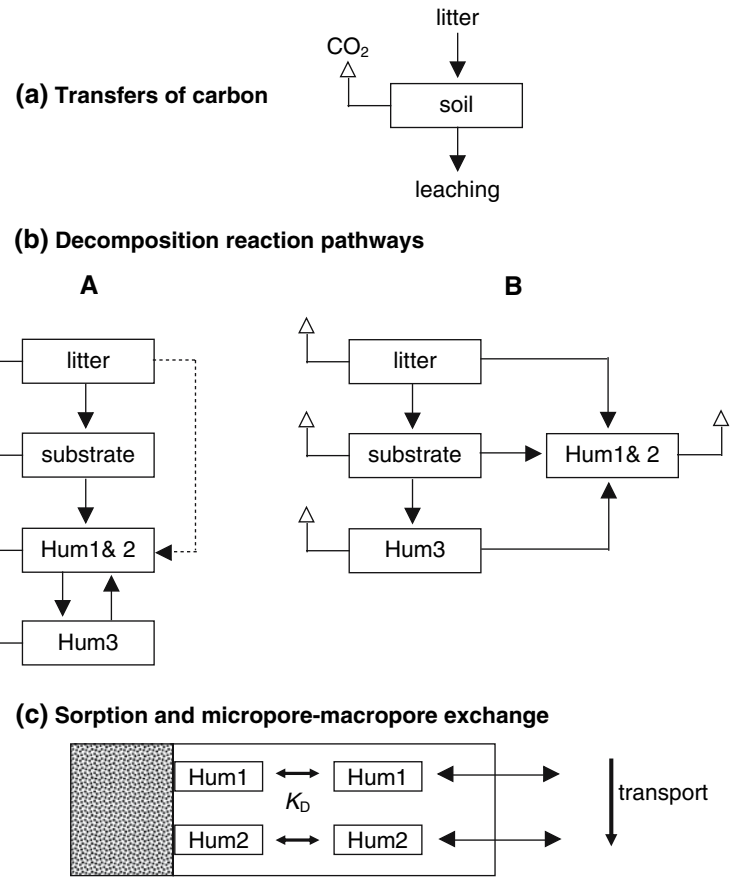

Fig. 1 Processes in DyDOC. Open and closed arrows indicate transfers of CO_2 and organic C respectively. The dotted line in (**b**) applies in DyDOC-02 but not in DyDOC-01

$$\Delta C = -k\, Q_{10}^{(T/10)}\, C_{\text{pool}}\, \Delta t \qquad (1)$$

where ΔC is the loss of carbon from the relevant pool, C_{pool} is size of the carbon pool, Δt is the time, T is the temperature in °C and Q_{10} is a constant. The effects of varying moisture on the metabolic reactions are not taken into account in the current version of DyDOC. The metabolism sub-model runs on a daily time step. (POC is not included in the current version of the model.) Humic fractions Hum1 and Hum2 adsorb reversibly to the soil solids and become DOC when passing into solution. The tendency to sorb to the soil is described by equilibrium partition coefficients (K_D), according to the equation

$$K_D = \frac{\text{g DOC sorbed per g soil}}{\text{solution concentration of DOC in g m}^{-3}} \qquad (2)$$

where the solution concentration refers to the micropore. The value of K_D for Hum1 is less than that for Hum2, reflecting the lesser tendency of hydrophilic organic solutes to undergo sorption reactions. The K_D values depend not only upon the type of DOC, but also on the nature of the solid phase and the soil solution composition, principally pH and Al concentration (cf. Lofts et al. 2001). The model tracks the ^{14}C contents of the different carbon pools, starting with the varying ^{14}C content of plant litter, which is estimated from the atmospheric $^{14}CO_2$ content in a given year (see above), combined with the average (integral) number of years the C resides in the living biomass.

The goodness-of-fit is judged by comparing simulated outputs with measured or estimated values of soil C pools, DOC flux, average ^{14}C signals, and the fraction of DOC that is hydrophobic. The objective function (OF) to be minimised is given by

$$\mathrm{OF} = \sum_i w_i \left(\frac{v_{i,\mathrm{meas}} - v_{i,\mathrm{sim}}}{v_{i,\mathrm{meas}}} \right)^2 \quad (3)$$

where v_i is the value of the variable and w_i is a weighting factor. In the present work, all values of w_i were set to unity, i.e., all variables were given equal weighting. However, to increase the precision of the ^{14}C values (expressed as % absolute modern ^{14}C), transformed variables were used for fitting, obtained by subtracting 85% from the total soil ^{14}C data, and 100% from the DO^{14}C data. Parameter optimisation was performed by the Nelder-Mead polytope procedure, using software published by Nash and Walker-Smith (1987). The method requires an initial set of trial parameter values, which are improved by formulated trial-and-error to minimise the objective function.

Results

Soil organic carbon

Carbon pools, including humic fractions, in four soils sampled at DHG in June 2002 are summarised in Table 1, together with isotope data. The leptosols contain 320 g kg^{-1} organic carbon, the podzols 140 g kg^{-1}. Combining these values with fine earth bulk densities of 0.24 g cm^{-3} for the leptosols, 0.22 g cm^{-3} for the podzol organic horizons, and 0.72 g cm^{-3} for the podzol mineral horizons, gave an average total C pool of 8,300 gC m^{-2}, slightly lower than an average of 10,300 gC m^{-2} for three leptosols and three podzols sampled at DHG in March 2002. Similar results were obtained for 14 other soil profiles from three other sub-catchments of the Duddon valley by Tipping et al. (2006a). The C pools for all 24 profiles range from 5,200 gC m^{-2} to 27,200 gC m^{-2}, with a mean and standard deviation of 10,800 gC m^{-2} and 4,800 gC m^{-2}, respectively. The organic matter of the leptosols at DHG comprises approximately 40% fulvic and humic acids, as judged by extraction with base, the remainder being classified as humin (Table 1). Overall, the ^{14}C contents of the three soil organic matter fractions increase in the order humin < humic acid < fulvic acid (Table 1), and this indicates that humin is, on average, the oldest fraction.

The insoluble humin could be little-transformed, fairly recent, plant litter, i.e., ''young humin'', or ''old humin'', material that has lost proton-dissociating groups and/or polar moieties, rendering the material insoluble. Since the young humin must reside primarily in the upper part of the leptosols, its maximum pool sizes are 1,500 gC m^{-2} in Leptosol #1 and 2,100 gC m^{-2} in Leptosol #2 (Table 1). However, the low ^{14}C contents of the upper soil humin mean that a considerable amount must be old humin, which implies that the young humin pools are considerably smaller than those maximum values, and are therefore no more than a few hundred gC m^{-2}.

The total ^{14}C values for the upper parts of the two leptosols differ appreciably, being 107.7% modern for Leptosol #1 and 92.6% for Leptosol #2 (Table 1). The value of 107.7%, being greater than 100%, unequivocally shows the presence of ''bomb carbon'', and the value of 101.2% value for the fulvic acid in Leptosol #2 (Table 1) shows that bomb carbon has also entered this soil. The ^{14}C contents of the two podzol samples are similar, and lie between the leptosol values. Interpretation of these data in terms of steady-state mean residence times (MRT) is illustrated by Fig. 2. Application of the MRT approach to all four upper layers, and to the four whole soils gave the results shown in Table 2. Taking all four soils together, the mean MRT is 814 years, and the average C input to the soil is 10.2 g m^{-2} a^{-1}.

Stream water organic carbon

Twenty-nine samples were collected during 1 year (2002–2003) and analysed for DOC. The average concentration was 0.85 mg l^{-1} (range 0.2–1.7 mg l^{-1}). Seasonality was not strongly apparent from this data set, partly because the values are close to the detection limit of the analytical method. However, other data are available for DHG and for neighbouring streams, and when these are combined a clear seasonality emerges, featuring a late summer/autumn maximum (Fig. 3). For Mosedale Beck, the mean DOC concentration in summer months (May–October) between 1993 and 2002 was 1.21 mg l^{-1} (n = 52) significantly (P < 0.025) greater than the winter value of 0.85 mg l^{-1} (n = 50); the low DOC concentrations preclude the detection of significant

Table 1 Carbon pools and isotope data for four soils at Doe House Gill, corrected for stones and rocks

	gC m^{-2}	$\delta^{13}C_{VPDB}$ ‰	^{14}C abs % modern	^{14}C age years BP[a]	Lab publication code
Leptosol #1, upper (7.75 cm)					
Fulvic acid	300	−26.1	112.79	Modern	AA-53499
Humic acid	1,900	−27.6	106.69	Modern	AA-53509
Humin	1,500	−27.5	101.87	Modern	SRR-6833
Total	3,700	−27.4	107.72	Modern	SRR-6819
Leptosol #1, lower (7.75 cm)					
Fulvic acid	400	−25.3	95.73	298 ± 52	AA-53500
Humic acid	1,200	−26.7	93.87	457 ± 44	AA-53510
Humin	2,000	−27.0	94.43	410 ± 49	SRR-6834
Total	3,500	−27.0	94.11	437 ± 44	SRR-6820
Leptosol #2, upper (5.5 cm)					
Fulvic acid	100	−25.0	101.22	Modern	AA-53501
Humic acid	600	−26.8	98.02	109 ± 41	AA-53511
Humin	2,100	−26.8	91.40	671 ± 35	SRR-6835
Total	2,800	−26.7	92.59	568 ± 45	SRR-6823
Leptosol #2, lower (5.5 cm)					
Fulvic acid	200	−25.0	92.84	545 ± 36	AA-53502
Humic acid	1,300	−27.3	82.07	1535 ± 54	AA-53512
Humin	3,900	−27.3	82.30	1514 ± 38	SRR-6836
Total	5,300	−27.3	81.38	1604 ± 44	SRR-6824
Podzol #1, O horizon (9 cm)					
Total	4,000	−26.8	98.70		SRR-6821
Podzol #1, mineral horizons (17 cm)					
Total	5,900	−26.8	88.08	969 ± 45	SRR-6822
Podzol #2, O horizon (11 cm)					
Total	5,900	−27.4	96.42	242 ± 37	SRR-6825
Podzol #2, mineral horizons (12 cm)					
Total	2,200	−27.7	87.41	1031 ± 49	SRR-6826

[a] Equivalent conventional ^{14}C ages (not applicable to results >98.5% modern carbon)

interannual variability. For 10 Duddon tributaries in 1998, the mean summer concentration of 1.22 mg l^{-1} (n = 246) was significantly ($P < 0.001$) greater than the winter value of 0.90 mg l^{-1} (n = 223).

Simple combination of the average DOC concentration with the total runoff gave a DOC flux of 2.3 g C m^{-2} a^{-1} for DHG in 2002–3. An improved estimate of the flux was made by taking into account seasonality and discharge dependence in DOC concentration. The mean [DOC] in summer (May–October) at discharges less than 5 mm day^{-1} was 0.74 mg l^{-1}, significantly ($P < 0.005$) less than the mean for higher discharges (1.21 mg l^{-1}). However there was no significant variation with discharge in winter (mean = 0.78 mg l^{-1}). Combining these average values with daily discharges gave a flux of 2.5 g C m^{-2} a^{-1}, the preferred value.

Particulate organic carbon (POC) concentrations, determined on 27 samples, were very low, with a mean of 0.19 mg l^{-1} (range 0.0–1.1). The POC load estimated from these data was 0.4 gC m^{-2} a^{-1}, although this is probably an underestimate because very high-discharge events were not adequately sampled.

Application of DyDOC

The soil was treated as a single mixed compartment, with properties averaged from the four soil samples

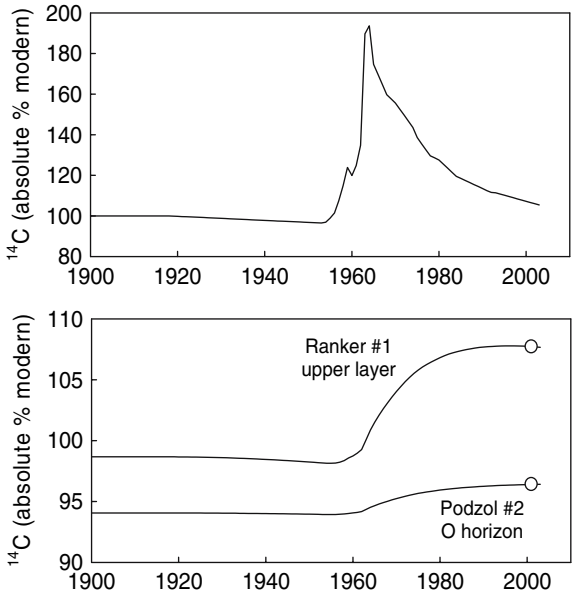

Fig. 2 Steady state interpretation of the ^{14}C data for the upper horizons of two DHG soils. The upper panel shows the atmospheric ^{14}C value, including the ''bomb carbon'' peak. The lower panel shows how the annual increment of C to the soil (assumed constant) was adjusted to force agreement between the modelled and observed ^{14}C values (see Modelling section)

Table 2 Carbon inputs in gC m^{-2} a^{-1}, and mean residence times (MRT) in years, calculated either for the upper soil or for the whole soil (Table 1)

	Upper layer		Whole soil	
	C input	MRT	C input	MRT
Leptosol #1	32.6	113	26.4	273
Leptosol #2	3.5	812	5.1	1,588
Podzol #1	10.3	388	11.8	839
Podzol #2	11.2	527	11.4	711

of Table 1. The system is taken to be in steady state, except for the ^{14}C inputs. The model was driven by daily rainfall, air and soil temperatures, and annual values of litter input and ^{14}C content. Meteorological conditions in the past were generated by repeatedly using the data for the sequence of years 1971–2002 for which full data are available. The rate of litter production (i.e., NPP) was assumed to be constant at 200 gC m^{-2} a^{-1} (see Site description).

The aim of the modelling with DyDOC was to reproduce the observed or assumed C pools and fluxes, and ^{14}C values, shown in Table 3. The assumed standing litter pool (above and below ground) is 100 gC m^{-2}, estimated from the results of Perkins et al. (1978) for similar sites in north Wales (see Site description). The substrate pool is set at the approximate value of 400 gC m^{-2}, based on the estimate of several hundred gC m^{-2} for ''young humin'' (see above). We assumed that the stream water DOC flux corresponded to the soil water flux, which is justified by the absence of deep mineral soil. The streamwater dissolved organic matter is assumed to comprise hydrophilic (Hum1) and hydrophobic (Hum2) components, present in equal amounts.

Hydrology

The soil porosity was estimated to be 73%, from the average bulk density of 0.40 g cm^{-3} and an assumed solids density of 1.5 g cm^3. The fraction of the pore space due to macropores, $f_{\text{macro,}}$ was set to 0.1, the default value, but equally good agreement between observed and simulated discharges could be achieved with the parameter set to 1/3 or 3 times this value, principally by modifying $k_{\text{drain,}}$ and with small adjustments of k_{evap}. The values of k_{evap}, k_{drain}, $k_{\text{drain, S}}$ and V_S were adjusted to simulate the stream discharge, by forcing the calculated total annual discharge to equal the measured value, and by reproducing peak and low discharges. Although detailed short-term simulation of the hydrograph was not achieved, the overall pattern was reproduced (Fig. 4), and this is adequate for the simple budgeting of DOC required in the present study.

Steady-state pools and fluxes

Starting at 2000 years BP, the system was run to steady state with respect to carbon pools, fluxes and ^{14}C contents, before the changes in atmospheric ^{14}C that occurred during the late 19th and 20th centuries (Fig. 2). This was done for different trial sets of metabolic parameter values (Table 4), their values being improved after each run using the optimisation software (see Methods). The objective function for fitting was created by linear combination of the residuals associated with the target variables of Table 3.

In the present version of the model, the average time between the incorporation of C into plants and

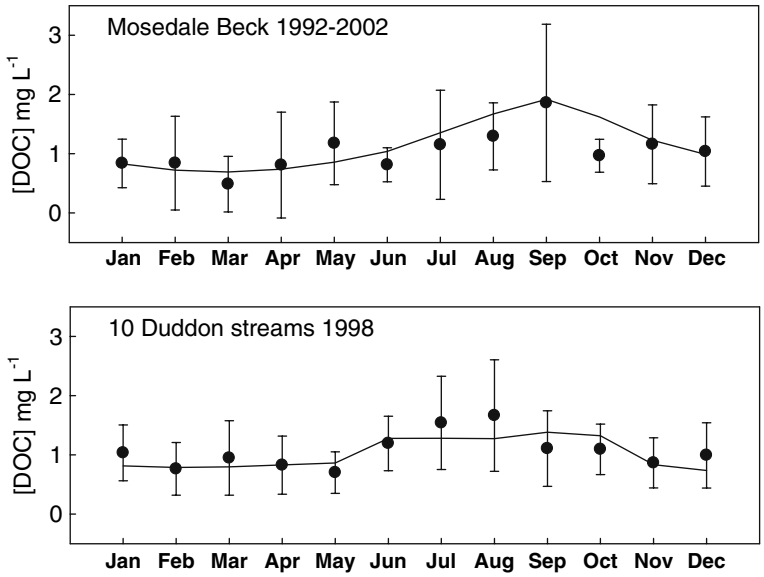

Fig. 3 Observed concentrations of DOC (shown by points) at Mosedale Beck (1992–2002) and in 10 tributaries of the main River Duddon, including Doe House Gill (1998). The values are averaged by month; the error bars indicate ±1 SD. The lines show monthly values simulated with DyDOC for Doe House Gill, for the same periods

Table 3 Observed, assumed (italicised) and model-simulated (parameter set I) variables for carbon cycling at Doe House Gill

	Units	Target	Simulated
Total C	g m^{-2}	8,300	7,800
Litter C	g m^{-2}	100	100
Substrate C	g m^{-2}	400	420
DOC flux	g m^{-2} a^{-1}	3.1[a]	3.2
Soil 14C	% Modern	93	94
DO14C	% Modern	107.5	106.6
Hydrophobic DOC	%	50	49

[a] DOC flux refers to ground covered with soil (80% of the total area)

its output in litter (t_{litter}) can only take on integral values. It was set to zero years for the main modelling, which means that the litter C input has a

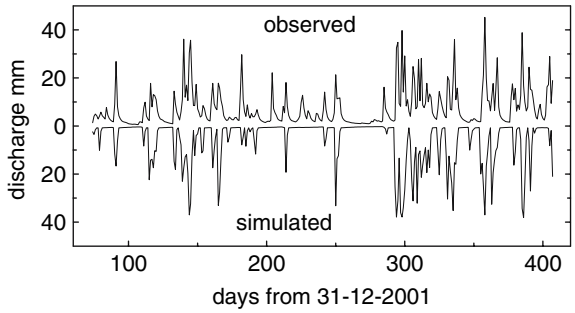

Fig. 4 Observed and simulated (parameter set II) discharge of Doe House Gill 2002–2003

^{14}C value equal to that of the atmosphere for the year in question. The exchange constant D_{exch} was set to 0.1, as optimised for forest soil by Tipping et al. (2005). The partition coefficients K_{D1} and K_{D2} (Eq. 2) were estimated from the results of laboratory and modelling studies on similar soils from the same area (Tipping and Woof 1991), in which the solid-solution distribution of potentially mobile organic matter was modelled in terms of 10 fractions; for this work, fractions 1 and 2 were assigned to Hum1 and 3–5 to Hum2, while the other fractions were completely insoluble under likely field conditions. The derived values of K_{D1} and K_{D2} were 0.0 and 1.2×10^{-5} m^3 g^{-1} respectively for soil at pH 4.4. In the main modelling, Q_{10} was fixed at the commonly used value of 2.0 (Schlesinger 1997) for all metabolic reactions, but the effect of selecting a higher value was explored (see below). Trials were made with DyDOC-01 and DyDOC-02 as previously used for forests (Fig. 1), but although acceptable fits could be achieved, the low pool sizes of Hum1 and Hum2 forced unrealistically high rates of conversion of these fractions to Hum3 (Scheme A, Fig. 1). Therefore the simpler metabolic scheme B (Fig. 1) of DyDOC-03 was adopted. Again, basing the model on previous findings for forest soils, we initially forced the formation of DOC to come equally from the three possible C pools (litter, substrate, Hum3), which has the advantage of reducing by two the number of fitted parameters, because only one of k_{LH12}, k_{SH12} and k_{H3H12} then needs to be optimised.

Table 4 DyDOC-03 parameters

Symbol	Units	Description	How found	Set I	Set II	Set III
t_{litter}	year	Time to convert plant C to litter	*a*	0	0	0
K_{D1} K_{D2}	$m^3\ g^{-1}$	Partition coefficients (equation 2)	*b*	0, 1.2×10^{-5}	0, 1.2×10^{-5}	0, varies
f_{macro}	–	Fraction of pore space due to macropores	*a*	0.1	0.1	0.1
k_{evap}	deg^{-1}	Evapotranspiration rate constant	*c*	3.8×10^{-4}	3.8×10^{-4}	3.8×10^{-4}
k_{drain}	*	Rate constant for soil drainage	*c*	0.15	0.15	0.15
V_S	m	Water store	*c*	0.02	0.02	0.02
$k_{drain,S}$	–	Rate constant for water store drainage	*c*	0.05	0.05	0.05
D_{exch}	h^{-1}	Exchange rate constant	*a,d*	0.1	0.01	0.01
Metabolic transformations						
k_{LCO2}	a^{-1}	litter → CO_2	*e*	1.0	1.0	1.0
k_{LS}	a^{-1}	litter → substrate	*e*	8.5×10^{-2}	8.4×10^{-2}	8.4×10^{-2}
k_{LH12}	a^{-1}	litter → Hum1 and Hum2	*e*	5.6×10^{-3}	5.6×10^{-3}	8.4×10^{-3}
k_{SCO2}	a^{-1}	substrate → CO_2	*f*	6.6×10^{-3}	6.5×10^{-3}	6.2×10^{-3}
k_{SH12}	a^{-1}	substrate → Hum1 and Hum2	*e*	1.4×10^{-3}	1.4×10^{-3}	2.1×10^{-3}
k_{SH3}	a^{-1}	substrate → Hum3	*e*	1.3×10^{-2}	1.3×10^{-2}	1.2×10^{-2}
k_{H3H12}	a^{-1}	Hum3 → Hum1 and Hum2	*e*	7.2×10^{-5}	7.1×10^{-5}	1.1×10^{-4}
k_{H12CO2}	a^{-1}	Hum1, Hum2→ CO_2	*a*	1.0×10^{-3}	1.0×10^{-3}	1.0
k_{H3CO2}	a^{-1}	Hum3 → CO_2	*e*	6.6×10^{-4}	6.5×10^{-4}	6.2×10^{-4}
f_{Hum1}	–	Fractional formation of Hum1	*e*	0.51	0.51	0.43

Key: *a* fixed *a priori*; *b* calculated from sorption data; *c* calibrated from discharge data; *d* calibrated from DOC short-term dynamics; *e* calibrated from C pools, fluxes and ^{14}C; *f* fixed at $10 \times k_{H3CO2}$

Fitting was first done by adjusting k_{LCO2}, k_{LS}, k_{LH12}, k_{SCO2}, k_{SH3}, k_{H12CO2}, k_{H3CO2} and f_{Hum1}, but it was found that neither k_{SCO2} nor k_{H12CO2} could be well-defined when the fitting was based on carbon pools and annual fluxes. The value of k_{SCO2} could be set to any value between zero and 10^{-2} a^{-1} without affecting the goodness of fit, and it was fixed at ten times k_{H3CO2}, to force the expected faster rate of mineralisation of substrate compared to humified organic matter. The value of k_{H12CO2} could be set to any value between zero and 1 without affecting the goodness-of-fit, and its value only affected the values of the other metabolic parameters when it was greater than 10^{-2} a^{-1}. It was therefore set to 10^{-3} a^{-1} for this part of the work. After fixing these two parameters, the number of adjustable metabolic parameters was reduced to 6, optimisation of which produced a reasonable fit, the difference between the 7 observed and simulated variables (Table 3) being 6% on average. Increasing t_{litter} from 0 to 1 or 2 years caused little change in the fitted parameters and did not worsen the goodness-of-fit. Finally, the model was refitted from a range of starting trial values, and this confirmed that a unique set of the adjusted parameters produced the optimal result. The parameter set (set I) found at this point is shown in Table 4, Table 3 compares the target and simulated variables, and the modelled pools and fluxes are shown in Fig. 5.

Although acceptable fits of annual DOC flux for 2002–2003 and $DO^{14}C$ for the same period were obtained by assuming that litter, substrate and Hum3 contribute equally to Hum1 and Hum2, equally good results could be achieved with the assumption that Hum1 and Hum2 are formed only from litter. The ambiguity arises because the measured $DO^{14}C$ values coincided with the atmospheric ^{14}C content during the study period. A range of intermediate combinations, with contributions from all three sources, would also provide good data matches. Since different $DO^{14}C$ values were both lower and greater than the atmospheric ^{14}C (Table 5), it seems likely that DOC is derived from several soil organic matter pools, with varying contributions in time (not captured by the model). Therefore, we maintained the assumption used above, and forced Hum1 and

Hum2 production to come equally from litter, substrate and Hum3.

Short-term variability in stream water DOC concentration

Parameter set I of Table 4 predicted greater seasonal variability in stream water [DOC] than observed (Fig. 3). The model generates seasonal variation in stream [DOC] because Hum1 and Hum2 accumulate in the soil during summer, due to (a) the higher rate of production of Hum1 and Hum2, a direct temperature effect, and (b) concentration increase because of the lower runoff, caused by a smaller rain input and greater evapotranspiration. Of these two effects, the second is dominant and therefore changing the Q_{10} values for processes generating Hum1 and Hum2 has a minor effect on the predicted seasonality. The variation of [DOC] with season can be controlled with D_{exch}, which governs the rate of exchange of Hum1 and Hum2 between mobile and immobile water, the optimal value of D_{exch} being 0.01. With D_{exch} set to 0.01, the entire model was refitted. The new optimised parameter values (set B of Table 4) were very similar to those for D_{exch} = 0.1 and the goodness-of-fit was the same. Neither the simulated values of Table 3 nor the pools and fluxes of Fig. 5 were affected. However, with D_{exch} = 0.01, agreement between observed and simulated monthly [DOC] is achieved (Fig. 3). The optimal value of D_{exch} depended little on the value of f_{macro} chosen for the hydrological sub-model (see above).

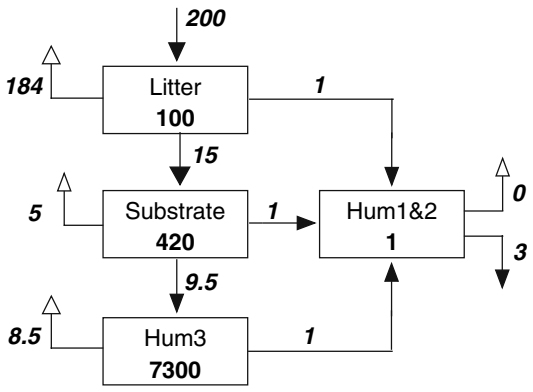

Fig. 5 Pools (gC m^{-2}) and fluxes (gC m^{-2} a^{-1}) of organic C at Doe House Gill, according to the DyDOC model, calculated using parameter set I (Table 4)

Effects of environmental change

The effect of increasing temperatures was investigated by running the model using parameter set II (Table 4) with an imposed linear temperature increase of 4°C between 2001 and 2100, followed by a further 100 years at constant higher temperature. This caused decreases of 25% in the litter and substrate C pools, but only 4% in the Hum3 pool, the overall decrease in soil carbon being 5%. The runoff is forecast to decrease by 11%, due to greater evapotranspiration, but the DOC flux to increase by 9%. According to Davidson and Janssens (2006), Q_{10} is probably greater for the decomposition of the more recalcitrant organic matter, and accordingly we re-fitted the model with Q_{10} set to 4.0 for the mineralisation of Hum3. An equally good fit was obtained, the only substantial difference in parameter values being a decrease in k_{H3CO2} from 6.5×10^{-4} to 3.6×10^{-4} a^{-1}, which compensated for the change in Q_{10}. As expected, the higher Q_{10} made the soil more sensitive to temperature change, with an overall decrease of 9% in total soil carbon over the 200 year period.

Litter input might increase due to faster plant growth, brought about by CO_2 or nitrogen fertilisation. To explore the effect on soil carbon we imposed a 25% increase in litter input from 2000 to 2050, followed by a further 150 years of constant input at the higher level. The model predicts proportional increases in the litter and substrate pools within 100 years, but only a small increase (ca. 2%) in the Hum3 pool. The DOC concentration and flux both increase by 17%.

According to Evans et al. (2006), increased DOC release from soil due to changing sorption strength may explain the observed correlation between the decline in sulphur deposition and the rise in surface water [DOC], observed for a number of UK sites. Modelling of the chemistry of acid soil in the Duddon valley (Tipping et al. 2006a) indicated a pH change from ca. 4.8 in 1900 to 4.2 in the 1970s, followed by a rise to 4.5 by 2000, associated mainly with the increase and subsequent decrease in soil water sulphate concentration. The results of laboratory measurements on such soils (Tipping and Woof 1991) suggest that K_{D2} would increase by a factor of 10 during the period of pH decline, and decrease by a factor of 2.7 during the recovery period. These factors

Table 5 Stream carbon isotope data for Doe House Gill, 2002–2003

Date	Q mm day^{-1}	[DOC] mg l^{-1}	$\delta^{13}C_{VPDB}$ ‰	^{14}C abs % mod	Lab. Publication code	[POC] mg l^{-1}	$\delta^{13}C_{VDPB}$ ‰	^{14}C abs % mod	Lab. Publication code
09-04-02	1.1	0.7	−28.1	94.65	AA-53476	0.8	−27.4	105.15	AA-50507
21-05-02	10.3	1.7	−26.5	104.51	AA-53479	0.1	−25.8	108.28	AA-53478
27-08-02	2.1	0.8	−27.9	107.32	AA-53560	0.2	−28.8	106.09	AA-53559
27-10-02	25.1	0.8	−27.8	106.62	AA-53563	Insufficient material for analysis			
06-11-02	23.8	1.2	−28.4	110.89	AA-54794				
03-12-02	9.4	1.1	−27.9	109.63	AA-55220				
11-02-03	16.3	0.6	−27.8	106.08	SUERC-1445				

were used in the construction of exploration scenarios, by assuming, for simplicity, linear changes in K_{D2}. The value of K_{D1} was kept at zero throughout the 100 year period.

The values of K_{D2} between 1900 and 2000 were scaled to the value of 1.2×10^{-5} m^3 g^{-1}, estimated for soil samples taken in 1987 (see above), and the model was optimised by adjusting the metabolic parameters as described above. The parameter values were hardly changed, neither was the goodness-of-fit. The model simulated only very slight changes in stream water [DOC] from 1900 to 2000. As mentioned above, the model optimisation is insensitive to k_{H12CO2}, and so this parameter was increased from its ''default'' value of 0.001 a^{-1}, to examine effects on [DOC]. Refitting with k_{H12CO2} set to 1.0 a^{-1} produced increases in the other parameters associated with the generation of Hum1 and Hum2 (k_{Lh12}, k_{SH12}, k_{H3H12} and f_{H1}) but hardly affected the other constants (see parameter set III of Table 4), and did not worsen the model fit. Parameter set III generated greater variability in [DOC] in response to the changes in K_{D2}. As shown in the upper panel of Fig. 6, [DOC] decreased as the soil became more acid, then increased again on acidification reversal, due to changes in the export of Hum2, the more hydrophobic fraction. Thus, the DOC became first more, then less, hydrophobic, during the period of simulation (Fig. 6, lower panel). Running the model to steady state for non-acidified soil gave pools and fluxes close to those of Fig. 5, the main differences being increases of about 50% in the fluxes of C from litter, substrate and Hum3 to Hum1 and Hum2, and a combined flux of 1 gC m^{-2} a^{-1} of CO_2 from Hum1 and Hum2. The seasonality of stream water [DOC] was very similar to that of Fig. 3.

Discussion

The steady state approximation

The modelling approaches used in the present work involve the approximation of steady state, and in this respect we are following a number of previous authors (e.g., Harkness et al. 1986; Jenkinson et al. 1992; Bol et al. 1999). The approximation is necessary in the absence of a detailed history of soil conditions and climate, which would require lengthy time-series data, but it may be questioned from a long-term perspective because of climatic variations, and changes in land-cover and land-use that have occurred since the first forest clearances c. 5,000 year BP (Pearsall and Pennington 1989). According to DyDOC calculations, the current DHG soil, if in steady state, would have taken c. 3,000 years to stabilise. If forest clearance and the establishment of grazing took place more recently, some of the present-day soil carbon may be derived from the original trees. On short time-scales, fertilisation due to recent increases in N deposition, or possibly increases in atmospheric CO_2 concentration, may have influenced the system (see DyDOC calculations above), although principally with respect to the relatively small litter and substrate pools, and DOC flux. Over the last 30 years, the temperature at DHG has risen by, on average, 0.03°C a^{-1}, and rainfall by 0.3% a^{-1} (ca. 10 mm a^{-1}); again according to DyDOC calculations, these changes will not have altered C pools or fluxes very much.

However, the recent work of Bellamy et al. (2005) suggests that the DHG soil may be far from steady state. After resurveying carbon contents of all soils of England and Wales, these authors estimated that

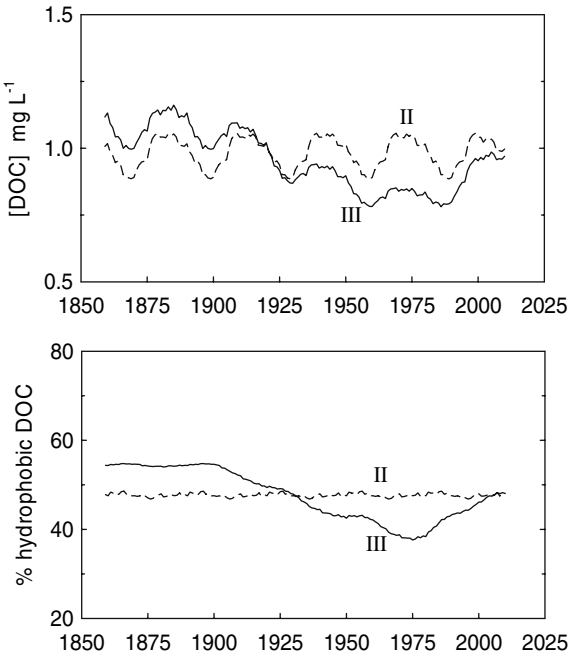

Fig. 6 Simulated [DOC] and %hydrophobic DOC over time, plotted as 10 year means. For parameter set II, the sorption strength (K_{D2}) of hydrophobic DOC was constant. For parameter set III it decreased from 1900 to 1975, then increased to 2000 (see text)

approximately one-third of the carbon in the top 15 cm of organic-rich soils was lost between 1978–1983 and 2003. In particular, the average linear rate of loss from soils with an organic carbon content of 200–300 gC kg^{-1} in the original sampling was 4.00 gC kg^{-1} a^{-1}. This figure implies that a soil now containing 203 gC kg^{-1} (the value for the top 15 cm of the combined leptosols and podzols at DHG), would 25 years ago have contained 303 gC kg^{-1}. This might mean that the soil organic matter studied in the present work is biased towards older, long-lived pools, and the overall rate of carbon turnover would be underestimated. However, in the generalised calculation method used by Bellamy et al., the measured carbon content (gC kg^{-1}) was combined with the bulk density, which was estimated from the carbon content using a regression equation. Although this procedure is sound for soils with low carbon contents, the interdependence of the carbon content and bulk density renders calculations for organic-rich soils less certain. Moreover, relatively few (c. 40) soils in the 200–300 gC kg^{-1} range were re-sampled. Therefore, we suggest that further work may be needed to confirm the large C losses from the DHG soils that are suggested by the study of Bellamy et al. Accordingly, we do not consider that the steady state approximation, used to analyse our data, need yet be abandoned. Nonetheless, we admit that our approximation, together with the averaging of soil properties (see below), mean that our estimates of MRT, and the modelling with DyDOC, provide only a broad picture of the pools and fluxes of carbon at DHG.

Soil organic matter

Carbon-14 can be used to characterise soil organic matter turnover by assuming a single carbon pool to calculate MRT. This is known to oversimplify a complex and depth-stratified situation (Harkness et al. 1986; Harrison 1996), specifically by ignoring a relatively small C pool with a high turnover rate. Nonetheless, the MRT values provide an idea of the rate of entry of organic matter into the soil (Bol et al. 1999), and permit comparisons among soils. The DyDOC model, operating with five C pools, is more realistic, but requires more data for calibration, and has less readily interpreted parameter values. By using the two approaches in parallel, some insight into the DHG soils is obtained.

The four DHG soil samples give a range of total ^{14}C contents, and corresponding MRTs, suggesting appreciable spatial heterogeneity within the catchment. However, in each case it is clear that the organic matter is, on average, turning over slowly, the MRTs being of the order of hundreds of years (Table 2). The averaging of soil properties for DyDOC modelling must mask the effects of spatial heterogeneity in the soil organic matter, but the variability is insufficiently characterised to justify a distributed model. Considering both MRT and DyDOC modelling, the steady-state calculations indicate that, if the NPP is taken to be 200 gC m^{-2} a^{-1}, then only about 8% of the NPP carbon is incorporated into the DHG soil, the rest being rapidly mineralised (Fig. 5). As indicated in the Site description section, the NPP value is uncertain, but it is surely of the order of hundreds of gC m^{-2} a^{-1}, and so the conclusion that most of the recently fixed C is rapidly remineralised will hold. In DyDOC modelling, the choice of a different NPP would result in a different rate of CO_2 generation from litter, requiring a different value of k_{LCO2}. The

absolute amount of C passing from litter to other organic forms (substrate, DOC) would stay the same. Thus, referring to Fig. 5, a change in the NPP input flux (200 gC m^{-2} a^{-1}) would be compensated only by a change in the value of the CO_2 efflux from the litter pool (184 gC m^{-2} a^{-1}), and not by a change in the fluxes from litter to substrate (15 gC m^{-2} a^{-1}), or from litter to Hum1 and Hum2 (1 gC m^{-2} a^{-1}).

Although the DHG soil receives little new C annually, even lower rates of incorporation are apparent from other results for organic-rich soils. Bol et al. (1999) reported total C contents of 13,800, 23,500 and 11,900 g m^{-2}, respectively for brown podzolic soils, stagnohumic gleysols and podzols from the Pennine moorlands (northern England), with overall C ages of the order of thousands of years. Schlesinger (1977) described the C pools (total 10,400 g m^{-2}) in the top 20 cm of a typical chernozem grassland soil, with an MRT of several thousand years. The reasons for such long-term stabilisation are not fully clear. Krull et al. (2003) favoured ''molecular recalcitrance'' as the principal long-term mechanism, but this notion was rejected by von Lützow et al. (2006), who considered inaccessibility to decomposer microorganisms, and reactions with soil inorganic components, to be the main governing factors. Bol et al. (1999) attributed the stability of the Pennine gley soil to its predominantly anaerobic status, but in the more freely draining podzolic soils, stabilisation by adsorption to mineral matter may be significant. In the chernozem, stabilisation of organic matter is promoted by interaction with calcium ions (Oades 1988). The soil C at DHG may be stabilised through interaction with abundant soil aluminium (Tipping et al. 2006a).

If it is accepted that the soil organic matter is currently approximately in steady state, then running the DyDOC model with changing environmental conditions can give indications about potential future changes. For a Q_{10} of 2.0, DyDOC predicts only a small effect of temperature over 200 years on the total soil carbon, because of the dominance of the pool with low turnover (the Hum3 fraction). With an assumed Q_{10} of 4.0 for the mineralisation of Hum3, a somewhat greater decrease (9%) in soil C is predicted. These changes are substantially smaller than suggested by the re-survey study of Bellamy et al. (2005), discussed above. However, Bellamy et al. attributed the large losses of C that they consider to have occurred during the past 25 years from organic-rich soils of England and Wales, to oxygenation, brought about by climatic warming and increased evapotranspiration. Similarly, Bol et al. (1999) suggested that warming, and drying of the Pennine peaty gley soil, anaerobic at depth, would cause it to release CO_2. The DyDOC model does not yet represent the dependence of metabolic transformation rates on soil moisture, and therefore we may be overlooking a significant process. However, the soils at DHG, although receiving high rainfall, and therefore often having high water contents, do not appear to be waterlogged, except in small areas with zero or low slope. Therefore it is unlikely that stabilisation due to permanent waterlogging is a major control on soil carbon at DHG, and consequently we would not expect drying per se to cause large carbon releases.

DyDOC parameters

Although it presents a simplified picture of the soil-water carbon cycle, DyDOC is quite a complex model, involving diverse parameters (Table 4), some of which are well-defined by the present data, and others less so.

Of the five parameters required for the hydrological sub-model, the least well-defined is f_{macro}, which was simply set to the default value of 0.1, i.e., 10% of the pore space was attributed to macropores. However, for any choice of f_{macro} within a wide range (0.033–0.3), a set of the other four parameters could be found to provide acceptable simulation of the rainfall-dependent short-term water balance of the soil compartment, and thereby the stream hydrograph (Fig. 4). This is because a change in f_{macro} can be compensated by an inverse change in k_{drain}, their product remaining nearly constant. The sub-model could be better constrained with additional soil porosity and field moisture content data, but it describes water movements sufficiently well to simulate both the annual DOC flux and seasonal variability in streamwater [DOC].

In principle, the residence time of carbon within living plants, t_{litter}, influences the transfer of the atmospheric ^{14}C signal to the soil organic matter. But because it is now several decades since there were rapid changes in atmospheric $^{14}CO_2$, associated with weapons testing, and because t_{litter} is short for grassland ecosystems, a value of zero suffices.

The value of Q_{10} (Eq. 1) was set to the widely adopted value of 2.0. Had a different value been chosen, the model would have compensated by adjusting the metabolic k values. The estimation of Q_{10} from field data, at least in terms of DOC generation, was not possible because, according to DyDOC, seasonal variations in streamwater [DOC] depend more on variations in rainfall and evapotranspiration than on the short-term production of DOC (HUM1 and HUM2). Insight into the temperature dependence of the metabolic reactions might be gained from realistic manipulation experiments.

The mineralisation rate constant for litter (k_{LCO2}) can be estimated because the CO_2 flux is a large proportion of NPP (see above), and k_{H3CO2} can be estimated from the ^{14}C content of Hum3, and because mineralisation is the main loss process for this pool. However, the size of the small substrate pool depends upon several fluxes (Figs. 1 and 5), and in the absence of a constraining ^{14}C value, the correct combination is unclear, rendering k_{SCO2} uncertain. Therefore a value of k_{SCO2} was assigned on the basis of expected molecular recalcitrance, with substrate falling between litter and Hum3. A better estimate of k_{SCO2} might be obtained if the soil could be fractionated to yield the substrate (and litter) pools, in particular to distinguish ''young humin'' from ''old humin'' (see Results). The mineralisation rate constant of Hum1 and Hum2, k_{H12CO2}, is also poorly defined, because faster transformation to CO_2 can be compensated by a faster rate of formation, without significantly affecting the larger fluxes of mineralisation (Fig 5). A high value of k_{H12CO2} makes streamwater [DOC] responsive to acidification and its reversal (see Results), but this does not adequately define the parameter. The measurement of mineralisation rates of soil water DOC from the study site would be helpful.

As discussed below, DOC is likely derived from a range of soil organic matter pools (litter, substrate and Hum3 in DyDOC), the relative contributions cannot be determined from the present data. The issue might partially be resolved by further monitoring of $DO^{14}C$, as the atmospheric ^{14}C signal continues to change, since different combinations of sources give different predictions of $DO^{14}C$. Isotope measurements on DOC extracted from the different SOM fractions could also provide constraining data.

The above discussion suggests that better characterisation of the metabolic reactions is required to improve the definition of model parameters. Information is especially required on temperature dependence, the mineralisation rates of substrate and Hum1 and Hum2, and the relative contributions of litter, substrate and Hum3 to Hum1 and Hum2. Extended field monitoring, manipulation experiments, and analysis of SOM fractions could provide the necessary data. Comparative studies on other systems might also help. Despite the parameter uncertainties however, DyDOC is already a useful tool with which to explore the functioning and possible evolution of the soil-water carbon cycle.

Dissolved and particulate organic carbon

The flux of DOC from the DHG soil, 3 gC m^{-2} a^{-1} (Fig. 5), is appreciable in that it represents about 20% of the C entering the soil, estimated from either the MRT or the DyDOC model, but is small in comparison with the NPP. The measured stream water flux of 2.5 gC m^{-2} a^{-1} is also less than those at other UK moorland sites. For example, Grieve (1984) reported 8 gC m^{-2} a^{-1} for a Scottish stream, Worrall et al. (2003) 9–15 gC m^{-2} a^{-1} for a Pennine stream, and Dawson et al. (2002) 8 g m^{-2} a^{-1} and 17 g m^{-2} a^{-1} for streams in Wales and Scotland, respectively. The POC flux at DHG (0.4 gC m^{-2} a^{-1}) is also lower than the values of 1.9 gC m^{-2} a^{-1} and 2.7 gC m^{-2} a^{-1} reported by Dawson et al. (2002).

Six of the seven measured $DO^{14}C$ values are greater than 100 % modern (Table 5), indicating the presence of ''bomb carbon'' in the DOC, and therefore that at least some of the material has formed during the last 50 years. The sample at the lowest flow had the lowest ^{14}C content, indicating much older C, but is representative of a very small part of the output flux. However, as noted in connection with DyDOC modelling, this observation, and the finding that some of the $DO^{14}C$ values are several % higher, and some several % lower, than the contemporary atmospheric CO_2 at the time of sampling (107% modern) suggests that the DOC is sourced from a range of soil C pools. The fact that the DOC is more depleted in the stable isotope ^{13}C than the whole soil could, however, suggest that some of it is formed directly from litter, which is generally ''lighter'' with respect to ^{13}C than soil organic matter (Ehleringer et al. 2000). Interestingly, the DOC is appreciably lighter in ^{13}C than soil fulvic acid,

implying that mobile DOC cannot be equated with soil fulvic acid. The three POC samples for which ^{14}C could be measured are enriched in bomb carbon, indicating that the material is relatively recent, and is presumably eroded from the soil surface.

The description of DOC formation and transport provided by DyDOC includes several mechanisms by which DOC concentrations and fluxes could increase, as is currently observed for many UK upland waters (see Introduction). These mechanisms are temperature increase, change in water throughput, increased NPP due to fertilisation by either carbon or nitrogen, and acidification reversal. Obviously, combinations of these drivers could operate. With regard to the acidification reversal mechanism, associated with a decrease in K_{D2}, the key point is that, under acidified conditions when K_{D2} is relatively high, adsorption to the soil prolongs the lifetime of Hum2 in the soil, thus favouring mineralisation of ''potential DOC'' over DOC export. For this process appreciably to influence DOC concentration and flux, the mineralisation rate needs to be high, which is why parameter set III (k_{H12CO2} = 1 a^{-1}) produces change in [DOC], while parameter set II (k_{H12CO2} = 0.001 a^{-1}) does not. Unfortunately, the monitoring data for DHG or other sites in the Duddon valley are of insufficient duration to test the model's predictions of [DOC] change. Application of the model to UK sites with longer records, and higher [DOC], is desirable.

Conclusions

[1] The thin leptosols and podzols of the Doe House Gill catchment have a mean C pool of 8,300 g m^{-2}. The carbon is present mainly as humic acid or older humin. Assuming steady state, the ^{14}C content of the whole soil (93% modern) yields a mean residence time of 800 years, although this varied from 300 to 1,600 years in the four samples studied.

[2] The soil flux of DOC is 3 g m^{-2} a^{-1}, which corresponds to about 20% of the carbon entering the soil, but only about 1.5% of the net primary production, and is lower than fluxes of DOC from some other UK moorland catchments. The POC flux is about 0.4 g m^{-2} a^{-1}. In most samples, DOC and POC were enriched in ''bomb carbon'', the average $DO^{14}C$ content in 2002–2003 being 107.5% modern. The similarity of this value to the contemporary atmospheric ^{14}C content is consistent with fresh litter being the main source of DOC, but the variability in $DO^{14}C$ means that DOC is more likely derived from several soil C pools.

[3] Application of the DyDOC model, again assuming steady state, permitted fluxes of carbon among soil pools to be estimated. The litter pool (ca. 100 gC m^{-2}) turns over quickly, and most (>90%) of the litter carbon is rapidly mineralised. The soil is calculated to gain only 16 gC m^{-2} a^{-1}, and to lose the same amount, about three-quarters as CO_2 and one quarter as DOC.

[4] Simulations with the parameterised model, assuming a Q_{10} of 2, suggest that the soil carbon is relatively stable; warming for 200 years would decrease the total C pool by only about 5%. With a Q_{10} of 4 for the major, recalcitrant soil organic matter pool, a decrease of 9% is predicted. Increased litter inputs would lead to a proportionally larger soil carbon store.

[5] The seasonal variability exhibited by stream water DOC concentration (maximum in September, minimum in January) is attributed mainly to variations in rainfall and evapotranspiration, rather than in the production rate of ''potential DOC''. DOC fluxes are predicted to increase in response to increased litter inputs and warming. If a high turnover rate of ''potential DOC'' is assumed, then decreased DOC concentrations and fluxes on soil acidification, and increases on acidification reversal, can be explained by changes in the strength of sorption of potential DOC to the soil solids.

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