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Modelling the production and transport of dissolved organic carbon in forest soils

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Abstract. DyDOC describes soil carbon dynamics, with a focus on dissolved organic carbon (DOC). The model treats the soil as a three-horizon profile, and simulates metabolic carbon transformations, sorption reactions and water transport. Humic substances are partitioned into three fractions, one of which is immobile, while the other two (hydrophilic and hydrophobic) can pass into solution as DOC. DyDOC requires site-specific soil characteristics, and is driven by inputs of litter and water, and air and soil temperatures. The model operates on hourly and daily time steps, and can simulate carbon cycling over both long (hundreds-to-thousands of years) and short (daily) time scales. An important feature of DyDOC is the tracking of ^{14}C, from its entry in litter to its loss as $DO^{14}C$ in drainage water, enabling information about C dynamics to be obtained from both long-term radioactive decay, and the characteristic ^{14}C pulse caused by thermonuclear weapon testing during the 1960s (″bomb carbon″). Parameterisation is performed by assuming a current steady state. Values of a range of variables, including C pools, annual DOC fluxes, and ^{14}C signals, are combined into objective functions for least-squares minimisation. DyDOC has been applied successfully to spruce forest sites at Birkenes (Norway) and Waldstein (Germany), and most of the parameters have similar values at the two sites. The results indicate that the supply of DOC from the surface soil horizon to percolating water depends upon the continual metabolic production of easily leached humic material. In contrast, concentrations and fluxes of DOC in the deeper soil horizons are controlled by sorption processes, involving comparatively large pools of leachable organic matter. Times to reach steady state are calculated to be several hundred years in the organic layer, and hundreds-to-thousands of years in the deeper mineral layers. It is estimated that DOC supplies 89% of the mineral soil carbon at Birkenes, and 73% at Waldstein. The model, parameterised with ″steady state″ data, simulates short-term variations in DOC concentrations and fluxes, and in $DO^{14}C$, which are in approximate agreement with observations.

Introduction

The important role of soil organic carbon dynamics in boreal and temperate forest ecosystems in the carbon cycle is beyond question and well documented (King et al. 1997; Schulze et al. 2000). These ecosystems account for about 25% of the global terrestrial ecosystem carbon, of which more than half is stored in soil organic matter (King et al. 1997). Soil organic C pools are correlated with climatic variables, positively with precipitation and negatively with temperature (Post et al. 1982; Moore et al. 1999), and are therefore likely to be sensitive to climatic change. They may also be affected by changes in soil acidification and nutrient status.

The significance of DOC (dissolved organic carbon) in forest ecosystems has been highlighted because of its ecological function in nutrient and element cycling (Qualls and Haines 1991; Michalzik and Matzner 1999), and because it is a major source of carbon to the mineral soil (McDowell and Likens 1988; Qualls et al. 1991; Guggenberger 1992; Guggenberger et al. 1994; Neff and Asner 2001). The identification of processes regulating the release of DOC from the forest floor and its fate in the mineral soil is therefore crucial for the prediction of organic C pools in soils and their development under varying environmental conditions, with obvious relevance to carbon sequestration.

Modelling plays a central role in the understanding and prediction of soil organic matter dynamics. Decomposition, or metabolic, models such as CENTURY (Parton et al. 1987) and the Rothamsted model (Jenkinson 1990) have focused on transformations among soil pools, and losses of C from the system as CO_2, although Currie and Aber (1997) pointed out the need to take into account leaching losses of DOC when modelling forest soils. The metabolic models can take advantage of ^{14}C measurements (e.g., Jenkinson et al. (1992)) to constrain turnover times. The physico-chemical SASD model of Santore et al. (1995) does not explicitly include metabolic transformations, but deals with down-profile transport and sorption reactions (dependent upon solution conditions), in order to simulate soil formation. At the catchment scale, DOC delivery to streams has been simulated by hydrological models incorporating simple temperature-dependent input terms for DOC (Grieve 1991; Taugbol et al. 1994). The soil DOC model of Neff and Asner (2001) applies to a layered soil, and uses the metabolic CENTURY model to simulate decomposition, DOC being generated by assigning solubility characteristics to different C pools. Transport of DOC is simulated with a model of soil hydrology, and both sorption and desorption are represented, with rates based on literature data.

The model presented here (DyDOC = Dynamic DOC model) is similar to that of Neff and Asner (2001) in terms of the processes that are represented. Thus, the formation, transport and retention of DOC in soil profiles are simulated, taking account of metabolism, sorption reactions and transport in percolating water. The models differ in the details of process representations, and the assumed carbon pools; DyDOC is based on chemically-differentiated fractions of humic substances whereas the Neff-Asner model utilises C pools characterised by their turnover times. However, the most significant difference between the models is that DyDOC tracks the passage of ^{14}C through the plant-soil-water system, thereby providing additional information about time scales. Furthermore, whereas Neff & Asner parameterised their model by combining and synthesising data from a variety of studies at different sites, our approach is to apply DyDOC to individual field sites. DyDOC is designed to use a variety of observational data, including soil carbon pool sizes, DOC concentrations and fluxes in different soil horizons, ^{14}C data, and the results of laboratory studies of DOC sorption reactions. It is hoped that DyDOC will be useful in exploring the implications for soil carbon – and DOC in particular – of changes in environmental variables such as temperature, litter and water inputs, and soil chemical conditions. This paper describes the model, and its preliminary application to two spruce forest sites.

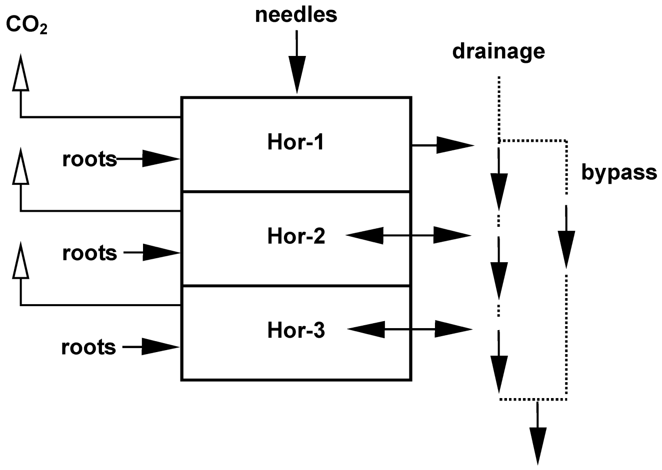
Model description

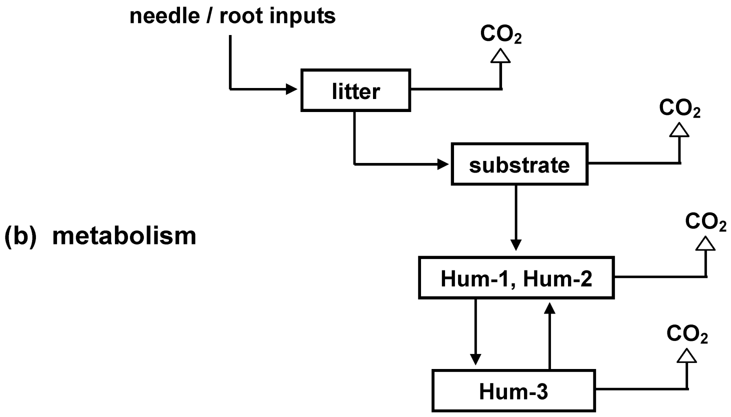
The structure of the model is shown schematically in Figure 1. The soil profile is conceptualised as consisting of three horizons (Figure 1a). Carbon entering each horizon undergoes metabolic transformations (Figure 1b) and sorption reactions (Figure 1c). Transport is by gaseous loss as CO_2 or by downward transport as DOC. Thus the model has three groups of processes, hydrology, metabolism and sorption (see below). The model parameters are listed in Table 1. They are of two kinds; some are fixed *a priori*, while others have to be determined by fitting the model to observed data.

Hydrology

Water enters Hor-1 as throughfall and snowmelt. Snow accumulates if the temperature is below 0 °C and melts if it is above 5 °C. The maximum amount of meltwater is proportional (via the constant k_{snow}) to the temperature in °C; if there is less snow than this maximum, all the snow melts. Apart from the freezing and thawing of snow, no special account is taken of the possible effects on soil hydrology of freezing. The pore space in each horizon comprises macropores, within which water moves due to gravity, and micropores, within which it is immobile. Incoming water enters a horizon and mixes with water already present in the macropores. Water then moves downwards through the soil profile until the macropores are filled to a single level. A first-order rate constant (k_{drain}) relates drainage loss from the base of the soil column to the total volume of macropore water. Under high moisture conditions, water leaving Hor-1 may pass directly to the stream and not interact with the lower soil horizons (bypass flow), this loss also being governed by a first-order rate constant (k_{drain}). Water can be lost by evaporation from the Hor-1 micropores, the rate of loss being proportional (via the constant k_{evap}) to air temperature. In Hor-1, water from the macropores can enter the micropores if they are not filled; for simplicity, it is assumed that the micropores in Hor-2 and Hor-3 are always fully filled with solution. Dissolved organic carbon exchanges between the macropores and micropores, according to a pseudo-diffu-

(a) transfers of carbon




(b) metabolism

(c) sorption and micropore-macropore exchange

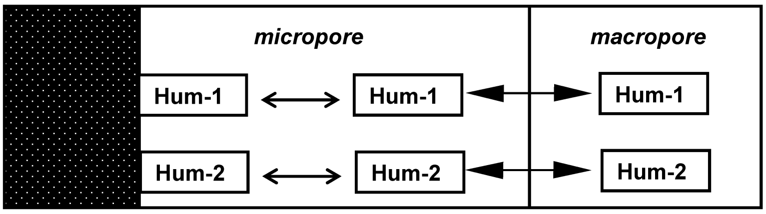


Figure 1. Scheme of processes governing carbon in DyDOC. Open arrows indicate formation and transport of CO_2, filled arrows formation and transport of organic C.

Table 1. Model parameters.

Symbol	Units	Description	How found
parameters with a single value			
t_{litter}	yr	time between C entering plant and leaving as litter	fixed *a priori*
k_{evap}	deg^{-1}	evaporation rate constant	calibrated
k_{snow}	$\mathrm{m\ deg}^{-1}\ \mathrm{hr}^{-1}$	rate constant for snow melt	calibrated
$f_{\mathrm{Hum\text{-}1}}$	–	fractional formation of Hum-1	calibrated
parameters that may have a different value for each horizon			
k_{drain}	hr^{-1}	drainage rate constant	calibrated
f_{macro}	–	fraction of pore space due to macropores	fixed *a priori*
D_{exch}	hr^{-1}	exchange rate constant	calibrated
K_{D1} K_{D2}	$\mathrm{m}^3\ \mathrm{g}^{-1}$	partition coefficients (Equation 2)	fixed *a priori*
k_{LCO2}	yr^{-1}	rate constant for litter → CO_2	calibrated
Q_{10LCO2}	–	temperature constant for litter → CO_2	fixed *a priori*
k_{LS}	yr^{-1}	rate constant for litter → substrate	calibrated
Q_{10LS}	–	temperature constant for litter → substrate	fixed *a priori*
k_{SCO2}	yr^{-1}	rate constant for substrate → CO_2	calibrated
Q_{10SCO2}	–	temperature constant for substrate → CO_2	fixed *a priori*
k_{SH}	yr^{-1}	rate constant for substrate → Hum-1 and Hum-2	calibrated
Q_{10SH}	–	temperature constant for substrate → Hum-1 and Hum-2	fixed *a priori*
k_{HCO2}	yr^{-1}	rate constant for Hum-1, Hum-2, Hum-3 → CO_2	calibrated
Q_{10HCO2}	–	temperature constant for Hum-1, Hum-2, Hum-3 → CO_2	fixed *a priori*
k_{123}	yr^{-1}	rate constant for Hum-1, Hum-2 → Hum-3	calibrated
Q_{10123}	–	temperature constant for Hum-1, Hum-2 → Hum-3	fixed *a priori*
k_{L312}	yr^{-1}	rate constant for Hum-3 → Hum-1, Hum-2	calibrated
Q_{10312}	–	temperature constant for Hum-3 → Hum-1, Hum-2	fixed *a priori*

sive process, governed by an exchange constant D_{exch}. The hydrology sub-model runs on an hourly time step.

Metabolism

Organic carbon can enter Hor-1 as DOC in throughfall, as above-ground litter, and as root litter and exudate. It can enter Hor-2 and Hor-3 as root litter and exudates, or in solution (DOC), from the horizon above. For simplicity, the different inputs are treated as a single component, entering the litter pool in each soil horizon. Thus, the model does not regard throughfall DOC as a direct contributor to soil DOC, but simply as a part of the C input to the soil; this assumption is also supported by the relatively high biodegradability of the organic components of throughfall (Qualls and Haines 1992). The litter, is transformed into ″substrate″ or CO_2 (Figure 1b). The substrate may be converted into two humic fractions (Hum-1 and Hum-2) or CO_2. The humic fractions Hum-1 and Hum-2 may be converted to Hum-3 or CO_2. Finally, Hum-3 may be converted back to Hum-1 and Hum-2, or to CO_2. The three humic fractions correspond approximately to hydrophilic acids (Hum-1), hydrophobic acids (Hum-2) and humic acid + aged humin (Hum-3). The substrate is equivalent to fresh humin. The scheme allows Hum-1 and Hum-2 to be both precursors and products of Hum-3. Only Hum-1 and Hum-2 are mobile, being transported downwards as DOC. 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

$$\Delta C = -kQ_{10}^{(T/10)}C_{pool}\Delta t \tag{1}$$

where ΔC is the loss of carbon from the relevant pool, C_{pool} is the size of the carbon pool, Δt is the time, T is the temperature in °C and Q_{10} is a constant. A Q_{10} value of 2 means that the rate of loss of C doubles for a temperature increase of 10 °C. The metabolism sub-model runs on a daily time step.

Sorption

Humic fractions Hum-1 and Hum-2 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

$$K_D = \frac{\text{g DOC sorbed per g soil}}{\text{solution concentration of DOC}} \tag{2}$$

where the solution concentration refers to the micropore. The value of K_{D} for Hum-1 is less than that for Hum-2, 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. Note that the formulation of Equation (2) means that sorption is not limited by a binding site capacity; thus we are assuming either that such a capacity is very high, or that the process of DOC removal is by aggregation, governed principally by hydrophobic interactions (Tipping and Woof 1991), rather than sorption by mineral surfaces.

The use of ^{14}C data

In the absence of anthropogenic influences on the atmospheric ^{14}C concentration, ^{14}C enrichment of soil organic material reflects the extent of radioactive decay of the isotope since death of the constituent organisms (plant, soil animal etc.) into which it had been incorporated. 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. During the late 19th and 20th centuries, the atmospheric ^{14}C concentration was diluted by the input of 'dead' carbon (containing infinitely small amounts of ^{14}C) from the burning of fossil fuels (Suess effect). More importantly, the atmospheric

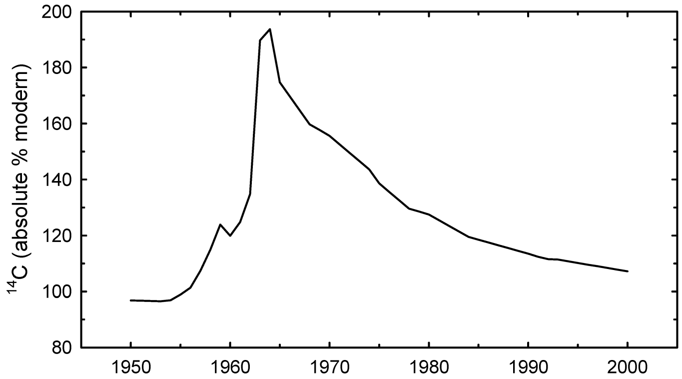


Figure 2. Variation in atmospheric ^{14}C concentration (30° to 60° N). From Baxter and Walton (1971) and Walton et al. (1970), Nydal et al. (1980), Levin and Kromer (1997).

^{14}C concentration was almost doubled during testing of thermonuclear weapons in the late 1950s to early 1960s. Figure 2 shows how fossil fuel burning decreased the ^{14}C signal to *c.* 97% modern by AD 1950, and how 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). Jenkinson (1963) first recognised that the bomb signal provides a means to track the processing of C through soils on relatively short time scales (O'Brien 1984; Harkness and Harrison 1989; Trumbore et al. 1989). To date, models developed to exploit bomb C have been based on ^{14}C measurements on whole soil horizons (e.g., Harkness et al. (1986)) or purely metabolic representations of C pools (e.g., Gaudinski et al. (2000)). The DyDOC model differs in that it incorporates hydrological and sorption processes as well as metabolism. In DyDOC, the ^{14}C signal of the incoming litter is treated as an input variable. Thus, in the assumed steady-state situation, the ^{14}C passes from litter to the different soil pools, and the model simulates the contents of those pools in each of the three soil horizons. Comparison of the observed and simulated ^{14}C signals is then used in deriving model parameters.

Parameterisation

In the present applications, the assumption is made that present soil properties, i.e., physical properties and carbon pool sizes, represent steady-state conditions. The current inputs of water and litter, and the temperature regime, are also assumed to be in steady state.

Some of the model parameters can be fixed *a priori*, on the basis of ancillary information, or by making reasonable assumptions. A default average time between the incorporation of C into plants and its output in litter (t_{litter}) of five years is used.

For a steady state simulation, this time does not influence the C pools and fluxes, only the ^{14}C values; for the ^{14}C values used to fit the model, times between three and eight years could be assumed without changing the ^{14}C of the Hor-1 whole soil (the most sensitive variable to t_{litter}) by more than 1%. The fraction of the total soil pore space that is due to macropores (f_{macro}) is required to define the macropore and micropore volumes, and thereby simulate heterogeneity in soil water and the presence of DOC at relatively high concentrations in the micropores. However, the model output is not very sensitive to its actual value, within the range 0.05–0.3. In the present work, f_{macro} was set to 0.1 for each horizon. The partition coefficients K_{D1} and K_{D2} for each horizon are estimated from results of physico-chemical experiments on soil suspensions (Lofts et al. 2001a, 2001b). These experiments showed that the affinity of the soil solids for DOC varies with horizon depth, due to differences in pH, Al concentration and DOC properties, and probably also the nature of the soil solids; the partitioning of DOC could be described with a model that employs 10 fractions of potentially-soluble organic matter. Conversion of results from the 10-fraction model to the two-fraction picture employed in DyDOC was performed by taking, for each horizon, the average K_{D} value for the two most soluble fractions, and the average K_{D} value for the remainder of the dissolved fractions.

The first step in applying the model is to simulate the passage of water through the soil, which can be done separately from the metabolic and sorption processes. The model is set up using soil physical properties (depth, bulk density, density of soil solids). It is then run with daily water inputs and air temperatures as driving variables, and with trial values of k_{snow}, k_{evap}, k_{drain}(Hor-1) and k_{drain}(Hor-3). The outputs are compared with observed or otherwise-generated hydrological data, and the parameters adjusted to obtain an acceptable simulation.

The metabolic sub-model is calibrated by the following sequence of operations:

1. A set of trial values of the parameters to be optimised is chosen, for Hor-1. The parameters in question are $f_{\mathrm{Hum\text{-}1}}$, D_{exch}, and the metabolic parameters (k_{LCO2} etc). In the absence of knowledge about the temperature dependences of individual reactions, values of Q_{10} are all fixed at 2, a value commonly adopted to characterise the temperature dependence of decomposition processes (Schlesinger 1997). The rate constants for conversion of the different C pools to CO$_2$ are constrained such that $\mathrm{k}_{\mathrm{LCO2}} \geqslant \mathrm{k}_{\mathrm{SCO2}} \geqslant \mathrm{k}_{\mathrm{HCO2}}$, implying that, as decomposition proceeds, the C becomes increasingly recalcitrant.
2. The model is run, driven by the following variables: daily observed water inputs, air and soil temperatures, above-ground and root litter inputs, annual atmospheric ^{14}C contents. It is arranged that steady state is reached before any anthropogenic influence on the ^{14}C signal (i.e., before 1800), and then up to the present day, so that the final outputs take account of the effects of fossil fuel burning and the input of bomb carbon. The model requires input data covering millennia, and of course these are not available. Therefore the available data (covering 2 to 3 years in the present examples) are used repeatedly; this implies that they are taken to be representative of the whole time period considered.

3. The goodness-of-fit is judged by comparing simulated outputs with measured or estimated values for Hor-1 of average C concentration in the micropore, soil C pools, DOC flux, average ^{14}C signals, and the fraction of DOC that is hydrophilic. The objective function (*OF*) to be minimised is given by

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

   where v_i is the value of the variable and w_i is a weighting factor (all values of w_i were set to unity in the present work). The DO^{14}C data, expressed as % absolute modern ^{14}C, were transformed to (v_i–80).
4. The parameter values are adjusted and the process repeated until the optimal fit is achieved. Adjustment is performed by the Nelder-Mead polytope procedure, using software published by Nash and Walker-Smith (1987). This method was not used to optimise D_{exch}, since measurements of the micropore concentrations of DOC were not available. However, there is evidence that micropore concentrations of DOC in organic horizons can be very high, as much as 500 mg l^{-1} (e.g., van Hees et al. (2000)). To represent this situation, a working value of 100 mg l^{-1} was chosen for Hor-1, and D_{exch} was adjusted in order to achieve this concentration (a value of 0.03 hr^{-1} was found). Micropore-macropore exchange in the deeper horizons had to be rapid (D_{exch} = 1) in order to maintain reasonably constant concentrations of DOC, in keeping with the observations.
5. With the model optimised for Hor-1, and therefore giving approximately correct output fluxes of DOC fractions, parameters for Hor-2 are optimised. In the present applications, it was assumed for simplicity that k_{LCO2}, k_{LS} and k_{SCO2} had the same values as in Hor-1, leaving k_{SH}, k_{HCO2}, k_{123} and k_{321} (the parameters governing humic substances) to be adjusted. This division of parameters can be partly justified on the grounds that the metabolic transformations of humic substances depend on their physical states, notably degree of sorption to mineral matter, which vary with horizon, whereas the transformations of litter and substrate are likely to be less horizon-dependent. The value of $f_{\mathrm{Hum\text{-}1}}$ was also assumed to be the same in each horizon, on the grounds that, ideally, it is simply a property of organic molecular structure. For Hor-2 at Birkenes, the objective function was derived from residuals in the output DOC flux, the total soil C content and the total soil ^{14}C value. For the Waldstein Hor-2, residuals in DO^{14}C were also included.
6. Parameters for Hor-3 are then optimised by the same procedure as for Hor-2. Objective functions were derived from residuals in the output DOC flux, DO^{14}C, the total soil C content and the total soil ^{14}C value.

In the two applications performed here, it was found that the same optimal parameter values were obtained for a range of different starting trial values, for each of the horizons, for each of the field sites.

Table 2. Variables used to drive and parameterise DyDOC.

Driving variables	Parameterisation variables
daily air temperature	*Horizon 1*
daily soil temperature	total soil C
daily throughfall	total soil ^{14}C
annual above-ground litter input	litter C
annual atmospheric ^{14}C values	substrate C
	C in humic substances
	[DOC] in soil micropores
For each soil horizon:	annual DOC flux
depth	average DO^{14}C
bulk density	fraction of DOC that is hydrophilic
density of soil solids	
porosity	*Horizon 2*
annual root and root exudate inputs	total soil C
	total soil ^{14}C (Waldstein only)
	annual DOC flux
	average DO^{14}C
	fraction of DOC that is hydrophilic
	Horizon 3
	total soil C
	total soil ^{14}C
	annual DOC flux
	average DO^{14}C
	fraction of DOC that is hydrophilic

Sources of data

We used data from two sites, Birkenes (southern Norway) and Waldstein (southern Germany), to illustrate the application of DyDOC. Full details of the sites, field monitoring, analytical procedures and results are presented by Mulder et al. (2000). A summary is given here. Table 2 summarises the data used to drive and parameterise the model.

The site at Birkenes (58°22′ N, 08°13′ E) is a 41-ha catchment, with granitic bedrock, partly covered by glacial till. Hill slopes are dominated by shallow podzolised acid brown earths and organic soils overlaying bedrock, whereas peat dominates the valley bottom (Leptosols, Cambisols, Podzols and Histosols, according to FAO classification, 1991). The vegetation is dominated by a 60–80 year-old stand of Norway spruce (*Picea abies* (L.) Karst.); the ground vegetation comprises shrubs (*Vaccinium myrtillus*) and laminaceae (*Deschampsia flexuosa*). During the study period (1995–1998), the mean air and surface soil temperatures were 5.3 and 5.5 °C respectively, and the mean annual throughfall was 1260 mm. The Waldstein catchment (50°08′ N, 11°52′ E), has an area of 400 ha and is dominated by a 140 year-old stand of Norway spruce (*Picea abies*), and ground vegetation similar to that at Birkenes. The bedrock is granitic, and the predominant soils are deeply weathered acid brown earths (Cambisols to Podzols). During the study period, the mean air and surface soil temperatures were 4.9 and 5.0 °C respectively, and the mean annual throughfall was 650 mm.

Determinations were made of average daily air and soil temperatures, annual above ground litter input, physical soil characteristics, and soil carbon contents. For the upper organic horizons, estimates of humic substances made by extraction with sodium hydroxide were assumed to be a good measure of the actual total humic matter. For the lower mineral horizons, the amounts of NaOH-extractable C (0.8–2.3%) were taken to be underestimates of the true values, bearing in mind the likelihood of strong adsorption and ageing effects that would, over long periods of time, render the humic matter non-extractable. Therefore most of the carbon in the mineral horizons was assumed to be humic substances. The measurements of solute concentrations and water fluxes in bulk and throughfall precipitation, in the forest floor and in sub-horizons were conducted fortnightly. Soil water was collected using zero tension lysimeters for the organic horizons, and tension lysimeters for the mineral soil. Fluxes of elements in throughfall and the humus layer were calculated using measured water volumes. Fluxes in the mineral soil were calculated using water flows estimated from stream discharge at Birkenes, and with a soil hydrological model based on Darcy flow (Manderscheid and Matzner 1995) at Waldstein. Dissolved organic carbon extractable with 0.001 M NaCl was determined by centrifuging soil suspensions.

Bulk soil samples were oven-dried and prepared 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 $-25‰$ $\delta^{13}C_{PDB}$. The mass spectrometer was calibrated with international reference materials to a precision of ± 0.1‰. Water samples and NaCl extracts were filtered through 0.7 μm glass fibre filters (Whatman GF/F) and the filtrates rotary evaporated and freeze-dried. Graphite targets for ^{14}C analysis by AMS were prepared at NERC RCL, 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 subsample of CO_2 was used to measure δ^{13}C as described above. Graphite was sent for ^{14}C analysis by Accelerator Mass Spectrometry to either the NSF-AMS Facility University of Arizona, Tucson, USA (Donahue 1990) or the Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, University of California, USA (Southon et al. 1990). In keeping with international practice the results (Table 3) 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). Overall analytical precision is quoted at 1σ. Quality control ^{14}C standards (bituminous coal and ANU

Table 3. Summary of ^{14}C data, expressed as % modern absolute (Stuiver and Polach 1977); n = number of samples, sd = standard deviation on mean ^{14}C data.

	Birkenes				Waldstein			
	horizon	n	^{14}C	sd	horizon	n	^{14}C	sd
soil solids[1]	F	2	126.0	0	L/F	1	120.5	–
	H	2	119.0	1.3	Ahe	1	96.5	–
	B	2	99.4	0.5	Bs	1	92.4	–
soil water DOC[2]	F	4	119.6	2.7				
	H	9	115.7	6.2				
	E	1	112.8	–				
	B	3	101.2	2.9				
NaCl-extracted DOC[3]	F	3	122.5	1.0	L/F	1	114.4	–
	H	4	120.4	1.0	Ahe	1	102.6	–
	B	2	104.4	1.6	Bs	1	99.9	–

[1] RCL codes: SRR-6029 to SRR-6034, AA-28986 to AA-28988.

[2] RCL codes: AA-27605 to AA-27613, AA-28920 to AA-28925, AA-30826, AA-30827.

[3] RCL codes: AA-25489 to AA 25491, AA-25498, AA-25499, AA-29840, AA-29841, AA-29844, AA-29845, AA-29850, AA-29852, AA-29855.

Table 4A. Physical attributes of Birkenes.

	Hor-1	Hor-2	Hor-3
soil horizons	L + F + H	E	B + BC
depth [cm]	9	10	42
bulk density [g cm^{-3}]	0.16	0.7	1.0
solids density[a] [g cm^{-3}]	1.5	2	2.5

[a] based on data given by Rowell (1994)

sucrose) were processed as for samples to check accuracy and precision of results, which were within normal analytical limits.

We assumed that the total root litter input per year equals the amount of above ground litter input (Persson 1978), and that the C input by roots into Hor-1, Hor-2 and Hor-3 amounted to about 75, 10 and 15% of the total annual root litter input, respectively (Persson 1978; Currie and Aber 1997). Root litter was assumed to enter each horizon at a constant daily rate; above-ground litter input into Hor-1 was assumed to occur at a constant daily rate only between June and December. The ratio of hydrophilic to total DOC is assumed to increase with depth in the soil profile, from ca. 0.4 in the organic layer to ca. 0.6 in the deeper mineral soil (Qualls and Haines 1991; Easthouse et al. 1992; Kaiser et al. 2001).

Comparison of the observations for the two field sites (Tables 4A and 5A) shows that Waldstein differs from Birkenes in having lower volumes of throughfall, greater litter inputs, larger soil C pools, lower ^{14}C values, and lower soil DOC fluxes.

Table 4B. Parameter values for Birkenes. Note that all Q_{10} values are set to 2.

	Hor-1	Hor-2	Hor-3
t_{litter}	5		
k_{evap}	2×10^{-4}	–	–
k_{snow}	10^{-4}	–	–
$f_{\text{Hum-1}}$	0.35		
k_{drain}	0.2	–	0.003
f_{macro}	0.1		
D_{exch}	0.03	1	1
K_{D1}	0	5×10^{-5}	10^{-4}
K_{D2}	10^{-5}	10^{-4}	2×10^{-4}
k_{LCO2}	0.040	0.040	0.040
k_{LS}	0.36	0.36	0.36
k_{SCO2}	0.027	0.027	0.027
k_{SH}	0.0066	0.0017	5.0×10^{-5}
k_{HCO2}	0.00088	0.0023	0.0015
k_{123}	1.3	0.17	0.024
k_{312}	0.020	0.0055	0.0017

Results

Parameter optimisation assuming steady state conditions

The model provided good agreements with the ″steady-state″ observations for Birkenes (Table 4C), using the parameter set shown in Table 4B. The metabolic rate constants for Hor-1 indicate that litter is transformed to substrate more rapidly than to CO_2. This reflects the fact that DyDOC treats all C inputs as a single component, and thereby does not explicitly describe processes operating on short time scales, notably CO_2 release from microbial biomass and the pool of ″active″ litter (cf. Trumbore (1997)). Substrate is transformed to CO_2 about 4 times faster than it is converted to humic substances. The parameter k_{123} has a high value, indicating that once Hum-1 and Hum-2 have been produced (primarily by the breakdown of substrate) they are rapidly converted to Hum-3. Hum-1 and Hum-2 are also lost by leaching as DOC, and therefore their pools in Hor-1 are calculated to be quite small, representing about 0.2% of the total soil C. Thus the supply of DOC to percolating water depends upon the continual metabolic production of Hum-1 and Hum-2. In the deeper soil horizons, the pools of Hum-1 and Hum-2 are much larger than in Hor-1, and concentrations and fluxes of DOC are principally controlled by sorption processes.

The metabolic constants for reactions involving humic substances tend to decrease in the sequence Hor-1 > Hor-2 > Hor-3, which might indicate lower microbial activity in the deeper horizons and/or a greater recalcitrance of the humic ma-

Table 4C. Observed and simulated C pools (g m^{-2}) and fluxes (g m^{-2} a^{-1}) at Birkenes; averages of values in December 1996, 1997 and 1998.

	Hor-1		Hor-2		Hor-3	
	obs	sim	obs	sim	obs	sim
Litter	400	410	–	17	–	32
Substrate[a]	4200	4200	–	220	–	420
Hum-1	–	3	–	42	–	220
Hum-2	–	10	–	78	–	310
Hum-3	–	1000	–	2600	–	4000
Total humic	1100	1000	–	2700	–	4500
Total	5700	5600	3100	3000	5100	5000
^{14}C for the whole horizon	123	122	–	102	99	98
^{14}C litter	–	113	–	113	–	113
^{14}C substrate	–	125	–	124	–	124
^{14}C Hum-1	–	118	–	111	–	103
^{14}C Hum-2	–	118	–	109	–	100
^{14}C Hum-3	–	109	–	100	–	95
DO^{14}C	118[b]	118	113	110	102[b]	102
DOC output flux	36	42	17	17	6	6
fraction hydrophilic DOC[c]	~0.4	0.4	~0.5	0.5	~0.6	0.6

[a] Observed value is the difference between total and (litter + humic substances)

[b] Mean of values from field-sampled soil waters and dilute NaCl soil extracts

[c] Simulated value is ratio of dissolved Hum-1 to dissolved (Hum-1 + Hum-2).

Table 5A. Physical attributes of Waldstein.

	Hor-1	Hor-2	Hor-3
soil horizons	L + F	Ahe	Bs + Bw
depth [cm]	12	9	45
bulk density [g cm^{-3}]	0.29	0.95	0.92
solids density[a] [g cm^{-3}]	1.5	2	2.5

[a] based on data given by Rowell (1994)

terials. The trend does not apply to k_{HCO2}, which varies comparatively little with depth.

The DO^{14}C values in Hor-1 are slightly lower than those for the whole horizon. According to the model, this is because the formation of Hum-1 and Hum-2 is not only from substrate, the fraction with the greatest content of bomb C, but also from Hum-3, which is low in bomb C. The DO^{14}C values decreases with depth in the soil, which the model explains by the mixing of Hum-1 and Hum-2 from Hor-1 with Hum-1 and Hum-2 derived from older C pools, low in bomb carbon, in the deeper horizons. However, Hum-1 and Hum-2 in the deeper soil are also derived from recent inputs of root litter, so the final ^{14}C signal reflects several sources.

The model could also be made to fit the data for Waldstein (Table 5C), using the parameter set shown in Table 5B. Most of the Waldstein and Birkenes parameter values are similar to one another, and show similar trends. However, appreciable differences between the two parameter sets are apparent in four cases. The significance of these differences was explored, for each parameter, by comparing steady state model outputs obtained using the optimised parameter values (Tables 4B and 5B) with those obtained using the geometric mean of the values for the two sites, keeping all other parameters at their optimised values.

1. The optimised value of k_{HCO2} (Hor-1) for Waldstein is an order-of-magnitude greater than that for Birkenes. When the geometric mean k_{HCO2} was used for Birkenes, there were modest decreases (up to 15%) in the Hum-1, Hum-2 and Hum-3 pools and DOC flux, and increases of up to 2% in ^{14}C values. However, the results for Waldstein were substantially different: lowering k_{HCO2} caused the Hum pools to increase considerably, the greatest effect being a 175% increase in Hum-3. The ^{14}C signals were also considerably changed, by up to 7%.
2. The Waldstein value of k_{SH} (Hor-2) is $\leqslant 10^{-4}$, whereas for Birkenes the value is 0.0017. When the geometric mean (calculated assuming $k_{\mathrm{SH}} = 10^{-4}$) is used, the simulated pools, fluxes and ^{14}C signals in Hor-2 are hardly altered at either site.
3. The Waldstein value of k_{SH} (Hor-3) is 0.0026, whereas for Birkenes the value is 5×10^{-5}. When the geometric mean is used for Birkenes, the simulated pools, fluxes and ^{14}C signals in Hor-3 are little affected. There are somewhat greater changes at Waldstein: the humic C pools are 15–30% lower, the humic ^{14}C values are changed by 1–3%, and the DOC flux is reduced by 20%.
4. The Waldstein k_{312} (Hor-3) is near to zero, the Birkenes value is 0.0017. Running the Birkenes simulation with the geometric mean k_{312} gives 30 and 45% respectively smaller Hum-1 and Hum-2, and a 30% larger pool of Hum-3. The DOC flux is decreased by 35% and the DO^{14}C increased by 4%. When the geometric mean k_{312} is used for Waldstein, there are negligible changes in pools, fluxes and ^{14}C signals.

Of the four cases considered, the discrepancy between parameter values is most significant in case (1), i.e., in k_{HCO2} for Hor-1. Thus, the model requires the rate constant for the mineralisation of humic matter at Waldstein to be greater than at Birkenes. In the other three cases it would be possible to adopt an intermediate parameter value that would provide reasonable results at both sites. In cases (2) and (3), this finding suggests that the conversion of substrate to humic matter in Hor-2 and Hor-3 is not as important as the delivery of humic carbon to these horizons by transport of DOC. However, the presence of litter and substrate, each containing post-bomb ^{14}C, in these horizons is important in explaining the total soil ^{14}C signals.

Table 5B. Parameter values for Waldstein.

	Hor-1	Hor-2	Hor-3
t_{litter}	5		
k_{evap}	2×10^{-4}	–	–
k_{snow}	10^{-4}	–	–
$f_{Hum\text{-}1}$	0.21		
k_{drain}	0	–	0.005
f_{macro}	0.1		
D_{exch}	0.03	1	1
K_{D1}	0	5×10^{-5}	10^{-4}
K_{D2}	5×10^{-6}	10^{-4}	2×10^{-4}
k_{LCO2}	0.025	0.025	0.025
k_{LS}	0.15	0.15	0.15
k_{SCO2}	0.016	0.016	0.016
k_{SH}	0.0032	$\leqslant 10^{-4}$	0.0026
k_{HCO2}	0.012	0.00059	0.00074
k_{123}	2.4	0.085	0.024
k_{312}	0.0092	0.0032	$\leqslant 10^{-6}$

Simulated development of soil carbon pools

The long-term development of soil carbon pools was simulated by setting each C pool to an initially low value, and by making the simplifying assumptions that (a) the litter inputs were constant at present-day values, and (b) the soil hydrology was the same throughout the period of simulation. Figure 3 shows the simulated developments of the total carbon pools in the three horizons at Birkenes. The time to reach steady state conditions increases considerably with increasing soil depth. In Hor-1, today's steady state C pool size was reached within 200 years, in Hor-2 the required time was 600 years, and in Hor-3 2000 years. Times for soil horizon carbon contents to reach steady-state values are greater at Waldstein than at Birkenes; 500 years for Hor-1, 1000 years for Hor-2 and 5000 years for Hor-3.

Simulated development of ^{14}C signals

Figure 4a shows DyDOC-simulated variations in whole-soil ^{14}C with time at Birkenes, due to the incorporation of ″bomb carbon″ into plants and subsequently into soil organic matter. The measured values for 1996 are also shown. Note that the incorporation of ^{14}C is taking place with the system assumed to be at steady state with respect to non-radioactive carbon; the ^{14}C is therefore providing information on the turnover rates of C pools of constant size. The greatest incorporation of bomb carbon is by Hor-1, with small but significant increases in ^{14}C in Hor-2 and Hor-3. The two deeper horizons have received bomb C from both percolating DOC and from root litter input; according to DyDOC, the latter process is essential

Table 5C. Observed and simulated C pools (g m^{-2}) and fluxes (g m^{-2} a^{-1}) at Waldstein; averages of values in December 1995, 1996 and 1997.

	Hor-1		Hor-2		Hor-3	
	obs	sim	obs	sim	obs	sim
Litter	1400	1400	–	57	–	130
Substrate[a]	9800	10000	–	530	–	1100
Hum-1	–	3	–	38	–	100
Hum-2	–	15	–	120	–	230
Hum-3	–	2000	–	3400	–	11000
Total humic	2000	2000	–	3600	–	11000
Total	13000	14000	4100	4100	13900	13000
^{14}C for the whole horizon	120	118	97	98	92	91
^{14}C litter	–	116	–	116	–	116
^{14}C substrate	–	120	–	118	–	120
^{14}C Hum-1	–	115	–	106	–	103
^{14}C Hum-2	–	115	–	102	–	103
^{14}C Hum-3	–	106	–	95	–	87
DO^{14}C	114[b]	115	103[b]	104	100[b]	103
DOC output flux	12	13	9	8	2	2
fraction hydrophilic DOC[d]	~0.4	0.4	~0.5	0.4	~0.6	0.5

[a] Observed value is the difference between total and (litter + humic substances)

[b] Value for dilute NaCl soil extracts

[c] Simulated value is ratio of dissolved Hum-1 to dissolved (Hum-1 + Hum-2).

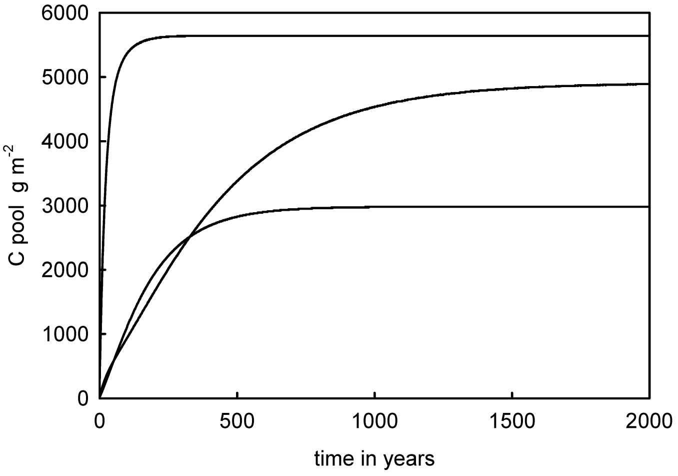


Figure 3. Simulated development of soil horizon C pools at Birkenes.

to explain the observed ^{14}C signal. Figure 4b shows the incorporation of bomb carbon into the different C pools in Hor-1 at Birkenes. The litter ^{14}C value increases rapidly to a maximum of c. 175, then falls to c. 110. The substrate value increases

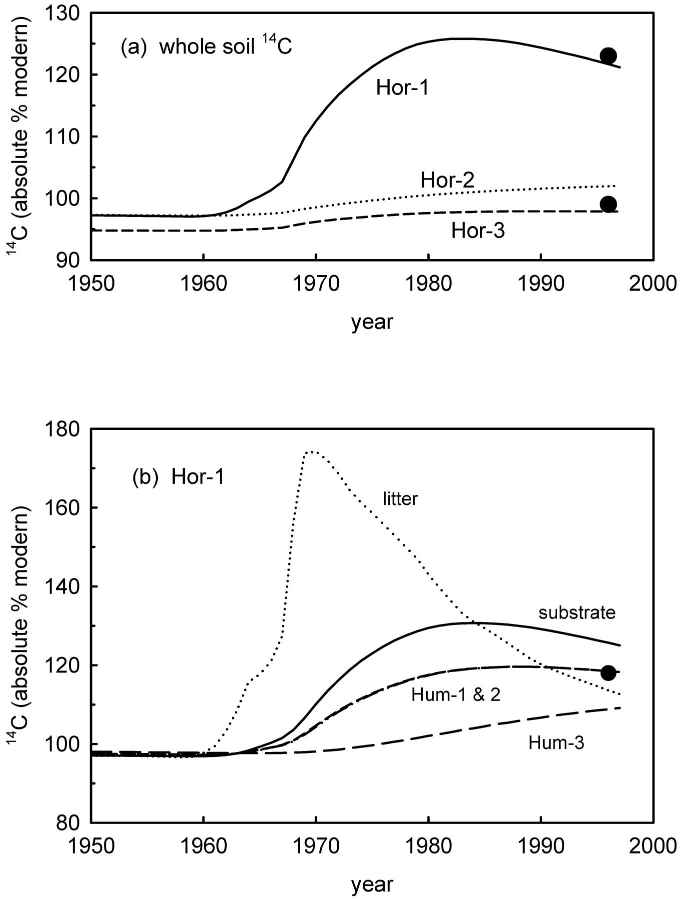


Figure 4. Simulated incorporation of ″bomb″ carbon into soil horizons (a) and carbon pools (b) in Hor-1, at Birkenes. The points are observations.

steadily to c. 130 and then falls slowly. The values for Hum-1 and Hum-2 lag behind the substrate, because they are derived also from Hum-3. The ^{14}C value of Hum-3 responds slowly to bomb carbon inputs because the pool is large, so that older C dilutes the bomb signal.

Values of ^{14}C tend to be lower at Waldstein (simulations not shown), due to greater dilution of bomb carbon by the larger soil C pools. The bomb carbon maximum in Hor-1 is calculated to have been lower and flatter than at Birkenes, and to have occurred somewhat later. Although Hor-3 is calculated to have received bomb carbon, its overall ^{14}C value is calculated to be appreciably less than 100 (Table 5C).

Contributions of DOC and roots to mineral soil carbon

The organic carbon accumulated in the mineral horizons Hor-2 and Hor-3 is, according to the model, supplied by root litter and by the downward transport of DOC. The parameterised model was run with the root litter inputs set to zero, in order to estimate the separate contributions of the two sources. For Birkenes, the calculation indicated that 89% of the mineral soil organic matter was due to DOC transport from Hor-1, while for Waldstein the figure was 73%. Thus for both sites DOC is the major source. This fits with the conclusion from parameter sensitivity analysis (see above) that the model output is not strongly dependent on the value of the rate constant for the conversion of substrate to humic substances.

Short-term variations in DOC concentrations and fluxes

The model has been optimised (calibrated) by minimising residuals in average concentrations and pool sizes, annual DOC fluxes and annual average ^{14}C signals, for an assumed steady state. In performing the optimisations, temporal variations in the concentrations and fluxes of DOC in soil water were necessarily simulated, but they were not used in the fitting procedure. Therefore, comparison of observed and simulated temporal variations (Figure 5) can be regarded as a test of the model. For [DOC] in Hor-1, the model produces less temporal variation in concentration than was observed (Figures 5a and 5b). In particular, it fails to reproduce the high concentrations observed in summer 1997 at Birkenes and in summer/autumn 1996 at Waldstein. Some other features of the temporal variations in [DOC] are, however, reasonably simulated. Fluxes of DOC (Figures 5c and 5d) are simulated better than the concentrations, reflecting the importance of water flow in their determination (Michalzik et al. 2001; Neff and Asner 2001).

It was observed that [DOC] in the deeper horizons at both sites varied relatively little with time. The model process available to reproduce such behaviour is sorption, as long as the percolating water is efficiently exchanged with the micropores (where sorption takes place). It was necessary to set D_{exch} to a high value (Tables 4B and 5B) in order to achieve the required efficient exchange.

Figure 6 shows the simulated dependence on discharge of DO^{14}C in drainage water from the soil profile at Birkenes, for the period 1996–1998. The ^{14}C signal switches between a baseline value of 101 to a maximum of 118, reflecting the dominance of Hor-3 at low drainage, and from Hor-1 (bypass flow) at high drainage. This pattern has been reported by Schiff et al. (1997) for DO^{14}C in stream and ground waters of a forested upland catchment in the Harp Lake Basin in Canada. Over a period of two years the authors found a wide range of ^{14}C from old groundwater values at baseflow under dry basin conditions to relatively modern values flushed from litter or A layers during high flow conditions. We observed similar behaviour for the stream draining the Birkenes site, over a period of four days in October 1997. The stream discharge increased from 0.001 to 0.26 m^3 s^{-1}, and the observed ^{14}C from 106 to 115; the simulated ^{14}C in soil drainage water showed a similar degree of change, from 102 to 117. The hydrological regime at Waldstein

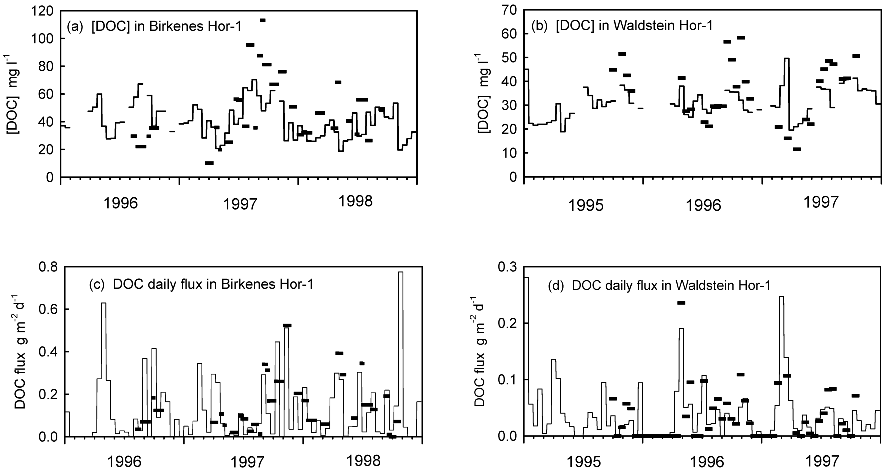


Figure 5. Short-term DOC concentrations and fluxes in Hor-1 at Birkenes and Waldstein. Measured values for lysimeter samples are shown by heavy bars, covering each observation period. The simulated values are 14-day averages, to provide similar resolution to the observations. Gaps in the simulations appear when the simulated water flows are zero.

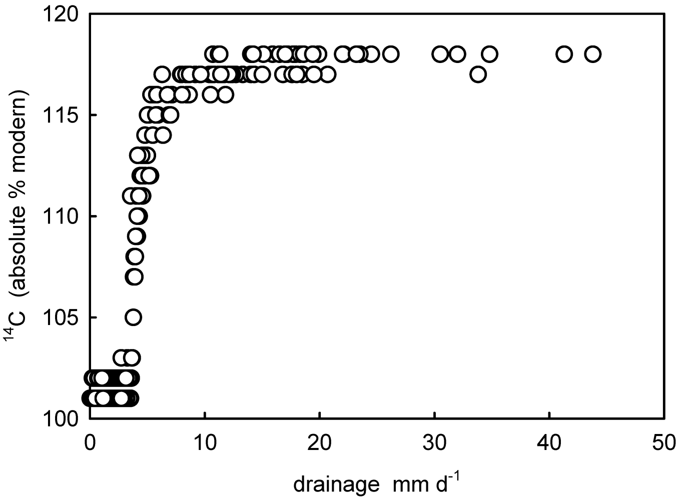


Figure 6. Simulated dependence of ^{14}C on total soil water discharge at Birkenes; daily values for 1996–1998.

differs from that at Birkenes in that there is no bypass flow. The model therefore simulates a steady value of DO^{14}C in total soil drainage.

Discussion

Carbon cycling in forest soils operates at a range of timescales, and can be studied by making measurements of transported components such as CO_2 and DOC, as well as by determining the amounts and isotopic signatures of whole soil, soil horizons, and organic matter fractions. Process-based modelling, as described here, provides a means to integrate the results of the different kinds of study. Thus DyDOC provides a description of the key long- and short-term processes governing DOC generation and transport within forest soils. The model is novel in that it includes ^{14}C signals within a dynamic, process-oriented, scheme involving several soil horizons. The use of ^{14}C provides a way to overcome the inevitable lack of long-term observations with regard to soil carbon cycling. Thus, by assuming that the forests and their soils at Birkenes and Waldstein are presently in steady state, we have gained information about the turnover times of soil C pools, through the use of ^{14}C signals. This has involved both long-term radioactive decay, leading to relatively low ^{14}C contents in Hor-3, especially at Waldstein, and the shorter-term input of ″bomb carbon″ which has enriched particularly Hor-1 in the isotope. Strictly speaking, ^{14}C data may not be essential for model parameterisation, but their use has been so valuable in the present applications, that it is difficult to envisage applying the model to a new field site without including ^{14}C measurements. Indeed more information could no doubt be extracted if ^{14}C contents of more carbon fractions were determined (cf. Gaudinski et al. (2000)).

Given present understanding and measurement techniques, we believe that DyDOC is at an appropriate level of complexity to conceptualise and analyse the production and transport of DOC in soils, and to relate these processes to the turnover of other long-term soil C pools. However, like previous soil carbon models, DyDOC simplifies complex processes. In particular, the metabolic reactions are formulated according to first-order decay reactions, commonly used in decomposition simulations (e.g., Parton et al. (1987) and Jenkinson (1990)), but not necessarily justified by empirical evidence (Arah and Gaunt 2001). They are also dependent only upon temperature, and might be improved if soil moisture were also taken into account. At present, the metabolic constants are best regarded as site-specific, but the values for the two study sites are, in most cases, either similar to one another, or not crucial to producing acceptable model output. Differences in the constants could arise from differences in variables ″external″ to the model such as nutrient status, soil chemical conditions (especially pH) and soil texture. By applying DyDOC to a greater range of field sites, it may be possible to relate variations in the metabolic constants to such properties. A more predictive model capability, i.e., less dependent upon site-specific fitting, might then be achieved.

Obviously, the response of forest ecosystems to climate change is a primary interest in the development of carbon cycling models, changes in temperature being of particular interest. In this respect, a key question is the extent of variation of the Q_{10} values for different metabolic processes. Although a universal value of 2 has been assumed in the present work, it may be that some transformations, or groups of transformations, are more temperature-sensitive than others; for example the production of CO_2 might be more temperature sensitive than that of DOC. In the first place, DyDOC could be used to explore the consequences of differences in Q_{10}. Secondly, ways should be sought to determine the temperature dependences of the metabolic processes. Other climate change related effects to which DyDOC could be applied include changes in litter and water inputs to the soil.

The present paper describes the model's application to forest systems, but it could also be used to simulate moorland, and possibly agricultural, soils. Another point regarding applications is that a modified version of DyDOC could be used to simulate soil development without assuming steady state. This would require scenarios of change, including plant growth and succession, climatic variations, and land use change. Elaboration of the model might be required, to take into account changes in soil properties with time.

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