



Article (refereed) - postprint

Tipping, E.; Rowe, E.C.; Evans, C.D.; Mills, R.T.E.; Emmett, B.A.; Chaplow, J.S.; Hall, J.R.. 2012 N14C: A plant-soil nitrogen and carbon cycling model to simulate terrestrial ecosystem responses to atmospheric nitrogen deposition. *Ecological Modelling*, 247. 11-26. [10.1016/j.ecolmodel.2012.08.002](https://doi.org/10.1016/j.ecolmodel.2012.08.002)

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REVISION submitted to Ecological Modelling 31 July 2012

N14C: a plant-soil nitrogen and carbon cycling model to simulate terrestrial ecosystem responses to atmospheric nitrogen deposition

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Abstract

The dynamic model N14C simulates changes in the plant-soil dynamics of nitrogen and carbon, brought about by the anthropogenic deposition of nitrogen. The model operates with four plant functional types; broadleaved and coniferous trees, herbs and dwarf shrubs. It simulates net primary production (NPP), C and N pools, leaching of dissolved organic carbon and nitrogen (DOC, DON) and inorganic nitrogen, denitrification, and the radiocarbon contents of organic matter, on an annual timestep. Soil organic matter (SOM) comprises three pools, undergoing first-order decomposition reactions with turnover rates ranging from *c.* 2 to *c.* 1000 years. Nitrogen immobilisation by SOM occurs if inorganic N remains after plant uptake, and leaching of inorganic N occurs if the immobilisation demand is met. SOM accumulates in the deeper soil by transport and sorption of DOM. Element soil pools accumulate with N inputs by fixation from 12,000 years ago until 1800, when anthropogenic N deposition begins. We describe the parameterisation of N14C with data from 42 published plot studies carried out in northern Europe, plus more general information on N deposition trends, soil radiocarbon, N fixation and denitrification. A general set of 12 parameters describing litter fractionation, N immobilisation, growing season length, DOC and DON leaching, denitrification and NH₄ retention was derived by fitting the field data. This provided fair agreements between observations and simulations, which were appreciably improved by moderate ($\pm 20\%$) adjustments of the parameters for specific sites. The parameterised model gives reasonable blind predictions of ecosystem C and N variables from only temperature, precipitation, N deposition, and vegetation type. The results suggest an approximate doubling of NPP due to N deposition, although the majority of the sites remain N-limited. For a given N deposition, leaching rates of inorganic N at conifer and shrub sites exceed those at broadleaf and herb sites.

Keywords: atmospheric deposition, carbon, leaching, NPP, nitrogen, radiocarbon, soil, turnover

1. INTRODUCTION

Contemporary enrichment of natural and semi-natural terrestrial ecosystems by nitrogen deposition is associated with acidification, eutrophication, carbon sequestration, loss of biodiversity and increasing emissions of the potent greenhouse gas N₂O (Vitousek et al., 1997; Matson et al., 2002; Galloway et al., 2004; Emmett, 2007; Schlesinger, 2009). Although natural or semi-natural terrestrial ecosystems are generally N-limited (Vitousek and Howarth, 1991; LeBauer and Treseder, 2008), in parts of the world with high N deposition, "nitrogen saturation" is a threat (Ågren and Bosatta, 1988; Aber et al., 1989, 1998), which means that there will be more available N than can be accommodated by biotic and abiotic sinks. To date, this has applied particularly to Europe, owing to long-term intensive agriculture and industrial emissions (Sutton et al., 2011), but the future threat is global (Galloway et al., 2004). In the early stages of enrichment, N may increase plant productivity, which may be followed by plant species losses associated with eutrophication (Bobbink et al., 1998), and the leaching of nitrate with acidifying effects (Curtis et al., 2005).

Nitrogen accumulation and its consequences are strongly linked to the cycling of carbon in both vegetation and soils. Therefore interactions between the two elements must be taken into account when attempting quantitative descriptions and forecasting future behaviour. For example, N leaching in forests was related to forest floor C:N ratio by Gundersen et al. (1998). Dise et al. (2009) reported the most consistent indicators of N leaching in European forests to be throughfall N deposition, organic horizon C:N ratio and mean annual temperature. However, different semi-natural UK ecosystems (grassland, heathland, deciduous woodland, coniferous woodland) display appreciable variation in the C:N ratio below which leaching occurs (Rowe et al., 2006). Therefore, bulk soil C:N is not a sufficient guide to leaching in general, and its use in prediction can be questioned, since it is a response to N loading as well as an indicator of leaching. The obverse of C control of N is C sequestration promoted by N enrichment, which has implications for climate responses; quantification of this process is currently controversial with a wide range of estimates (De Vries et al., 2006, 2009).

To understand these issues, a long-term perspective would be helpful, taking into account the build up of both N and C in affected terrestrial ecosystems. This requires dynamic modelling.

If the current N and C status of soils, together with associated variables such as net primary productivity (NPP) and inorganic N leaching, can be explained in terms of site histories, we would be in a better position to forecast responses to changes in inputs, and thereby to guide N emissions policy.

Many models already exist that describe plant-soil C and N turnover. The level of detail required for our purposes would be categorised by Manzoni and Porporato (2009) as "E-3-4", i.e. a coupled soil-plant dynamic model operating at a spatial scale of 1-100 m and a time scale of 100-1000 days. Manzoni and Porporato (2009) identified 11 such models (out of a total of c. 250) of which four describe most of the variables of interest to us. Of these the TCS model of Luo and Reynolds (1999) and G'DAY (Comins and McMurtrie, 1993; McMurtrie et al., 2001) are based on the CENTURY model (Parton et al., 1987), the driving data demands of which are high compared to those available at the broad scale which interests us. The VEGIE model of Aber et al. (1991) is a relatively detailed model designed for forest ecosystems and focusing on N. The model of Wang et al. (2007) focuses on nutrient-plant interactions with only a rudimentary description of soil organic matter turnover. Thus, we could not find an existing model that would readily carry out the required simulations, especially when considering that we wanted to (a) achieve a "general" parameterisation, i.e. to derive a parameter set that could operate on multiple sites, (b) to run the model from historical pristine conditions into the contemporary period (from 1800) of N enrichment, (c) utilise measurements of soil radiocarbon, and (d) drive the model with readily-available data on N deposition, mean annual temperature and precipitation (MAT, MAP), and plant functional type and element stoichiometry. Therefore we combined existing modelling concepts into a new model, which we refer to as N14C to connote the linking of C and N and the use of radiocarbon data. The key underlying assumption of N14C is that vegetation type determines the turnover properties of soil organic matter, firstly through the element stoichiometry of the plants, and secondly through the different decomposition properties of plant litter derived from tree and non-tree vegetation.

In this paper, we describe the model and report its parameterisation and partial testing. We used plot-scale observations of soil C and N contents, and leaching of DOC, DON and inorganic

N at 42 sites covering natural and semi-natural terrestrial ecosystems of northern Europe, and with a range of N deposition rates, together with representative soil radiocarbon data. We developed separate versions of N14C for plant-soil systems of broadleaved and coniferous trees, herbs and shrubs.

2. MODEL DESCRIPTION

The N14C model simulates annual plant growth and turnover and soil C and N cycling starting at the onset of soil formation. Contemporary pools and fluxes depend upon the NPP at the site in question, long-term N-fixation and more recent N enrichment by atmospheric deposition. The plant type determines the C:N stoichiometry of litter, and how it adds to soil organic matter (SOM). The schematic of Figure 1 shows the model pools and interconnecting annual fluxes. Table 1 lists the variables, Table 2 the model constants. For clarity, units are given in the Tables but not always in the text. The model tracks ^{14}C from atmospheric CO_2 entering plant biomass and flowing through the carbon pools. Element transfers during designated within-year periods, or a single year, are designated with a leading Δ , and have units of g m^{-2} .

Each calendar year is divided into three periods, namely dormant (pre-growth), growth, and dormant (post-growth). Although the post-growth dormant period for a given year is followed immediately by the pre-growth dormant period for the subsequent year, they do not always make a single dormant period because at the mid-point the atmospheric N input may change. The fraction of time taken by the growth period is denoted by f_{gr} , the remaining time is split equally between the two dormant periods. A mean temperature is calculated for dormant and growth periods, taking into account f_{gr} and the temperature difference (ΔT_{sw}) between mean summer (April-September) and winter (October-March).

In general parameterisation of N14C, the value of f_{gr} for a given site was initially assumed to be related to mean annual temperature (MAT) by the following simple model;

$$\text{for } \text{MAT} \leq T_{gr} \quad f_{gr} = f_{gr,1} + (f_{gr,2} \times \text{MAT} / T_{gr}) \quad (1)$$

$$\text{for } \text{MAT} > T_{gr} \quad f_{gr} = f_{gr,1} + f_{gr,2} \quad (2)$$

Here, $f_{gr,1}$ and $f_{gr,2}$ are constants and T_{gr} is a threshold temperature above which the growing season fraction is constant. For positive values of $f_{gr,1}$ and $f_{gr,2}$, f_{gr} is less than maximal at lower temperatures, i.e. the growing season is shortened. For site-specific parameterisation, f_{gr} has only a single value.

2.1. C and N inputs and outputs

Carbon enters the ecosystem by the generation of plant biomass. There are two sources of N, fixation (ΔN_{fix}) and deposition (ΔN_{dep}). It is assumed that anthropogenic inputs of N began in 1800. Thereafter, any anthropogenic N inputs substitute for N fixation, i.e. down-regulation occurs (DeLuca et al., 2008), and so only when ΔN_{dep} exceeds the pristine ΔN_{fix} does net N enrichment take place. For woodland, the term ΔN_{dep} takes into account the scavenging effects of tree foliage.

Carbon is lost as CO_2 (including dissolved carbonate species in drainage water) from decomposition, and leached as dissolved organic carbon (ΔDOC). Nitrogen leaves as N_2 or N_2O (ΔN_{gas}), and is leached in organic and inorganic forms (ΔDON , ΔN_{inorg}). Some ΔN_{dep} can bypass the plant-topsoil system and this is characterised by $f_{\text{N,bypass}}$, the fraction of the input flux that does not interact with the soil.

2.2. Plants

Four plant functional types (PFT) are recognised, namely broadleaved trees (B), conifers (C), herbs (H) and shrubs (S) (Whittaker, 1970). By herbs, we mean sites dominated by herbaceous plants, and by shrubs we mean dwarf shrubs, as typical of heaths and mountain regions. Plant tissue is divided into "coarse" and "fine". The former comprises larger woody parts, which provide litter that is assumed not to contribute to soil C. The latter consists of foliage, twigs, fine roots etc that supply C and N to the soil. For herbs and shrubs, all biomass is in the fine category. For trees, a substantial fraction is coarse; the entire stem and half of the branches are assumed to decay on the soil surface, while half of the coarse roots are assumed not to contribute to topsoil C. The C:N ratio of coarse tissue is assumed constant, whereas that of the fine tissue can become enriched in N, so C:N varies. Thus, two end-members are defined for each PFT, corresponding to plants with different nutrient contents, i.e. high and low C:N ratios. This creates stoichiometric flexibility, which can arise in two ways; (i) change N-poor to N-rich plant species; (ii) N enrichment of the same plant species. In either case, the site vegetation becomes progressively enriched in N (C:N falls) as N availability increases.

Maximum net annual primary productivity (NPP_{max}) at a site is determined by temperature or precipitation (Section 3.1), while the actual NPP may depend on the availability of nitrogen, ΔN_{avail} , during the growth period (Section 2.4). The demand for N to build biomass is given by;

$$\Delta N_{demand,i} = \{f_{coarse,i}/(C:N)_{coarse,i} + (1-f_{coarse,i})/(C:N)_{fine,i}\} \times NPP_{max} \quad (3)$$

where i is the PFT end-member (1 or 2), $f_{coarse,i}$ is the fraction of NPP carbon going into the coarse parts of the plant ($f_{fine} = 1 - f_{coarse}$), and C:N is the carbon:nitrogen mass ratio of the plant tissue.

The fractions of NPP carbon entering plant biomass are f_{NPP1} and f_{NPP2} ($f_{NPP1} + f_{NPP2} = 1$), and the greater the availability of N, the more is plant 2 favoured, according to;

$$f_{NPP2} = k_{P1P2} \times \Delta N_{avail} \quad (4)$$

where k_{P1P2} is a constant. If the calculated value of f_{NPP2} exceeds unity, the value is set to unity. The potential NPP for the two end-members is given by

$$NPP_{pot,1} = (1 - f_{NPP2}) \times \Delta N_{avail} \times NPP_{max} / \Delta N_{demand,1} \quad (5)$$

$$NPP_{pot,2} = f_{NPP2} \times \Delta N_{avail} \times NPP_{max} / \Delta N_{demand,2} \quad (6)$$

If the sum of $NPP_{pot,1}$ and $NPP_{pot,2}$ exceeds NPP_{max} , i.e. if N availability exceeds demand, then the values are scaled such that $NPP_{pot,1}$ and $NPP_{pot,2}$ sum to NPP_{max} . If ΔN_{avail} is low, then end-member 1 is favoured, and as enrichment occurs, more NPP is through end-member 2. This enables the model to simulate not only increased NPP due to pollutant N supply, but also the enrichment of plant biomass with N, i.e. the decline in nutrient use efficiency (Aerts & Chapin, 2000). The total amount of N taken up to build new biomass is ΔN_{plant} .

A fraction of coarse biomass ($f_{coarse,litter}$) is converted to litter at the end of each year, and a fraction of fine biomass ($f_{fine,litter}$) at the end of each within-year period (pre-growth, growth, post-growth). When litter is created from fine biomass, a fraction ($f_{Nretained}$) of the biomass N is retained (Aerts & Chapin, 2000) and added to the available N pool for subsequent plant growth ($\Delta N_{retained}$).

2.3. Soil C dynamics

Coarse litter C is assumed not to contribute to soil organic matter. It is lost as CO₂ by a first-order rate process, with modification by temperature via a conventional Q₁₀ relationship, so the loss of C is given by;

$$\Delta C_{\text{coarse}} = k_{C,\text{coarse}} C_{\text{coarse}} \times Q_{10}^{T/10} \times f_k \quad (7)$$

where $k_{C,\text{coarse}}$ is the decomposition rate constant, C_{coarse} is the coarse carbon pool, T is temperature in °C, and f_k is f_{gr} during the growing season and $(1 - f_{\text{gr}}) / 2$ during the two dormant periods. This process is inconsequential for the soil, but the related release of N from coarse litter does enter the soil (see below).

In our simplified picture of SOM, the topsoil (typically 20 cm in depth) contains carbon that has been derived from fine plant litter while carbon deeper in the soil is only from DOC downward transport, and therefore is in organic material that has been lost from the topsoil pool. Topsoil organic matter is divided into fast, slow and passive soil organic matter (SOM) fractions. The SOM pool structure follows that proposed by Van Veen and Paul (1981), and is also used in the CENTURY model (Parton et al., 1987). By using three pools with differing turnover rates, the range of SOM turnover can be represented efficiently, i.e. with few parameters. We maintain the nomenclature for the pools suggested by Amundson (2001), and to be consistent with our own work on soil C cycling (Tipping et al., 2010; Mills, 2011).

The input flux of fine litter C is fractionated into three types, depending upon which soil pool it enters; thus

$$f_{\text{fast}} + f_{\text{slow}} + f_{\text{passive}} = 1 \quad (8)$$

Once entered, the C remains in the specified pool, i.e. inter-pool transfers do not occur. The values of f_{fast} , f_{slow} and f_{passive} are characteristic of a given plant type. Each of the pools (C_{fast} , C_{slow} , C_{passive}) has a characteristic temperature-dependent first-order turnover rate constant for C, k_j . Thus the loss of C from pool j (fast, slow or passive) in a particular period (dormant or growth) is given by

$$\Delta C_j = k_j C_j \times Q_{10}^{T/10} \times f_k \quad (9)$$

Effects of soil moisture on decomposition are not modelled.

The output of DOC from the topsoil depends upon the releases of C from the three SOM pools, according to the equation;

$$\Delta\text{DOC} = f_{\text{DOC}} (\Delta C_{\text{fast}} + \Delta C_{\text{slow}} + \Delta C_{\text{passive}}) \quad (10)$$

The remaining (and majority) of the C loss is as CO₂. The DOC leaving the topsoil either enters or bypasses the lower soil. The bypassing fraction is $f_{\text{DOC,bypass}}$. The entering DOC adds to an accumulated pool of carbon, C_{lower} , which loses carbon by first-order decomposition, governed by the rate constant k_{lower} . The carbon is lost either as CO₂ or DOC, the fractional loss to DOC being denoted by $f_{\text{DOC,lower}}$.

2.4. Soil N dynamics

Nitrogen is released from decaying coarse tissue in proportion to C release (equation 7), and enters the soil as available N. Organic nitrogen accompanies litter C into the three soil SOM pools (N_{fast} , N_{slow} , N_{passive}), the litter C:N proportion depending upon the N status of the biomass, taking $\Delta N_{\text{retained}}$ into account. During decomposition of the SOM pools, N is released in proportion to C (equation 9). In the topsoil, DON is released from the three SOM pools in proportion to the total loss, via the equation;

$$\Delta\text{DON} = f_{\text{DON}} (\Delta N_{\text{fast}} + \Delta N_{\text{slow}} + \Delta N_{\text{passive}}) \quad (11)$$

The input of inorganic N to soil water is then obtained as;

$$\Delta N_{\text{inorg}} = \Delta N_{\text{dep}} + \Delta N_{\text{fast}} + \Delta N_{\text{slow}} + \Delta N_{\text{passive}} - \Delta\text{DON} \quad (12)$$

Some N can be lost by denitrification, according to a temperature-dependent first order reaction;

$$\Delta N_{\text{gas}} = k_{\text{denitr}} \Delta N_{\text{inorg}} \times Q_{10}^{T/10} \times f_k \quad (13)$$

We then obtain the flux of N available for plant growth as;

$$\Delta N_{\text{avail}} = \Delta N_{\text{inorg}} - \Delta N_{\text{gas}} + \Delta N_{\text{retained}} \quad (14)$$

After removal of N to build biomass, which only occurs during the growing season, and if the amount of N required to do this is greater than $\Delta N_{\text{retained}}$ (which is invariably the case), then excess N is given by

$$\Delta N_{\text{excess}} = \Delta N_{\text{avail}} - \Delta N_{\text{plant}} \quad (15)$$

If for some reason $\Delta N_{\text{retained}}$ exceeds the N demand for plant growth, then the unused retained N continues to be retained. If ΔN_{excess} exceeds zero, then uptake (immobilisation) of N by SOM occurs according to the equation;

$$\Delta N_{\text{immob}} = k_{\text{immobN}} \Delta N_{\text{excess}} (C_{\text{fast}} + C_{\text{slow}} + C_{\text{passive}}) \times Q_{10}^{T/10} \times f_k \quad (16)$$

where k_{immobN} is a constant, the N being incorporated into SOM in proportion to the C pools.

In addition, a restriction is placed on the leaching of inorganic N released during each of the dormant periods, to take account of the fact that some or most of the released N_{inorg} will be NH_4 which can be retained by sorption rather than immediately leached. Thus $\Delta N_{\text{immob2,max}}$ is the maximum additional flux of N_{inorg} that can enter the fast N pool. Then

$$\text{for } \Delta N_{\text{excess}} - \Delta N_{\text{immob}} \leq \Delta N_{\text{immob2,max}} \quad ; \quad \Delta N_{\text{immob2}} = \Delta N_{\text{excess}} - \Delta N_{\text{immob}} \quad (17)$$

$$\text{for } \Delta N_{\text{excess}} - \Delta N_{\text{immob}} > \Delta N_{\text{immob2,max}} \quad ; \quad \Delta N_{\text{immob2}} = \Delta N_{\text{immob2,max}} \quad (18)$$

Strictly, the subsequent desorption of this additional N is a different process to mineralization (cf. equation 9), but must take place on a similar time-scale and so counting the additional N as fast N is justifiable. Also, in principle $\Delta N_{\text{immob2,max}}$ might be related to the length of the growing season, but this is a subtle variation in comparison to setting $\Delta N_{\text{immob2,max}}$ equal for all soils, which is necessary in order to fit available field data.

The final leaching flux of inorganic N is given by

$$\Delta N_{\text{inorg}} = \Delta N_{\text{excess}} - \Delta N_{\text{immob}} - \Delta N_{\text{immob2}} \quad (19)$$

In the lower soil, DON follows DOC into the sorbed pool, from which it can escape only by leaching. This contrasts with sorbed DOC, which can also be mineralized, and so the deeper SOM becomes relatively enriched in N. The inorganic N flux from the topsoil is unaffected by processes in the deeper soil.

2.5. Radiocarbon

The accumulation and loss of ^{14}C in the organic matter pools is calculated by keeping a budget based on the annual inputs of $^{14}\text{CO}_2$. Each C pool is assumed to be fully mixed, and changes in ^{14}C due to inputs and losses are tracked. Radioactive decay is also taken into account. More details are given by Michalzik et al. (2003) and Tipping et al. (2012).

3. DATA AND PARAMETERISATION

3.1. General data

Data characterising the four PFTs are summarised in Table 3, and details of their derivation are given Table S1. The maximum NPP at a given site is assumed to depend upon MAT or MAP, whichever is limiting, following Lieth (1975). Data compiled by Chapin et al. (2002) were used to derive temperature and precipitation functions, assuming that the 90% quantile at a given MAT or MAP represents the maximum NPP (Figure S1). We chose a value of 8°C for T_{gr} in equations (1) and (2), i.e. for sites with $MAT > 8^{\circ}\text{C}$ the growing season was assumed to be independent of temperature. Model runs began with zero plant and soil pools at 12000 yrs BP, i.e. approximately at the end of the last glaciation, which would apply to most of the study sites. This length of time was sufficient for all the simulated ecosystems to reach near-steady state conditions.

For the pristine period before anthropogenic N deposition, i.e. before 1800, it is assumed that the only N input is from fixation, at a constant annual rate ($\Delta N_{\text{fix,pris}}$). Data for N fixation under the temperature and precipitation or evaporation conditions of our study sites are sparse. The compilation of Cleveland et al. (1999) contains only two examples, with values of 0.27 and 1.6 $\text{gN m}^{-2} \text{a}^{-1}$, the second of which is considered unrepresentative (Galloway et al., 2004). DeLuca et al. (2008) report rates for Swedish boreal forest in the range 0-0.35 $\text{gN m}^{-2} \text{a}^{-1}$. Cleveland et al. (1999) proposed that N fixation is proportional to evaporation rate, while Houlton et al. (2008) demonstrated a strong temperature dependence of nitrogenase activity. But in each case the relationship refers to large ranges of the explanatory variable, and is not evident over the relatively small ranges that apply to N. Europe. The selection of sensible values is hampered by the possibility that N fixation is down-regulated by N deposition, which has been shown for boreal forests (DeLuca et al., 2008; Gundale et al., 2011), and may mean that measured contemporary N fixation rates are lower than those under pristine conditions. However, this is hard to quantify. Based on the value of 0.27 $\text{gN m}^{-2} \text{a}^{-1}$ mentioned above, and the value of 0.37 $\text{gN m}^{-2} \text{a}^{-1}$ estimated by linear extrapolation of the data of DeLuca et al. (2008) to zero N deposition, we chose a default pristine N fixation rate of 0.3 $\text{gN m}^{-2} \text{a}^{-1}$. After

1800, N deposition is assumed to have increased with the same pattern everywhere (Figure 2), based on the analysis of Schöpp et al. (2003) for Europe as a whole.

Denitrification (gaseous loss of N_2O , N_2 etc) is a significant loss process of N from soils, and data are needed to constrain the model, but are available for only one of the specific sites modelled here (Butterbach-Bahl et al., 2002). On the basis of several reviews and studies (Barton et al., 1999; Helliwell and Ferrier, 2001; Butterbach-Bahl et al., 2002; Groffman et al., 1992; Denier van der Gon and Bleeker, 2005; de Vries et al., 2006) we concluded that an average contemporary value for the study sites would lie in the range 0.1 to $1 \text{ gN m}^{-2} \text{ a}^{-1}$.

3.2. Site-specific data

Field data for fitting (summarised in Table 4, presented in full in Table S2, mapped in Figure S3) were taken from sites that had experienced negligible recent land use change. Data were assembled for a total of 42 sites for which at least the following data were available or could be derived; dominant plant functional type, soil type, mean annual temperature and precipitation, contemporary N deposition, topsoil C, N and inorganic N leaching. For some sites DOC and DON fluxes from the topsoil were also available and were used for fitting. The study sites have an average N dep of $2.1 \text{ g m}^{-2} \text{ a}^{-1}$, representing a seven-fold increase over the assumed pristine N inputs by fixation (see above). The medians and ranges of N deposition are fairly similar for each PFT, although shrub sites tend to have lower values. Over all sites, N deposition is positively correlated ($r^2 = 0.39$) with MAT. The topsoil depths differ among sites. Forest soil average depths were 25 and 24 cm for broadleaf and conifer respectively, whereas for herbs and shrubs the average depths were both 16 cm. However the average soil C pools were more similar, ranging from 6.8 kg m^{-2} (shrubs) to 7.9 kg m^{-2} (herbs), with intermediate values for the forested sites.

The tendency of sites to exhibit topsoil bypass flow was assessed from information in the source literature, or from the general characteristics of the landscape where they are located. Bypass flow was assumed to account for 20% of N deposition at sites with high relief and/or rocky terrain. This applied to 13 of the 42 sites, of which 12 were in the herb or shrub PFT. The value of ΔT_{SW} at each site was assigned using country averages, values ranging from 7°C

(UK, France) to 13°C (Norway, Czech Republic). If the calculated average winter temperature was negative, the actual soil temperature was assumed to be 0 °C.

The ¹⁴C contents of soil organic matter differ between soils that have developed under trees and non-trees, leading to greater “bomb carbon” contents of the former (Bol et al., 1999; Tipping et al., 2007, 2010; Mills, 2011). On the basis of the available data (Table S3) we assumed ¹⁴C contents of 110 % modern for tree sites and 100 % modern for non-tree sites as typical values for the year 2000. Precise assignments for individual sites were not attempted since the available representative data refer largely to sites other than those used in the present analysis.

3.3. Model parameters for topsoils

We aimed to minimise the number of adjustable parameters, and to obtain general values either applicable to all sites and vegetation types, or to all sites within a vegetation type. Site-specific parameterisation was explored subsequently. Account was taken of the different years of observation, which ranged from 1993 to 2005.

Parameters for plants, derived from external sources, are given in Table 3. Other *a priori* parameters were as follows. A Q_{10} of 2.0 was assigned to all temperature-dependent processes (equations 7, 9, 13, 16). Values of k_{fast} , k_{slow} and k_{pass} were fixed at 0.25, 0.025 and 0.0005 a⁻¹ respectively, to give mean residence times of 2, 20 and 1000 years when applied at 10°C with $Q_{10} = 2$. Coarse litter was assumed to lose 10% of its carbon per annum (i.e. $k_{C,coarse} = 0.1$). The value of k_{P1P2} was set to 0.05 m² g⁻¹, since trial model runs showed this to give complete transitions from plant 1 to plant 2 during enrichment by N for some sites.

To fit the data, 13 general parameter values were optimised; k_{immobN} for each vegetation type (4 parameters), f_{fast} and $f_{passive}$ each for trees and non-trees (4 parameters), k_{denitr} , f_{DOC} , $\Delta N_{immob2,max}$, $f_{gr,1}$ and $f_{gr,2}$ (5 parameters). The following objective function was minimised;

$$\begin{aligned} & \alpha \sum (C_{obs} - C_{calc})^2 \\ & + \beta \sum (N_{obs} - N_{calc})^2 \\ & + \gamma \sum (C:N_{obs} - C:N_{calc})^2 \\ & + \delta \sum (\Delta N_{inorg,obs} - \Delta N_{inorg,calc})^2 \end{aligned}$$

$$\begin{aligned}
& + \varepsilon ((110 - {}^{14}\text{C}_{\text{calc},\text{B}})^2 + (110 - {}^{14}\text{C}_{\text{calc},\text{C}})^2 + (100 - {}^{14}\text{C}_{\text{calc},\text{H}})^2 + (100 - {}^{14}\text{C}_{\text{calc},\text{S}})^2) \\
& + \zeta (\Delta\text{DOC}_{\text{mean,obs}} - \Delta\text{DOC}_{\text{mean,calc}})^2 \\
& + \eta (\Delta\text{DON}_{\text{mean,obs}} - \Delta\text{DON}_{\text{mean,calc}})^2 \\
& + \theta (\Delta\text{N}_{\text{denitr,mean}} - \Delta\text{N}_{\text{denitr,mean,calc}})^2 \\
& + \kappa (\text{NPP}_{75\%} - \text{NPP}_{\text{calc}})^2
\end{aligned}$$

We used soil C:N ratio as well as C and N pools as criteria for fitting, because the measurements of topsoil C and N pools are somewhat arbitrary, depending upon the choice of a representative soil depth, whereas the C:N ratio is a more robust variable. The mean values of ΔDOC , ΔDON and $\Delta\text{N}_{\text{denitr}}$ refer to the whole dataset, i.e. averages over all 42 sites, and $\text{NPP}_{75\%}$ is $526 \text{ gC m}^{-2} \text{ a}^{-1}$, i.e. 75% of the average maximum NPP. The average NPP is assumed (a) to be greater than the average current observed NPP from global data (see Section 3.1) because the study sites are N-enriched, but (b) less than maximal given that N-limitation is widespread (LeBauer and Treseder, 2008). The 75% of maximal NPP is therefore chosen as a reasonable intermediate value.

The first four terms of the objective function are summations over all 42 sites, the fifth is from ${}^{14}\text{C}$ values for each of the four PFTs, and the last four involve single differences of average values. The weighting factors α , β , γ , δ , ε , ζ , η , θ and κ were set to 2.5×10^{-8} , 10^{-5} , 0.005, 2.5, 1, 500, 0.25, 5×10^{-4} and 500 respectively, i.e. approximately the inverse of the mean value for each measurement, to factor out the differing units and magnitudes. Parameter optimisation was performed using the Nelder-Mead polytope method. For the work described here, the model was coded in TurboBASIC. A FORTRAN version is planned, which will be made available to other researchers.

After the above optimisation, and selection of $\Delta\text{N}_{\text{denitr,mean}}$, site-specific fitting was done by permitting modest variations around general parameter values, together with variations in $\Delta\text{N}_{\text{fix,pris}}$. Optimisation was performed by minimising the sum of the first four terms of the above objective function.

3.4. Parameterisation for deeper soil

For deeper soil, the model assumes that all soil C comes from the immobilisation of DOC in water percolating from the topsoil (Sections 2.3 and 2.4). Typically, there are several kg m⁻² of deeper soil C, with an output DOC flux of c. 2 g m⁻² a⁻¹, a bulk ¹⁴C content of 90-100% modern and a C:N ratio lower than that of the topsoil (see e.g. Neff and Asner, 2001; Michalzik et al., 2003; Swanston et al., 2005; Tipping et al., 2007). Some of the DOC from the topsoil can bypass the mineral soil (e.g. Fröberg et al., 2007; Tipping et al., 2012). These processes are governed in the model by three parameters, namely a first order rate constant for decomposition, a constant that partitions C released by decomposition into CO₂ and DOC, and a bypass constant for DOC and DON. Nitrogen can only be lost as DON, in proportion to the DOC flux.

3.5. Testing data for topsoils

We tested the parameterised model by its ability to predict observed ecosystem variables, with mean annual temperature and precipitation, N deposition in 2000, and vegetation type as inputs. Testing data for European forests came from the CANIF and NIPHYS projects (Schulze, 2000; Bauer et al., 2000; Harrison et al., 2000; Persson et al., 2000; Scarascia-Mugnozza et al., 2000), for which plant, soil and nitrate leaching data were available for 11 beech and conifer forests in Europe (summarised in Table S5, mapped in Figure S3). Data from the Countryside Surveys of Great Britain for 1998 (Carey et al., 2008; Emmett et al., 2010) were also used, a total of 806 soil samples with data on soil C and N pools and C:N ratios, for six natural or semi-natural vegetation types (Table S6, Figure S4).

4. RESULTS

4.1. General parameterisation for topsoils

Optimisation of the 13 parameters identified in Section 3.3 was performed with $\Delta N_{\text{fix,pris}}$ set to $0.3 \text{ g m}^{-2} \text{ a}^{-1}$, and for target values of $\Delta N_{\text{denitr,mean}}$ in the range 0.1 to $1 \text{ gN m}^{-2} \text{ a}^{-1}$. All denitrification rates in the range 0.4 to $0.7 \text{ gN m}^{-2} \text{ a}^{-1}$ gave about the same minimum value (90) of the objective function, and so we adopted $0.5 \text{ gN m}^{-2} \text{ a}^{-1}$ as a rounded target value for average denitrification. The value of $f_{\text{gr},2}$ (equations 1 and 2) was found to be small (0.01), and the parameter could be set to zero with no worsening of the fit. Therefore a value of zero was adopted for the present study. However, it may be that application of the model to sites with a wider range of MAT than considered here will require variation in f_{gr} and therefore the formulation of equations (1) and (2) is worth preserving.

Table 5 shows the parameter values obtained, Table 6 summarises the observed and simulated mean values, and Figure 3 shows plots of soil C, N, C:N and ΔN_{inorg} for individual sites. The variable giving the largest error was ΔN_{inorg} , which accounted for 52% of the total. This was followed by the soil C:N ratio (21%), soil N pool (13%), soil C pool (10%). The remaining five variables (see Section 3.3) together contributed only 4%, primarily because they are obtained from average values of variables, not summed over all sites.

The values of f_{fast} , f_{slow} and f_{passive} differ between tree and non-tree vegetation, reflecting the differences in soil ^{14}C contents summarised in Table S3. Of particular importance is the difference in f_{passive} , since although the passive C pool only receives small additions from litter each year, its slow turnover (c. 1000 years) means that it represents a large part of soil C. For the year 2000, the simulated passive pool C accounts for 36, 44, 60 and 63% of the total soil C for soils under broadleaved trees, conifers, herbs and shrubs respectively, i.e. there is substantially more passive C in soils under non-tree vegetation, while soils under broadleaved trees and conifers have relatively more carbon in the slow pool. The fast pools account for only 4–6% of SOM. The differences in the rates of entry of carbon into the slow and passive pools are also reflected in those of nitrogen, so more N is transferred into the passive pool in soils under non-tree vegetation.

The soils under the different vegetation types differ in their abilities to immobilise N, as reflected in k_{immobN} , this being about twice as efficient in soil under broadleaved trees and herbs as under conifers and shrubs. In this way, N14C accounts for observed differences in soil C:N ratios and in N_{inorg} leaching.

The fraction of time taken by the growing season was found not to depend significantly on the site MAT values (see above), and averaged 0.517, i.e. the growing and dormant seasons are nearly equal in length.

The values of f_{DOC} and f_{DON} were forced to be equal, since data on DOC and DON leaching were insufficient to distinguish the two parameters. The overall value, based on average leaching rates was 0.0274, which means that 2.74% of decomposition goes to dissolved organic forms, the remaining 97.3% leaving as CO_2 or inorganic N. The value of 0.0472 for k_{denitr} means that about 5% of cycling inorganic N is lost as gas.

The parameter $\Delta N_{\text{immob2,max}}$ causes inorganic N to be retained by the soil, and although not explicitly stated this is taken to mean NH_4^+ retention by cation-exchange. The optimised value of 1.15 gN m^{-2} corresponds to about 0.1 eq m^{-2} of NH_4^+ . This is a relatively small fraction of the total cation-exchange capacity (CEC) of typical soils; based on representative measured values of CEC per gram of dry soil (Rowell, 1994), conversion to topsoil CEC pool gives values of at least 3 eq m^{-2} . Therefore this estimated retention appears reasonable.

With regard to performance, from Table 6 we see that the model is reasonably successful at reproducing average results. However for individual sites (Figure 3 left panels) there are no significant correlations for C pools ($r^2 = 0.05$) or C:N ratios ($r^2 = 0.08$) and only weak relationships for N pools ($r^2 = 0.28$) and N_{inorg} leaching ($r^2 = 0.31$). The simulated fluxes of DOC vary from 7.3 to $13.6 \text{ g m}^{-2} \text{ a}^{-1}$, appreciably less than the observed range of 3.1 to $23.7 \text{ g m}^{-2} \text{ a}^{-1}$, and the same relative contrast is found for DON.

The model was constrained to target an overall average NPP of 75% of the maximum estimated to be possible, an average of 71% being obtained. The simulated average NPP for broadleaved trees is 75%, and all sites are estimated to be N-limited, while for conifers, the simulated average NPP is 94% of the maximum, and only for five of the 13 sites is NPP limited

by N. For herbs and shrubs, the average NPP values are 49% and 58% of the maximum respectively and all sites are calculated to be N-limited.

4.2. Site-specific parameterisation for topsoils

For site-specific fitting we used general parameter values, together with $\Delta N_{\text{fix,pris}}$, as starting points, permitting small variations ($\pm 20\%$) in f_{fast} , f_{passive} , k_{immobN} , f_{gr} , k_{denitr} , $\Delta N_{\text{immob2,max}}$, and also in $\Delta N_{\text{fix,pris}}$. Values of f_{DOC} and f_{DON} were maintained at the general values. The full objective function was not used for judging the goodness-of-fit, only errors in the site-specific values of C, N, C:N and ΔN_{inorg} . However the full objective function could still be calculated, and the optimisation reduced its value from 90 to 15.

Agreement between observed and calculated average values (Table 6) was improved for soil C, N, C:N and ΔN_{inorg} , and hardly changed for SO^{14}C , DOC and DON, neither was the average simulated denitrification rate much altered. However, agreements for individual sites were greatly improved for C, N, C:N and ΔN_{inorg} (Figure 3), with new r^2 values of 0.81, 0.96, 0.89 and 0.92 respectively. The calculated overall average contemporary NPP differed from the general value by only 1%. Six of the conifer sites are now calculated to be N-limited, but as with the general parameterisation, all non-conifer sites are N-limited.

Site-specific parameters and their distributions are provided in Table S4 and Figure S5. Individual values of k_{immobN} , f_{fast} , f_{slow} , f_{passive} and f_{gr} , and also $\Delta N_{\text{fix,pris}}$, are evenly distributed around the means, which are of course similar to the general values shown in Table 5. Average k_{denitr} and $\Delta N_{\text{immob2,max}}$ were also similar to the general means, but site-specific values clustered at both the lower and upper imposed parameter limits. Only one significant correlation between a pair of parameters was found, which was a negative relation between k_{denitr} and $\Delta N_{\text{fix,pris}}$ ($r^2 = 0.28$, $p < 0.001$). No significant trends of parameter values with MAP, MAT or soil pH were seen.

4.3. Temporal variations in C and N variables

The model fits are to contemporary observations, but the model simulates soil C and N starting with soil formation 12,000 years ago. During the period before widespread anthropogenic N deposition, i.e. before 1800, soil element pools accumulated driven by nitrogen fixation, to

reach or closely approach steady state. Figure 4 illustrates simulated changes in key variables during the period of N enrichment. The calculations were performed with the general parameter set, and with average site conditions for the whole data set, thereby comparing the general responses of ecosystems with different vegetation types.

The model calculates an overall approximate doubling of NPP due to N enrichment, with 2.7, 1.8, 2.3 and 2.1-fold increases for broadleaved trees, conifers, herbs and shrubs respectively. Consequently, soil C and soil N pools both increased, but by similar amounts, so that changes in soil C:N ratios were minor. Leaching fluxes of both DOC and DON increased because the model assumes DOC and DON production to be proportional to decomposition rates and therefore to the sizes of the soil C and N pools. Leaching of inorganic N occurred much later than the other changes, because until the mid 20th century the ecosystems were able to absorb the additional N in biomass and soil organic matter.

For all four PFTs, the vegetation in 1800 was calculated to be dominated by plant end-member 1 (high C:N ratio; Table 3), which accounted for 80-90% of the NPP. But by 2000, N enrichment had increased the fraction of end-member 2 (low C:N ratio) so that for broadleaved trees, herbs and shrubs the two end-members were about equal in their capture of NPP, while for conifers end-member 2 captured about 40% of NPP.

4.4. Inorganic nitrogen leaching

This phenomenon is one of the main indicators of N saturation, and therefore an important goal of N14C is to simulate its response to N enrichment. The observations show a general tendency of leaching to increase with N deposition, but there is considerable scatter (Figure 5, top panel). The model with general parameters predicts strong monotonic relationships (Figure 5, middle panel), with an order of leaching; conifer ~ shrub > herb > broadleaf. However, this refers to actual N inputs, i.e. using throughfall for the trees. Comparison in terms of N deposition measured in the open, with enhanced inputs due to scavenging by tree foliage, would change the order to conifer > broadleaf ~ shrub > herbs. As would be expected, the site-specific parameter adjustments caused the simulations to agree better with the observations, and to become more scattered (Figure 5, bottom panel).

Inorganic N (primarily nitrate) leaching is commonly related to soil C:N ratio using the ratio of leaching flux to N deposition (Gundersen et al., 1998; Dise et al., 1998; Lovett et al., 2002; Rowe et al., 2006). The observations for our study sites (Figure S6) show a strong relationship for broadleaved tree sites, the leaching/deposition ratio falling to near zero at and above a soil C:N of about 20. The same tendency is shown by coniferous sites but with a cut-off at C:N ratios of 30–35. The herb and shrub sites do not produce well-defined thresholds. The model produces reasonable agreement, including examples where soil C:N is low but no leaching occurs. Neither the observations nor the simulations show any dependence of the leaching / deposition ratio on mean annual temperature.

4.5. Carbon and nitrogen dynamics in deeper soil

Processes in the deeper soil are not the main focus of the present work, but a description is included for completeness. Simple parameterisation was performed assuming the same constants for all plant types, aiming to produce reasonably typical deeper soil conditions. By setting the bypass constant ($f_{\text{DOC,bypass}}$) to 0.1, the lower soil decomposition constant (k_{lower}) to 10^{-3} , and the fraction of decomposition lost by DOC leaching ($f_{\text{DOC,lower}}$) to 0.5, results in approximate agreement with observed conditions (Section 3.4) were obtained (Table 7).

4.6. Testing

The N14C model was tested with independent observations of European forest ecosystems and various UK ecosystems, by using the general parameter set of Table 5 to predict site variables from MAP, MAT, contemporary N deposition, and vegetation type. Note that MAP is rarely significant, since according to the model, it would limit the maximum NPP at only about 10% of all the sites considered in this work. Temperature is much more significant, not only by limiting maximum NPP but also as a control on process rates, via Q_{10} .

Considering data averaged by vegetation type, reasonable agreement between simulated and observed soil C and N pools, and C:N ratios are obtained (Figure 6). Overall there is a slight underestimation of soil C pools, but variations in the three variables are approximately reproduced. The model captures the differentiation of the averaged soil C:N ratios into two

groups, low values ($\sim 15 \text{ g g}^{-1}$) occurring in soils under broadleaved trees and grassland, and high values ($\sim 25 \text{ g g}^{-1}$) under conifers and shrubs.

For the 11 individual forest ecosystems in Europe studied in the NIPHYS and CANIF projects (Schulze, 2000), data on additional variables were available for testing (Table S5). Average inorganic N leaching was predicted to be greater for the 6 conifer sites than for the 5 sites with broadleaved trees, and although in both cases the predicted rates were lower than the observed ones the differences were not significant ($p > 0.05$). Predictions of average NPP were reasonable, while average biomass was underestimated by 30% for the broadleaved trees and overestimated by 50% for the conifers.

The model underestimated soil C pools measured in the GB Countryside Surveys (Emmett et al., 2010) by about 8% overall, and the soil N pools by 4%. Consequently the overall soil C:N ratio was also underestimated, by 7% (Table S6). Ranges of the observed soil variables were greater than those of the simulated ones in nearly all cases (Table S6). The model predicts negative dependences of soil C and N pools on MAT, and positive dependences on N deposition, but few significant trends emerge from the observations (Table S7); note that the input data showed no relation between MAT and N deposition. The overall averaged slopes of soil C vs MAT, soil C vs N_{dep} and soil N vs N_{dep} have the same signs for both observations and simulations. However, the observations show almost no average dependence of soil N pool on MAT whereas this is the strongest dependence predicted by the model. Note that in this exercise, Countryside Survey sites designated "bog" are assumed to fall into the shrub category of N14C. However some of them will be ombrotrophic peats with different C and N cycling properties, and this will likely cause discrepancies between observation and simulation.

5. DISCUSSION

As stated in the Introduction, we assume that vegetation type determines the turnover properties of soil organic matter, firstly through the element stoichiometry of the plants, and secondly through the different decomposition properties of plant litter derived from tree and non-tree vegetation. The former determines N demand and the N content of litter, the latter the partitioning of litter into SOM fractions with different turnover rates. Moreover, the empirical fitting results indicate that SOM under different vegetation types varies in its ability to immobilise N. Thus, at one extreme, coniferous trees have foliage low in N (Table 3), supply a lower proportion of their litter to the passive soil pool (Table 5), and produce SOM that immobilises N poorly (Table 5). At the other, herbs are richer in N, put more litter into the passive pool, and their SOM can immobilise N better. Consequently N does not build up so much in SOM under coniferous trees, while the demand for N is more easily satisfied, for a given NPP. This leads to higher soil C:N ratios, a greater propensity to reach N saturation, and a greater tendency to leach inorganic nitrogen (Figures 4 and 5). This simple picture of plant-soil interactions can provide reasonable fits of observed data, while using minimal input information to make predictions of average soil C, N, C:N ratio and other variables that agree fairly well with independent observations. The strong relationships between plants and soil C and N cycling that emerge from this empirical analysis accord with ideas summarized by Ehrenfeld et al. (2005) and Chapman et al. (2006).

5.1. Simplifications

Despite its simplicity, N14C can sensibly be parameterised to produce a clear quantitative description of the plant-soil interactions of C and N, without the need for detailed input data. This makes the model useful for understanding gross interactions among elements and processes, and offers potential for large-scale application. However it is important to recognise the simplifications and consider their possible consequences.

A major simplification, widely used in soil C and N modelling, is that the theoretical soil pools used for conceptualisation and modelling can be equated with measured values. In order to make use of data from many disparate studies, we have assumed that the topsoil receives all

fine plant litter, and is where all plant nutrient uptake occurs. But in most cases the topsoil cannot be equated with one or more recognisable soil horizons, and this can lead to inconsistencies. Notably, in studies of forest soils, detailed fieldwork usually entails sampling of soil and soil solution with the O horizon, often further subdivided, as a distinct functional unit, whereas in our approach if the O-horizon is relatively thin parts of the underlying mineral horizons are included in the topsoil. If N fertilization or some other factor caused thickening of the O-horizon, then over time topsoil properties might change in ways not accounted for by the model. But in cases where the C concentration in soil is low, and mineral matter dominates, then changes in topsoil SOM might be confined to essentially the same soil depth even if additional litter entered. These points need to be borne in mind when comparing observed and simulated soil C and N pools; arguably more weight should be attached to agreements between observed and simulated C:N ratios.

A core simplification is that soil C and N processes are not explicitly modelled in terms of microbial biomass or faunal activity. Of course, soil biota are responsible for decomposition, but their activities are quantified through simple rate expressions, rather than the passage of the elements through biomass. Our approach is consistent with Manzoni and Porporato (2009), who suggest that "simple linear decomposition functions and fewer variables describing microbial biomass may be suitable at long time scales", by which they mean yearly or longer.

In N14C, rates of decomposition of the three SOM fractions (fast, slow, passive) are fixed, and not affected by C:N ratio or N availability. Literature reviews indicate that litter decomposition rates decline with C:N ratio at a global scale (Aerts, 1997; Zhang et al., 2008), although Aerts (1997) found no evidence for such dependence if only temperate regions were considered. Berg and McClaugherty (2003) have shown that N-rich litter undergoes fast initial decomposition, but longer-term decomposition is relatively slow; however, their studies only cover a few years, much less time than is required for the long-term processes included in N14C. Hagedorn et al. (2003) reported that increased N deposition retards decomposition of older SOM, while Keeler et al. (2009) found for eight forest and grassland sites that added N had negative or no effect on litter and SOM decomposition, with no correspondence between

effects of N on enzyme activity and decomposition across sites. It is difficult to draw simple general rules from this evidence, which justifies, at least for now, our neglect of any compositional dependence of turnover rates.

Two omitted variables that are widely-recognised to affect SOM turnover, but which are currently neglected in N14C, are soil pH and moisture. We did not include these explicitly in the model as presented here in view of their relatively small variations among the 42 sites providing data for parameterisation (Table S2). But future modifications would be possible, given appropriate observations. In the case of pH, this might allow the model to be used to analyse the temporal effects of sulphur deposition and consequent acidification on soil C and N cycling (Oulehle et al., 2011). Related to soil moisture is water leaching flux which is a factor in the fluxes of N_{inorg} , DOC and DON. In the case of DOC at least, the average annual flux does not appear to depend upon water flux (Buckingham et al., 2008), rather the DOC concentration varies.

Other process simplifications include the following; neglect of the complexities of higher plants and their responses to changing N availability (Sterner and Elser, 2002); the assumption that only inorganic N is available to plants, whereas organic N appears significant in low-N systems (Schimel and Bennett, 2004); neglect of other nutrients notably phosphorus, but also trace elements; no account of inter-site variations in soil texture; no account of erosion. Neither have the effects of atmospheric ozone been considered, nor grazing, fire, parasites, diseases and management. Each of these factors could contribute to errors in the fitting, with different degrees of effect at individual sites. To incorporate some or all of them might be feasible in principle, but would require data for many more field sites, together with quantification of or assumptions about the effects. We also simplified the histories of the sites, by assuming that soil formation began 12,000 years ago at every site, and that the current vegetation type has always been present, i.e. possible land-use changes have been ignored, although possible effects could be explored with the model by imposing realistic past variations.

An aspect of historical conditions that we found to be of especial importance is $\Delta N_{fix,pris}$, the (constant) nitrogen fixation rate under "pristine" conditions, i.e. before any significant N deposition. The chosen value of $\Delta N_{fix,pris}$ exerts a strong influence on the contemporary soil N

pool and C:N ratio. The rate is doubtless more variable than we have assumed, and its variations may account for some of the unexplained differences between observations and simulations. The other side of this coin is the assumption of the overall average denitrification rate, which permits balancing of the N budget, and responds to variations in the assumed value of $\Delta N_{\text{fix,pris}}$. As noted in Section 3.1, we surveyed the literature for information on these two fluxes, but did not reach firm conclusions about the appropriate rates. Widely-representative data on contemporary denitrification rates for natural and semi-natural systems are needed to resolve this issue.

A final point is that the model as presently formulated does not apply to ombrotrophic peat, a major ecosystem of northern Europe. Peat differs from other soils due to the importance of waterlogging and the accumulation of organic matter in the anaerobic catotelm, which, from the viewpoint of the topsoil (acrotelm), acts as an additional loss process of organic matter (cf. Clymo, 1978; Jones and Gore, 1978; Heinemeyer et al., 2010). A modified version of N14C to describe peats is in progress.

Inevitably, all these simplifications must limit accuracy and precision. However, even though the simulations could be improved by incorporating additional processes and associated observational data, incomplete information about site history might ultimately determine how well contemporary observations could be captured by a model. This difficulty might limit the applicability of the kind of detailed information called for by Schmidt et al. (2011), in order to understand SOM persistence. The N14C model offers a simple means to explore the effects on prediction of possible past variations, to establish sensitivity and uncertainty.

5.2. Parameterisation and parameter values

A novel aspect of the application of N14C has been the fitting of a general parameter set from the field observations of a variety of ecosystem types. Other modelling, notably with CENTURY (Parton et al., 1987), has relied more on combining parameterisations of individual processes. The recently-introduced VSD+ (Bonten et al., 2009), like N14C aimed at describing and predicting N deposition effects, has been constructed using parameterisations of individual processes together with fitting to chronosequence data for forests. Although the general fitting

of N14C with 13 optimised parameters was moderately successful in matching observations (Table 6, Figure 3) and in making predictions on the basis of simple input data (Figures 6 and 7), small modifications of the general parameter values, or of $\Delta N_{\text{fix,pris}}$, could greatly improve the descriptions of individual sites (Figure 3, bottom panel). In applying CENTURY to a number of differing grassland sites, Parton et al. (1993) also found the need for site-specific adjustments. This suggests that ecosystems are too variable to be faithfully predicted without local adjustments, and by the same token, care should be taken in making general predictions on the basis of one or a few site studies. Further complications will arise if the site-specific adjustments compensate for incorrect assumptions about ecosystem development. An obvious way to address these issues is to parameterise and test N14C on more sites, covering fully representative ranges of soil properties, N deposition and climatic conditions, and where possible temporal variations.

The modelling does not produce strong dependences of growing season on temperature, and the overall average values are close to 0.5, i.e. plant growth occurs during half of the year. This is a reasonable overall value, but the values do not follow the temperatures of the sites. An important role of f_{gr} in the model is to balance N uptake into soil and plants, i.e. it does more than simply define growing conditions according to usual definitions (see e.g. Tivy, 1993), and in the site-specific fitting this is probably why the full allowed range ($\pm 20\%$) of the values are used.

Control of DOC and DON fluxes within N14C depends upon the parameters f_{DOC} and f_{DON} , which were forced to be equal in this exercise. This produces the correct average fluxes, but does not explain differences among sites. This might partly be due to the considerable interannual variability in actual fluxes, dependent upon water flux (Buckingham et al., 2008), which would produce differences among sites if only short monitoring periods are involved (which applies to the sites here). This aspect of the model could also be developed using DO^{14}C data, as in the more detailed DyDOC model (Michalzik et al., 2003; Tipping et al., 2007; 2012).

In most studies with soil radiocarbon, steady state is assumed in order to estimate approximate turnover rates (e.g. Harkness et al., 1986; Baisden et al., 2012), i.e. to relate changes in ^{14}C inputs in litter to observed soil ^{14}C . The N14C model provides a means to

escape this constraint, by permitting more realistic site histories to be used, particularly of course with respect to N enrichment and the consequent changes in productivity and litter inputs. Use of the model with simple site characterisation data (MAT, MAP, N deposition, vegetation type) might in the future be a useful means of improving radiocarbon-based turnover estimates in general, and thereby explaining observed variations in soil ^{14}C contents.

5.3. Model outputs

The N14C produces many outputs covering long time periods, detailed reporting of which is beyond the scope of the present paper. Instead, we confine this discussion to the major outputs directly related to anthropogenic N enrichment.

The approximately two-fold increases in NPP simulated as a result of enrichment by nitrogen deposition (Section 4.3) are of the same order as found by Throop et al. (2004) in applications of CENTURY to a herbaceous ecosystem, and by Pepper et al. (2005) who applied the G'DAY & DAYCENT models to several ecosystems. The modelling results are supported by long-term increases in forest C storage observed for Europe (Spiecker et al., 1996) and North America (Thomas et al., 2010). In some cases, other factors, notably soil acidification, might restrict the nutrient response of N (e.g. Bedison and McNeil, 2009), but these are not yet represented in N14C.

The calculated increases in NPP arise because the systems were N-limited before anthropogenic influence, and we find that most are still N-limited, the exceptions being almost all among the conifer sites. The model correctly identifies two of the conifer sites, Flakaliden and Strasan, to be N-limited; in both cases this has been demonstrated through fertilisation experiments (Hyvönen et al., 2008). It also finds that the Klosterhede conifer site is N-saturated, in agreement with the results of Gundersen (1998). The Ruabon shrub site is modelled to be N-limited, in accord with Pilkington et al. (2005). More generally, N limitation is apparently widespread, in accord with the conclusions of the review by LeBauer and Treseder (2008) of world-wide N addition experiments, supported specifically for grassland ecosystems by Lee et al. (2010). Most of the N. European sites included in the LeBauer and Treseder (2008) review were N-limited, the only exceptions being two (out of 11) conifer sites.

Time-series observations are not available to test the model's simulations showing temporal increases in soil C and N as a result of the increased NPP (Section 4.3, Figure 4), but this issue can be addressed by space-for-time substitution, taking advantage of the range of N deposition rates at field sites sampled in the GB Countryside Surveys (Emmett et al., 2010). According to N14C, soil C and N pools should show positive dependences on annual N deposition, with average gradients of $1.1 \text{ kgC (g N}_{\text{dep}})^{-1}$ and $60 \text{ gN (g N}_{\text{dep}})^{-1}$, respectively about four times and twice the observed average values (Table S7). The discrepancy could of course reflect inaccuracy in the model formulation, but NPP-controlling factors other than N could also explain the differences. A noteworthy outcome of N14C application to the Countryside Surveys data is that both soil C and N pools are predicted to decline with MAT, owing to the temperature dependence ($Q_{10} = 2$) of decomposition and denitrification reactions. Such dependences are not seen in the observations (Table S7), which suggests that the assumed Q_{10} value may be too high. In the case of denitrification, a major loss process for soil N in N14C, this possibility, and wider uncertainties about rates in natural and semi-natural ecosystems (Section 3.1), mean that systematic field surveys are urgently required.

Leaching of inorganic N (section 4.4), simulated with the general parameter set, is in reasonable agreement with observations. In terms of differences among soils under different vegetation types, the results agree with the findings of Rowe et al. (2006) for UK ecosystems. The model predicts that leaching increases with N in throughfall, in agreement with the finding of Dise et al. (2009) from their analysis of large European forest datasets that N input was the most significant driver of nitrate leaching. We also found that N_{inorg} leaching is inversely related to soil C:N ratio, in agreement with the Dise et al. (2009) study. However, we conclude that soils under conifers leach inorganic N more readily than those under broadleaved trees, whereas Dise et al. (2009) did not find a difference. Rothe et al. (2002) compared leaching at co-located spruce and beech sites, and reported that the ratio of N_{inorg} leaching to N input was greater under spruce, although inputs were greater because of more efficient scavenging of N in rain. If the leaching response is assumed linear with respect to inputs, these findings agree with N14C outputs (Figure 5). Dise et al. (2009) found a significant negative influence of temperature on N leaching in forests, but neither the observations nor the simulations for our (relatively few) study sites showed any significant effect. Only small

temperature effects were simulated by the model for the four plant types under idealised conditions, differing only in MAT.

The model assumes that vegetation C:N ratios will fall as a result of N enrichment, and forces a relationship between N demand and N availability (equation 4). Therefore it is no surprise that the simulations show vegetation to be enriched in N (Section 4.3). Field evidence for such enrichment due to N deposition comes from (a) measurements of the foliar N contents of individual species (Baddeley et al., 1994; Hicks et al., 2000; Pitcairn et al., 2001, 2006), and (b) shifts towards plant species associated with high N availability (reviewed by Emmett, 2007). The effect is not tested quantitatively in the present work, but there is scope to use observational data, collected for different N deposition rates, to parameterise this part of the model, with space-for-time substitution. Coupling vegetation C:N ratios with measurements of NPP would be especially useful as a means of constraining the N14C parameters.

6. CONCLUSIONS

- (a) The N14C model, which is based on the idea that plant functional type is the major control on soil C and N cycling and takes the long term development of soil C and N pools into account, can be parameterised for four plant functional types (PFTs), to obtain a general set of 13 parameters for tree, herb and shrub natural or semi-natural ecosystems of northern Europe. The general version of the model accounts approximately for soil C, N, C:N, inorganic and organic N leaching, and DOC leaching.
- (b) Key outcomes of the parameter optimisation are PFT-specific rate constants for the immobilisation of N by soil, and differences between trees and non-trees in the supply of litter to soil pools with different turnover rates. In particular, small differences between PFTs in incorporation rates into the passive pool result in substantial differences in mean C residence time.
- (c) Agreements between observations and simulations can be much improved by modest site-specific parameter adjustments, which suggests considerable heterogeneity in ecosystem characteristics, and that faithful simulation and prediction on the basis of results for relatively few sites should not be expected.
- (d) According to model simulations, N deposition has increased NPP by about two-fold since 1800 and this has led to increases in soil C and N pools and the leaching of dissolved organic C and N. Leaching of inorganic N has occurred where the capacity of ecosystems to retain N in biomass or in soil has been exceeded. Most of the study sites are, however, still N-limited with respect to biomass growth. The highest rates of inorganic N leaching are found for N-saturated conifer ecosystems.
- (e) The model can be used to predict plant-soil C and N dynamics using only MAP, MAT, contemporary N deposition, and PFT as inputs. This approach is supported by the reasonable agreement between its simulations and observations of C and N in European forests and British semi-natural ecosystems.

Acknowledgements

This work was funded by the UK Department for Environment Food and Rural Affairs (Defra) and the Natural Environment research Council as part of the “Terrestrial Umbrella” (TU) and Critical Loads Dynamic Modelling II (CLDMII) projects (Contract Numbers AQ0802 and AQ0801). Thanks are due to P Gundersen (University of Copenhagen) and N Dise for the provision of field data (ECOFEE and IFEF datasets). We are grateful to PJ Coleman (Defra), TU and CLDMII participants, the Joint Expert Group on Dynamic Modelling (United Nations Economic Commission for Europe, Convention on Long-range Transboundary Air Pollution, Working Group on Effects), and two anonymous referees for constructive criticism.

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Table 1 Glossary of variables

<i>Term</i>	description	units
C_{coarse}	coarse litter C pool	g m^{-2}
C_{lower}	C pool in the lower soil	g m^{-2}
ΔC_{coarse}	loss of C from coarse litter	g m^{-2}
C_j	soil C pools (fast, slow, passive)	g m^{-2}
ΔC_j	loss of C from soil SOM pools (fast, slow, passive)	g m^{-2}
ΔDOC	output of DOC from soil SOM pools	g m^{-2}
ΔDON	output of DON from soil SOM pools	g m^{-2}
f_{gr}	growth period, fraction of year	-
f_k	variable equal to f_{gr} or $(1 - f_{\text{gr}})$ in equation (7)	-
$f_{\text{NPP},i}$	fraction of NPP to plant i (1 or 2)	-
MAP	mean annual precipitation	mm
MAT	mean annual temperature	$^{\circ}\text{C}$
N_j	soil N pools (fast, slow, passive)	g m^{-2}
ΔN_j	loss of N from soil SOM pools	g m^{-2}
ΔN_{avail}	plant-available N	g m^{-2}
$\Delta N_{\text{demand},i}$	demand for N by plant i (1 or 2)	g m^{-2}
ΔN_{dep}	N input from deposition	g m^{-2}
ΔN_{excess}	inorganic N remaining after plant growth	g m^{-2}
ΔN_{fix}	N input from fixation	g m^{-2}
ΔN_{gas}	N lost by denitrification	g m^{-2}
ΔN_{immob}	N taken up into SOM	g m^{-2}
$\Delta N_{\text{immob}2}$	N taken up into fast SOM by sorption	g m^{-2}
ΔN_{inorg}	inorganic N leached	g m^{-2}
ΔN_{plant}	N taken up into biomass	g m^{-2}
$\Delta N_{\text{retained}}$	nutrient N retained at litter fall	g m^{-2}
NPP_{max}	maximum annual net primary production	g m^{-2}
$\text{NPP}_{\text{pot},i}$	potential annual net primary production of plant i (1 or 2)	g m^{-2}
ΔT_{SW}	mean summer temperature minus mean winter temperature	$^{\circ}\text{C}$

Table 2 Glossary of parameters

Symbol	Description	Units
$f_{\text{coarse},i}$	fraction of NPP carbon entering coarse part of plant i (1 or 2)	-
$f_{\text{coarse,litter}}$	annual fraction of coarse biomass converted to litter	-
f_{DOC}	fractional release of DOC in decomposition	-
$f_{\text{DOC,bypass}}$	fraction of DOC from topsoil bypassing the deeper soil	-
$f_{\text{DOC,lower}}$	fractional release of DOC in decomposition, lower soil	-
f_{DON}	fractional release of DON in decomposition	-
f_{fast}	fraction of litter entering the fast SOM pool	-
f_{slow}	fraction of litter entering the slow SOM pool	-
f_{passive}	fraction of litter entering the passive SOM pool	-
$f_{\text{N,bypass}}$	fraction of N deposition bypassing the topsoil	-
$f_{\text{Nretained}}$	fraction of biomass N retained at litterfall	-
f_{fine}	fraction of NPP carbon entering fine part of plant	-
$f_{\text{fine,litter}}$	fraction of fine biomass converted to litter, per dormant or growth period	-
$f_{\text{gr},1}$	constant defining f_{gr} (equations 1 and 2)	-
$f_{\text{gr},2}$	constant defining f_{gr} (equations 1 and 2)	-
$k_{\text{C,coarse}}$	rate constant for loss of C from coarse litter	a^{-1}
k_{denitr}	rate constant for denitrification	a^{-1}
k_j	rate constant for C and N release from SOM pool j (fast, slow or passive)	a^{-1}
k_{immobN}	rate constant for N uptake by SOM	$\text{g m}^{-2} \text{a}^{-1}$
k_{lower}	rate constant for C release from lower SOM	a^{-1}
k_{P1P2}	parameter relating growth of plants 1 and 2 to ΔN_{avail} (equation 4)	$\text{m}^2 \text{g}^{-1}$
$\Delta N_{\text{immob2,max}}$	maximum secondary immobilisation of N	g m^{-2}
$\Delta N_{\text{fix,pris}}$	annual N fixation rate before anthropogenic N deposition	g m^{-2}
Q_{10}	factor describing rate response to temperature	-
T_{gr}	temperature defining f_{gr} (equations 1 and 2)	-

Table 3. Plant functional type properties used in the model. See Table S1 for the sources of information for these assignments. C:N ratios are in g g^{-1} .

	broadleaf	conifer	herb	shrub
C:N coarse	250	250	-	-
C:N fine low nutrient	42	63	35	49
C:N fine high nutrient	30	50	24	35
f_{coarse}	0.35	0.45	0.00	0.00
f_{fine}	0.65	0.55	1.00	1.00
$f_{\text{coarse,litter}}$	0.004	0.005	-	-
$f_{\text{fine,litter}}$	0.1	0.1	0.3	0.1
$f_{\text{Nretained}}$ low nutrient	0.30	0.19	0.32	0.29
high nutrient	0.36	0.25	0.38	0.35

Table 4. Summary of plot data (medians and ranges) used for parameterisation. See Table S2 for information about individual sites.

	units	Broadleaf	Conifer	Herbs	Shrubs
<i>n</i>		8	13	10	11
MAT	°C	9.9 8.2 - 11.0	7.8 2.1 - 9.6	7.0 5.3 - 8.5	7.4 4.7 - 10.1
MAP	mm a ⁻¹	1250 610 - 2230	860 580 - 1400	2280 1230 - 3650	1200 760 - 2300
N deposition	g m ⁻² a ⁻¹	2.8 1.1 - 3.6	2.1 0.2 - 4.7	2.3 1.6 - 3.5	1.6 0.9 - 2.8
topsoil depth	cm	26 14 - 30	30 12 - 30	12 8 - 37	17 10 - 22
topsoil C pool	kg m ⁻²	6.9 5.0 - 11.0	7.3 2.2 - 11.7	7.2 5.3 - 13.4	8.2 3.4 - 12.2
topsoil N pool	g m ⁻²	380 260 - 770	270 70 - 500	460 200 - 760	270 140 - 820
topsoil C:N	g g ⁻¹	19 13 - 25	30 17 - 35	18 12 - 28	23 12 - 48
N _{inorg} leaching	g m ⁻² a ⁻¹	0.3 0.1 - 1.3	0.6 0.0 - 3.2	0.6 0.0 - 1.2	0.1 0.0 - 1.2
DOC leaching ^a	g m ⁻² a ⁻¹	9.9 3.1 - 13.7	9.7 9.7	8.5 3.6 - 11.3	8.8 4.1 - 23.7
DON leaching ^a	g m ⁻² a ⁻¹	- -	0.17 0.06 - 0.28	0.29 0.14 - 0.46	0.43 0.11 - 0.60
NPP _{max} ^b	g m ⁻² a ⁻¹	476 715-849	413 491-789	389 613-743	401 590-810

^a incomplete data

^b calculated (see Figure S1)

Table 5. Values of optimised parameters.

	broadleaf	conifer	herbs	shrubs
f_{fast}	0.471			0.614
$f_{\text{slow}}^{\text{a}}$	0.515			0.360
f_{passive}	0.014			0.026
k_{immobN}	2.25×10^{-4}	9.18×10^{-5}	1.79×10^{-4}	8.20×10^{-5}
$f_{\text{gr},1}$		0.517		
$f_{\text{gr},2}$		0.0		
$f_{\text{DOC}} f_{\text{DON}}$		0.0274		
k_{denitr}		0.0472		
$\Delta N_{\text{immob2,max}}$		1.15		

^a obtained by difference; $f_{\text{slow}} = 1 - f_{\text{fast}} - f_{\text{passive}}$

Table 6. Summary of observed or assumed and simulated NPP and soil variables. Simulated values obtained with the general parameter set of Table 5 are denoted by "sim1", those with site-specific parameters by "sim2".

		Broad			Conifer			Herbs			Shrubs		
		obs	sim1	sim2	obs	sim1	sim2	obs	sim1	sim2	obs	sim1	sim2
NPP ^a	gC m ⁻²		595	604		649	624		333	347		404	391
soil C	kg m ⁻²	7.49	6.02	6.71	6.98	7.60	7.26	8.32	7.87	8.23	8.08	9.82	9.03
soil N	g m ⁻²	416	372	396	276	261	282	474	585	477	362	415	390
soil CN	g g ⁻¹	18.5	16.5	17.6	27.0	29.7	27.1	18.6	14.1	18.5	25.8	24.6	26.5
ΔN_{inorg}	g m ⁻²	0.49	0.25	0.41	1.09	0.91	0.98	0.53	0.57	0.57	0.32	0.59	0.43
soil ¹⁴ C	% mod	110	111	111	110	109	108	100	101	101	100	101	102
DOC flux ^b	g m ⁻² a ⁻¹	9.1	10.6	11.3	9.7	8.7	8.8	7.7	9.0	9.2	10.4	11.1	10.4
DON flux ^c	g m ⁻² a ⁻¹	-	-	-	0.17	0.22	0.21	0.30	0.30	0.30	0.39	0.27	0.27
denitrification	g m ⁻² a ⁻¹	-	0.65	0.62	-	0.51	0.48	-	0.49	0.54	-	0.45	0.52

^a NPP overall mean target is 526 gC m⁻² a⁻¹ (Section 3.3), overall weighted means are 499 gC m⁻² a⁻¹ (sim1) and 499 gC m⁻² a⁻¹ (sim2).

^b numbers of samples are 5 (B), 1 (C), 7 (H), 10 (S)

^c numbers of samples are 0 (B), 2 (C), 6 (H), 5 (S)

Table 7. Simulated soil pools, fluxes and radiocarbon in deeper soil, calculated with the parameters given in Section 4.5, for the average conditions (MAP, MAT, N deposition) of the four different vegetation types.

		SOC kg m ⁻²	SON g m ⁻²	C:N g g ⁻¹	DOC g m ⁻² a ⁻¹	DON g m ⁻² a ⁻¹	SO ¹⁴ C % mod	DO ¹⁴ C % mod
Broadleaf	1800	2.43	184	13.2	1.6	0.10	92	94
	2000	2.70	194	13.9	2.3	0.12	96	104
Conifer	1800	3.74	185	20.2	2.4	0.10	91	93
	2000	4.07	194	20.9	3.0	0.12	94	101
Herbs	1800	2.77	209	13.3	1.8	0.12	91	93
	2000	3.07	220	13.9	2.5	0.14	94	102
Shrub	1800	3.67	212	17.4	2.4	0.12	91	93
	2000	4.05	222	18.2	3.2	0.14	94	102

FIGURE CAPTIONS

Figure 1. Schematic of the N14C model.

Figure 2. Pattern of nitrogen deposition derived from data given by Schopp et al. (2003).

Figure 3. Simulated vs. observed soil C and N variables for the four plant functional types; B broadleaved trees, C conifers, H herbs, S shrubs. Left panels, general parameter set; right panels site-specific data set.

Figure 4. Simulated NPP and topsoil changes over time. For each of the four plant functional types (B, C, H, S; see legend to Figure 3), the calculations were performed for the same MAP and MAT, and for equal amounts of input N, i.e. no account is taken of additional scavenging of N by trees. The dotted and full lines are used only for contrast, and therefore vary among panels. The ^{14}C plots for B and C, and H and S, are nearly coincident so only results for B and H are shown.

Figure 5. Observed and simulated contemporary variations of inorganic N leaching with N deposition (throughfall for B and C).

Figure 6. Model testing by comparison of predicted and observed average topsoil C and N pools and C:N ratios (see Section 4.6). NI-CA: data from the NIPHYS and CANIF projects, CS: GB Countryside Surveys (separate points for 1998 and 2007). Figures in parentheses indicate the number of data contributing to the average values. 1:1 lines are shown.

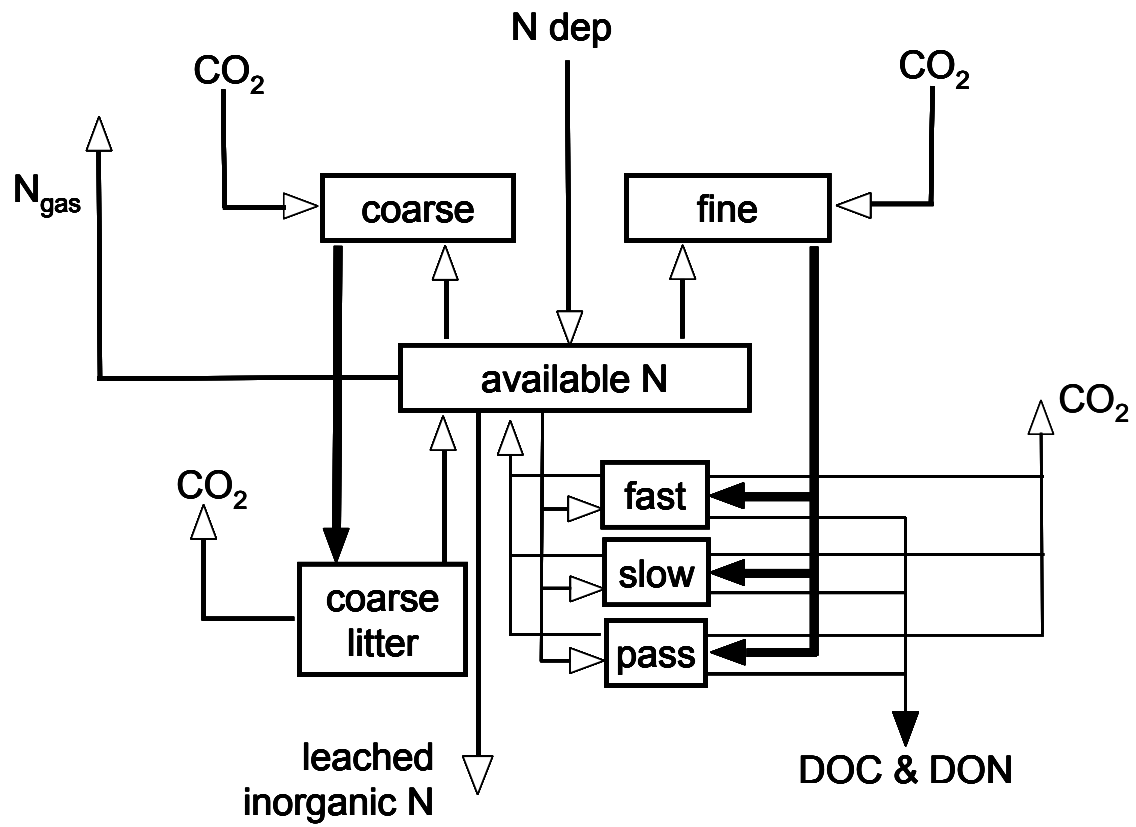


Figure 1.

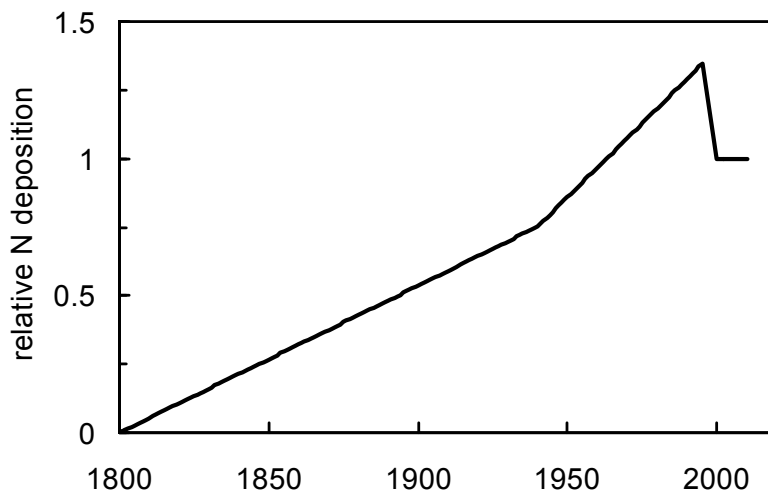


Figure 2.

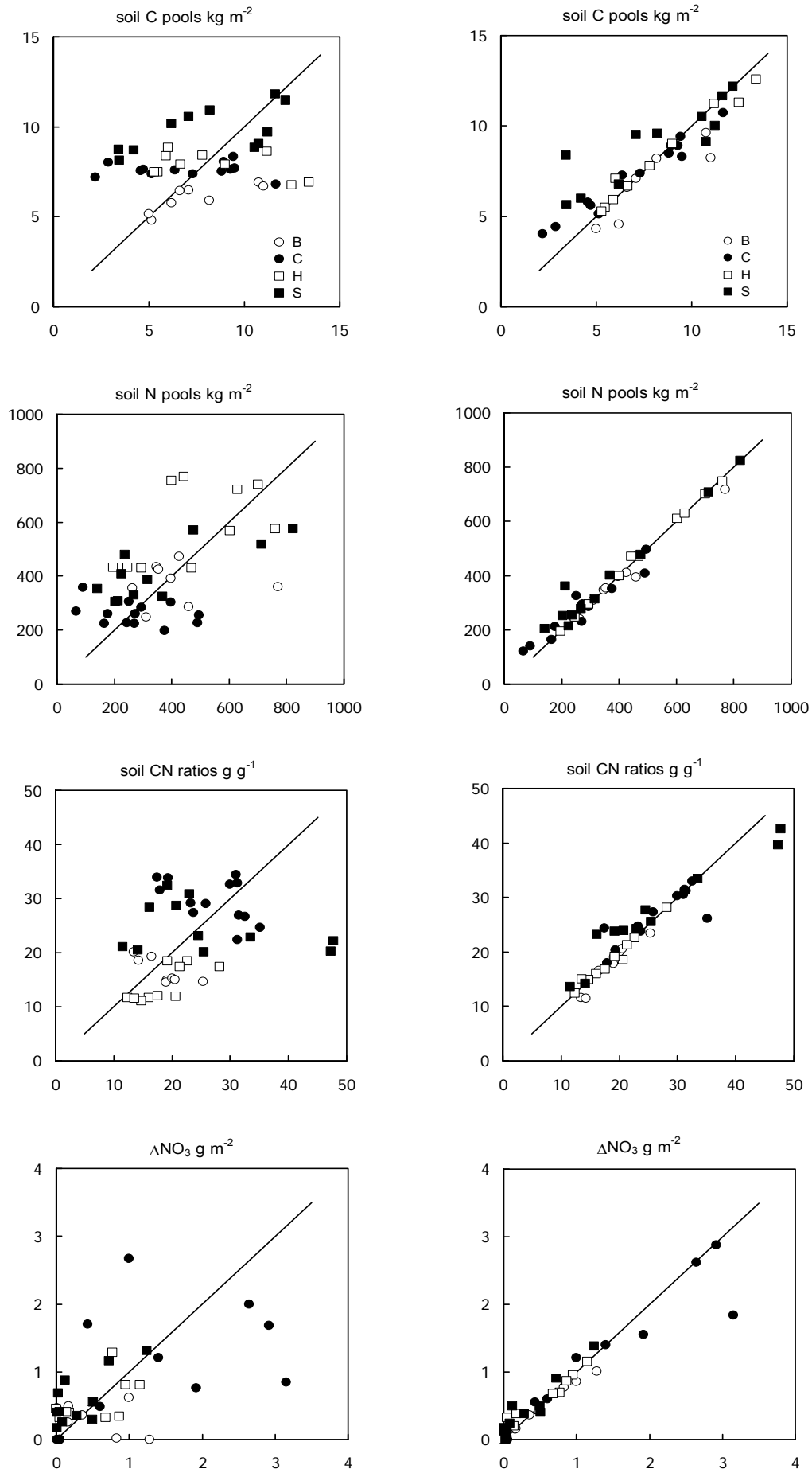


Figure 3.

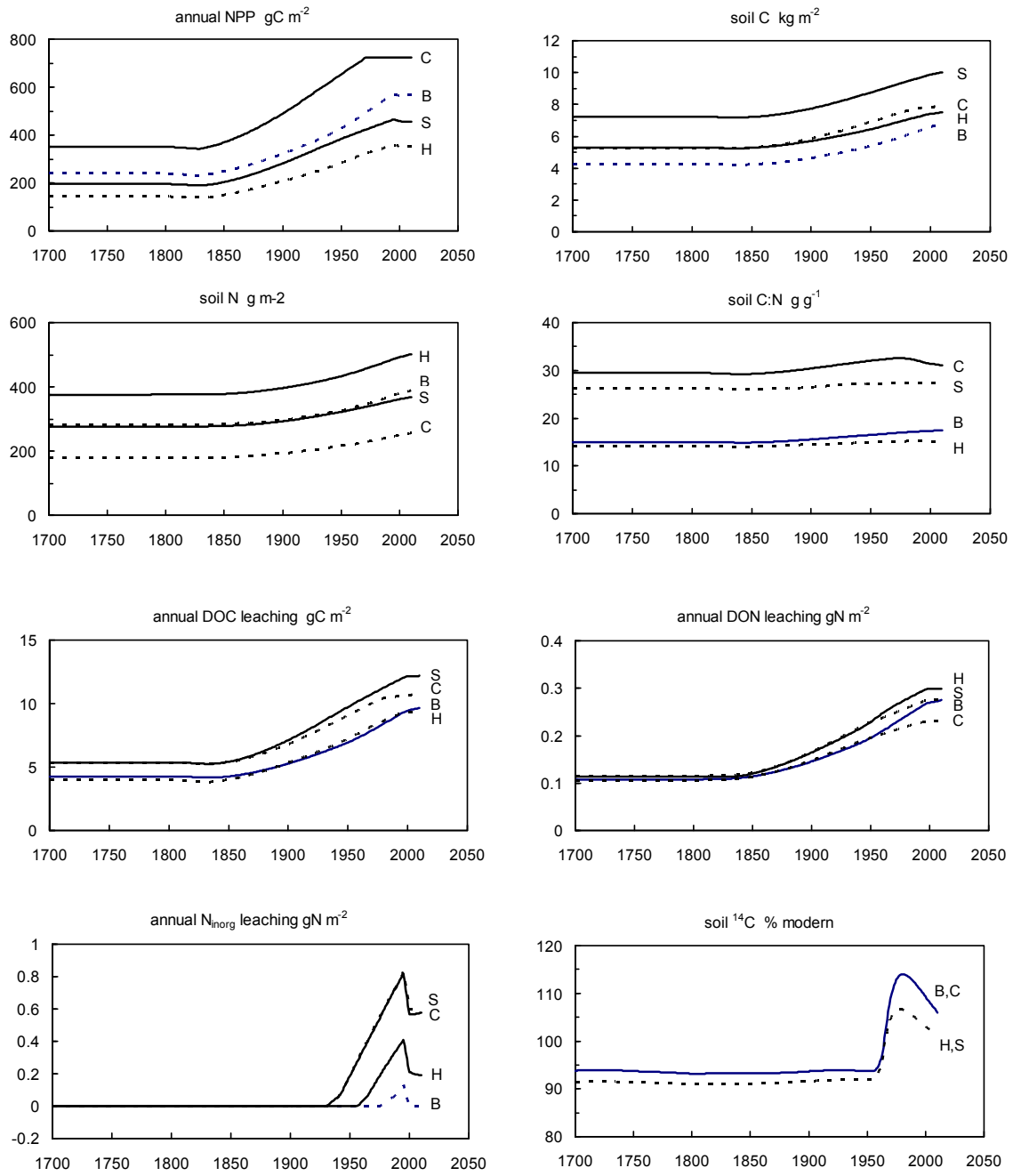


Figure 4.

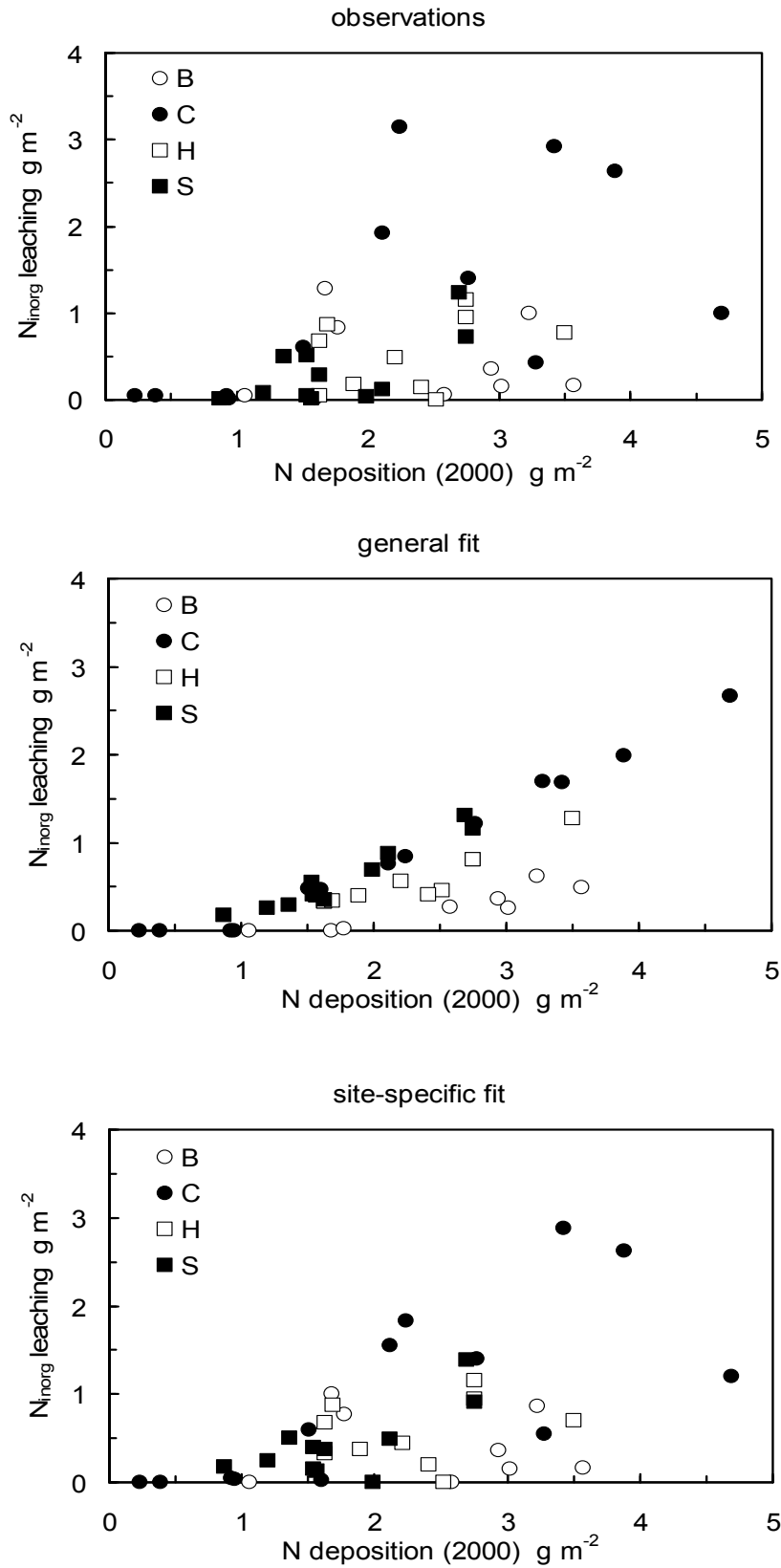


Figure 5.

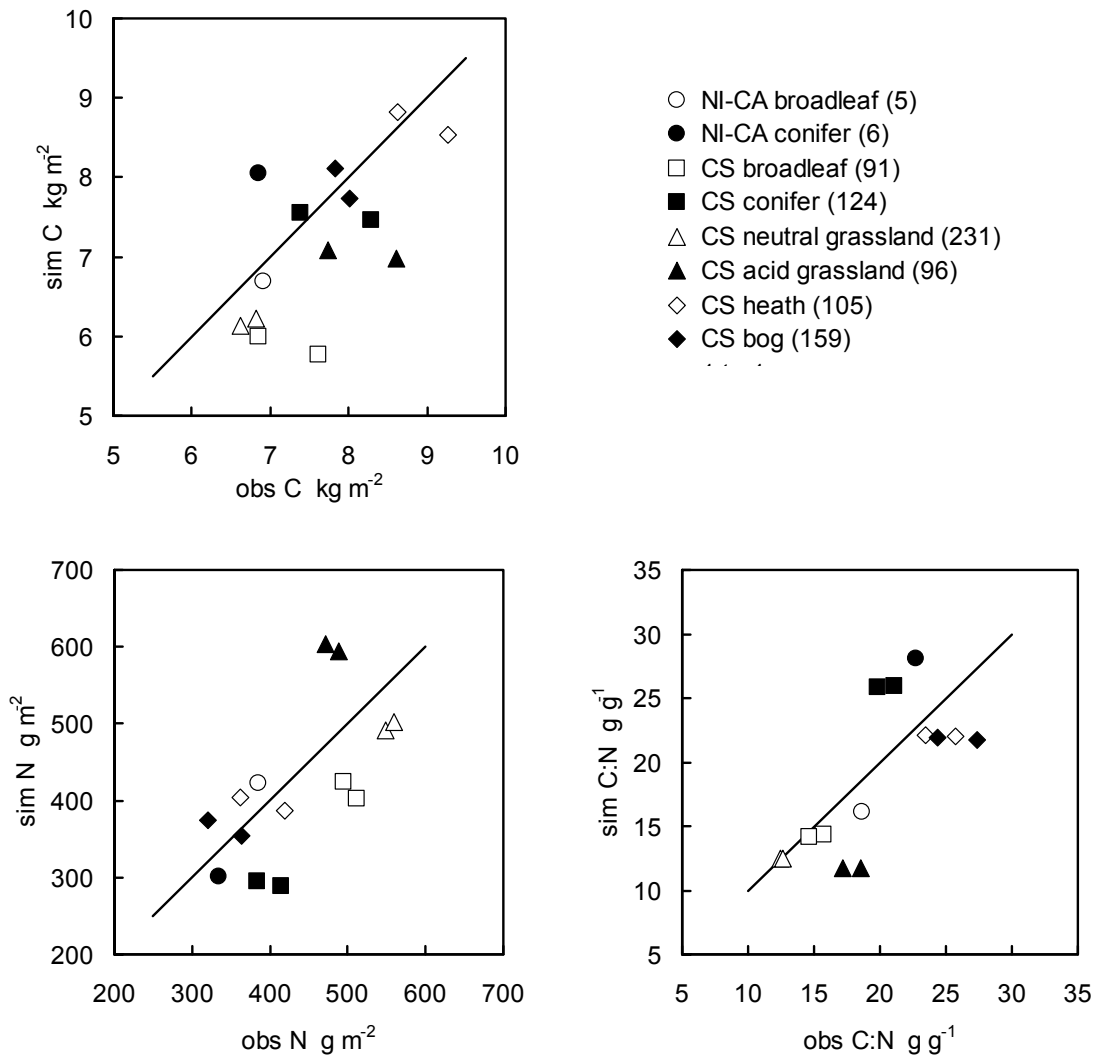


Figure 6.