Modelling impacts of atmospheric deposition and temperature on long-term DOC trends

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The MADOC model description

MADOC (Rowe et al., 2014) was developed to simulate long-term changes of elements of carbon and nitrogen cycling, soil acidity and their impact on plant productivity on the annual-time step basis. The model was built by integrating three existing process-based models of soil and vegetation dynamics: N14C (Tipping et al., 2012), VSD (Posch and Reinds, 2009) and DyDOC (Michalzik et al., 2003) for simulating dynamics in one-dimensional soil and vegetation column (Figure S1). Here the general principles of modelling approach are described. The three models the MADOC was built on represent key processes the DOC undergoes: production, mobility and transport.

N14C (Tipping et al., 2012) simulates C and N dynamics assuming that vegetation type determines the turnover properties of SOM through the basic balance of the plants-soil interaction dependent on forest/no forest habitat. The changes are essentially driven by N deposition. Current pools and fluxes depend upon NPP, long-term N fixation and more recent N enrichment by anthropogenic deposition. The N14C simulates annual plant growth and turnover and soil C and N cycling starting with the soil formation. The turnover of the pools is split between quantity to be mineralized and a proportion becoming potentially dissolved organic matter (PDOM) and the leaching of DOC and DON are predicted.

The VSD model (Posch and Reinds, 2009) was designed to simulate acidification and recovery via computation of critical loads for S and N. Critical loads as steady-state quantities define upper limits for S and N deposition that do not have ‘harmful effects’ on specified ecosystems. They are calculated with simple mass balance equations that assume that soil processes are in equilibrium with deposition (UBA, 2004). Simulated soil solution chemistry depend on deposition input, nutrient uptake, net immobilization, denitrification and geochemical interaction in soil described by equations defining competition among cations for exchange sites and thus the partitioning of ions between the solution and adsorbed phases.

DyDOC model (Michalzik et al., 2003) simulates carbon formation, retention and transport in three-horizon profile. Humic substances are divided into three pools, one of which is immobile, while the other two (hydrophilic and hydrophobic) can pass into solution as DOC. Processes described in DyDOC are driven by inputs of substrate (litter), water and temperature. In MADOC, DyDOC component has been simplified by removing the hydrological detail.

Inputs and outputs circulating among component models are shown in Figure S2. MADOC is capable of simulating processes in both top- and subsoil (organic and mineral horizon). In MADOC, a pool of PDOM is calculated as annual changes in C and N stocks determined from input fluxes together with mineralization and leaching (Equation S1 and S2):

$$\Delta C_{pd} = k_{inpdC} T_C - k_{minpd} C_{pd} - W_d \times c_{DOC}$$

(eq.S1)

$$\Delta N_{pd} = k_{inpdN} T_N - k_{minpd} N_{pd} - W_d \times c_{DON} \tag{eq.S2}$$

where:
C_{pd}, N_{pd} - single pools of potentially dissolved C and N [g m^{-2}],
T_C, T_N - net annual turnovers of C and N [g m^{-2} yr^{-1}] (as in N14C),
k_{inpdC}, k_{inpdN} - proportions of C and N turnovers entering the potentially-dissolved pools,
k_{minpd} - rate constant for annual mineralization of both C_{pd} and N_{pd} pools,
W_d - water drainage flux [g m^{-2} yr^{-1}]
c_{DOC}, c_{DON} - concentrations in the soil water [g g^{-1}].

c_{DOC} and c_{DON} are calculated from the stocks of potentially-dissolved C and N, assuming that in the absence of soil the whole stock would be dissolved, resulting in a concentration determined by water mass. Soil decreases this concentration according to soil mass and a pH-dependent coefficient determining partitioning between solid and solution phases (Equations S3 and S4):

$$c_{DOC} = \frac{C_{pd}}{(k_D \times M_S) + M_w} \tag{eq.S3}$$

$$c_{DON} = \frac{N_{pd}}{(k_D \times M_S) + M_w} \tag{eq.S4}$$

where:
M_w – water mass [g m^{-2}], constituting both annual average soil water content and annual drainage flux,
M_s – soil mass [g m^{-2}],
k_D – partitioning coefficient.

MADOC allows to simulate through the soil profile (i.e. processes occurring in both organic and mineral horizons), so k_D is calculated as the average coefficient for organic and mineral horizon, weighted by their thickness (Equation S5):

$$k_D = \frac{k_{Dorg} \times L_{org} + k_{Dmin} \times L_{min}}{L_{org} + L_{min}} \tag{eq.S5}$$

where:
k_{Dorg}, k_{Dmin} - partitioning coefficients for organic and mineral soil,
L_{org} and L_{min} are the thicknesses in m of the organic and mineral horizons.

The partitioning coefficients were conditional on soil water H^+ activity, and were calculated for organic and mineral horizons using different values for a partition constant (Equations S6 and S7).

$$k_{Dorg} = \alpha_{org} \times a_{H^+} \tag{eq.S6}$$

$$k_{Dmin} = \alpha_{min} \times a_{H^+} \tag{eq.S7}$$

where:

k_{Dorg}, k_{Dmin} - partitioning coefficients for organic and mineral horizon,

α_{org}, α_{min} - partition constants [$m^3\ g^{-1}\ L\ mol^{-1}$] for organic and mineral horizon,

$a_H{}^+$ - soil water H^+ activity [$mol\ L^{-1}$] (assumed to be the same for organic and mineral upper layers).

MADOC was primarily designed to tackle N and S deposition influence on ecosystems. The original N14C model calculates a flux of dissolved organic matter (DOM), which in MADOC was assumed to enter a PDOM pool as described above. The VSD model governs ion exchange dynamics dependent on the supply of N, deposition rates of S and other elements, and DOC concentration and flux as calculated by DyDOC. A constant proportion, P_{sites}, of the DOC was assumed to be able to form acid anions, i.e. a fixed value for dissociation site density. The value of pH influenced DOC dissolution in the DyDOC model. The MADOC model now uses a two-step integration method to prevent oscillations caused by the interaction between pH and DOC concentration (Rowe et al., in prep.).

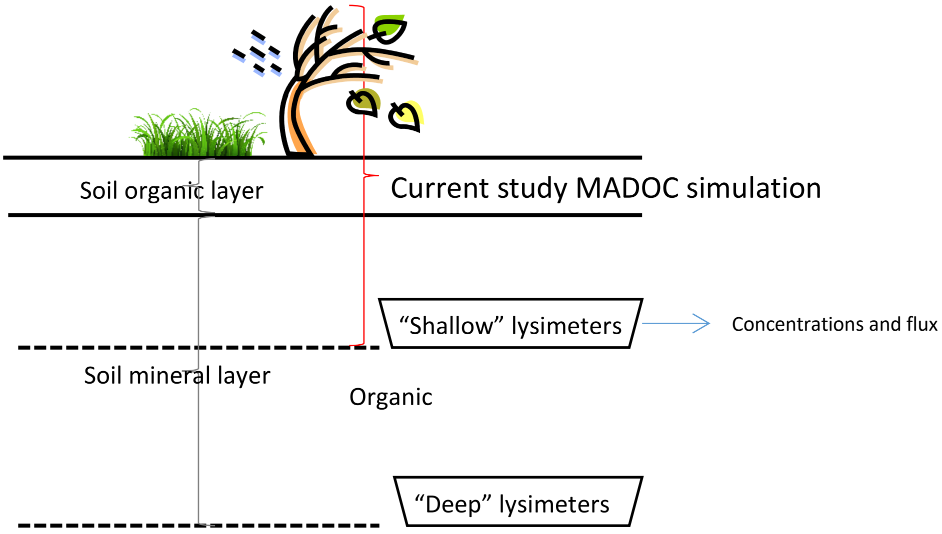

Figure S1 Diagram of soil layer simulated by MADOC in the current study.

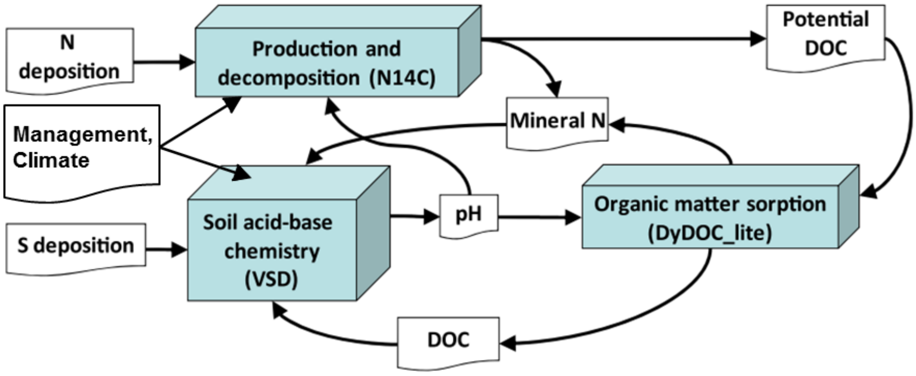

Figure S2 Model of Acidity Dynamics and Organic Carbon (MADOC): structure in terms of component models (N14C, VSD and DyDOC) and quantities passed among these. Modified from Rowe et al. (2014).

The FRAME model description

The FRAME Atmospheric Transport Model (Dore et al., 2009) has been developed as a flexible multiple scale tool. The model can be applied to estimate the concentration and deposition of sulphur and nitrogen compounds at resolutions of 1 km and 5 km over the UK and at 50 km resolution over the EMEP European domain.

The domain of the model covers the British Isles with a grid resolution of 5 km and grid dimensions of 172 x 244. Input gas and aerosol concentrations at the edge of the model domain are calculated using FRAME-EUROPE, a larger scale European simulation which was developed from TERN to run a statistical model over the entirety of Europe with a 150 km scale resolution. FRAME is a Lagrangian model that simulates an air column moving along straight-line trajectories. The atmosphere is divided into 33 separate layers extending from the ground to an altitude of 2500 m. Layer thicknesses vary from 1 m at the surface to 100 m at the top of domain. Separate trajectories are run at a 1^{o} resolution for all grid edge points. A year-specific wind rose is used to give the appropriate weighting to directional deposition and concentration for calculation of total deposition and average concentration (Dore et al., 2009).

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