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# Environmental Pollution

# Predicting nitrogen and acidity effects on long-term dynamics of dissolved organic matter

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## ARTICLE INFO

## ABSTRACT

Increases in dissolved organic carbon (DOC) fluxes may relate to changes in sulphur and nitrogen pollution. We integrated existing models of vegetation growth and soil organic matter turnover, acid–base dynamics, and organic matter mobility, to form the 'MADOC' model. After calibrating parameters governing interactions between pH and DOC dissolution using control treatments on two field experiments, MADOC reproduced responses of pH and DOC to additions of acidifying and alkalising solutions. Long-term trends in a range of acid waters were also reproduced. The model suggests that the sustained nature of observed DOC increases can best be explained by a continuously replenishing potentially-dissolved carbon pool, rather than dissolution of a large accumulated store. The simulations informed the development of hypotheses that: DOC increase is related to plant productivity increase as well as to pH change; DOC increases due to nitrogen pollution will become evident, and be sustained, after soil pH has stabilised.

## 1. Introduction

Observed increases in dissolved organic carbon (DOC) concentration in many north-temperate surface waters (Evans et al., 2005; Findlay, 2005; Oulehle and Hruska, 2009) may indicate changes in soil carbon storage (Freeman et al., 2001), and give rise to increased water treatment costs (Chow et al., 2003). These increases have been attributed to various factors (Clark et al., 2010), such as pH increase (Reynolds et al., 2013) resulting mainly from a decline in sulphur (S) pollution (De Wit et al., 2007; Evans et al., 2006, 2008a; Haaland et al., 2010; Monteith et al., 2007; SanClements et al., 2012); climate change (Freeman et al., 2001); nitrogen enrichment (Bragazza et al., 2006; Findlay, 2005; Pregitzer et al., 2004); changes in precipitation patterns (Hongve et al., 2004; Ledesma et al., 2012); or changes in management such as burning (Clutterbuck and Yallop, 2010; Holden et al., 2012). While it is doubtful that all of these proposed drivers have combined to cause

an increase in DOC in all locations, it is likely that interactions among some factors, in particular recovery from acidification and factors affecting plant productivity, will affect DOC fluxes. Several models of DOC dynamics have been developed (Futter et al., 2007; Jutras et al., 2011; Michalzik et al., 2003; Neff and Asner, 2001; Xu et al., 2012) but these focus mainly on seasonal dynamics and require detailed inputs describing hydrological processes. There remains a need for a simple model, which simulates long-term controls on DOC fluxes and is suitable for large-scale applications. In the current study, we summarised key processes affecting DOC into a simple annual-timestep model, and applied this to experimental and long-term monitoring studies in which DOC and acid–base dynamics could be related.

Dissolved organic matter is defined as particles that pass through a 0.45 μm filter (Sleutel et al., 2009), and includes molecules of 100–100,000 Da (Aitkenhead-Peterson et al., 2003) with variable C/N ratio and surface charge. The formation and loss of DOC are affected by biological and surface exchange processes. The sorption and flocculation of potentially-dissolved organic carbon (PDOC) is mediated by hydrophobicity, ligand exchange between surface hydroxyl groups and organic acids, electrostatic

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interactions, and coadsorption and competition with other anions (Tipping, 1990). Several of these processes are influenced by soil solution acidity. At low pH, much low-molecular-weight organic matter stays in the solid phase, flocculated or adsorbed onto larger particles, in particular iron and/or aluminium oxyhydroxides (Sleutel et al., 2009). As pH increases, this organic matter tends to de-flocculate and desorb. In solution, acid groups on DOC partially buffer pH increases (Evans et al., 2008b; Krug and Frink, 1983).

Fluxes of DOC are greater from more organic soils, and correlate well with soil total C/N ratio (Aitkenhead-Peterson et al., 2005; van den Berg et al., 2012). Concentrations of DOC are determined not simply by soil solution acidity but also by the dynamics of soil C. During decomposition, DOC is produced by the action of microorganisms on plant litter and soil organic matter. Decomposition in organic soils is commonly impeded by anaerobic conditions, and may only proceed as far as soluble forms of C. Studies of $^{14}C$ concentration indicate that much of the DOC in streams (Raymond et al., 2007; Tipping et al., 2010) and in peat pipes (Billett et al., 2012) results from recent inputs of plant-derived C. This recent origin implies that, other factors being equal, DOC concentrations are likely to be correlated with plant productivity. This inference is supported by the conclusion of Larsen et al. (2011a) from a study of Norwegian lakes that a correlation of DOC concentration with temperature was primarily due to increased vegetation cover. In a related study, by far the best predictor of lake DOC concentration among a set of catchment properties that included annual mean temperature, slope, and fractions of bog, forest and arable land, was the normalised-difference vegetation index, which indicates photosynthetic capacity (Larsen et al., 2011b). Evidence that DOC fluxes are correlated more strongly with solar radiation 1–2 months previously than with air or soil temperature (Harrison et al., 2008) also indicates the importance of recently fixed C.

Nitrogen deposition has variable effects on DOC flux. It has been suggested that N pollution will increase DOC flux due to the suppression of phenol oxidase activity by nitrate (DeForest et al., 2004), but no evidence was found for this effect in an experimental study (DeForest et al., 2005). Increased N deposition has been observed to decrease (De Wit et al., 2007), increase (Filep and Rekasi, 2011), or have no net effect on (Emmett et al., 1998; Fernandez and Rustad, 1990; Stuanes and Kjonaas, 1998) DOC flux. None of these studies reported effects on plant productivity, so it is difficult to judge which of these systems were N-limited. Productivity is limited by N supply in many terrestrial ecosystems, since N is energetically expensive to obtain through fixation and easily lost through leaching and gaseous pathways (LeBauer and Treseder, 2008; Vitousek and Howarth, 1991), but at a given site other limitations may predominate such as growing season length (Kerkhoff et al., 2005) or availability of other nutrients (Menge et al., 2012). Increases in plant productivity as a result of chronic pollution with reactive N have however been observed at least in the short term in many forest ecosystems (Bontemps et al., 2011; Hogberg et al., 2006; Lu et al., 2012; Wei et al., 2012) and are likely in other habitats where N has historically been limiting. Where increased N supply increases productivity, there will potentially be an increase in DOC flux, although this also depends on soil and hydrological properties that determine the retention, transport and mineralisation of DOC.

Soils often change considerably in organic matter content, biotic activity and surface chemistry with depth. Mineral soil horizons with large concentrations of iron and/or aluminium oxyhydroxides generally have greater DOC sorption capacity than organic horizons. In a study of Belgian forests, sorption was responsible for substantial retention (67–84%) of DOC entering the mineral soil profile with forest floor leachate (Sleutel et al., 2009). Reductions in S pollution and sulphate concentrations may free up anion

exchange sites in lower soil horizons, increasing the sorption of DOC (Borken et al., 2011). Much of the retained organic matter is likely to be mineralised before it can be leached, resulting in lower DOC concentrations in streams than in soil solution. This process also releases mineral N, which may be re-immobilised or taken up by plants, depending on the amount of labile C-rich organic matter and the presence of plant roots within deeper soil layers. These processes can result in considerable decoupling between fluxes of dissolved organic N (DON) and DOC (Kalbitz et al., 2000).

The concentrations of DOC in rivers and lakes are affected by DOC efflux from different landscape elements depending on the flow regime (Laudon et al., 2011). Flow pathways through soil vary with rainfall intensity. During high-flow periods, much of the streamflow derives from near-surface drainage through more organic horizons (Hagedorn et al., 2000), resulting in greater stream DOC concentrations and considerably greater DOC fluxes during storm events (Buffam et al., 2001). Conversely, during periods of low water flow, DOC concentrations in streams are reduced by surface interactions and mineralisation within the mineral soil. As well as affecting flow pathways and (via effects on anaerobiosis) DOC formation, water flux directly affects the solubilisation of DOC since greater volumes of water allow more dissolution of PDOC. Thus DOC concentrations do not show a strong decline with precipitation (Haaland et al., 2008; van den Berg et al., 2012), as would be expected from simple dilution.

Previous approaches to modelling DOC fluxes (Futter et al., 2007; Jutras et al., 2011; Michalzik et al., 2003; Xu et al., 2012) have most often focused on seasonal and episodic variation in DOC production and in flow pathways through soil layers, and consequently require detailed hydrological and meteorological parameterisation. For modelling long-term changes in DOC flux we assume that the key processes are the production, mineralisation and solubilisation of DOC. A similar approach was taken by Neff and Asner (2001), who based their DOC model on a three-pool soil C model instantiated in four soil layers and with an hourly-timestep hydrology model. In the current study we propose a much simpler approach to modelling DOC changes using a Model of Acidity Dynamics and Organic Carbon (MADOC), developed by integrating models of: a) plant production and soil total C and N dynamics; b) partitioning of DOC between solid and dissolved phases; and c) acid–base kinetics. The MADOC model simulates the effects on long-term trends of DOC of large-scale ecosystem drivers such as air pollution by N and S. The aim of the study was to determine whether observed changes in soil solution and stream chemistry across a range of experimental and long-term monitoring sites can be simulated using a combination of these relatively simple models.

## 2. Methods

### 2.1. Model development

Three annual-timestep models of vegetation and soil dynamics were dynamically integrated in Fortran90 to form the MADOC model: N14C (Tipping et al., 2012), VSD (Posch and Reinds, 2009), and a simplified version of DyDOC (Michalzik et al., 2003). The model simulates dynamics within a one dimensional vegetation-soil column and is suitable for simulating experimental plots, and larger-scale areas where spatially-lumped parameters can be used. Data for calibrating the model were obtained from control treatments on experimental N addition sites, and the model was tested against data from acidified and alkalised treatments from these sites, and from long-term monitoring sites.

The VSD model (Posch and Reinds, 2009) was developed as the simplest dynamic model compatible with the computation of critical loads for S and N deposition by simple mass balances (UBA, 2004), and is based on solving equations that describe competition among cations for exchange sites and thus the partitioning of ions between the solution and adsorbed phases. The model was run using Gapon exchange kinetics. A retained fraction of deposited S can be specified to simulate retention of reduced and organic S.

The N14C model (Tipping et al., 2012) simulates C and N dynamics in vegetation and soils, tracking three organic matter pools with mean residence times at 10 °C of