A long-term simulation of the effects of acidic deposition and climate change on surface water dissolved organic carbon concentrations in a boreal catchment

M. N. Futter, M. Forsius, M. Holmberg and M. Starr

ABSTRACT

Concentrations of dissolved organic carbon (DOC) are increasing in many surface waters across Europe. Two of the main mechanisms proposed to explain this increase are declines in sulfate (SO_4^{2-}) deposition and changes in climate. Many of the reductions in SO_4^{2-} have already occurred; climate change related effects are occurring now and will continue in the future. This paper presents the first application of a new version of INCA-C, the *In*tegrated *Ca*tchments model for *C*arbon, which simulates the effects of both climate and SO_4^{2-} deposition on surface water DOC concentration ([DOC]). The model was applied to Valkea-Kotinen, a small headwater catchment in Finland, where it was able to simulate present-day (1990–2007) trends in [DOC] in the lake and catchment outflow as functions of observed climate and European Monitoring and Evaluation Programme (EMEP)-modelled SO_4^{2-} deposition. Using a parameter set derived from a present-day calibration, the model was run with two climate scenarios from the Special Report on Emissions Scenarios (SRES) and three EMEP deposition scenarios to simulate surface water [DOC] between 1960 and 2100. The results show that much of the historical increase in [DOC] can be explained as a result of historical declines in SO_4^{2-} deposition and that surface water [DOC] will continue to increase as climate changes.

Key words | acidification, climate change, dissolved organic carbon, Finland, model, Valkea Kotinen

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INTRODUCTION

Concentrations of dissolved organic carbon (DOC) are increasing in surface waters across Europe and in parts of North America. There has been considerable debate as to the mechanisms responsible for the observed increase (Roulet & Moore 2006). It has been suggested that declining sulfate (SO_4^{2-}) deposition (Skjelkvåle *et al.* 2005; De Wit *et al.* 2007; Monteith *et al.* 2007), changing climate (Hongve *et al.* 2004; Köhler *et al.* 2008; Lepistö *et al.* 2008), changes in hydrology (Laudon *et al.* 2004; Ågren *et al.* 2008; Dawson *et al.* 2008; Lepistö *et al.* 2008), land use (Mattsson *et al.* 2005) and combinations of these factors (Erlandsson *et al.* 2008) can explain many of the observed trends.

Large-scale empirical studies in many parts of Europe have identified correlations between increasing surface water DOC concentrations ([DOC]) and declining SO_4^{2-} deposition (Skjelkvåle *et al.* 2005; Monteith *et al.* 2007). The hypothesis that deposition of strong acid anions can control surface water [DOC] is strengthened by observations of declining surface water [DOC] during periods of high chloride (Cl^-) deposition (Monteith *et al.* 2007).

Analyses of long-term organic matter time series from Nordic rivers and lakes show the effects of climate, hydrology and SO_4^{2-} deposition on surface water [DOC]. Both direct effects of warmer temperatures and increasing

precipitation as well as indirect effects caused by changes in hydrology have been reported. Ågren *et al.* 2008 analysed 14 years of data from a river in northern Sweden. They found positive correlations between total organic carbon concentration [TOC] and runoff when data were examined on a seasonal basis. Lepistö *et al.* (2008) analysed a 43-year time series of TOC and total organic nitrogen (TON) from a northern Finnish river that received low levels of acid deposition. They ascribed the increase in TOC and TON flux to a combination of increasing runoff, warmer soil temperatures and more intensive forestry in the catchment (Lepistö *et al.* 2008). In a study of long-term monthly organic matter time series from 28 large rivers in Sweden, Erlandsson *et al.* (2008) showed an effect of flow and [SO_4^{2-}] on organic matter concentrations but did not find an effect of temperature or [Cl^-].

Understanding historical and future changes in surface water [DOC] requires information about past and future climate, land use and atmospheric deposition of SO_4^{2-} and Cl^-. While records of historical land use, climate and hydrology are readily available, deposition data are less accessible. Vuorenmaa (2004) has presented records of deposition in Finland from 1973–2000. The north of the country receives less deposition than the south. In southern Finland, SO_4^{2-} deposition has declined by as much as 60% from peak values in the early 1980s. There was little change in acid deposition during the 1970s and 1980s. The most pronounced decline was in the 1990s. Deposition of base cations was also declining. Possible future patterns of acid deposition in Finland have been presented by Syri *et al.* (2004) and Posch *et al.* (2008). Neither Syri *et al.* (2004) nor Posch *et al.* (2008) suggest that SO_4^{2-} deposition is likely to increase in Finland in the future.

There have been a number of studies of acidification and recovery of Finnish lakes (Forsius *et al.* 1997; Vuorenmaa *et al.* 2006; Vuorenmaa & Forsius 2008). These have shown that most water bodies in Finland are recovering from the effects of excess acidic deposition. However, rates of recovery will be affected by changes in organic acidity (Evans *et al.* 2008; Vuorenmaa & Forsius 2008).

Projected climate change effects in Finland (Jylhä *et al.* 2004) include an increase in annual average temperature of 1–3° and an increase in mean annual precipitation of 0–15% by the 2020s relative to a reference period of 1961–1990. By the 2050s, mean annual temperature is projected to have increased by 2–7° and annual precipitation by 0–30%. By the 2080s, annual average temperatures may have increased by 2–7° and precipitation by 5–40%. Changes in precipitation are projected to be larger during winter months than during the summer.

Futter *et al.* (2008) presented an application of an earlier version of the *In*tegrated *Ca*tchments model for *C*arbon, INCA-C. They applied the model to Valkea-Kotinen, a headwater catchment in Finland, to simulate the combined effects of climate and hydrology on surface water [DOC]. They showed that the pattern in surface water [DOC] between 1990 and 2003 could be explained as a function of climatic controls on production of DOC in the catchment and microbial mineralization of DOC in the lake. This paper presents an application of a new version INCA-C to Valkea-Kotinen. The new model simulates the effects of [SO_4^{2-}], hydrology and climate on soil and surface water [DOC] and temperature-dependent microbial mineralization of DOC in the open water. The model was calibrated to present-day climate and deposition. The parameter set from the present-day calibration was used with climate and deposition projections to simulate the long-term effects of projected changes in climate and deposition on surface water [DOC].

MODEL DESCRIPTION

INCA-C is a dynamic, daily time-step, semi-distributed catchment scale process-based model for simulating seasonal and long-term patterns in soil and surface water DOC (Futter *et al.* 2007). The initial model application to catchments in Canada (Futter *et al.* 2007), Norway (Futter & De Wit 2008) and Finland (Futter *et al.* 2008) simulated climate controls on DOC. A detailed description of the INCA-C hydrology, climate controls and carbon processing routines is presented by Futter *et al.* (2007). The new version of the model presented here simulates the effects of both climate and SO_4^{2-} on soil and surface water DOC.

Daily time series of air temperature, precipitation, soil moisture deficits (SMD) and hydrologically effective rainfall (HER) are required to run INCA-C. The SMD (mm) and HER (mm d^{-1}) time series may be simulated using the HBV

rainfall–runoff model (Sælthun 1996). When available, the version of INCA-C presented here can make use of daily time series of SO_4^{2-}. Daily time series of total global radiation can be provided as user input, or may be calculated from the site latitude and longitude.

The INCA-C model is calibrated against time series of surface water [DOC] and flow. Briefly, INCA-C simulates the hydrological fluxes within a catchment or subcatchments and the masses and fluxes of solid organic (SOC), dissolved organic (DOC) and dissolved inorganic carbon (DIC) in soils and surface waters (Futter *et al.* 2007). HER is that water arriving at the soil surface as precipitation or snowmelt which will eventually contribute to runoff. It may flow directly into the surface water or percolate into the upper soil box. Water in the upper soil box may enter the stream through diffuse runoff or percolate to the lower soil box. All water in the lower soil box eventually enters the surface water via groundwater flow. The breakdown of litter and root material contributes SOC and DOC in the upper soil box. Sorption and desorption processes control the transformation of organic carbon between DOC and SOC, and mineralization controls the transformation of SOC and DOC to DIC, which is lost to the atmosphere through degassing. DOC and DIC are transported advectively by water movement from the upper to lower soil boxes and from the soil to surface waters. Within surface waters DOC may be lost by either photolytic or temperature-dependent biological mineralization.

Within INCA-C, all carbon transformations in soils and surface waters are modelled as a series of first-order differential equations. All in-soil rate coefficients are dependent on soil temperature and moisture status. Soil temperature is simulated using observed air temperature and a model developed by Rankinen *et al.* (2004). The effect of soil temperature on the rate coefficients in INCA-C is simulated using a Q_{10}-type model. The rate coefficient for the effect of soil moisture is a linear function of soil moisture content. The processes operate at a maximum rate when the simulated SMD is equal to zero. Processes cease when the SMD is greater than SMD_{Max}, a calibrated threshold representing the maximum soil moisture deficit at which carbon processing may occur. The effect of soil temperature is simulated using a calibrated Q and modelled soil temperature (T_{Soil}, °C). The effects of soil moisture are simulated using daily values of SMD and a calibrated SMD_{Max} (Equation (1)):

$$m = Q^{(T_{Soil}-20)}\left(\frac{SMD_{Max} - \min(SMD, SMD_{Max})}{SMD_{Max}}\right). \quad (1)$$

Changes in the mass of organic carbon in a soil box are simulated as a combination of soil temperature and moisture effects (m), and the mass of organic carbon sorbed ($k_S DOC$, kg C d^{-1}) and desorbed ($k_D SOC$, kg C d^{-1}) (Equation (2)). The base rates of the desorption (k_D, d^{-1}) and sorption (k_S, d^{-1}) coefficients are estimated during model calibration:

$$\frac{dDOC}{dt} = m(k_D SOC - k_s DOC). \quad (2)$$

The modifications to INCA-C described here simulate the effect of soil solution chemistry on organic matter sorption/desorption dynamics. In the application presented here, atmospheric SO_4^{2-} deposition is used as a surrogate for soil water [SO_4^{2-}]. The relationship between SO_4^{2-} and sorption/desorption has been specified in as general a manner as possible. This has been done as there is still considerable debate as to the actual mechanism by which [SO_4^{2-}] influences organic matter sorption and desorption in soil waters. Equations (3) and (4) are simplified representations of the changes in mass of DOC (Equation (3)) and SOC (Equation (4)) as functions of soil solution chemistry controls on organic matter sorption/desorption rates. The full equations are described in Futter *et al.* (2007). Briefly, they have been modified to include the effect of [SO_4^{2-}] on the rate at which DOC is transformed to SOC. At higher [SO_4^{2-}], the transformation of DOC to SOC will be more rapid:

$$\frac{dDOC}{dt} = m\left(k_D SOC - \left(b_1\left[SO_4^{2-}\right]^{b_2} + k_S\right)DOC\right) \quad (3)$$

$$\frac{dSOC}{dt} = m\left(\left(b_1\left[SO_4^{2-}\right]^{b_2} + k_S\right)DOC - k_D SOC\right). \quad (4)$$

When $b_1 = 0$, the effects of [SO_4^{2-}] are not included in simulating the rate at which organic matter moves from the dissolved to the solid phase. Thus, the version of the model presented here is backwards-compatible with earlier

INCA-C applications which only simulated the effects of climate on DOC.

DOC is lost from the open water through a combination of microbial and photo-mineralization. In open water, the DOC photo-mineralization rate is simulated as a function of total global solar radiation (R, kJ m^{-2}) and surface water [DOC]. The photo-mineralization rate (k_P, d^{-1}) is a linear function of solar radiation. As high surface water [DOC] can lower rates of photo-mineralization, actual rates of photo-mineralization are calculated by multiplying the potential rate by a [DOC]-dependent self-shading factor, $a/(a + [DOC])$. Equation (5) shows the rate at which [DOC] changes in surface waters as a function of global radiation (R), water temperature (T_w, °C), microbial (k_M, d^{-1}) and photolytic (k_P, d^{-1}) mineralization coefficients:

$$\frac{\mathrm{d}[DOC]}{\mathrm{d}t} = -\left(k_M T_W + k_P R\left(\frac{a}{a + [DOC]}\right)\right)[DOC]. \qquad (5)$$

Microbial mineralization of DOC is linearly dependent on water temperature (T_W). Water temperature is assumed to be equal to air temperature so long as the air temperature is above a user-specified threshold. When air temperatures are below this value, the water temperature is set to the threshold value.

STUDY SITE

Valkea-Kotinen is a small headwater catchment situated within a protected area of old-growth forest in southern Finland (61°14′N, 25°04′E; Figure 1). Land use and management effects are therefore excluded and the catchment only receives background levels of long-range transported air pollution. The catchment and monitoring activities are described in Ukonmaanaho et al. (1998). Stream flow is monitored at the catchment outflow and water chemistry monitored in the lake and at the catchment outflow. The catchment has an area of 30 ha. The lake elevation is 156 m above sea level (a.s.l.). The long-term mean annual temperature in the area is +3.1°C and the annual amount of precipitation is 618 mm, of which
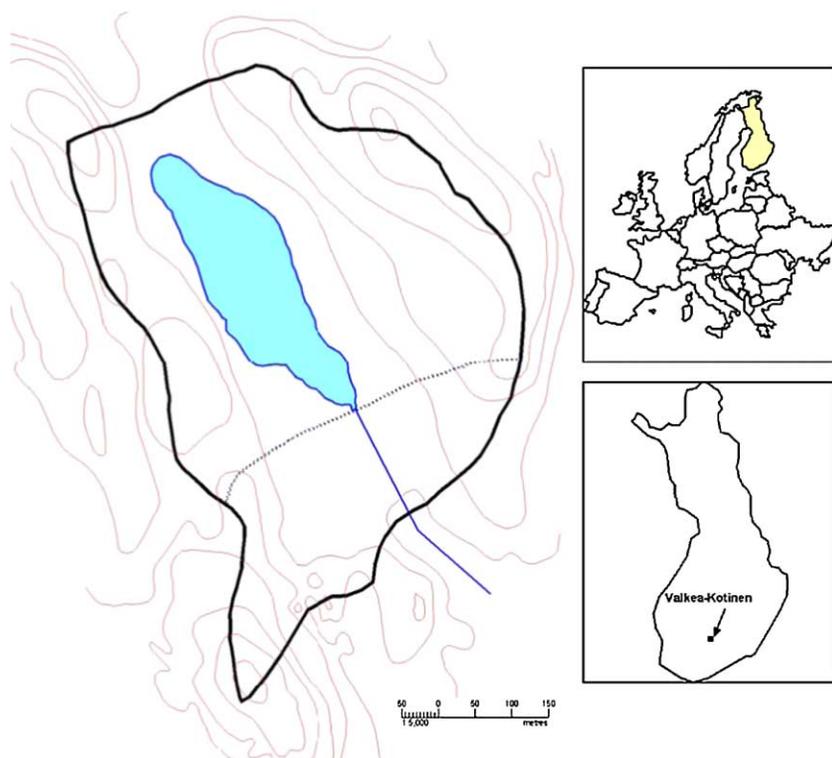

Figure 1 │ Map of the Valkea-Kotinen catchment. There are two subcatchments, the lake and catchment outflow.

approximately 30% falls as snow, giving rise to a distinct snowmelt peak in runoff at the end of April. Global radiation averages $3,300\,\text{MJ m}^{-2}\,\text{yr}^{-1}$.

Valkea-Kotinen is typical of glaciated boreal landscapes. The catchment contains areas of forested mineral soil (17 ha, higher elevations), forested and open peatlands (7 ha, lower elevations and adjacent to the lake and stream) and a discharge lake (4 ha) with stream. The mineral soils in the catchments are predominately Podzols, developed on shallow glacial drift (till) deposits (Starr & Ukonmaanaho 2001). The forest cover consists mainly of old-growth mixed stands of Norway spruce and deciduous species (birch and aspen) with large individuals of Scots pine present. The lake has a mean depth of 3 m, a volume of $7.7 \times 10^4\;\text{m}^3$ (Keskitalo *et al.* 1998) and is fringed by peatland. The waters in the lake and outlet stream are humic (average $[\text{TOC}] = 17\,\text{mg L}^{-1}$), and have low pH (4.5) and alkalinity ($< 40\,\mu\text{mol L}^{-1}$).

The Valkea-Kotinen catchment has been the subject of much biogeochemical research. (Keskitalo *et al.* 1998; Starr & Ukonmaanaho 2001, 2004; Holmberg *et al.* 2006) and is part of the UN/ECE ICP Integrated Monitoring program in Finland (http://unece.org/env/wge/im.htm). Because of this, detailed data on soil and stand carbon stocks, litter production and soil-water [DOC] are available (Starr & Ukonmaanaho 2001, 2004). The lake has been the subject of numerous limnological studies, especially on greenhouse gas production (Vähätalo *et al.* 2003).

DATA SOURCES

Meteorological data used in this study were obtained from nearby Finnish Meteorological Institute weather stations; temperature (*T*) and precipitation (*P*) data from the Lammi meteorological station (61°10′ N 25°02′ E 129 m a.s.l.) and *P*, *T* and total global radiation data from Jokioinen (60°48′ N, 23°30′ E, 104 m a.s.l.). The Lammi station is closer to the Valkea-Kotinen site but data from Jokioinen were also used, as radiation data were not available at Lammi. Stream flows were measured at the catchment outflow by SYKE.

The climate scenarios used here were obtained from the Prudence project (http://prudence.dmi.dk/). Climate data from 1961–2100 were derived from the RCAO Regional

Climate model (RCM) using the Special Report on Emissions Scenarios (SRES) A2 and B2 scenarios. Additional information on the climate models and scenarios is provided by Posch *et al.* (2008).

Instrumental data from Lammi and Jokioinen were available from 1965–2007. The average annual *T* from the RCM climate scenarios for this period was 4.7°, $\sigma^2 = 1.3°$ for the A2 scenario and 4.4°, $\sigma^2 = 1.2°$ for the B2 scenario. For both the A2 and B2 scenarios, modelled *P* was much higher than measured (Figure 2(a)). Between 1965 and 2007, the modelled annual average *P* for the A2 scenario was 960 mm, $\sigma^2 = 105$ mm and 967 mm, $\sigma^2 = 111$ mm for the B2 scenario. Annual average radiation recorded at Jokioinen between 1971 and 2007 was $9170\,\text{kJ m}^{-2}$, $\sigma^2 = 436\,\text{kJ m}^{-2}$. For both the A2 and B2 scenarios, annual average global radiation was $7{,}663\,\text{kJ m}^{-2}$, $\sigma^2 = 440\,\text{kJ m}^{-2}$.

There was good correspondence between the measured *T* and *P* at Jokioinen and Lammi. The annual average *P* at Lammi was 628 mm with a standard deviation (σ^2) of 88 mm while the annual average *P* at Jokioinen was 597 mm, $\sigma^2 = 85$ mm. Annual average *T* at the two sites during the same time period was 4.0° and 4.3°, respectively, with standard deviations of 1.0°.

Climate data used in the long-term (1961–2100) simulations will not reproduce observed daily weather patterns. They should, however, have similar annual and seasonal means and variances to observed data from the site they represent. While there was good agreement between observed and modelled *T*, there were large discrepancies between average monthly observed and modelled *P* and radiation (Figure 2(a, b)). Radiation and *P* from the downscaled climate scenarios were adjusted so as to match the average observed values. Daily modelled precipitation and radiation were scaled to match observed data by multiplying by the ratio of average monthly observed to modelled data.

Large increases in annual average *T* were projected under both the A2 and B2 SRES scenarios (Figure 3(a)). There is little difference in average *T* projected by the two scenarios until around 2050, after which temperatures are projected to increase more rapidly under the A2 scenario. Between 2070 and 2100, annual average *T* projected under the A2 scenario was approximately 1°C warmer than the B2 scenario. There is little difference in projected *P* between
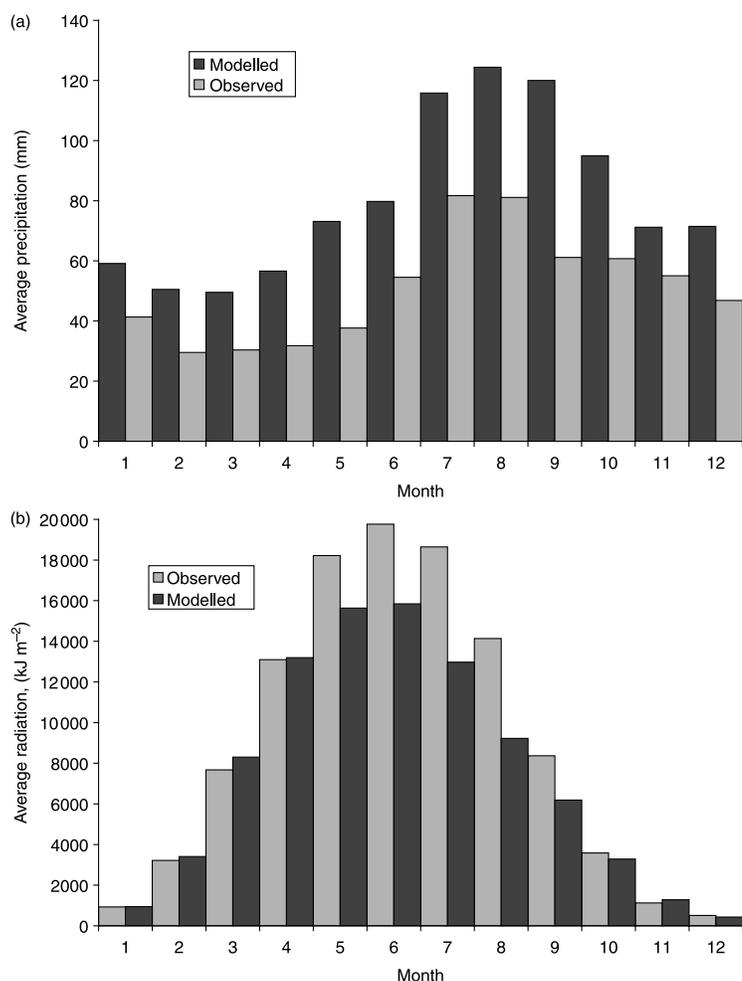
Figure 2 │ (a) Monthly average measured and RCM-modelled precipitation between 1965 and 2007. Measured precipitation is from Jokioinen and Lammi. Modelled results are the average of A2 and B2 scenarios. (b) Monthly average measured at Jokioinen and RCM modelled radiation, 1971–2007.

the two scenarios (Figure 3(b)). Overall, P is projected to increase slightly under both scenarios but there is large inter-annual variability.

Three deposition scenarios from the Emissions Monitoring and Evaluation Programme (EMEP) were used (Figure 4). These were currently legislated emissions (CLE), maximum feasible reductions (MFR) and CAFÉ (D23) deposition scenarios. The scenarios and the manner in which data were generated have been described by Posch *et al.* (2008). Deposition for the forest land cover type was used as an input to the modelling exercise. Estimated deposition peaked in the 1980s and has declined sharply since then. The deposition scenarios are identical from 1850

to 2010. There is little difference between deposition estimates for the three scenarios between 2010 and 2020. Deposition is assumed to remain constant after 2020. Annual deposition was used as a surrogate for soil-solution $[SO_4^{2-}]$ in the INCA-C modelling. Using deposition data as a surrogate for in-soil $[SO_4^{2-}]$ makes a number of simplifying assumptions. The effects of SO_4^{2-} adsorption and any possible effects of drought and redox mediated SO_4^{2-} pulses on [DOC] were not considered.

The input time series for long-term model projections are correlated. Increasing annual average T and P from the SRES scenarios are correlated with declining SO_4^{2-} deposition in all deposition scenarios. Radiation is negatively
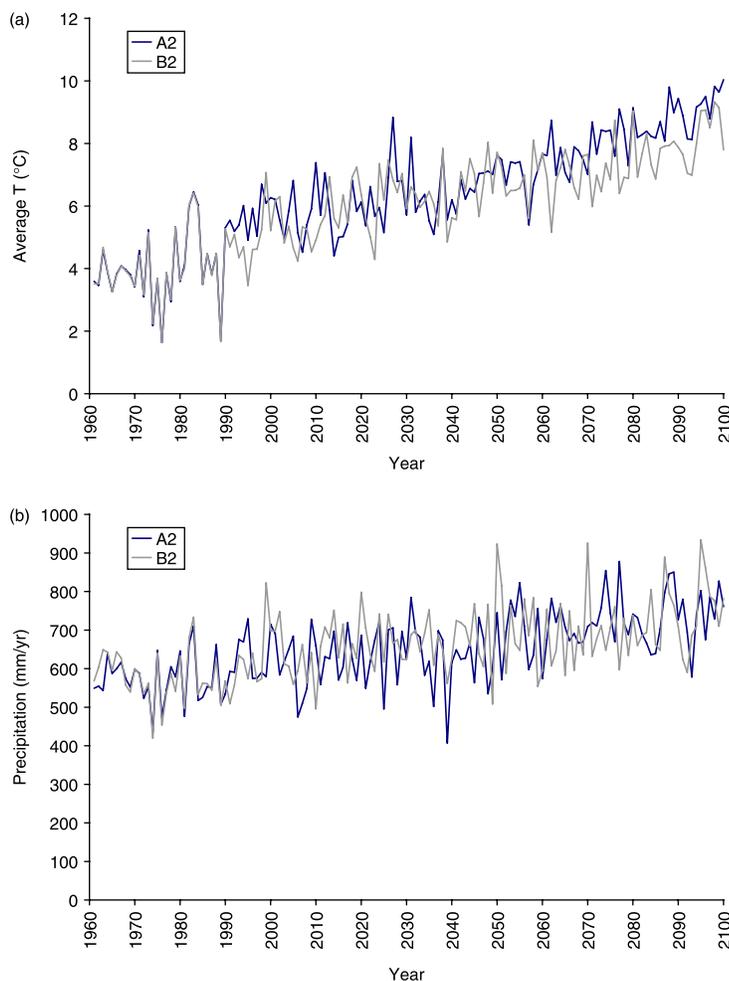
Figure 3 | (a) Projected annual average temperatures at Valkea-Kotinen under the SRES A2 and B2 scenarios. (b) Projected annual precipitation at Valkea-Kotinen from RCM output adjusted to match observed data. There is a slight upwards trend in projected precipitation under both the A2 and B2 SRES scenarios.

correlated with both T and P, but positively correlated with deposition. This has implications for interpreting the relative importance of climate and deposition on [DOC] using linear methods such as stepwise multiple regression (SMR).

HBV AND INCA-C MODEL CALIBRATION

Calibration to present-day conditions followed the procedure described by Futter *et al.* (2008). Stream flow at the catchment outlet and [DOC] from the lake and catchment outflow from 1990–2007 were used in model calibration.

Estimates of HER and SMD were obtained using HBV (Sælthun 1996). HBV is a conceptual rainfall–runoff model

that has been extensively used in Finland and Scandinavia. In HBV, time series of P and T and a description of the catchment are used to simulate daily runoff, HER and SMD. HBV is calibrated by adjusting snowmelt, water residence time in the conceptual soil reservoirs and evapotranspiration-related parameters so as to minimize the difference between modelled and observed flow. The estimate of HER generated by HBV is the depth of water entering the soil on any given day which eventually contributes to runoff. It is the sum of precipitation and snowmelt minus losses due to evapotranspiration. SMD is the difference between the amount of water in the soil and its water holding capacity, expressed as a depth of water. Runoff estimates were only used for HBV model calibration. They were not used in
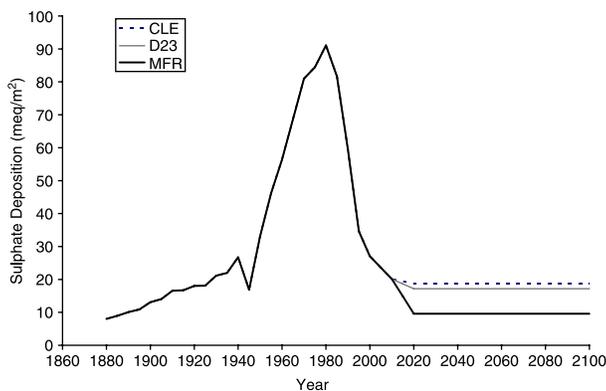
Figure 4 | Sulfate deposition scenarios for forest land cover type at Valkea-Kotinen. Intermediate values are obtained by linear interpolation.

the INCA-C application, as INCA-C includes routines to route HER through the catchment to provide estimates of stream flow.

Observed T and P from Lammi as well as modelled HER and SMD from HBV were used as input time series for the INCA-C simulations. In the application presented here, the catchment was divided into two sub-catchments representing the lake at the top of the catchment and the peat lands and forest draining into the stream below the lake outflow (Figure 1). Three land-cover classes were simulated representing (i) forests on upland, freely draining soils in both subcatchments, (ii) peatlands around the lake and (iii) the organic-rich soils and peat downstream of the lake outflow. INCA-C was manually calibrated to match observed [DOC] in the lake and flow and [DOC] at catchment outflow. In-lake mineralization rates were obtained from Futter *et al.* (2008). The exponent for soil solution [SO_4^{2-}] effects on organic matter solubility (b_2 from Equations (3) and (4)) was fixed at a value of 1. The parameter set obtained from the manual calibration to current data and measurements was used for projecting DOC concentrations under future climate and deposition scenarios.

Long-term (1961–2100) simulations of [DOC] were performed in the following manner. First, climate scenario data were adjusted so as to have the correct number of days in each year. The available climate data used a 360-day year. Every 72nd record in the data set was duplicated to produce 365-day years. Leap years were accounted for by simulating every 1,440th record. Estimates of SMD and HER were

obtained by running HBV with the parameter set obtained during calibration to current-day conditions, and daily temperature and precipitation from the SRES scenarios. These estimates were used with SRES temperature, precipitation and radiation data and the parameter set obtained during calibration to present conditions as inputs to INCA-C.

MODEL RESULTS

There was good correspondence between HBV-modelled and observed runoff. The Nash–Sutcliffe (NS) R^2 equalled 0.65 and 0.53 for untransformed and log-transformed data, respectively. Overall, there was a difference of 10 mm between observed and modelled runoff between 1990 and 2007. The HBV simulation failed to capture some of the large runoff peaks but did capture inter-annual variability in low flows.

The manual INCA-C calibration produced a parameter set capable of simulating the observed temporal patterns of [DOC] in the lake (Figure 5(a)) and catchment outflow (Figure 5(b)). The NS and Pearson product moment correlations for observed and modelled [DOC] in the lake and outflow were 0.25, 0.76 and 0.3, 0.56, respectively. The INCA-C model over-estimated [DOC] in the lake between 2000 and 2001 but otherwise reproduced both the intra- and inter-annual trends. At the catchment outflow, the INCA-C model did a better job of simulating low concentrations of [DOC].The model simulation did not always capture the timing or magnitude of summer-time peaks in [DOC] in the catchment outflow.

Long term simulations (Figure 6(a, b)) using SRES climate and EMEP deposition scenarios to drive the model showed the most rapid increase in [DOC] between about 1980 and 2000. Increases continued after 2000 but the rate of increase slowed. After 2020, concentrations remained relatively stable. There are large increases in within-year variance in the later years of modelled [DOC] for the lake. Within-year variance of modelled [DOC] also increased with time at the catchment outflow, but to a lesser extent.

Daily modelled flows and [DOC] were multiplied and summed to estimate annual areal organic carbon fluxes for the lake and catchment outflow. Figure 7 shows annual

areal exports of DOC projected from the SRES A2 and MFR deposition scenarios. Projected exports under the other climate and deposition scenarios followed a similar pattern. The largest increases in DOC flux were modelled between the late 1980s and 2005. Fluxes continued to increase until around 2050, but at a much lower rate. Post-2050, there are no trends in flux. On an areal basis, more organic carbon is always exported through the catchment outflow than is exported from the lake sub-catchment. This is a result of simulated in-lake mineralization of DOC. There does not appear to be any trend in the differences in areal export between the lake and the catchment outflow.

The trends in climate, SO_4^{2-} deposition and modelled [DOC] are not independent (Figure 8). While deposition has been declining, climate has been warming. In Finland, SO_4^{2-} deposition was relatively constant though the 1970s and 1980s. Declines in deposition started to be observed in the late 1980s and have continued since then (Vuorenmaa 2004). It should be noted that measured declines in deposition started somewhat later than the decline in the EMEP modelled deposition data used in this analysis.

Similar trends in [DOC] were seen for all combinations of SRES and deposition scenarios. The projected [DOC] reflect patterns in temperature and deposition. Warmer,
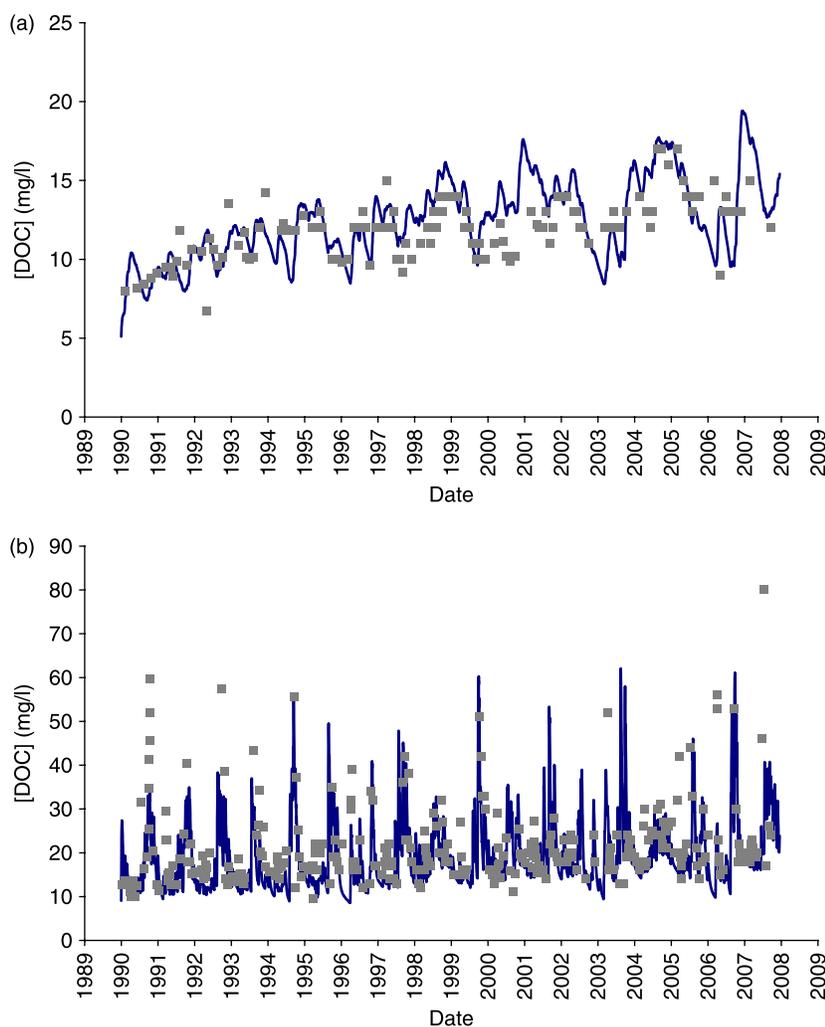

Figure 5 │ (a) Observed (dots) and modelled (line) DOC concentration in the lake at Valkea-Kotinen. (b) Observed (dots) and modelled (line) DOC concentration in the Valkea-Kotinen catchment outflow.

wetter conditions and lower deposition all resulted in higher projected [DOC]. The small differences in deposition post-2020 resulted in slightly higher [DOC] being projected under the MFR scenario than either CLE or D23. While [DOC] projections under the D23 scenario were slightly higher than those for CLE, the effect was almost too small to be noticed. Very similar projections were obtained using the A2 and B2 SRES scenarios. Projected [DOC] was marginally higher under A2 as projected temperatures were, in general, warmer than those under the B2 scenario.

STATISTICAL ANALYSIS

Despite the concerns expressed by statisticians, Stepwise Multiple Regression (SMR) is often used to select candidate predictor variables in environmental modelling. Interpreting the results of SMR analyses using correlated predictor variables, such as those used in the analysis presented here, can be less than straightforward. In a forward-selection SMR analysis, the first variable entered into the model is that which explains the largest amount of variability.
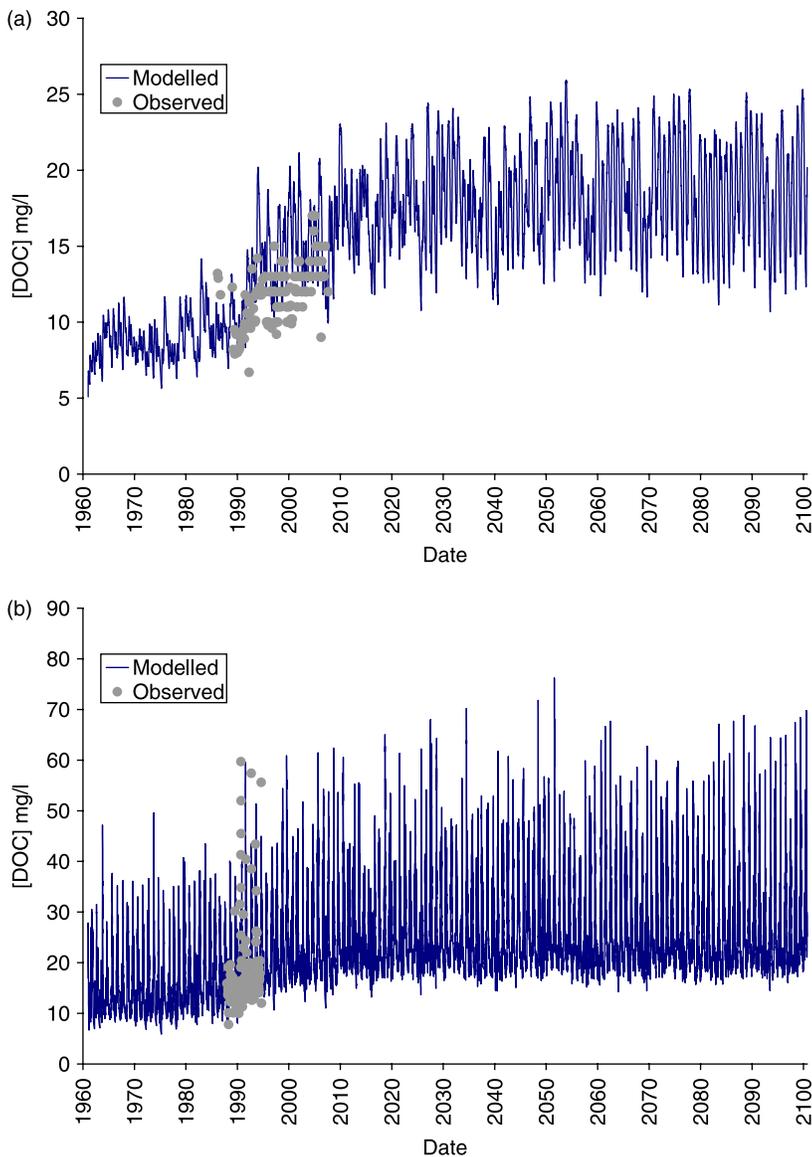

Figure 6 | (a) Modelled (line) and observed (dots) daily [DOC] in the lake from 1961–2100 under the SRES A2 scenario and maximum feasible reductions (MFR). (b) Modelled (line) and observed (dots) daily [DOC] at the catchment outflow between 1961 and 2100 under the SRES A2 scenario and maximum feasible reductions (MFR).
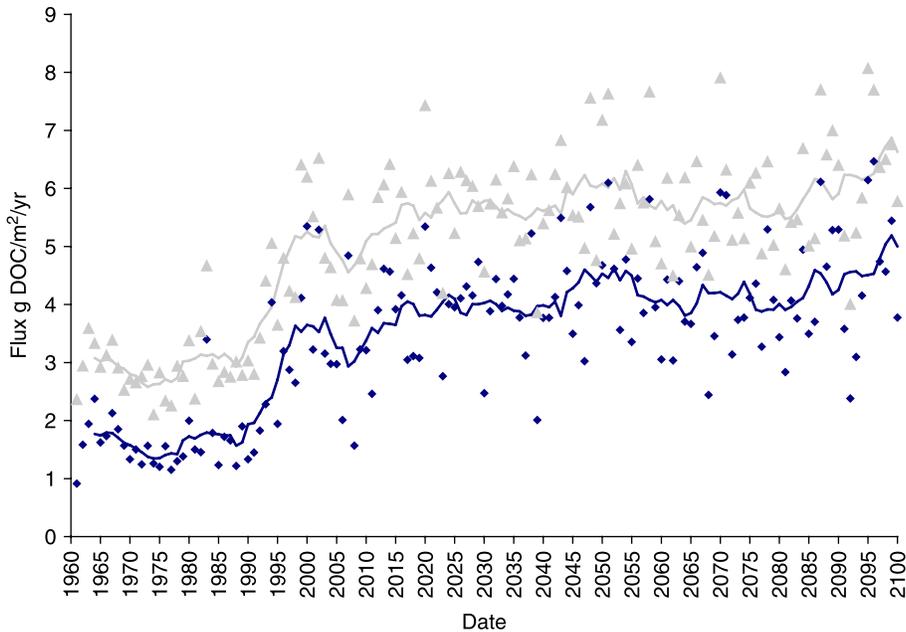
Figure 7 │ Modelled DOC flux from the lake (diamonds) and catchment outflow (grey, triangles) from the SRES B2 scenario and maximum feasible reductions of deposition (MFR). Symbols represent the annual areal export and the lines are a 9-year running mean. There is no trend in the difference between areal export from the catchment outflow and the lake.

Subsequent variables to be entered only explain residual variability. In an SMR analysis of the data set used in long-term projections, deposition explained most of the variability. As the climate parameters were correlated with deposition, they explained much of the same trend in [DOC] as deposition. Deposition was the first variable to be entered, and had an $R^2 = 0.94$ for an SMR analysis using climate and deposition data. Cumulatively, the climate variables explained less than 1% of the remaining variation. When an SMR analysis was conducted using only the climate variables as predictors they were able to explain approximately 70% of the variability in annual average
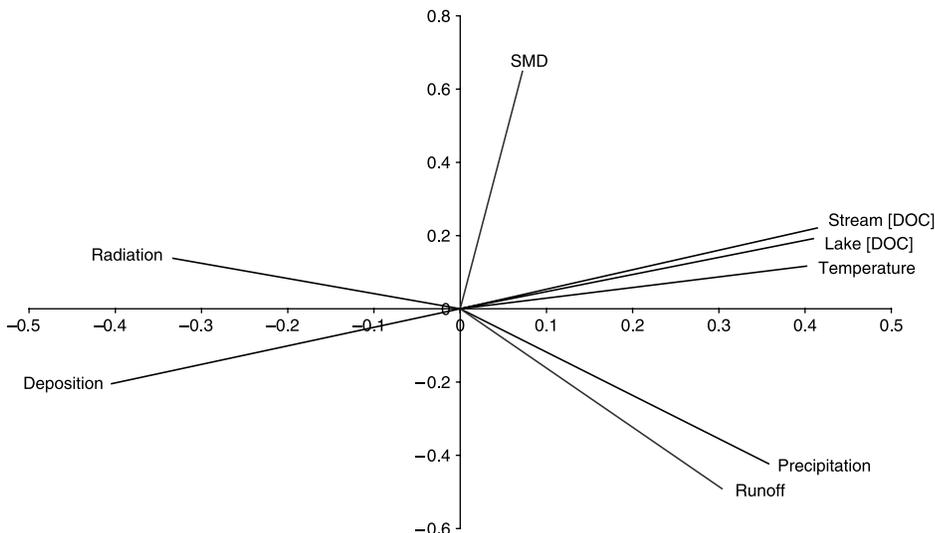
Figure 8 │ Plot of first two axes from PCA on correlations of annual modelled [DOC], climate and deposition. The first two axes show 60% and 21% of the variation, respectively.

[DOC]. Given the difficulties in interpreting model output using SMR, the decision was made to perform a Principal Components Analysis (PCA) on the correlation matrix of predictor time series and [DOC] in the lake and catchment outflow.

The PCA (Figure 8) showed a strong positive relationship between annual average modelled [DOC] in both the lake and stream and temperature. Deposition and T were negatively correlated. Warmer temperatures and lower deposition were both associated with higher [DOC]. Both deposition and radiation were negatively correlated with annual average modelled [DOC] in the lake and stream. Precipitation and runoff had similar loadings and were positively correlated with lake and stream [DOC]. Annual average SMD was not strongly correlated to any of the other time series.

DISCUSSION

The authors believe that this is the first modelling study to simulate both the effects of declining acid deposition and changing climate on surface water [DOC] and fluxes at a catchment scale. This study is important as it shows possible effects of both changing SO_4^{2-} deposition and climate on surface water [DOC]. Changes in atmospheric deposition are a stronger driver than climate for the modelled long-term changes in surface water [DOC] presented here. It has been shown that a model simulation of the present-day climate and deposition controls on surface water [DOC] in a boreal catchment can be used to make inferences about historic and future trends in [DOC]. The present-day [DOC] simulations presented here extend the modelling exercise conducted by Futter *et al.* (2008) at Valkea-Kotinen. The results presented here include the effects of both climate and deposition on surface water [DOC] and there is a more realistic simulation of the effects of water temperature on rates of biological mineralization of DOC. The results presented here provide a better fit to post-2003 data than was obtained with the climate-only parameter set presented by Futter *et al.* (2008). This corroborates the hypothesis that both reductions in SO_4^{2-} deposition and a changing climate are causing the observed increase in [DOC] in European boreal surface waters and highlights

the difficulties of interpreting causal relationships when parameters are correlated.

Further work is required to (i) provide estimates of the uncertainty associated with the model projections; (ii) confirm the projected effects of changing climate and deposition on surface water [DOC], (iii) elucidate the mechanism by which deposition controls organic carbon dynamics in soils and surface waters and (iv) improve the link between modelled surface water [DOC], estimates of the future patterns of soil carbon sequestration and potential litter inputs to the forest floor.

There has been very little consideration of uncertainty in the model results presented here, which are based on single HBV and INCA model runs. More credible results would have been obtained had an ensemble of behavioural parameter sets been available for use during model projection. While the two climate projections do represent different SRES scenarios, no attempt has been made to simulate stochastic weather effects. All of the deposition scenarios assume constant inputs post-2010. There will doubtless be some amount of year-to-year variability surrounding these projections, that will in turn influence modelled [DOC].

The model results presented here provide corroboration for one set of hypotheses as to the possible relationship between climate, atmospheric deposition and surface water [DOC]. The unambiguous effects of declining deposition and the more complex effects of changing climate is due, in part, to model structure. In the model, there is a simple relationship between deposition and [DOC]. Higher soil solution $[SO_4^{2-}]$, for which deposition was used as a surrogate, affects the rate at which dissolved organic matter associates with the solid phase. Climate effects are more difficult to disentangle as they have direct and indirect effects in the model. Process rates in the model are positively dependent on temperature and soil moisture. In the simulations presented here warmer, wetter conditions will lead to more DOC production but wetter conditions will also lead to lower soil water residence times and shorter contact times between water and soil.

There have been suggestions that the period of most rapid climate change began in the 1970s (Henson 2006). While it can be difficult to disentangle the effects of two simultaneous drivers, the results presented here corroborate

the hypotheses that deposition (i.e. Skjelkvåle *et al.* 2005; Monteith *et al.* 2007), climate (Hongve *et al.* 2004; Köhler *et al.* 2008) and their interactions (Erlandsson *et al.* 2008) control inter-annual and long-term patterns in surface water [DOC]. The largest increases in [DOC] were projected to occur between the mid-1980s and 2005 (Figure 6(a, b)). This is consistent with the observed increases reported by Monteith *et al.* (2007) and Skjelkvåle *et al.* (2005). It is also the period during which modelled deposition was declining most rapidly.

While projected annual average [DOC] did not increase appreciably after about 2020, fluxes of organic carbon continued to increase until about 2050. The continued increase in modelled organic carbon flux was caused mostly by changes in timing as opposed to overall increase in runoff amount. The projected smaller snow pack and shorter winters resulted in smaller spring freshets.

The stronger effects of deposition versus climate change may be due in part to the range in model inputs. Modelled deposition ranged between 7.5 and 90 meq m^{-2} yr^{-1} while annual average temperature varied by less than 8°C. The overall variability in average temperatures should be contrasted with the annual average temperature range of in excess of 35°C. Similarly, there is a relatively small increase in precipitation of approximately 1 mm yr^{-1} which is much less than the year-on-year variability of over 70 mm. Modelled radiation does decrease slightly but has a minimal effect on model projections.

The difficulties encountered in attempting to match observed to modelled meteorological data from the RCM scenarios are worthy of further exploration. Climate model output currently provides very credible present-day T data for biogeochemical modelling. Unfortunately, there is not as good agreement between modelled and observed P and radiation. Projecting future biogeochemical conditions that are driven by a changing climate requires better estimates of P and radiation in climate projection datasets.

The model presented should be applied to sites that have been subject to a range of climate and deposition effects and for which long-term surface water [DOC] data are available. Ideally, the model will be applied to a North American site at which long term declines in SO_4^{2-} deposition are not correlated with a long-term increase in surface water [DOC]. Applying the model at a range of sites

should refine or corroborate the estimates of the effects of climate and deposition on [DOC] that are presented here.

The EMEP SO_4^{2-} deposition data were used in this study as a surrogate for in-soil [SO_4^{2-}]. There are a number of possible problems with this. While deposition and soil-solution data should be correlated, there are many processes occurring in the soil including adsorption and redox-mediated mobilization of SO_4^{2-} that will not be represented by deposition data. There are also differences between EMEP-modelled and measured deposition data. The EMEP data show much less inter-annual variability than the measured deposition presented by Vuorenmaa (2004). While deposition chemistry will influence soil-solution chemistry, the two are not the same thing. Improved results could be obtained if soil-solution [SO_4^{2-}] were used to drive the model. The actual mechanism by which SO_4^{2-} influences surface water [DOC] is still a matter of some debate. The model presented here uses a simple, empirical, representation of the effects of SO_4^{2-} on organic matter solubility. Further experimental and monitoring efforts are required to elucidate the mechanism. Without a clear knowledge of the mechanism, the processes presented here should be considered as conditional.

INCA-C projections are sensitive to assumptions made about long-term patterns of soil C sequestration. Behavioural parameter sets obtained during model calibration may predict widely varying patterns of soil C sequestration when long-term climate projections are made. Constraining soil carbon estimates using "soft" calibration of the sort advocated by Futter *et al.* (2008) can help in identifying behavioural parameter sets during model calibration but may be of little use when making long-term projections. Small changes in modelled soil C stocks during the calibration period can have large effects when the model is run over a much longer time period. Modelled soil C stocks were projected to follow a parabolic path between 1961 and 2100. The size of the soil C pool was projected to increase between 1961 and the middle of the 21st century, after which declines were projected to occur. Liski *et al.* (2006) have shown that the size of the soil C pool in Finland was increasing between 1922 and 2004 but that much of this was an increase in the area of land covered by forest. They reported slight overall increases in carbon density from 6.1 to 6.3 kg m^{-2}. Ideally, the surveys conducted by

Starr & Ukonmaanaho (2001, 2004) should be repeated to determine possible changes in the rates of litter input and carbon sequestration in the Valkea-Kotinen catchment.

In some cases, changing climate can lead to elevated soil and surface water $[SO_4^{2-}]$. Over the long term, deposition will tend to drive soil water $[SO_4^{2-}]$ but the approach here neglects many potentially important in-soil processes. Instead of incorporating additional soil processes into INCA-C, it could be more productive to pursue the model-chaining approach presented by Aherne *et al.* (2008) in which HBV and INCA-C were used to provide inputs to the MAGIC model. Such an approach could deal with the findings of Eimers *et al.* (2008) who noted a confounding of S and climate in forested catchments which had not been subject to high levels of acid deposition. In these catchments, there can be a large pool of reduced S which can be re-mobilized after drought events, leading to lowered surface water [DOC].

Despite the concerns discussed, the model and model application presented here are a major step forward in understanding long-term patterns of surface water [DOC]. The modelling results presented here have shown that two of the main hypotheses proposed to explain the increase in surface water [DOC] are compatible with data from the European boreal environment. Both reductions in atmospheric deposition of SO_4^{2-} and changing climate are leading to increases in surface water [DOC]. Future research must address the links between climate, deposition, land management, organic matter production, soil carbon sequestration and dissolved organic matter fluxes if there are to be credible long-term projections of surface water [DOC].

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REFERENCES

Ågren, A., Jansson, M., Ivarsson, H., Bishop, K. H. & Seibert, J. 2008 Seasonal and runoff-related changes in total organic carbon concentrations in the River Öre, Northern Sweden. *Aquatic Sci.* **70**, 21–29.

Aherne, J., Futter, M. N. & Dillon, P. J. 2008 The impacts of future climate change and dissolved organic carbon on acidification recovery at Plastic Lake, Ontario. *Hydrol. Earth Syst. Sci.* **12**, 383–392.

Dawson, J. J. C., Soulsby, C., Tetzlaff, D., Hrachowitz, M., Dunn, S. M. & Malcolm, I. A. 2008 Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. *Biogeochemistry* **90**(1), 93–113.

De Wit, H. A., Mulder, J., Hindar, A. & Hole, L. 2007 Long term increase in dissolved organic carbon in streamwaters in Norway is response to reduced acid deposition. *Environ. Sci. Technol.* **41**, 7706–7713.

Eimers, M. C., Watmough, S. A., Buttle, J. M. & Dillon, P. J. 2008 Examination of the potential relationship between droughts, sulfate and dissolved organic carbon at a wetland-draining stream. *Global Change Biol.* **14**, 938–948.

Erlandsson, M., Buffam, I., Fölster, J., Laudon, H., Temnerud, J., Weyhenmeyer, G. A. & Bishop, K. H. 2008 Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by flow and sulphate. *Global Change Biol.* **14**, 1191–1198.

Evans, C. D., Monteith, D. T., Reynolds, B. & Clark, J. M. 2008 Buffering of recovery from acidification by organic acids. *Sci. Total Environ.* **404**, 316–325.

Forsius, M., Johansson, M., Posch, M., Holmberg, M., Kämäri, J., Lepistö, A., Roos, J., Syri, S. & Starr, M. 1997 Modelling the effects of climate change, acidic deposition and forest harvesting on the biogeochemistry of a boreal forested catchment in Finland. *Boreal Environ. Res.* **2**, 129–143.

Futter, M. N., Butterfield, D., Cosby, B. J., Dillon, P. J., Wade, A. J. & Whitehead, P. G. 2007 Modelling the mechanisms that control in-stream dissolved organic carbon dynamics in upland and forested catchments. *Water Res. Res.* **43**(2), W02424.

Futter, M. N. & de Wit, H. A. 2008 Testing seasonal and long-term controls of streamwater DOC using empirical and process-based models. *Sci. Total Environ.* **407**(1), 698–707.

Futter, M. N., Starr, M., Forsius, M. & Holmberg, M. 2008 Modelling long-term patterns of dissolved organic carbon concentration in the surface waters of a boreal catchment. *Hydrol. Earth Syst. Sci.* **12**, 437–447.

Henson, R. 2006 *A Rough Guide to Climate Change.* Rough Guides, London.

Holmberg, M., Forsius, M., Starr, M. & Huttunen, M. 2006 An application of artificial neural networks to carbon, nitrogen

and phosphorus concentrations in three boreal streams and impacts of climate change. *Ecol. Modell.* **195**, 51–60.

Hongve, D., Riise, G. & Kristiansen, J. F. 2004 Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water: a result of increased precipitation? *Aquatic Sci.* **66**, 231–238.

Jylhä, K., Tuomenvirta, H. & Ruosteenoja, K. 2004 Climate change projections for Finland during the 21st century. *Boreal Environ. Res.* **9**, 127–152.

Keskitalo, J., Salonen, K. & Holopainen, A.-L. 1998 Long-term fluctuations in environmental conditions, plankton and macrophytes in a humic lake, Valkea-Kotinen. *Boreal Environ. Res.* **3**, 251–262.

Köhler, S. J., Buffam, I., Laudon, H. & Bishop, K. H. 2008 Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscapes. *J. Geophys. Res.* **113**.

Laudon, H., Köhler, S. J. & Buffam, I. 2004 Seasonal TOC export from seven boreal catchments in northern Sweden. *Aquatic Sci.* **66**, 223–230.

Lepistö, A., Kortelainen, P. & Mattson, T. 2008 Increased organic C and N leaching in a northern boreal river basin in Finland. *Global Biogeochem. Cycles* **22**, GB3029.

Liski, J., Lehtonen, A., Palosuo, T., Peltoniemi, M., Eggers, T., Mukkonen, P. & Mäkipää, R. 2006 Carbon accumulation in Finland's forests 1922-2004 – an estimate obtained by combination of forest inventory data with modelling of biomass, litter and soil. *Annals Forest Sci.* **63**, 687–697.

Mattsson, T., Kortelainen, P. & Räike, A. 2005 Export of DOM from boreal catchments: impacts of land use cover and climate. *Biogeochemistry* **76**, 373–394.

Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopácek, J. & Vesely, J. 2007 Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* **450**, 537–540.

Posch, M., Aherne, J., Forsius, M., Fronzek, S. & Veijalainen, S. 2008 Modelling the impacts of European emission and climate change scenarios on acid sensitive catchments in Finland. *Hydrol. Earth Syst. Sci.* **12**, 449–463.

Rankinen, K., Karvonen, T. & Butterfield, D. 2004 A simple model for predicting soil temperature in snow covered and seasonally

frozen soil: model description and testing. *Hydrol. Earth Syst. Sci.* **8**, 706–716.

Roulet, N. T. & Moore, T. R. 2006 Browning the waters. *Nature* **444**, 283–284.

Sælthun, N. R. 1996 *The "Nordic" HBV Model. Description and Documentation of the Model Version developed for the Project Climate Change and Energy Production*. NVE Publication 7, Norwegian Water Resources and Energy Administration, Oslo.

Skjelkvåle, B. L., Stoddard, J. L., Jeffries, D. S., Tørseth, K., Høgåsen, T., Bowman, J., Mannio, J., Monteith, D. T., Mosello, R., Rogora, M., Rzychon, D., Vesely, J., Wieting, J., Wilander, A. & Worsztynowicz, A. 2005 Regional scale evidence for improvements in surface water chemistry 1990-2001. *Environ. Pollut.* **137**, 165–176.

Starr, M. & Ukonmaanaho, L. 2001 Results from the first round of the integrated monitoring soil chemistry subprogramme. In: Ukonmaanaho, L. & Raitio, H. (eds) *Forest Condition in Finland. National Report 2000*. Finnish Forest Research Institute, Helsinki, pp. 140–157, Research Papers 824.

Starr, M. & Ukonmaanaho, L. 2004 Levels and characteristics of TOC in throughfall, forest floor leachate and soil solution in undisturbed boreal forest ecosystems. *Water Air Soil Pollut. Focus* **4**, 715–729.

Syri, S., Fronzek, S., Karvosenoja, S. & Forsius, M. 2004 Sulphur and nitrogen oxides emissions in Europe and deposition in Finland during the 21st century. *Boreal Environ. Res.* **9**, 185–198.

Ukonmaanaho, L., Starr, M. & Ruoho-Airola, T. 1998 Trends in sulphate, base cations and H^+ concentrations in bulk precipitation and throughfall at integrated monitoring sites in Finland 1989-1995. *Water Air Soil Pollut.* **105**, 353–363.

Vähätalo, A. V., Salonen, K., Münster, U., Järvinen, M. & Wetzel, R. G. 2003 Photochemical transformation of allochthonous organic matter provides bioavailable nutrients in a humic lake. *Arch. Hydrobiol.* **156**, 287–314.

Vuorenmaa, J. 2004 Long-term changes of acidifying deposition in Finland (1973-2000). *Environ. Pollut.* **128**, 351–362.

Vuorenmaa, J. & Forsius, M. 2008 Recovery of acidified Finnish lakes: trends, patterns and dependence on catchment characteristics. *Hydrol. Earth Syst. Sci.* **12**, 465–478.

Vuorenmaa, J., Forsius, M. & Mannio, J. 2006 Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. *Sci. Total Environ.* **365**, 47–65.