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Changes in soil dissolved organic carbon affect reconstructed history and projected future trends in surface water acidification

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ABSTRACT

Pre-industrial (1850´s) and future (2060) streamwater chemistry of an anthropogenically acidified small catchment was estimated using the MAGIC model for three different scenarios for dissolved organic carbon (DOC) concentrations and sources. The highest modeled pH = 5.7 for 1850´s as well as for 2060 (pH = 4.4) was simulated given the assumption that streamwater DOC concentration was constant at the 1993 level. A scenario accounting for an increase of DOC as an inverse function of ionic strength (IS) of soilwater and streamwater resulted in much lower pre-industrial (pH=4.9) and future recovery to (pH=4.1) if the stream riparian zone was assumed to be the only DOC source. If upland soilwater (where significant DOC increase was observed at –5 cm and –15 cm) was also included, DOC was partly neutralized within the soil and higher pre-industrial pH=5.3 and future pH = 4.2 were estimated. The observed DOC stream flux was 2 – 4 times higher than the potential carbon production of the riparian zone, implying that this is unlikely to be the sole DOC source. Modeling based on the assumption that stream DOC changes are solely attributable to changes in the riparian zone appears likely to underestimate pre-industrial pH.

KEYWORDS

Acidification, surface waters, soils, dissolved organic carbon, MAGIC model, pre-industrial water chemistry

1. INTRODUCTION

Over the last two decades, concentrations of dissolved organic carbon (DOC) have shown widespread increases in surface waters in several regions in Europe (Pärn and Mander 2012; Hruška et al. 2009; Monteith et al. 2007) and North America (SanClements et al. 2012). The increases in DOC have been ascribed primarily to decreased acid deposition (Hruška et al. 2009; Monteith et al. 2007; Evans et al. 2005), and the mechanism appears to be increased solubility of DOC due to decreased ionic strength of soil solution. Concentrations of DOC in acidified surface waters were thus probably higher in pre-industrial times relative to present-day levels and may increase further in the future if acid deposition continues to decline.

DOC decreases soil solution and surface water pH, increases concentrations of base cations and thus acid neutralizing capacity (ANC). Over the long term, soil base saturation is also affected. These parameters influence the health and vitality of aquatic and terrestrial organisms. The EU Water Framework Directive (2000/60) mandates achievement of good ecological status of all water bodies, including with respect to acidification. Assessment of good ecological status requires setting of the unpolluted reference condition to which the present-day state is to be compared. The question of historical DOC concentrations is therefore important for quantifying present-day acidification and determining potential future recovery of surface waters.

Due to the paucity of historical data, estimates of pre-acidification chemical and biological status usually come from modeling applications. This is also the case for DOC. Modeling DOC concentrations is predicated upon understanding the factors driving the observed changes. Determination of the origin of DOC in surface waters is key. Erlandsson et al. (2011) and Löfgren and Zetterberg (2011) have argued on the basis of data from Sweden that riparian zone processes account for the increased DOC in surface waters. Alternatively, increased concentrations of DOC in organic layers across the entire catchment could cause the observed increases in DOC in surface waters. The cause of the observed increases in surface water DOC concentrations affects the calibration and application of models to reconstruct past and project future surface water chemistry.

Here we use the long-term observed soil, soil solution and streamwater chemistry data from the Lysina catchment, Czech Republic, to develop empirical relationships between DOC and ionic strength in soil- and streamwater. We then use the process-oriented acidification model MAGIC (Cosby et al. 2001; Cosby et al. 1985) to evaluate the potential effect on soil- and streamwater acidification on the alternative possible sources of the increased DOC -

riparian versus organic layers. Lysina is a well-documented catchment in the formerly heavily polluted “Black Triangle” region in Central Europe (Oulehle et al. 2008). The streamwater shows chemical recovery from acidification and concurrent increases of soil- and streamwater DOC since 1990´s as a result of declining atmospheric deposition in the region (e.g. Hruška et al. 2009). Acidification of freshwaters is addressed by both the UN-ECE Convention on Long-range Transboundary Air Pollutants (LRTAP) and the European Union’s Water Framework Directive (WFD). Both of these international environmental policies strive to achieve good ecological quality in European freshwaters. Both are underpinned by scientific assessments of present-day acidification status relative to past reference conditions and to possibilities of achieving recovery from acidification in the future. For example, for surface waters in Sweden a contemporary pH<0.4 units below the 1860 reference pH is regarded as the threshold value for good ecological status according to the WFD with respect to acidification (Fölster et al. 2007, SEPA 2010). Realistic estimates of effect of DOC on historical pH are therefore essential. Thus reconstruction of the past and prognosis for the future requires application of models such as MAGIC.

2. SITE DESCRIPTION

The Lysina catchment (Table 1) is located in the Slavkov Forest, a mountainous region in the western Czech Republic (Figure 1). Lysina is an acid-sensitive site underlain by base-poor bedrock and soil with even-aged Norway spruce (*Picea abies*) plantations. Local soil is classified as a Folic Albic Skeletic Podzol with a sandy loam structure and a depth of about 120 cm. Organic layer thickness varied typically between 4-7 cm. Soil pH_w increases with depth from 3.4. to 4.2 (Banwart et al. 2012). Lysina is part of several catchment monitoring networks, e.g. in the Czech GEOMON (Oulehle et al. 2008), the international SoilTrEC Critical Zone Observatories (Banwart et al. 2012), and the International Cooperative Programmes on Waters and Integrated Monitoring (ICP Waters and ICP IM) (Holmberg et al. 2013).

3. MATERIAL AND METHODS

3.1. Deposition, soil- and streamwater sampling

Bulk precipitation (since 1990) and throughfall (since 1991) were collected monthly. Soilwater samples were collected monthly since 1992 by means of zero-tension lysimeters at 5 (beneath O horizon, two lysimeters) and 15 cm (below E horizon, two lysimeters) depth, and by tension lysimeters at 80 cm (lower B horizon, two lysimeters) depth. The lysimeters are located at the hillslope representing the most common soil type (skeletic podzol) and forest stand age (40-50 years old). Streamwater samples for chemical analysis were collected monthly in 1989 and weekly since 1990. Streamwater samples were also collected irregularly during high flow events (storms and intensive snowmelt). Streamflow from the catchment was monitored continuously since 1989 using a V-notch weir and a mechanical water level recorder. All annual mean concentrations for streamwater are discharge-weighted and are based on a November – October water year. Annual arithmetic means based on water year were used for soilwater. Oulehle et al. (2008) provide additional details on catchment chemistry.

3.2. Chemical analyses

Concentrations of Cl^-, SO_4^{2-}, and NO_3^- in water samples were determined by ion-exchange HPLC, F^- by ion-selective electrode after TISAB buffer addition, and concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, and Al by atomic absorption spectroscopy (AAS) in unfiltered samples (Oulehle et al. 2008). Solution pH was determined using a combination glass electrode. DOC (filtered 0.45 µm) was determined using platinum-catalyzed, high-temperature oxidation using the non-purgeable organic carbon method (Hruška et al. 2009).

3.3. Ionic strength (IS)

Ionic strength was calculated from the chemistry of inorganic constituents (mol L^{-1}):

$$IS = 1/2 \sum_{i=1}^{n} c_i Z_i^2 \qquad \text{(Eq. 1)}$$

where c is the concentration and Z is the ionic charge of ion i. The IS was calculated from the measured concentrations of major cations and anions: Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, Al^{n+}, H^+, SO_4^{2-}, NO_3^-, Cl^- and F^-. The inorganic Al fraction was determined by the Al speciation method of Driscoll et al. (1984) modified for high Al concentrations (Hruška et al. 1994). The concentrations of inorganic Al species (mostly Al-F and Al-OH complexes) were calculated using the chemical equilibrium model ALCHEMI (Schecher and Driscoll 1987). Thus the effect of DOC and F on Al charge was included in IS calculation.

3.4. Acid neutralizing capacity (ANC)

ANC was calculated on an equivalent basis as the difference between base cations and strong acid anions (μeq L^{-1}):

$$ANC = (Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}) - (Cl^{-} + SO_4^{2-} + NO_3^{-}) \qquad \text{(Eq.2)}$$

Although F^- is also a strong acid anion, it was not used in the calculation of ANC, as concentrations are low and assumed not to change over time; these assumptions are usual in MAGIC model applications (e.g. Cosby et al. 1985, 2001).

3.5. The MAGIC model

3.5.1. Model description

MAGIC (Model of Acidification of Groundwater in Catchments) is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on soil and surface water chemistry (Cosby et al. 2001; Cosby et al. 1985). The model simulates soil and surface water chemistry in response to changes in drivers such as deposition of S and N, silvicultural practices, and climate. MAGIC calculates for each time step (annual time steps were used for this study) the concentrations of major ions under the assumption of simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation-speciation of aluminum and dissolution-speciation of inorganic and organic carbon compounds. MAGIC accounts for the mass balance of major ions in the soil by accounting for the fluxes from atmospheric inputs, chemical weathering, net uptake in biomass and loss to runoff. Data inputs required for calibration of MAGIC comprise catchment characteristics, soil chemical and physical characteristics, input and output fluxes for water, concentrations of major ions, and net uptake of base cations and N by vegetation.

3.5.2. MAGIC calibration

Measured data for catchment characteristics, soil, deposition and streamwater volume and chemistry were used to calibrate MAGIC. The fixed parameters (constant values that must be specified) were measured or estimated (such as soil depth and cation exchange capacity) (Table 2) or obtained by optimization as part of the calibration procedure (such as cation exchange coefficients and base cation weathering rates) (Table 3). Cosby et al. (2001) give definitions and details. MAGIC was calibrated to the average streamwater and soilwater chemistry for the period 1990 – 1991. The calibration proceeded by sequential steps. The first steps involved calibration of the strong acid anions; Cl^-, SO_4^{2-} and NO_3^- were calibrated by adjusting the deposition inputs and/or ecosystem uptake as described by Wright and Cosby (2003). This procedure resulted in the modeled sum of strong acid anions (SAA) in water equal to that observed. The next steps involved calibration of the base cations Ca^{2+}, Mg^{2+}, Na^+, and K^+. Here the model was run from an assumed steady-state condition in year 1850 to year 2010. A trial and error process was used to adjust the weathering rates of Ca^{2+}, Mg^{2+}, Na^+, and K^+ and initial soil exchange pools of these four cations until modelled concentrations of base cations in the streamwater, soilwater and modelled pools of base cations in the soil matched the observed for the calibration period 1990-2010. This step calculated the soil-soilwater selectivity coefficients for base cations and Al exchange and the weathering rates for the four base cations (Table 2). At this point the modelled sum of base cations (SBC) equalled the observed for the calibration period, and thus also the modelled acid neutralising capacity (ANC) equalled the observed ANC (ANC was defined as SBC – SAA, Eq. 2). The final step entailed calibration of the weak acids (DOC) such that the simulated concentrations of H^+, Al^{n+} and organic anions (A^-) matched observations. This was achieved by adjusting the dissociation constants for organic acids, aluminum hydroxide, fluoride, and sulfate species, and organic aluminum complexes. We used a tri-protic model for organic acids with dissociation constants given by Hruška et al. (2003, Table 2).Relationships between DOC and IS in soilwater and streamwater were calculated using a power regression model for the period 1993-2010 (streamwater: $DOC = 749.2*IS^{-0.5540}$ $p<0.01$, soilwater – 5cm: $DOC = 494068*IS^{-1.3504}$, $p<0.01$, soilwater -15 cm: $DOC = 41974*IS^{-1.0049}$, $p<0.01$) Long-term DOC concentrations were calculated using estimates of IS from the inorganic chemistry simulated by the MAGIC model for the period 1850-2060.

In a study based on $H_2{}^{18}O$ measurements in precipitation, soilwater and runoff, Buzek et al. (1995) calculated that on an annual basis streamwater at Lysina consists of about 5% direct overland flow and 95% leachate from soil. Of the latter, 40% drains from the upper mineral soil layer (-15 cm). The measured increase of DOC concentration in this layer was 192% between 1994 and 2010 (Figure 2). As there is no evidence of changes in DOC concentration in deep mineral soil (-80 cm), we assumed this to be constant and very low (measured data from 1993-4 and 2012 between 2.3-3.4 mg L^{-1}). Thus the observed 192% increase of DOC flux in upper mineral soil was assumed to lead to a 36% increase in concentration of DOC in leachate from soil entering the stream from 1993-2010.

3.6. Scenarios for DOC in soil and streamwater

Three scenarios were modeled for the period 1850-2060 using different sets of assumptions concerning soil and streamwater DOC concentrations:

A. Constant stream and soilwater DOC concentration as measured in 1993 (stable DOC scenario)
B. Changing DOC over time inversely to IS only in stream (Figure 4) and not in soilwater for the catchment as a whole (riparian DOC scenario)
C. Changing DOC over time inversely to IS in soilwater (Figure 3) throughout the catchment as well as in streamwater (Figure 4, soil DOC scenario)

The MAGIC model was calibrated first for stable DOC in the stream using scenario A and then recalibrated to fit observed streamwater chemistry using changes of DOC parameters (scenarios B and C).

For calibration and recalibration the measured or estimated parameters used were always identical for all three scenarios. The optimized parameters (cation exchange coefficients and base cation weathering rates) were changed to fit measured soil and stream chemistry data. Scenario B represents riparian source of DOC solely, with no connection with upland soils within the catchment. Thus optimized parameters connected to soil properties (all of them in Table 3) did not differ between scenarios A and B. Only acid-base characteristics connected with DOC (e.g. pH at Figure 5) has changed.

4. RESULTS

4.1. Observed chemical trends

The Lysina catchment was strongly acidified by atmospheric deposition during the second half of the 20th century (Hruška and Krám 2003; Krám et al. 1995; Krám et al. 2012); sulfur (S) and nitrogen (N) deposition (as estimated by throughfall fluxes) peaked in the late 1980's. Deposition of S then declined from 30-34 kg ha^{-1} to 5-7 kg ha^{-1} in 2008-2010. (Figure 6) Inorganic N deposition decreased from 12-14 kg ha^{-1} to 7-10 kg ha^{-1} over the same period. In the stream, recovery was manifest mainly by a major decrease in sulfate concentrations from 568 µeq L^{-1} in 1990 to 116 µeq L^{-1} in 2010. This 80% decline relative to 1990 mirrors the 77-85% decline in atmospheric S deposition. The lower concentrations of strong acid anions were balanced by decreasing concentrations of sum of base cations (SBC = Ca^{2+} + Mg^{2+} +Na^{+} + K^{+}) from 434 µeq L^{-1} in 1990 to 144-174 µeq L^{-1} in 2008-2010, dissolved aluminum (from 56 µmol L^{-1} to 28-29 µmol L^{-1}), and to a lesser extent H^{+} (from 126 µeq L^{-1} to 80 µeq L^{-1}). Streamwater pH increased from 3.9 in the early 1990's to 4.1 in 2010. Chemical recovery at Lysina is described in detail by Hruška and Krám (2003) and Krám et al. (2012) and is typical for recovery from acidification of poorly-buffered catchments (e.g. Moldan et al. 2013). More detailed streamwater chemistry is available (Online Resource 1).

During the recovery the mean annual DOC concentrations increased significantly in streamwater as well as in soilwater ($p<0.001$, Figure 2). There are large year-to-year variations due to variations in precipitation amount with higher DOC concentrations in wet years (see Online Resource 2). The annual mean streamwater DOC concentration increased from 15.6-16.9 mg L^{-1} (1993-1994) to 21.8-24.5 mg L^{-1} in 2010-2011, an average annual increase of 0.6 mg L^{-1} $year^{-1}$ ($p<0.001$). Even stronger DOC trends were observed for water draining the upper soil horizons (Figure 2). Mean annual DOC increased from 41-42 mg L^{-1} in 1993-1994 to 67-74 mg L^{-1} in 2010-2011 at 5 cm depth beneath the O horizon, an annual increase of 2.7 mg L^{-1} $year^{-1}$ ($p<0.001$). At 15 cm depth below the E horizon DOC concentrations increased from 31-34 mg L^{-1} to 68-73 mg L^{-1}, an annual increase of 1.9 mg L^{-1} $year^{-1}$ ($p<0.005$). Hruška et al. (2009) showed that change in ionic strength (IS) is the best predictor of observed changes in DOC at this site.

4.2. Scenarios for DOC in soil and streamwater

The resultant optimized parameters for the soil DOC scenario C include higher weathering rates for Ca, Mg, Na and K compared to the constant DOC scenario A, but with lower initial (year 1850) Ca and Mg % saturation of the soil cation exchange complex (Table 3). The simulated streamwater DOC concentrations agreed fairly well with the observed for the period 1993-2010 (Figure 4). The higher observed versus modeled DOC concentrations in 2002 and 2007 may be due to weather conditions during this time. The extremely wet year 2002 (annual runoff 747 mm was highest recorded since 1989) and the high number of summer storms in 2007 resulted in positive residuals from the DOC-IS relationship.

All modeled scenarios satisfactorily reproduced measured mean annual chemistry for the period 1990-2010 (Figure 5).The most striking changes in DOC - sharp decrease between 1950´s – 1980´s and increase between 1990´s and 2010´s - was caused mainly by changes in S deposition in the region (Figure 6). Historical estimate of S deposition was derived from Kopáček and Veselý (2005) for the period 1860-1990. The leveling of DOC concentrations (Figure 3 and 4) for the future corresponds with model predictions of future S deposition in Europe where only slight decreases are expected from 2010 to 2030 under the scenario of full implementation of current legislation (CLE) (Schöpp et al. 2003).

4.3. Streamwater acidity

The three DOC scenarios gave different simulated values for pre-industrial (1850) streamwater acidification parameters (Figure 5). Under the constant DOC scenario A pre-industrial streamwater pH was simulated to be 5.7 (Figure 5) and future pH (to 2060) was estimated to be 4.4. Under the riparian only scenario B pre-industrial streamwater pH was simulated to be 4.9 and future pH only 4.1. Under the scenario with DOC changes in both soil and streamwater (scenario C) a pre-industrial streamwater pH of 5.3 and a future pH of 4.2 was simulated.

4.4. Base cations and soil base saturation.

The stable DOC scenario A and riparian DOC scenario B gave estimated pre-industrial base cation concentrations of about 185 μeq L^{-1} and a future prediction of about 160 μeq L^{-1} after 2020 (Figure 5). When changes in soilwater DOC were taken into account (scenario C), historical estimated base cation concentrations increased to 220 µeq L^{-1}, and the future prediction was 185 µeq L^{-1}. Historical soil base saturation (Figure 5) was estimated to be 27.5% and future prediction of 5.5% for both A and B scenarios after 2020. Inclusion of soilwater DOC dynamics resulted in pre-industrial base saturation of 23.5% and future prediction of 7.0%.

4.5. Acid neutralizing capacity (ANC)

ANC was modeled at 130 µeq L^{-1} for the pre-industrial period for both A and B scenarios, decreased significantly during period of high acidic deposition (minimum –235 µeq L^{-1} in 1986) and was predicted to increase to 15-25 µeq L^{-1} after 2020 (Figure 5). A slightly higher ANC was estimated for scenario C: 165 µeq L^{-1} for 1850, with substantially greater predicted recovery to 40-50 µeq L^{-1} after the year 2020.

5. DISCUSSION

5.1. DOC trends.

The increases in concentrations of DOC in streamwater as well as soilwater at Lysina (Figure 2) are among the largest reported from acid-impacted sites in the Northern Hemisphere. The widespread increases in surface water DOC concentrations reported from many regions are widely believed to be due to decreasing acid deposition and associated decreased acidity of soilwater and streamwater (Monteith et al. 2007; Clark et al. 2011; SanClements et al. 2012). Although a number of other climatic and land-use related factors have also been invoked as possible explanations for some or all of the observed changes (Pärn and Mander 2012; Eimers et al. 2008; Sarkkola et al. 2009; Zhang et al. 2010), recent data from field manipulation experiments provide strong support for deposition change as a major driver (Evans et al. 2008; Evans et al. 2012; Evans et al. 2005; Ekström et al. 2011; Moldan et al. 2012; Kopáček et al. 2009; Bragazza et al. 2006). It is hard to disentangle IS and acidity control on DOC mobility. It is not trivial (even not possible) to use acidity as driving force for estimating historical DOC concentration. DOC, as weak acid acid-base system, contributes significantly to stream and soilwater acidity, and the depletion of soil cations-exchange complex and Al mobilization by high deposition of strong acids has changed soil and water acidity (e.g Hruška et al. 2009; Evans et al. 2005). Present soil and streamwater pH is significantly lower compared to similar deposition loads in the beginning of the 20th century. The effect of IS on DOC coagulation is another potentially important mechanism affecting DOC concentrations. Decreasing IS as a result of decreasing deposition should lead to lower concentrations of divalent ions in soils and streams (Ca^{2+}, Mg^{2+}, SO_4^{2-}) and thus a lower IS (eq. 1). Several studies have shown explicitly that increasing IS reduces DOC concentrations (e.g. Hruška et al.2009). Regional studies, and intensive evaluation of catchment monitoring attributed observed increases in DOC concentrations to reduced atmospheric deposition, but they do not distinguish between the effects of pH and Al, nor the effects of ionic strength alone (Monteith et al. 2009). At Lysina the majority of the IS decrease was caused by declining SO_4^{2-} deposition and consequently a decline of SO_4^{2-} and base cation concentrations in soilwater and streamwater (see Online Resource 1). For both SO_4^{2-} and base cations, long-term trends are possible to model with MAGIC independently of acid-base characteristics. Thus IS provides a reasonable proxy for DOC. Nevertheless, it is not yet completely resolved whether the key mechanism responsible for observed DOC responses to changing deposition is the decrease of acidity itself, resulting in lower H^+ and dissolved Al (Evans et al. 2012; Clark et al. 2011), or the decrease in ionic strength (e.g. (Hruška et al. 2009; Moldan et al. 2012). This uncertainty arises in part from the fact that both possible mechanisms respond simultaneously to changes in ambient deposition, making their relative importance difficult to disentangle from monitoring data. Data from experiments where alkaline treatments have been applied (reducing acidity but increasing IS), indicate a rise in DOC, providing some support for the role of acidity as the dominant control on DOC mobility (Ekström et al. 2011). However, evidence of DOC increases from base-rich catchments (where IS responds more strongly than pH to deposition changes) suggests an important role for ionic strength (Hruška et al. 2009). In practice, since pH and IS are both strongly linked to S deposition, assumptions made about their relative importance would not fundamentally alter the trajectory of modeled DOC change.

5.2. Reconstruction of historical DOC.

Water chemistry, represented by IS or SO_4^{2-} concentrations, has been used by several authors as a proxy for long-term DOC changes. Kopáček et al. (2009) used SO_4^{2-} concentrations to estimate the long-term change of DOC at Plešné Lake in the Bohemian Forest, Czech Republic. Their results indicated that decreases in DOC concentrations of 70-80% during acidification in comparison to pre-industrial levels. Evans et al. (2005) used the combination of SO_4^{2-} deposition, rainfall and summer temperature to estimate temporal DOC changes for an upland stream in UK. The simulated decline in DOC concentrations during acidification was ca. 70% relative to the pre-industrial concentrations. Based on experimental evidence of increased DOC leaching in response to nitrogen addition (Bragazza et al. 2006), and theoretical links between nitrogen availability, net primary productivity and DOC production in low-nutrient systems, Tipping et al. (2012) used the N14C model to simulate a long-term increase in DOC leaching since the pre-industrial period. As noted by the authors, the model omits acidity controls on carbon cycling, and further work is needed to establish the importance of N deposition as a driver of increased DOC leaching. A recent extension of N14C to incorporate acidity effects on DOC mobility (Rowe et al., in review) suggests that the acidity effect dominates historical and recent DOC variations, whilst any nitrogen effect might become more evident in the future, as S deposition stabilizes at low levels. Paleolimnological reconstructions of DOC by near infrared spectroscopy from lake sediments in Sweden (Cunningham et al. 2011) also support a dominant role of acidification on historical DOC variations, suggesting that pre-industrial lake water DOC concentrations were two times higher compared to present. Thus our estimate of the reduction in stream DOC by 58% with respect to pre-industrial concentrations during the 1980s falls within the range of most published data. Positive residuals in observed versus modeled DOC in recent wet years, as well as negative residuals during dry years, also highlight the potential sensitivity of DOC leaching to inter-annual hydrological variation (see also Erlandsson et al. (2008); any future climatic shift towards wetter or drier conditions at this site could, therefore, moderate the long-term trajectory of DOC change shown in Figures 3-4.

5.3. DOC origin

Soils, in particular shallow organic soils, are thought to be the main source of DOC in most headwater catchments (Cunningham et al. 2011). Recent studies from Sweden (Erlandsson et al. 2011; Löfgren et al. 2010), however, suggested only a minor contribution of soilwater DOC to streamwater concentrations. Instead, they argue that most of the DOC derives from the riparian zone around streams. This hypothesis, however, is not supported by available long-term soil solution data. The majority of reported DOC trends in the organic layers in areas recovering from acidification suggest increases similar in magnitude to those observed in surface waters (Hruška et al. 2009; Borken et al. 2011; Stutter et al. 2011). For mineral soil horizons the picture is more mixed, with increases at some sites (Stutter et al. 2011; Hruška et al. 2009), but decreases at others (Löfgren and Zetterberg 2011; Stutter et al. 2011; Borken et al. 2011).

There are limits to how much DOC a riparian zone could produce alone without replenishment of DOC by leachate from upland soils. At Lysina, the total length of riparian zone along the stream channel and associated artificial ditches is estimated to 2700 meters (Figure 1). Along these channels the riparian zone is irregularly developed. We estimate the area of the riparian zone (based on width between 0.25-1 m along the stream) to be between 1400 and 5500 m^2, comprising 0.5 to 2% of the total catchment area). *Sphagnum* species which dominate those wet environments typically have an annual net primary productivity (NPP) of carbon ranging between 200 and 400 g C m^{-2} yr^{-1} (Gunnarsson 2005). Thus 400 to 1700 kg C yr^{-1} could be produced by the riparian zone each year. This amount of C, assuming steady state conditions, is then available for heterotrophic respiration (with subsequent partitioning between CO_2 and DOC). Annual average export of DOC (2007-2009) was 118 kg ha^{-1} yr^{-1}, thus total annual export from the whole catchment was 3221 kg C yr^{-1}, which is 2 – 4 times more than our estimate of total NPP of *Sphagnum* species along stream channels. It is thus unlikely that the riparian zone is the sole source of DOC exported in streamwater. Based on the ^{18}O study (Buzek et al. 1995), consistent and coherent increases of shallow mineral soilwater DOC concentration and streamwater DOC, and the insufficient spatial extent of riparian wetlands to provide the full observed DOC flux, we believe that substantial part of DOC in the stream is derived from upland forest soils by lateral transport through the shallow mineral soil, which contributes around 40% to annual catchment runoff. The 36% increase in soil DOC leachet entering the stream (derived from observed soilwater DOC increases and ^{18}O data) agrees very well with 37% observed increase of streamwater DOC (Figure 2). This result suggests that there is no need to invoke additional sources or biogeochemical processes within the riparian zone in order to explain observed DOC trends.

5.4. Weak acid-base chemistry and base cation fluxes

Organic acids are represented in MAGIC by a triprotic acid analogue (Hruška et al. 2003; Driscoll et al. 1994). The total organic acid concentration is based on charge density and the observed DOC in runoff. The charge density is calibrated such that the simulated and observed weak acid anion concentrations agree. The higher soil solution concentration of organic acids in scenario C resulted in more acidic soil conditions in the beginning of simulation (1851) with subsequently more negative Al-base cations (Al-BC) selectivity coefficients (Table 3). As a consequence, higher calibrated weathering rates of base cations and slightly lower initial base saturation were required to fit the observed values (Table 2 and 3). From the conceptual point of view, as accommodated in the MAGIC model, it is clear that changing soil solution organic acid concentration affects Al-BC selectivity coefficients, thus affecting the calibrated weathering rates and consequently modeled concentrations of streamwater base cations and soil base saturation (Figure 5). Adjusted BC fluxes to fit the observed data in scenario C resulted in higher initial pH (pH of 5.3) when compared to scenario B where only a DOC increase in streamwater was modeled (pH of 4.9). Soil processes are sensitive to organic acid concentrations and omitting their long-term changes could lead to unrealistic estimates of pre-acidification conditions (Evans et al. 2005).

5.5. Comparison of stream-water chemistry among scenarios

As illustrated by the example here from the Lysina catchment (Figure 5), an understanding of the processes controlling DOC concentrations in soil and water is central to such modeling. Based on documented time series from the last two decades, it seems clear that estimates based on stable DOC from the 1990s (solid black lines in Figure 5) give unrealistically high simulated pre-industrial pH (5.7) as well as future predicted pH increases. Scenarios based on an IS-DOC relationship (Figure 3) give a better fit to observations, and result in higher simulated pre-industrial DOC and lower pH (dotted black and dotted grey lines in Figure 5). The scenario taking account of soilwater contributions to streamwater DOC resulted in a pre-industrial estimate of pH=5.3. The estimate based on a riparian-only DOC contribution to the stream resulted in a pre-industrial pH of only 4.9. We consider this later scenario also unrealistic, because there is insufficient potential carbon supply from the riparian zone to generate the observed DOC exports, and because observed DOC changes in streamwater could be effectively reproduced by simple mixing of observed DOC leachate chemistry from the upper soil with a fixed lower soilwater input, without the need to invoke additional riparian processes. Thus, the most plausible scenario appears to be the change in soilwater DOC in the organic soil horizon throughout the catchment. This may help to explain previous observations that the MAGIC model tends to give a higher simulated pre-industrial pH estimate than paleolimnological techniques (Battarbee et al. 2005). On the other hand, this scenario slightly increased the estimated pre-industrial ANC as a result of higher weathering rate of base cations (Table 3). Modeling pre-industrial pH based on the assumption that stream DOC changes are solely attributable to changes in the riparian zone (Erlandsson et al.

2011) appears likely to result in a substantial under-estimate of pre-industrial pH, because this assumption does not account for the increased loss of base cations from the soil. To arrive at present-day concentrations of base cations, therefore, one must start with higher weathering rates of base cations in the past, and thus higher pH in the past.

Finally, our study has some implications for catchment management. In relation to both acid-base chemistry and DOC leaching, our results suggest that water quality is controlled by processes operating at the whole-catchment scale, and by external (i.e. atmospheric deposition) drivers. It is thus highly doubtful whether it would be possible to arrest recent increases in surface water DOC (which are often viewed as detrimental, for example from a water treatment perspective) through altered riparian zone management. While this conclusion may not necessarily apply to other water quality issues such as eutrophication or organic pollutants, we argue that, in general, a whole-catchment approach to water quality management is likely to be more effective than a focus solely on riparian ‘buffer zones’.

6. CONCLUSIONS

We show that changes in DOC concentrations in soilwater within the forest catchment can significantly affect predictions of past and future streamwater chemistry. Taking into account soilwater contributions to streamwater chemistry and modeled long-term changes in DOC concentrations in response to changing deposition chemistry, the historical pH of streamwater was estimated to be lower than if DOC had remained constant over time (pH=5.3 versus pH=5.7). Incorporating variable DOC also resulted in lower estimates of historical soil base saturation (23.5% versus 27.5%) and higher base cation weathering rates (80.5 meq m^{-2} yr^{-2} versus 66.5 meq m^{-2} yr^{-2}).

The hypothesis that riparian zone is the sole source of DOC in streamwater was rejected, as there was insufficient potential carbon supply from the riparian zone. Observed DOC stream flux was 2-4 times higher than the potential carbon production in riparian zone.

7. ACKNOWLEDGEMENTS

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Figure captions

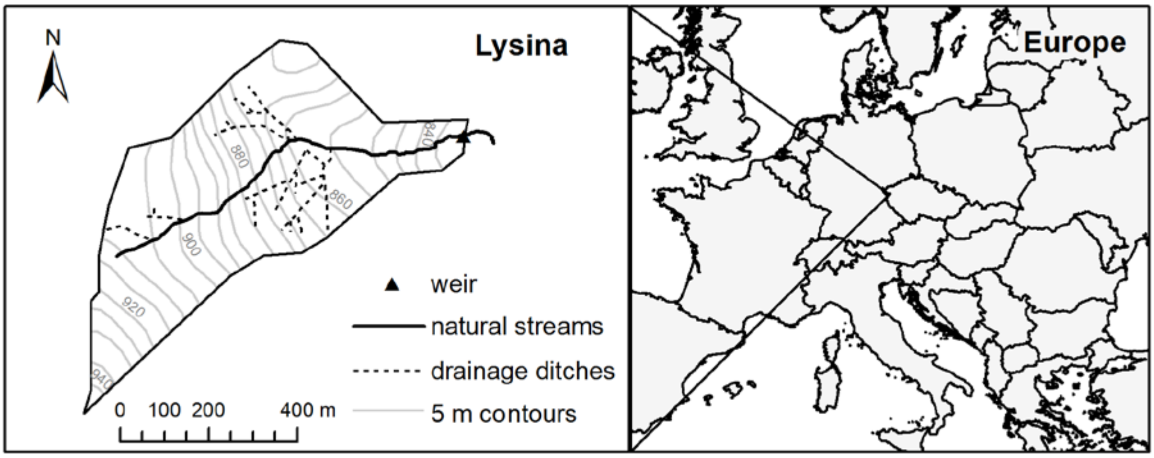


Figure 1. Map of Europe showing Lysina catchment with natural streams and drainage ditches.

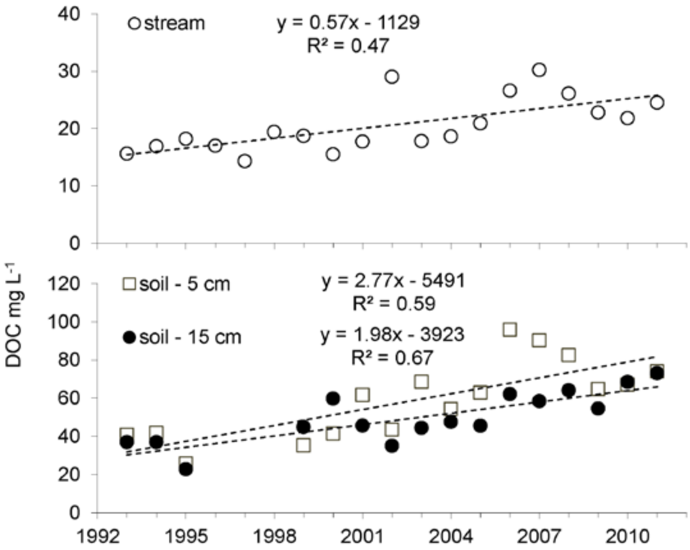


Figure 2. Trends in mean annual DOC is streamwater (open circles) and soilwater (squares: -5 cm depth, black circles: -15 cm depth) for the period 1993-2011 at the Lysina catchment.

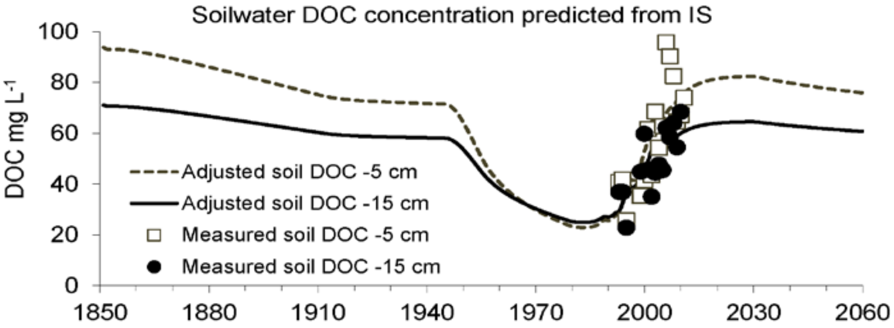


Figure 3. Reconstructed and predicted trends of DOC in soilwater at -5 and -15 cm for the period 1851-2060. DOC was adjusted by IS derived from MAGIC calibration.

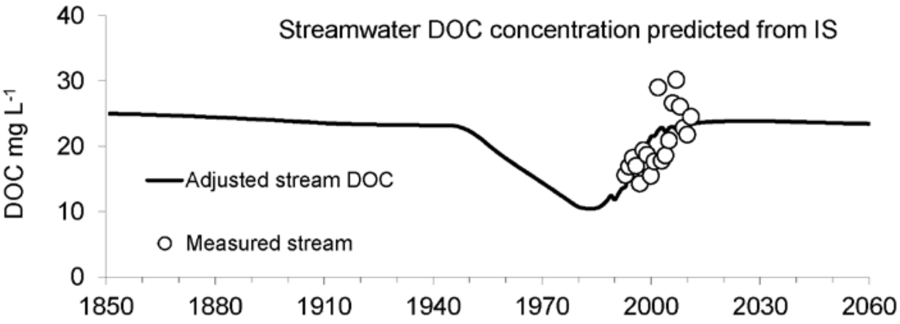


Figure 4. Reconstructed and predicted trends of DOC in streamwater for the period 1851-2060. DOC was adjusted by IS derived from MAGIC calibration.

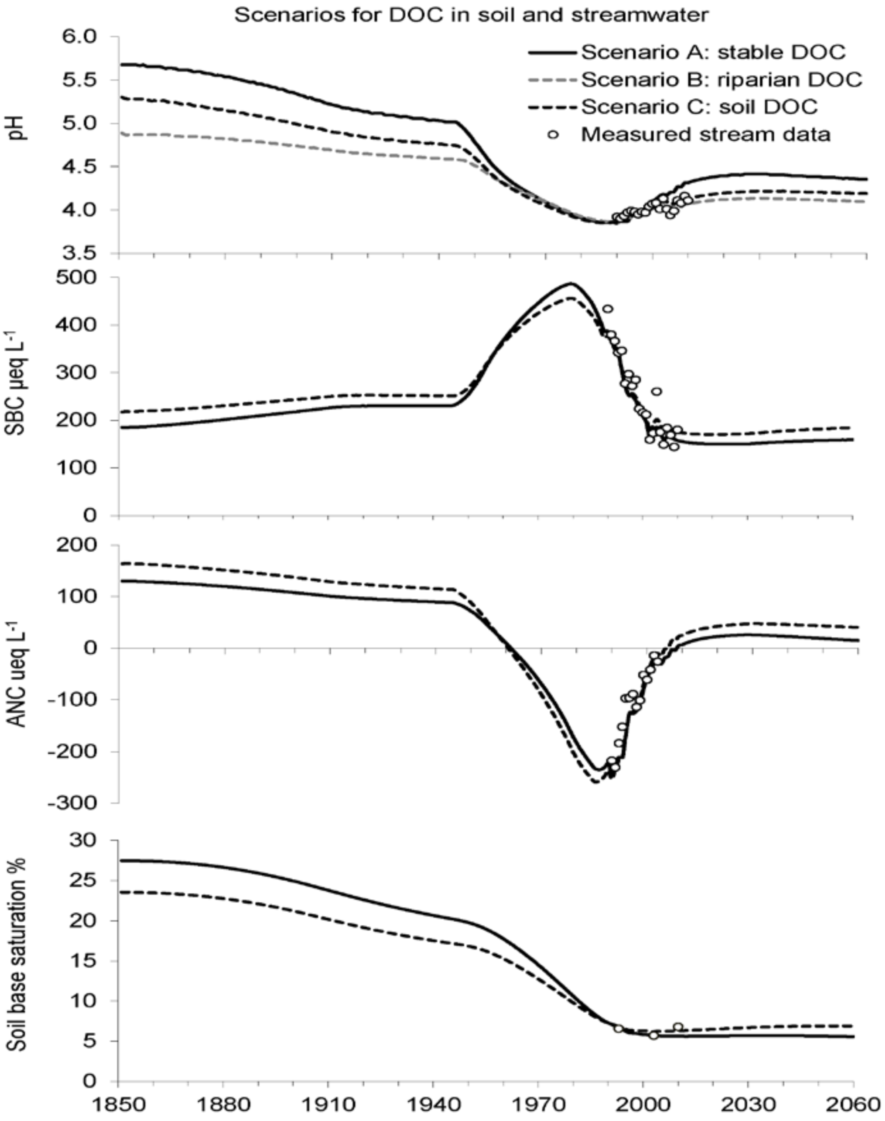


Figure 5. Simulated and observed pH, concentrations of sum base cations (SBC) and ANC in streamwater and % base saturation in soil at Lysina between 1851-2060. The solid black line depicts the simulation with constant DOC concentrations as measured in 1993 (scenario A). The gray dotted line depicts the situation when all streamwater DOC was derived from riparian zone only (scenario B). The dotted black line shows the scenario with simultaneous increases of DOC in soilwater and streamwater (scenario C). Scenario B is not shown where it is identical with scenario A.

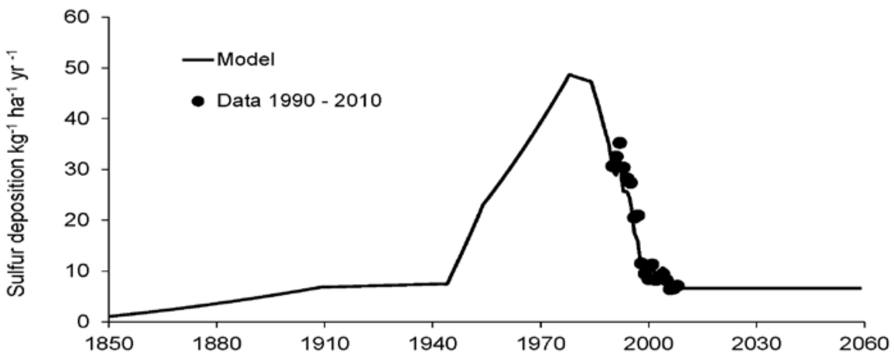
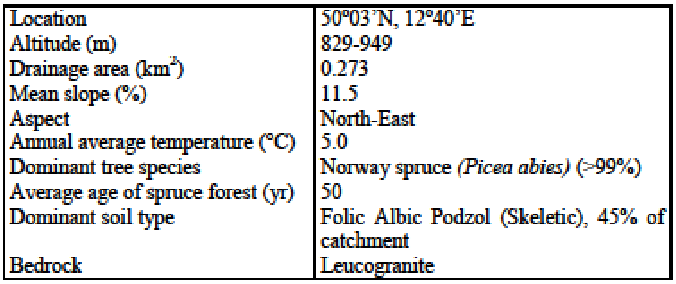


Figure 6. Deposition of S at Lysina over the period 1850 - 2050. The estimated historical trend between 1860-1990 is from Kopáček & Veselý (2005), and the future trends assume full implementation of the CLE scenario (solid line). Circles show the measured annual deposition (1991-2010).

Table captions:

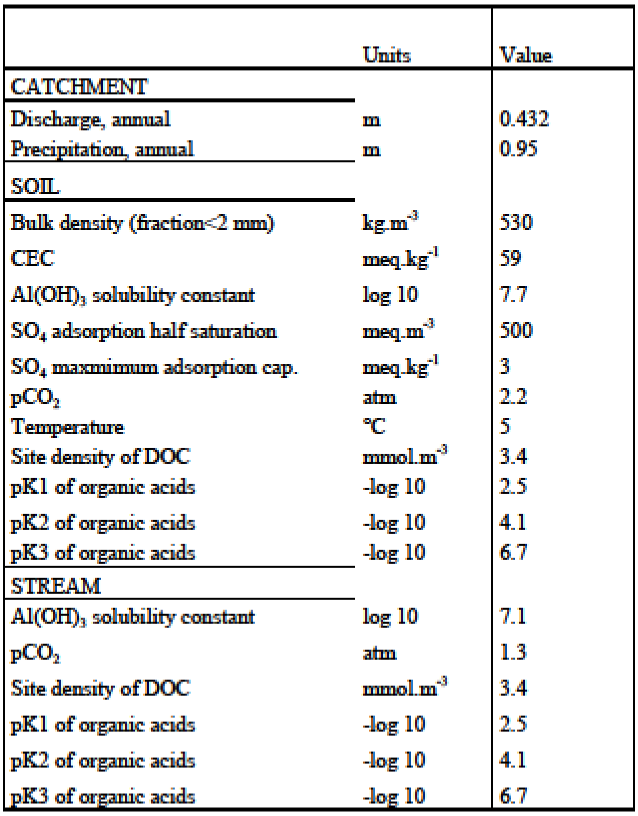
Table 1. Characteristics of the Lysina catchment

Tab. 1.



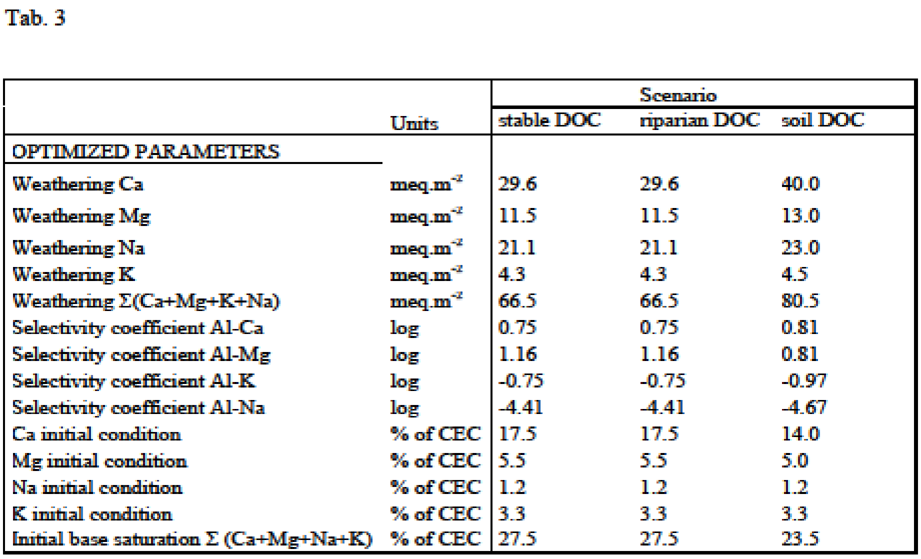
Location	50°03'N, 12°40'E
Altitude (m)	829-949
Drainage area (km^2)	0.273
Mean slope (%)	11.5
Aspect	North-East
Annual average temperature (°C)	5.0
Dominant tree species	Norway spruce *(Picea abies)* (>99%)
Average age of spruce forest (yr)	50
Dominant soil type	Folic Albic Podzol (Skeletic), 45% of catchment
Bedrock	Leucogranite

Tab. 2



	Units	Value
CATCHMENT		
Discharge, annual	m	0.432
Precipitation, annual	m	0.95
SOIL		
Bulk density (fraction<2 mm)	kg.m^{-3}	530
CEC	meq.kg^{-1}	59
$Al(OH)_3$ solubility constant	log 10	7.7
SO_4 adsorption half saturation	meq.m^{-3}	500
SO_4 maxmimum adsorption cap.	meq.kg^{-1}	3
pCO_2	atm	2.2
Temperature	°C	5
Site density of DOC	mmol.m^{-3}	3.4
pK1 of organic acids	-log 10	2.5
pK2 of organic acids	-log 10	4.1
pK3 of organic acids	-log 10	6.7
STREAM		
$Al(OH)_3$ solubility constant	log 10	7.1
pCO_2	atm	1.3
Site density of DOC	mmol.m^{-3}	3.4
pK1 of organic acids	-log 10	2.5
pK2 of organic acids	-log 10	4.1
pK3 of organic acids	-log 10	6.7

Table 2. Selected fixed parameters used to calibrate MAGIC to Lysina.



Tab. 3

	Units	Scenario		
		stable DOC	riparian DOC	soil DOC
OPTIMIZED PARAMETERS				
Weathering Ca	meq.m^{-2}	29.6	29.6	40.0
Weathering Mg	meq.m^{-2}	11.5	11.5	13.0
Weathering Na	meq.m^{-2}	21.1	21.1	23.0
Weathering K	meq.m^{-2}	4.3	4.3	4.5
Weathering Σ(Ca+Mg+K+Na)	meq.m^{-2}	66.5	66.5	80.5
Selectivity coefficient Al-Ca	log	0.75	0.75	0.81
Selectivity coefficient Al-Mg	log	1.16	1.16	0.81
Selectivity coefficient Al-K	log	-0.75	-0.75	-0.97
Selectivity coefficient Al-Na	log	-4.41	-4.41	-4.67
Ca initial condition	% of CEC	17.5	17.5	14.0
Mg initial condition	% of CEC	5.5	5.5	5.0
Na initial condition	% of CEC	1.2	1.2	1.2
K initial condition	% of CEC	3.3	3.3	3.3
Initial base saturation Σ (Ca+Mg+Na+K)	% of CEC	27.5	27.5	23.5

Table 3. Parameters optimized in the three scenarios such that simulated and observed soil and streamwater chemistry match for the reference year 1991.