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Atmospheric pollution histories of three Cumbrian surface waters

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Summary

1. The CHemistry of the Uplands Model (CHUM), driven by measured and estimated atmospheric deposition, was used to simulate the chemical compositions of three upland Lake District surface waters, Devoke Water (DW), Levers Water (LW) and Mosedale Beck (MB) over several hundred years.
2. “Natural acidification” combined with human activities, notably forest clearance, was assumed to have brought about chemically stable acid moorlands by the period 1000–1500 A.D. Deposition of sulphur, nitrogen, chlorine and heavy metals, released into the atmosphere by coal-burning and industrial processes, then took place, gradually increasing to maximum levels in the late 20th century.
3. Surface water concentrations of chloride are consistent with depositional inputs, whereas the transfer of atmospherically deposited sulphur to the surface waters is delayed by temporary retention processes within the catchment. Over the last 40 years, concentrations of pollutant (non-marine) sulphate in the surface waters declined to one-third of their maximum levels. Atmospherically deposited pollutant N continues to accumulate in catchment soils, although a significant fraction appears in surface waters as nitrate. Annual average surface water bicarbonate concentrations were 20 - 60 μmol L^{-1} in the pristine past, fell nearly to zero in all three waters when acidification was most intense, but now are increasing.
4. Combined data from several Lake District upland waters suggest substantial recent increases in concentrations of dissolved organic carbon (DOC). If this can be attributed to acidification reversal, a corresponding decline in DOC concentrations would have occurred as acidification intensified, and pristine surface waters would have been comparatively rich in DOC.
5. Major cationic elements enter the soil-water system in deposition (H^+, Na, Mg, K, Ca), from organic matter decomposition (H^+), or by chemical weathering (Mg, Al, Ca), and are much affected by sorption to soil organic matter (SOM). The surface soils of all three catchments are acid (current pH ~ 4.5) and so variations in surface water chemistry among sites reflect differences in mineral dissolution rates deeper in the soil-rock profile. The simulations indicate pH values of 6.9, 6.1 and 6.4 for DW, LW and MB respectively in the period up to 1800, followed by declines to minima of c. 6.0, 4.7 and 5.0 in around 1980, then acidification reversal in agreement with observations.
6. The transfer of atmospherically deposited heavy metals to surface waters depends upon their sorption by SOM. Nickel, zinc and cadmium adsorb relatively weakly and

therefore are quite readily leached, and sensitive to changes in acidification status. The higher affinities of organic matter to Cu and Pb promote retention and these two metals are continuing to accumulate in soil, despite major declines in deposition over the past several decades.

7. The WHAM-F_{TOX} model was used to estimate the maximum number of Ephemeroptera, Plecoptera and Trichoptera species in MB through time, as influenced by chemical variability. The maximum number is estimated to have fallen from 14-15 under pristine conditions to 9-10 when acidification was greatest and a modest recovery to 10-11 species since then.

Introduction

Britain has been affected by atmospheric pollution for a long time (Mannion, 1991; Thorsheim, 2006). Coal burning already took place on a significant scale in the 17th century, adding sulphur, nitrogen and metals to the atmosphere, while the mining and smelting of metal ores, especially of lead, was also widespread. Emissions increased during the Industrial Revolution of the 18th and 19th centuries, and into the 20th century. To the effects from power generation and manufacturing industry were added those of transport and intensifying agriculture, especially with respect to nitrogen (Sutton *et al*., 2008). The effects of pollutants were localised at first, but then spread to more remote areas. Thus the English Lake District has been subjected to various forms of atmospheric pollution for several centuries, and has also contributed through its own mining activities (Cameron, 2000). Direct evidence for the long-term deposition of pollutants to the area comes from lake sediment records showing the increasing deposition of metals until the latter part of the 20th century (Hamilton-Taylor, 1979; Ochsenbein *et al*., 1983; Yang & Rose, 2005). More recent pollutants include radionuclides, notably caesium-137, due to atmospheric weapons testing and reactor accidents (Beresford *et al*., 1992), and organic contaminants such as polychlorinated biphenyls and polycyclic aromatic hydrocarbons (Gevao *et al*., 2000).

Monitoring and process studies of atmospheric pollutant deposition and its effects go back to the 1950s, and the work of E. Gorham (1955, 1958), who described rain composition at various sites, relating it to sources and pointing out the high acidity of rain. Extensive monitoring and analytical work during the 1970s and 1980s, led by D.W.Sutcliffe, documented spatial and temporal variation in the chemistry of Lake District surface waters and rainfall (Carrick & Sutcliffe, 1982, 1983; Sutcliffe & Carrick, 1983, 1988; Sutcliffe *et al*., 1982). Spatial variations in surface waters were studied by Thornton & Dise (1998). Continuation of temporal monitoring demonstrated the reversal of surface water acidification, attributed to declines in sulphur deposition (Tipping *et al*., 1998, 2000); this was one of the first documented occurrences of such reversal, reflecting the responsiveness of Lake District catchments. Monitoring of two small lakes is now also performed by the UK Acid Waters Monitoring Network (Monteith & Evans, 2005).

As well as being useful in themselves, to delineate changes and spatial differences, the monitoring programmes provide data for the running and testing of simulation models, which by quantitatively relating depositional inputs to surface water composition, permit the testing of hypotheses about catchment processes that generate surface waters. Simple modelling of water chemistry in terms of deposition and soil-rock processes, sorption and weathering was performed by Tipping (1989, 1990). The MAGIC acidification model has also been applied both to specific Lake District sites (Whitehead *et al*., 1997) and as part of regional-scale analyses (Evans *et al*., 1998). The more comprehensive biogeochemical model CHUM has been used to explore acidification (Tipping *et al*., 2006a), heavy metals (Tipping *et al*., 2006b) and radionuclides (Tipping, 1996). The behaviour of radiocaesium derived from Chernobyl has also been studied by modelling (Smith *et al*., 1995).

In the present paper, we report new applications of the CHUM model, which takes into account deposition compositions and amounts, soil chemistry, chemical weathering, and relevant parts of the C, N and S cycles. We focus on three catchments that receive little or no direct input of chemicals such as fertilisers, so any contamination comes from the atmosphere as wet and dry deposition. We apply and test assumptions about the combination of biogeochemical and hydrological processes that determine element retention and transport within the catchments. To calibrate and assess the model, we use stream and lake chemistry monitoring data starting in the 1970s, and in a few cases even earlier, making a record of 40 years or more. The main aim is to explain how several centuries of pollution by atmospheric deposition have affected the catchments, starting from the near-pristine conditions that we assume prevailed in the middle of the last millennium, and arriving at the present day. Thus, for each of the catchments a quantitative history of surface water chemistry is constructed.

The field sites

The present landscape of the Lake District was shaped by glaciation, which ended14,500 years BP (Pearsall & Pennington, 1989; Millward & Robinson, 1974). According to palaeoecological records, vegetation establishment and succession led to most of the area being forested to an altitude of 600-650 m by about 7000 BP. Human settlement in the Stone, Bronze and Iron Ages involved extensive tree removal to obtain wood for fuel and construction, and to create grazing and arable land. This led to the development of acid moorland soils by *c.* 3000 BP. Tree clearance continued until about 1000 BP, by which time the land was mainly used for the grazing of sheep, and the vegetation was principally grasses, with some bog-associated plants. Thus the main character of the rough-grazed land is acid-loving plant types on acid soil. Although there has been tree planting in recent years, each of the catchments considered here is moorland.

Our model runs begin in 1400, at which point the soils are assumed to have been in steady state with respect to “pristine” atmospheric deposition, weathering reactions, and C, N and S cycling. The concept of a steady-state soil is a useful construct that is probably never actually realised. The principal soil component in terms of controlling depositional impacts is the soil organic matter (SOM). On the basis of contemporary estimates of SOM turnover in deciduous woodlands of the UK (Tipping *et al*., 2010a), there would have been ample time to establish SOM in steady state to a depth of several tens of centimetres by the time that tree clearance began, the average mean residence time of carbon in the topsoil being about 90 years. However, SOM turnover under moorland vegetation is slower than under woodland, with a mean residence time for Lake District soils of about 800 years, assuming them to be in steady state (Tipping *et al*., 2007a). Therefore, in areas where tree clearance had been carried out several thousand years ago, a situation close to steady state is likely, but more recent clearance might mean that the SOM in 1400 AD was derived from both woodland and non-woodland vegetation sources, or the pool might not have been so great as it is presently. Non-steady state will also have arisen due to climatic variation, Britain having experienced appreciable changes in both temperature, notably the Little Ice Age (*c.* 1590-1850), and rainfall during the past 1000 years (e.g. Roberts, 1998). Nonetheless, we assume that such variations are insufficient to cause significant deviations from an approximate steady state for SOM.

The modelling reported here was conducted on the catchments of a stream, Mosedale Beck, and two small lakes, Devoke Water and Levers Water (Fig. 1). Mosedale Beck (MB) drains part of the upper Duddon Valley, an area of high relief, underlain by rocks of the Ordovician Borrowdale Volcanic Group. These rocks range in composition from basalt to dacite, and have been affected by low-grade metamorphism and secondary alteration, so that important secondary minerals with respect to chemical weathering are calcite and dolomite (Stidson *et al*., 2002). Duddon Valley soils comprise rankers, peat and peaty gleyed podzols of the Coniston Association, (Hall & Folland; 1970); those of the MB catchment are largely rankers and peats (85%), the remaining 15% being more mineral soils. The vegetation comprises grasses, bracken and *Sphagnum* moss and the land is used as rough pasture for the low-density grazing of sheep. MB drains an area of 3.7 km^2 with an altitude range of 219 - 764 m. Although the Duddon Valley is now sparsely populated, there was considerable activity in the past (Duddon Valley Local History Group, 2009). However, for the most part this seems to have been in the lower part of the valley, with little major settlement in the area drained by Mosedale Beck. Pollen records from the sediments of six surrounding tarns (small lakes) suggest that trees were largely absent, grasses, *Calluna* and *Sphagnum* being the dominant plant species, and soils were acid by 2000 years BP (Pennington, 1984).

Levers Water (LW), a natural corrie tarn enlarged for use as a reservoir, is located in the Coniston catchment, adjacent to the Duddon Valley. Its catchment is also underlain by rocks of the Borrowdale Volcanic Group, and ranker soils dominate. The lake has a surface area of 0.15 km^2 and a mean depth of 21 m, the land drainage area is 2 km^2, the catchment altitude range is 411 - 802 m, and average annual rainfall is 3250 mm. The relatively high altitude means that the catchment was probably never fully forested, and has likely been treeless with acid soils for 2000 years.

The catchment of Devoke Water (DW) is partly underlain by rocks of the Borrowdale Volcanic Group and partly by Eskdale granite. The soil is 86% by area rankers and 14% podzols. The lake has a surface area of 0.34 km^2 and a mean depth of 4 m, the land drainage area is 3.1 km^2, the catchment altitude range is 233 - 487 m, and average annual rainfall is 2600 mm. This catchment saw more recent human activity than those of the other two sites, with partial regeneration of woodland *c.* 2200 years BP and cereal cultivation during the period 200-600 AD (Pearsall & Pennington, 1989).

A few surface water chemical data are available for the 1950s in the two lakes, but the main monitoring was performed since the mid-1970s. Data collection was conducted initially by the Freshwater Biological Association (FBA), and subsequently the Natural Environment Research Council Institute of Freshwater Ecology (IFE) and Centre for Ecology (CEH). The principal published data are in the following references: Sutcliffe & Carrick (1973); Carrick & Sutcliffe (1982, 1983); Sutcliffe *et al*. (1982); Tipping *et al*. (1998, 2000). Unpublished CEH data have also been used in the present study. The full data set is available through the CEH Information Gateway (www.gateway.ceh.ac.uk; CEH:EIDC:1252669286585). This paper is concerned with annual mean surface water chemistry, and plotted data points represent simple averages, derived from between four and 50 individual samples in a given year. Throughout the paper we use square brackets – [ ] – to denote concentrations. We use DOM (dissolved organic matter) or POM (particulate organic matter) when referring to the entities that participate in chemical reactions, but DOC or POC when referring to the measured variables, dissolved or particulate organic carbon. We assume that OM is 50% C.

Deposition histories

Daily amounts of precipitation for the years 1932-2009 were available for a weather station at Ambleside, *c.* 20 km from the study sites, and these were used to estimate amounts at the study sites by correcting for altitude (Tipping *et al*., 1998). Annual totals were calculated, and the average of these was used for all years before 1932.

Temporal variations in deposition chemistry (exemplified for MB in Fig. 2) were obtained as follows. Volume-weighted annual concentrations of H^+, Na, Mg, K, Ca, NH_4, Cl, NO_3, SO_4 were obtained from the monitoring programmes of FBA, IFE and CEH, for the years 1975-1976 and 1989-2009. For the period before 1650, rainfall was assumed to have been diluted sea water, with solute concentrations estimated from contemporary mean values. Sulphur deposition from 1650 onwards was estimated by scaling S deposition to known or estimated S emissions (Tipping *et al*., 2006a); for the period 1650-1850, a linear increase in emissions from zero to 500 tonnes a^{-1} was assumed reflecting escalation in the demand for coal in the early 18th century, while for 1850 onwards, data were taken from UKRGAR (1990) and the UK National Air Emissions Inventory (http://www.naei.org.uk). The approach used for N is described below. Pollutant Cl was estimated by correcting for sea-salt inputs, assuming all Na to be of marine origin. Concentrations of non-marine K and Ca were assumed to have risen linearly from zero in 1650 to the observed levels (1975 onwards). Note that this procedure differs from that employed by Tipping *et al*. (2006a), who only used observations from 1989 onwards, and assumed that non-marine K and Ca were scaled to pollutant S; the method used here provides significantly better simulations of streamwater Ca in particular. Non-marine Cl deposition was scaled to non-marine S. The DW lakewater is richer in sea salts than anticipated from the rain chemistry. Therefore sea salt ion concentrations were increased in the DW deposition to achieve the correct surface water [Na] and [Cl].

The multiple sources of N make construction of an accurate long-term N deposition scenario difficult. In previous work (Tipping *et al*., 2006a) we drew on the results of Pitcairn *et al*. (1995) who estimated that there was a major increase in N deposition at rural sites from 1950. But a subsequent publication by Fowler *et al*. (2004) estimated that deposition in 1900 was already fairly high, especially of reduced N. We used measured wet deposition data from 1989 onwards for Cockley Beck, located in the upper Duddon Valley, and dry deposition data from Concentration Based Estimated Deposition (Smith *et al*., 2000; Smith and Fowler, 2001), quoted in Dore *et al*. (2007). We assumed a background “pristine” level of 0.5 gN m^{-2} a^{-1} for the period to 1850 and a linear increase to the value for 1989. Wet and dry deposition were kept throughout in proportion to values for 2001-2003, and a constant relation between oxidised and reduced N was also assumed.

Heavy metal (Ni, Cu, Zn, Cd and Pb) concentrations in bulk deposition at sites near to or in the upper Duddon Valley have been measured since 1972 (Baker, 2001; Lawlor and Tipping, 2003; Malcolm *et al*., 2010). Procedures for the estimation of dry deposition and the construction of historical deposition scenarios, based on estimates of deposition under pre-industrial conditions and using lake sediment profiles, are given by Tipping *et al*. (2006b).

Model descriptions

The main model used in the present work, CHUM-AM (CHemistry of the Uplands Model - Annual, Metals), was described in detail by Tipping *et al*. (2006a,b; 2007b). It deals with hydrology, C, N, S, cation sorption to SOM, mineral precipitation, weathering, and processes associated with lake sediments. An improved model of plant-soil N dynamics is described below. The model (Fig. 3) considers a soil-rock profile consisting of three completely mixed layers (L1, L2, L3) through which water percolates, streamwater being drainage from L3. The model is run with annual average input data, and produces annual average outputs. Atmospherically deposited elements and species are assumed to be in solution on entering the plant-soil system; dry-deposited gases NH_3, NO_2 and SO_2 dissolve in rainwater to form NH_4^+, NO_3^- and SO_4^{2-} respectively. Extra deposition of major solutes from cloud water is taken into account.

Water percolates at a constant rate from L1 to L2 to L3 and then to the stream. At each time-step (4-7 days depending upon catchment and rainfall) the available pore space in the soil layer is emptied of water, and solutes are removed in drainage water. Then the pore space is refilled, new solutes are added in the input water, and from decomposition and weathering reactions, and the new equilibrium distribution of chemical species calculated.

Elements (N, S, metals) associated with SOM transfer annually from L1 to L2, to take into account mineralization and water transport losses of organic matter from L2. Annual outputs of organic carbon from L1 and L2, as DOC and particulate organic carbon (POC) in percolating water, are specified in the input file, as is the soil pCO_2. Dissolved CO_2 in percolation water from L2 enters L3, where it may be supplemented by CO_2 from carbonate dissolution. Outgassing of CO_2 occurs in the stream, to a specified partial pressure. Annual soil uptake of sulphur in L1 is directly proportional via k_{S1} (dimensionless), to input $[SO_4^{2-}]$. Release depends upon the product of the soil S:C ratio and the pool of soil S, via the adjustable rate constant k_{S2} (yr^{-1}).

The chemical “master species”, i.e. the inorganic species on which all the chemical reactions are based, consist of major cations (H^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Fe^{3+}, NH_4^+), trace cations (Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}), and anions (OH^-, Cl^-, NO_3^-, SO_4^{2-}, F^-, CO_3^{2-}) and the neutral species $Si(OH)_4$. In L1 and L2, solutes may bind to organic matter, which may be in the solid phase, in solution (DOM) or in suspension (POM). The interactions are described using the soil version of WHAM / Model VI (Tipping, 1998; Tipping, 2002). Account is also taken of reactions among inorganic species in solution. In addition, precipitation and dissolution of $Al(OH)_3$, $Fe(OH)_3$ and carbonates may occur. In L3, the same reactions are possible, together with surface complexation at the surfaces of Al and Fe oxides. In streamwater, the reactants are the inorganic components, together with DOM and POM.

Weathering inputs of major and trace metals, and carbonate, are described with the formulation of Schnoor & Stumm (1986), in which the rate is given by the product of a constant (k_w) and H^+ activity raised to the power n_w. Values of n_w for different solutes were taken from Stidson *et al*. (2002), while values of k_w (which includes the effects of mineral type and available surface area) were adjusted to match observations.

The lakes are assumed to be of constant volume and completely mixed. Their chemical compositions are determined by atmospheric deposition directly to the water surface, streamwater input, lake water output, particle sedimentation and sediment-water exchange of solutes. Nitrate, sulphate and ferric iron are reduced within the accumulating sediment.

We formulated a new plant-soil nitrogen model (Fig. 4), able to account both for long-term soil storage of N while also simulating short-term variability in nitrate leaching in response to varying deposition and temperature. This drew on published work on catchment N modelling, including short-term simulations of nitrate leaching (Sloan *et al*., 1994), annual time-step models with one or more soil N pools (Cosby *et al*., 1997, 2001; Kros *et al*., 2004), and more detailed process-based models (e.g. Wade *et al*., 2002). The new model is more realistic than the model used previously (Tipping *et al*., 2006a, b), which simulated slow changes in NO_3 leaching governed by the total soil N pool, but remains sufficiently simple to permit calibration with available data. Water transport was modelled with the hydrological sub-model from the soil carbon model DyDOC (Michalzik *et al*., 2003; Tipping *et al*., 2007a). Two soil N pools are postulated, a small labile pool comprising plants, microbes and fast-turnover soil organic N, and a larger stable pool. Any wet or dry deposited reduced N, and dry oxidised N, is taken up directly into the labile pool. The uptake rate (mol m^{-2} hr^{-1}) of NO_3 by the labile pool is given by the expression $k_{up}\ P_{NO3}\ T^{n}\ /\ P_{N\text{-labile}}$ where k_{up} is the rate constant, P_{NO3} and $P_{N\text{-labile}}$ are the pools (mol m^{-2}) of soil solution nitrate and labile N respectively, T is the soil temperature (°C) and *n* is an adjustable exponent. Nitrate is released from the labile N pool according to the expression $k_{rel}\ P_{N\text{-labile}}^{2}$ thereby rendering the pool more “leaky” as it grows in size. “Other N losses” (Fig. 4), which include releases of gaseous N and DON, are represented by a simple net first order process governed by k_L ; it is recognised that N gas losses actually go through nitrate, but this process cannot be parameterised with available information. Nitrogen also leaves the labile pool by first-order transfer to the stable pool, from which first-order release again occurs, governed by k_S (Fig. 4). The model allows two soil types - here rankers and podzols - in each catchment, and stream water is generated by simple mixing of the two drainage waters. Direct deposition of nitrate to the lake (if present) is also included. The model is driven by daily rainfall amount, daily temperature, and fortnightly or monthly rainfall chemistry. The key output of the nitrogen model is the daily leaching flux of NO_3, which was used to compute the volume-weighted annual $[NO_3]$ required by CHUM-AM.

The modelling strategy was first to deal with the anionic components Cl, N, S and DOM, which are assumed to behave independently. Next, the major cationic elements (H^+, Na, Mg, Al, K and Ca) were considered, with calibration of weathering rates. Finally, heavy metal behaviour was predicted. Soil and streamwater pCO_2 values were assumed to be constant, at 10 times and twice the atmospheric value respectively.

Lake mixing, sedimentation and sediment chemistry were simulated as described by Tipping *et al*. (2007b). A single average stream was assumed to drain each catchment, with additional inputs from direct precipitation. A sedimentation rate of 132 g m^{-2} a^{-1} was used for both DW and LW, based on a parameterisation for the nearby Scoat Tarn (Ashmore *et al*., 2007). Lakewater pCO_2 was assumed to be in equilibrium with the atmosphere.

To apply the nitrogen sub-model, daily soil temperatures required for the N model were estimated as described by Tipping *et al*. (2007a) from air temperatures at the Ambleside meteorological station adjusted for altitude with a lapse rate of 0.006 deg m^{-1}. Nitrate leaching was assumed to occur only from ranker soils (Tipping *et al*., 2008). The biomass N pool for typical upland moorland vegetation on soils of the study sites is approximately 10 gN m^{-2} (Perkins *et al*., 1978), and we estimated a labile pool of N in soil of approximately 35 gN m^{-2} from a labile carbon pool of *c.* 500 gC m^{-2} (Tipping *et al*., 2007a) with a C:N ratio of *c.* 15 g g^{-1} (Tipping *et al*., 2008), to produce a present-day total labile N pool (Fig. 4) of about 45 gN m^{-2}. To achieve this with the known N inputs to the system, and NO_3 losses, it was required that $k_L + k_{LS} = 2\times10^{-4}$ d^{-1}. In the absence of other information, and for convenience, we assumed that $k_L = k_{LS}$. A value of k_S of 10^{-6} d^{-1} produced the required stable N pool of *c.* 600 gN m^{-2}. With these values of k_L, k_S and k_{LS} fixed, adjustments were made of k_{up}, k_{rel} and n in the ranker soils to simulate surface water $[NO_3]$. The value of k_{rel} was assumed to be the same for each of the three catchments, while k_{up} was allowed to vary.

Results and discussion

The 20th century saw increasing rates of deposition of S, Ca and heavy metals until around 1970, after which substantial declines took place (Fig. 2). The peak for N was about 20 years later, in agreement with wider UK observations (Fowler *et al.*, 2010). Model application mainly used the scenarios of Fig. 2, except that for DW additional seasalt and pollutant S inputs were required (see below).

Chloride

Tolerable predictions of interannual variations in [Cl] in the three surface waters were obtained from depositional inputs and concentrative evapotranspiration, but assuming no interactions with vegetation or soil. Results for DW and LW are shown in Fig. 5; results for MB were similar to those of LW. Rain collected in winter 1989-1990 was extremely salty, (as also found elsewhere in western Europe), and although this is reflected in both DW and LW, the model predictions of lakewater [Cl] in 1990 were too high (Fig. 5), suggesting short-term retention of chloride either due to hydrological heterogeneity within the catchment (Neal & Kirchner, 2000) or biological uptake (Bastviken *et al.*, 2009) and subsequent release. Non-marine (pollutant) Cl contributes a small but significant amount to the acidity of Lake District rain, the average of 4 μeq L^{-1} over the period 1989-2000 corresponding to *c.* 5% of the total acidifying equivalents of N + S + Cl in the three surface waters. The presence of acidifying Cl was noted by Gorham (1958), and widespread decreases in Cl deposition in recent decades have contributed to acidification reversal in the UK (C.D. Evans, personal communication).

Nitrate

In applying the nitrogen model, the best results, judged by minimising the sum of the squared differences between observed and simulated [NO_3], were obtained with n = 2 and k_{rel} = 2.5×10^{-6} m^2 mol^{-1} d^{-1}. The values of k_{up} were 1.6×10^{-3}, 3×10^{-5} and 4×10^{-4} mol m^{-2} d^{-1} deg^{-2} for DW, LW and MB respectively.

Simulated [NO_3] in the surface waters (Fig. 5) reproduced differences among the catchments in terms of the average values. The increase in surface water [NO_3] in the order DW < MB < LW is accounted for in the model by corresponding decreases in the uptake N rate constant (k_{up}, Fig. 4). Variations in this parameter among the three catchments follow factors that strongly influence N retention, i.e. likely terrestrial productivity (LW < MB < DW), mean slope (LW > MB > DW) and rockiness (LW > MB > DW). Thus the high-altitude, high-relief LW catchment, with its higher proportion of rock outcrops, is especially poor at retaining atmospherically deposited N, in contrast to the lower-altitude, flatter, less rocky catchment of DW, which retains N quite well (Fig. 5). The model correctly simulates declines in [NO_3] that have occurred over recent years, due to decreases in inputs (Fig. 2). This is achieved through the assumption of the small labile N pool (accounting for less than 10% of the total plant-soil N) which permits N to be taken up and released rapidly, and in response to short-term changes in deposition and temperature. The model predicts considerable interannual variability in [NO_3], driven by variations in both N input and temperature, but agreement with the observations is not fully convincing (Fig. 5), and therefore unidentified drivers may be missing. Over timescales of less than one year, winter maxima and summer minima in [NO_3] are successfully simulated (results not shown).

The fraction of total deposited N calculated to be leached as NO_3 in 1800 at DW was 4%, rising to 11% in 2000. The corresponding increase at LW was from 29 to 41% and at MB from 10 to 24%. Leaching of NH_4 is negligible, and thus the acidifying effect of N has increased over the past two centuries. There are additional losses of N as dissolved organic nitrogen (DON) and probably also as gas (N_2, N_2O), but most of the deposited N has been retained by the soil. The model assumes this stored N to be mainly in the stable pool, from which it can only leave as DON or gas. If this is so, then a massive re-acidification due to N-saturation, as considered by Tipping *et al*. (2006a) would not occur, but research is urgently needed to improve our understanding of the fate of the soil N store.

Sulphate

By permitting uptake by and release from a soil pool of S, the sulphur sub-model dampens the response of [SO_4] in the surface waters to variations in atmospheric S deposition. The effect is illustrated for LW and MB in Fig. 5. The constants required to achieve a match between observations and predictions (k_{S1} = 0.4 and k_{S2} = 0.8 yr^{-1}) result in a residence time of soil S of *c.* 200 years under pristine conditions, falling to *c.* 100 years as more soil S accumulated, although this only applies to the 40% of SO_4 that is calculated to be taken up. However, when the uptake is optimised for surface water [SO_4] the calculated corresponding contemporary soil S:C ratios of *c.* 0.01 mol mol^{-1} exceed the mean measured value of 0.004 mol mol^{-1} for upper Duddon Valley topsoils (Tipping *et al*., 2006a). Possible uptake mechanisms are (a) removal of incoming SO_4 by reductive incorporation into SOM (measured in the topsoils), and oxidative release under dry conditions, as seems likely in Pennine catchments (Tipping *et al*., 2003, 2010b), and (b) reversible adsorption onto the surfaces of Al and/or Fe(III) oxides at greater depths within the soil. It is possible that mechanism (a) controls the topsoil S, giving rise to the 0.004 mol mol^{-1} S:C ratio, while mechanism (b) accounts for the remaining S. However, this is speculative and there is a need for more research into S retention.

The behaviour of S in the DW catchment, which results in substantially higher surface water [SO_4] than found for the other two waters (Fig. 5), was harder to reproduce with the model. Simply increasing the sea-salt contribution of SO_4 in deposition, as done for Cl (see above), while maintaining the pollutant deposition at the same level as for the other two catchments, led to underprediction of lake [SO_4] in all years. Increasing the retention of S in soil, by adjustment of the S sub-model parameters, improved agreement for later years, but not for the 1980s. Therefore the S model parameters were held at the values derived for LW and MB, and the assumed deposition input of pollutant S was increased. An additional 60% produced agreement with the observations, but it is not clear why the pollutant deposition needs to be greater at DW.

Of the two principal acidifying elements, N and S, the latter is more important. Although depositional inputs are similar on a molar basis (Fig. 2) the anion equivalents associated with S are twice those for N, while the removal and storage of N by the soil amplifies the difference. Thus if the surface waters themselves are considered then over the 20th century pollutant sulphate contributed 95%, 71% and 84% of the leached acidity for DW, LW and MB respectively. Between 2001 and 2009 however, N became more important, the SO_4 contributions falling to 81%, 56% and 71% of the leached N+S acidity.

Bicarbonate

The final major inorganic anion to consider is bicarbonate (HCO_3^-), which is derived mainly from the atmosphere, via plant growth and subsequent decomposition, and to a lesser extent from the weathering of Ca and Mg carbonates. Water emerging from the soil-rock profile has CO_2 partial pressures greater than atmospheric, and so tends to release CO_2. This loss is rarely complete in streams because of the short transit times, but approximate equilibrium may be obtained in the lakes. Concentrations of carbonate (CO_3^{2-}) are negligible in these waters and the bicarbonate concentration is essentially equivalent to alkalinity. Concentrations of HCO_3^- were calculated from the [H_2CO_3] value corresponding to the assumed pCO_2 and the concentrations of the other solutes, in the course of which surface water pH was obtained. For the most acid water, LW, calculated [HCO_3^-] was 19 μmol L^{-1} in 1400, falling to 1 μmol L^{-1} in 1980 and then rising to 2 μmol L^{-1} in 2009. For MB the corresponding values were 31, 1 and 6 μmol L^{-1}, and for DW 60, 5 and 23 μmol L^{-1}.

Dissolved organic matter

Tipping *et al*. (2006a,b) assumed constant concentrations of DOM in percolation water. Here we also explore the possible effects of temporal changes in DOM, based on the widespread recent increases of [DOC] in upland surface waters (Freeman *et al*., 2001; Worrall *et al*., 2004; Monteith *et al*., 2007). Results for Lake District waters are available for the three study sites, and also from the UK Acid Waters Monitoring Network (AWMN; Monteith & Evans, 2005) for Burnmoor and Scoat Tarns, both within 15 km of our study sites and with similar water chemistries. Data for the five waters were amalgamated by normalising [DOC] to the mean values for the commonly sampled years 1998-2006 (Fig. 6). Increasing trends in [DOC] for the two AWMN sites are clear, but less apparent in the results for DW, LW and MB. However, the shorter monitoring period for DW, LW and MB may correspond to a period during which there was not much change in [DOC] for any of the five waters, and so a recent general increase in [DOC] in Lake District waters is plausible.

Temporal changes in DOM leaching may arise from the increasing solubility of DOM with pH (Tipping & Woof, 1991), as soil becomes less acid in response to decreasing S deposition (Evans *et al*., 2006; Monteith *et al*., 2007). Tipping *et al*. (2007a) showed that this could be explained if “potential” DOM held in the soil by adsorption under more acid conditions was preferentially lost by conversion to CO_2, while weaker adsorption under less acid conditions favoured leaching. If so, then in the pristine past, [DOC] in Lake District waters would have been greater than it is today, and there would have been a minimum in [DOC] coinciding with the lowest surface water pH. We constructed a relative scenario of changing surface water [DOC] on this basis, scaled to the data for 1988 to 2009, and assuming that under pristine conditions [DOC] was twice the average value for 1998-2006 (Fig. 6). The pristine surface water [DOC] values estimated in this way were 5.7, 1.7 and 2.0 mg L^{-1} for DW, LW and MB respectively.

For DOM movement within the soil profile, CHUM-AM includes a flux from L1 to L2, and another from L2 to L3 and thence to the stream (Fig. 3). A contemporary flux of 4 gC m^{-2} a^{-1} for the first was used, based on the range of estimates (2 to 6 gC m^{-2} a^{-1}) for a site in the upper Duddon Valley (Buckingham *et al*., 2008), while the second takes the same value as the streamwater flux. These were modified in proportion when creating the varying [DOC] scenarios.

The generation and transport of DOM within the soil is an internal acidifying process, but DOM differs from nitrate and sulphate because it is a weak acid and therefore is complexed with protons and cationic metals, although it still provides a net negative charge to the percolating water (Tipping, 2002). Concentrations in Lake District surface waters are low compared to those from other upland acid-sensitive sites (see e.g. Monteith & Evans, 2005 and references therein), but DOM is still of significance in the charge balance and acidity of the surface waters studied here. The CHUM calculations (Table 1) indicate that the net negative charge on DOM could have contributed as much as 20 μeq L^{-1} to the total anionic charge in DW in the pristine past. Generally, the organic anion contribution declined as pH decreased, but has grown again over the past 30 years, with greater relative changes in the scenarios that include variations in [DOM].

Weathering inputs of Mg, Al, Ca and Si

Mineral dissolution supplies Mg, Al and Ca to the soil and underlying rock or till. In principle, Na and K could also be acquired by the percolating water, but surface water concentrations of these elements can be sufficiently accounted for by rainfall inputs. Weathering rate constants, k_w, were optimised to match simulated and observed soil and surface water chemical compositions, using the modelled time series concentrations of anionic species. CHUM-AM was run both with constant [DOC], set to the contemporary average for each surface water, and with [DOC] scaled to the suggested trend of Fig. 6.

We only have detailed soil data for sites in the Duddon Valley, including the MB catchment, and so we assumed that the same weathering rate constants apply to all three catchments. This is justified by the similar observed soil pH values for topsoils of the three catchments, with values of 4.5, 4.6 and 4.6 respectively in DW, LW and MB during 1998-2000 (Tipping *et al*., 1999; 2006a). These were matched satisfactorily (pH values of 4.4, 4.5, and 4.6) using the L1 and L2 weathering constants for Mg, Ca, and Al of Table 2, which are close to those estimated for MB by Tipping *et al*. (2006a). Calibration to the surface water chemistry was performed by adjusting the L3 weathering rate constants in the individual catchments (Table 2). Again for MB, the L3 weathering rate constants are close to those estimated by Tipping *et al*. (2006a) from a shorter time series. The same weathering constants could be used for constant or varying [DOC]. Predicted pH values differed only slightly in the two cases, but temporal variations in surface water [Al] in LW and MB were captured better in the constant [DOC] scenario.

Silica plays a minor role in surface water chemistry because it is unreactive and uncharged, but its weathering fluxes were used to estimate catchment inputs of heavy metals (see below). In estimating Si release from catchment minerals the removal of Si due to diatom growth within the surface waters must be taken into account. It was simplest to do this by considering only the streamwater (MB) for which Si removal during spring and summer was well-defined by the temporal pattern of [Si]. Thus [Si] data for the rest of the year were assumed simply to reflect Si through weathering, fluxes being derived from the products of concentration and runoff. A single weathering rate constant was derived, assuming each soil-rock layer to contribute equally (Table 2).

The history of acidification

To reach the “pristine”, i.e. not atmospherically polluted, state that is the starting-point for our simulations, upland Lake District soils were first converted “naturally” to an acid state. Soils on which the former vegetation was oak and other deciduous trees, evidenced by sediment pollen records, are thought to have been richer in base cations because of deeper root activity and base cation cycling (Pennington, 1984). Thus tree clearance might have been an acidifying process. Another factor is simply the high runoff which will drive “natural” acidification by depleting soils of base cations and exhausting the supply of base cations from underlying minerals. This would explain the diatom record for DW (Atkinson & Haworth, 1990) which shows that shortly after the last glaciation the lake pH was *c.* 7.5, which would have required substantially greater inputs of base cations than currently found, implying higher weathering rates from freshly exposed mineral surfaces.

As shown in Fig. 7, the model calculations for the pre-pollution period suggest that the surface waters were mildly acid (LW, MB) or neutral (DW). Concentrations of non-marine SO_4 and Cl were zero, and anionic charge not provided by sea salts was due mainly to HCO_3 and DOM (see above), with small contributions (0.3-2.0 μmol L^{-1}) from NO_3, balanced by weathering inputs of Mg, Al and Ca. The calculated pristine pH of DW, 6.9, agrees with the range of 6.5-7.0 for the period 1200-1800 AD deduced by Atkinson & Haworth (1990) from analysis of the lake’s sedimentary diatom record. Although a diatom-based reconstruction of past pH is not available for LW, results for three lakes of similar present-day acidity in nearby Wasdale indicate pre-industrial pH values of *c.* 6.0 (Haworth & Lishman, 1991), similar to our calculated value of 6.1.

Acidification of soil and water occurred principally because weathering rates could not neutralise the inputs of sulphuric and nitric acids derived from the atmospheric deposition of S and N, and their processing by soil as described above. Neutralisation of incoming acidity by the exchange of SOM-bound cations for H^+ also contributed, as “stored” weathering products came into play, but only temporarily. Once these cations were depleted, weathering became the only neutralising process within the catchment, assisted to some extent by the small increase in base cation deposition. Two feedback processes, the tendency for weathering rates to increase with falling pH, and the possible suppression of DOM transport from topsoils, had only minor influences on the progress of acidification.

Soil and water pH values showed only small declines until *c.* 1850, but over the next 130 years surface water pH fell by over one unit in both LW and MB, reaching minima by about 1980 (Fig. 7). The decline in DW was less, because of greater mineral weathering rates in this catchment. The temporal developments are matched by the lake diatom records (Atkinson & Haworth, 1990; Haworth & Lishman, 1991). After 1980, pH was observed to increase in all three surface waters, and this is satisfactorily reproduced by the model. The reversal was mainly driven by the marked decline in [SO_4], reflecting a substantial decrease in emissions (Fowler *et al*., 2010). Such acidification has been widely observed in affected regions (Stoddard *et al*., 1999; Monteith & Evans, 2005), but Lake District sites have been especially responsive (Tipping *et al*., 1998, 2000). More recent declines in surface water [NO_3] have contributed further to water quality improvement, although this has been offset to some extent by a decline in Ca deposition.

Heavy metals

Time-series monitoring data are not available for heavy metals, which means there are limited possibilities for model calibration, and we are restricted to comparing the limited observations with predictions. Previous work (Tipping *et al*., 2006b; 2007b; 2010b) has demonstrated reasonably good agreement for both surface water metal levels and soil metal pools, using default metal binding parameters for SOM, for 13 catchments throughout Great Britain, including three streams of the Upper Duddon Valley. The one metal for which calibration has been required is Pb, which has to be made to bind somewhat more strongly to SOM than expected from the default parameters.

Here we simply present simulations for two metals, Zn and Pb in MB (Fig. 8). The patterns are very similar to those obtained previously for Duddon streams (Tipping *et al*., 2006b). Broadly, Cu is calculated to behave similarly to Pb, while Ni and Cd behave like Zn. All the metals are calculated to have passed through maximum dissolved concentrations during the late 20th century. For Ni, Zn and Cd, the maxima reflect both the deposition patterns (Fig. 2), and the fact that they sorb relatively weakly to SOM, so that acidification caused their soil pools to decline. The stronger sorption affinities of Cu and Pb mean that their soil pools have continued to increase, and variations in their surface water concentrations are due to relatively small changes in proton competition for binding to SOM, as soil pH passed through a minimum.

The modelling suggests that by 2000, the catchment soils of MB had retained 90% or more of the total previously deposited anthropogenic Cu and Pb, but less than 60% of the other three metals. The streamwater heavy metal concentrations are calculated to be due predominantly to depositional inputs (as opposed to weathering); for example, in the year 2000 the fractional contributions by deposition were Ni 0.90, Cu 0.77, Zn 0.99, Cd 0.99 and Pb 0.70.

The choice of [DOC] scenario makes little difference to the predictions for Ni, Zn and Cd. However, both Cu and Pb are affected, calculated streamwater concentrations for the past 50 years being about 50% lower when the model is driven with varying [DOC]. This arises because anthropogenic Cu and Pb depositions during the twentieth century were better-retained in soil layer L1, due to lower output fluxes of DOM-bound metal.

Biological responses

Unfortunately, biological monitoring of these upland waters has not been conducted to the same extent as chemical monitoring. Macroinvertebrate diversity is the variable for which most information is available; Minshall & Kuehne (1969) reported on communities in several tributaries of the River Duddon, and Sutcliffe & Carrick (1973) showed diversity to be lower in the more acid Duddon Valley streamwaters. Tipping *et al*. (2002) offered evidence of an increase in invertebrate diversity following acidification reversal.

Using outputs from the biogeochemical modelling, we estimated long-term changes in the species richness of Ephemerotera, Plecoptera and Trichoptera (SR_{EPT}) with the WHAM-F_{TOX} model (Stockdale *et al*., 2010), which relates SR_{EPT} to the bioavailability of the potentially toxic cations H^+, Al^{3+}, Cu^{2+} and Zn^{2+}. The model quantifies the toxic effects of mixtures of cations through F_{TOX}, the sum of the products of the amount of each biologically accumulated cation and its toxic potency. Below a lower threshold in F_{TOX} no toxicity occurs, while above an upper threshold, all EPT species are absent. For MB, F_{TOX} is calculated to have been appreciably greater than the lower threshold even in the pristine past, i.e. the stream was never able to host a full complement of EPT species. The value of F_{TOX} is calculated to have increased during the 20th century, due almost entirely to acidification, heavy metals contributing less than 0.5% to F_{TOX} in this stream. According to the model, there would have been 14-15 different EPT species under pristine conditions, but only 9-10 when acidification was greatest around 1980, with a modest increase to 10-11 for the present day. It is important to note that the model deals only with the effects of toxic cations; other factors, e.g. food availability, extremes in physical conditions, predation, may cause SR_{EPT} to be lower than the predicted values.

Other atmospheric pollutants

The atmospheric pollutants considered here have almost certainly had the greatest long-term effect on both terrestrial and freshwater ecosystems of the upland Lake District. However there have been others. Perhaps the best-known of all is radiocaesium, especially ^{137}Cs, derived from thermonuclear weapons testing in the 1950s and 1960s, and from the reactor accidents at Windscale (Cumbria) in 1957, and Chernobyl in 1986. In combination, these events delivered several tens of kBq m^{-2} to the Lake District. Considerable research into the fate of this radioactivity has been conducted (see e.g. Beresford *et al*., 1992; Hilton *et al*., 1993; Smith *et al*., 1995), including the transfer of ^{137}Cs to fish in DW (Elliott *et al*., 1992). What made ^{137}Cs different from other metals was its peculiarly strong affinity towards illitic clay minerals, which played a major role in in its post-depositional behaviour. A radioactive half-life of *c.* 30 years makes radioactive decay the main “sink” of ^{137}Cs, and much will be lost before reaching surface waters. Other possibly significant pollutants that have been of concern in similar locations, but not yet studied from biogeochemical or hydrochemical perspectives in Lake District catchments, include mercury, organic contaminants and ozone.

The future

Agreement between observations and simulations of surface water solutes, including acidification reversal, over the 40-year period from 1970 (Fig. 7), and the good correspondence with diatom-based estimates of historical lake pH values provide support for the choice of biogeochemical processes represented in the model. There is undoubtedly scope for improvement, for example from further research into the soil N and S cycles, the prediction of weathering processes using more fundamental information on mineral components (cf. Sverdrup & Warfvinge; 1993), and by introducing catchment spatial variability. However, the present calibrated versions of CHUM-AM for these three catchments are suitable for use in predicting the future behaviours and effects of atmospherically deposited pollutants. More widely, the model could be used to explore how changes in soil carbon, caused by changes in climate or vegetation, might affect element retention and solute transport.

Whereas mathematical description of the biogeochemical processes that control surface water composition is fairly advanced, quantitative prediction of biological responses to chemical change remains rudimentary. The WHAM-F_{TOX} approach, mentioned above, shows promise as a way to link chemistry and biology mechanistically, while allowing for the fact that non-chemical factors, often unidentified, will influence biological variables.

There would clearly be merit in further monitoring and modelling of these three sensitive sites, building upon the work reported here, which itself draws upon a wealth of data from earlier studies. Thus we could continue to learn the lessons of environmental history.

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Table 1. Calculated net anionic charge (μeq L^{-1}) due to dissolved organic matter (DOM) complexed with cations, for scenarios with constant and varying [DOM], in Devoke Water (DW), Levers Water (LW) and Mosedale Beck (MB)

	DW		LW		MB	
[DOM]	const.	var.	const.	var.	const.	var.
year						
1400	10.3	20.7	2.7	5.4	3.6	7.1
1980	7.7	1.7	1.0	0.2	1.8	1.4
2009	9.5	12.5	1.2	1.6	2.3	5.5

Table 2. Weathering rate constants for soil layers L1, L2 and L3. The units depend upon the exponent n_w; in general they are l^n mol$^{(1-n)}$ m^{-2} a^{-1}.

	n_w	k_w for L1 & L2 all sites	k_w for L3		
			DW[1]	LW[1]	MB[1]
Na	0	0	0	0	0
Mg	0.35	0.7	0.55	0.1	0.2
Al	0.7	8	-[2]	60	15
K	0	0	0	0	0
Ca	0.35	0.7	5.5	0.1	0.7
Si	0	0.043	0.043	0.043	0.043

[1] DW = Devoke Water, LW = Levers Water, MB = Mosedale Beck

[2] For DW, k_w (L3) for Al was not defined, since the pH in L3 is always high enough for precipitation of $Al(OH)_3$ to occur and control surface water [Al], via the assumed solubility product (a_{Al3+} / a_{H+}^3) of $10^{9.5}$ at 25 ^{o}C (Tipping, 2005).

Figure captions

Fig. 1. Map showing the locations of Devoke Water (DW), Levers Water (LW) and Mosedale Beck (MB)

Fig. 2. Historical deposition scenarios used to drive the model for Mosedale Beck. Note that information on interannual variability depends upon the availability of meteorological and/or chemical monitoring data.

Fig. 3. Schematic of CHUM-AM. See text for explanation.

Fig. 4. Schematic of the nitrogen sub-model. See text for explanation.

Fig. 5. Observed and simulated surface water concentrations of chloride, nitrate and sulphate. The periodicity in simulated [NO_3] arises from the repeated use of 1989-2009 rainfall and temperature patterns to simulate daily variations in years before 1989. Nitrate data represented by open symbols were not used in model optimisation because measured N deposition data were not available.

Fig. 6. Measured [DOC] for five Lake District surface waters, normalised to the mean values for each site between 1998-2006 (points), and fitted by linear regression ($r^2 = 0.43$, $P < 0.001$). The dashed line is a suggested scenario for the response of [DOC] to soil acidification (see text).

Fig. 7. Observed (points) and simulated (lines) pH and concentrations of cations, for constant-[DOC] scenarios. Note that the base cation data are plotted logarithmically.

Fig. 8. Simulated dissolved concentrations of Zn and Pb in Mosedale Beck.

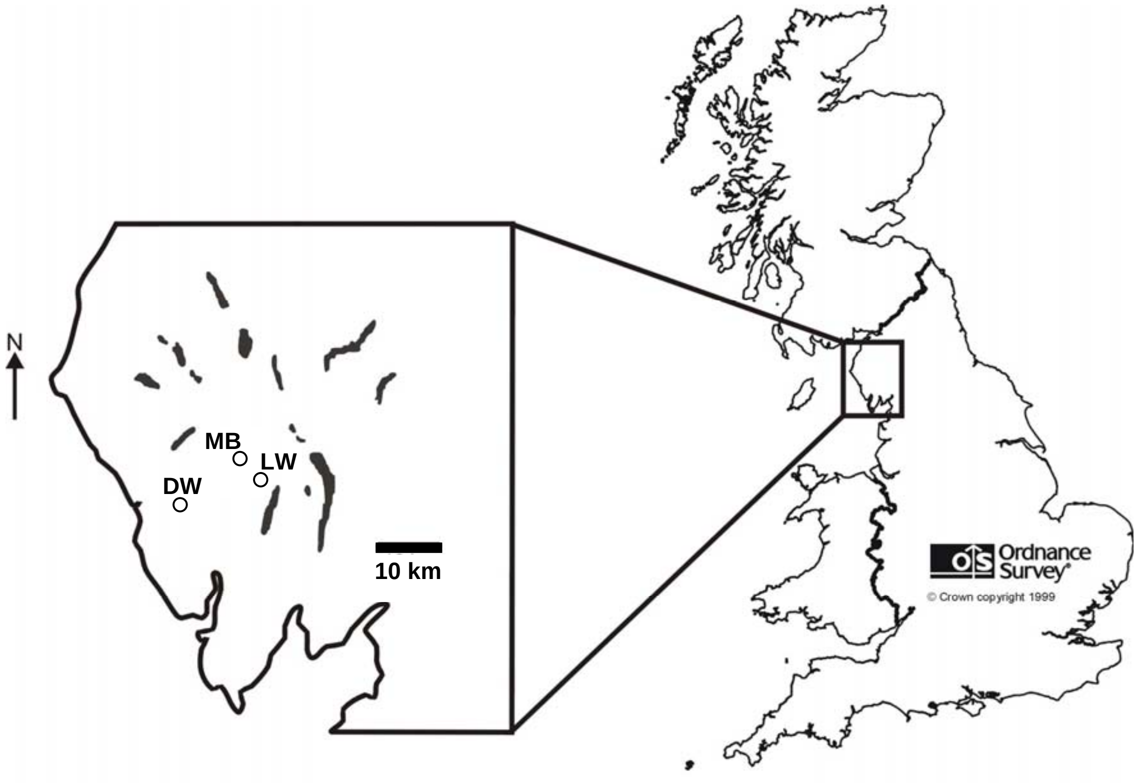

Fig 1

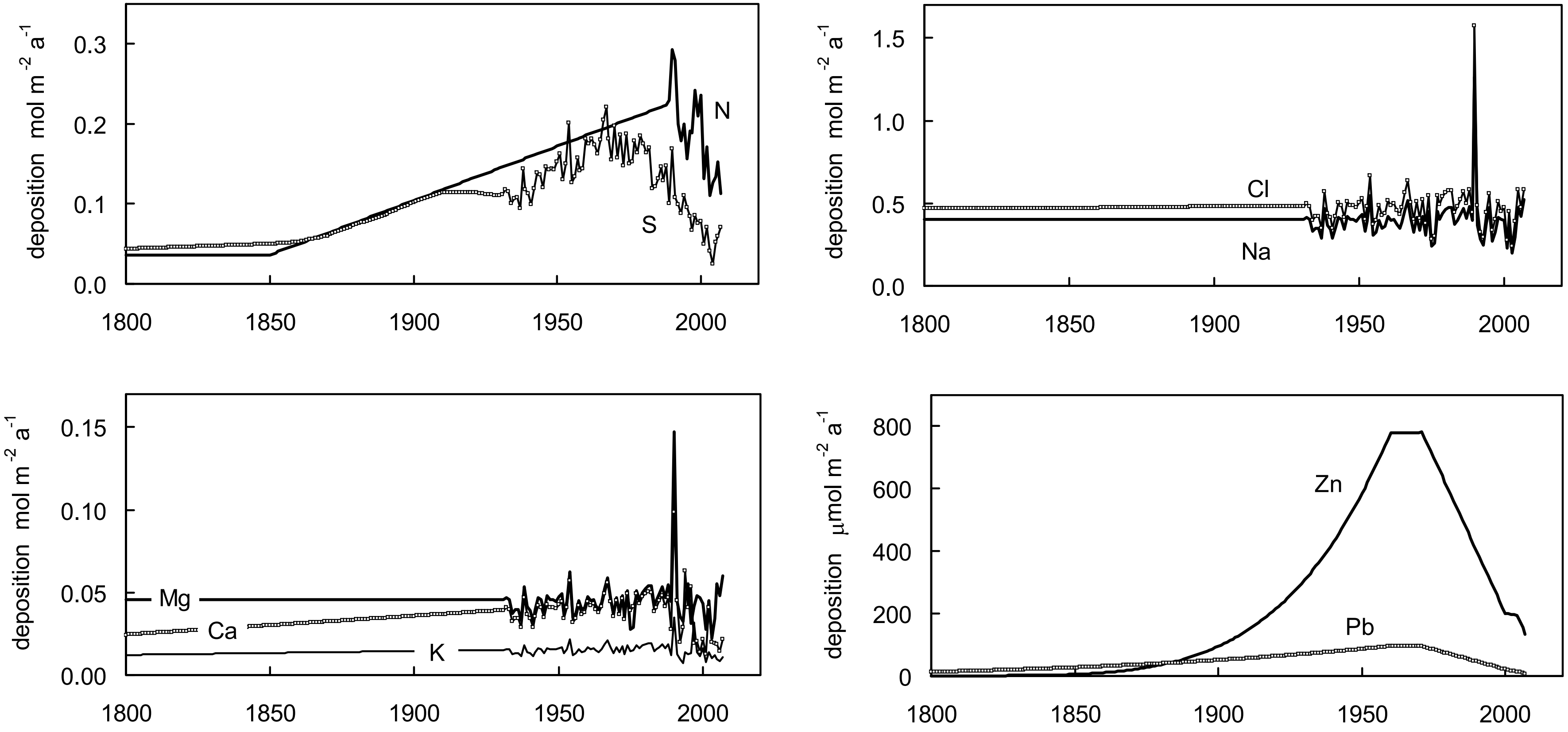
deposition mol m^{-2} a^{-1}
0.3
0.2
0.1
0.0
N
S
1800
1850
1900
1950
2000
deposition mol m^{-2} a^{-1}
1.5
1.0
0.5
0.0
Cl
Na
deposition mol m^{-2} a^{-1}
0.15
0.10
0.05
0.00
Mg
Ca
K
deposition μmol m^{-2} a^{-1}
800
600
400
200
0
Zn
Pb

Figure 2

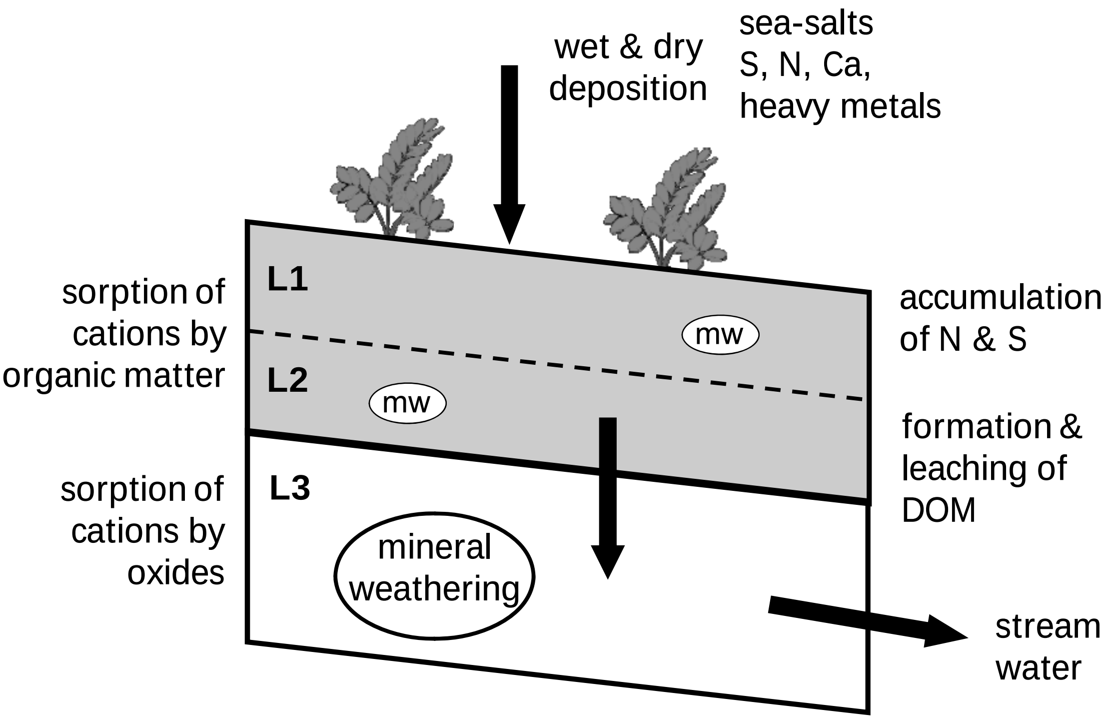
wet & dry
deposition
sea-salts
S, N, Ca,
heavy metals
L1
L2
L3
mw
mw
sorption of
cations by
organic matter
sorption of
cations by
oxides
accumulation
of N & S
formation &
leaching of
DOM
mineral
weathering
stream
water

Figure 3

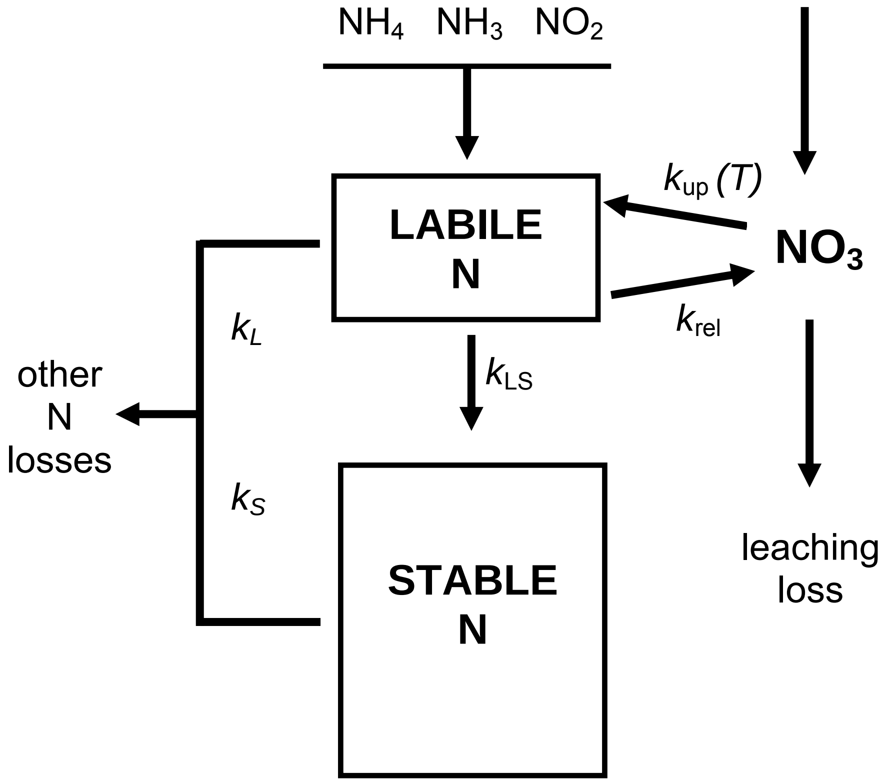
NH_4 NH_3 NO_2
LABILE N
k_{up} (T)
NO_3
k_{rel}
k_L
k_{LS}
other N losses
k_S
STABLE N
leaching loss

Figure 4

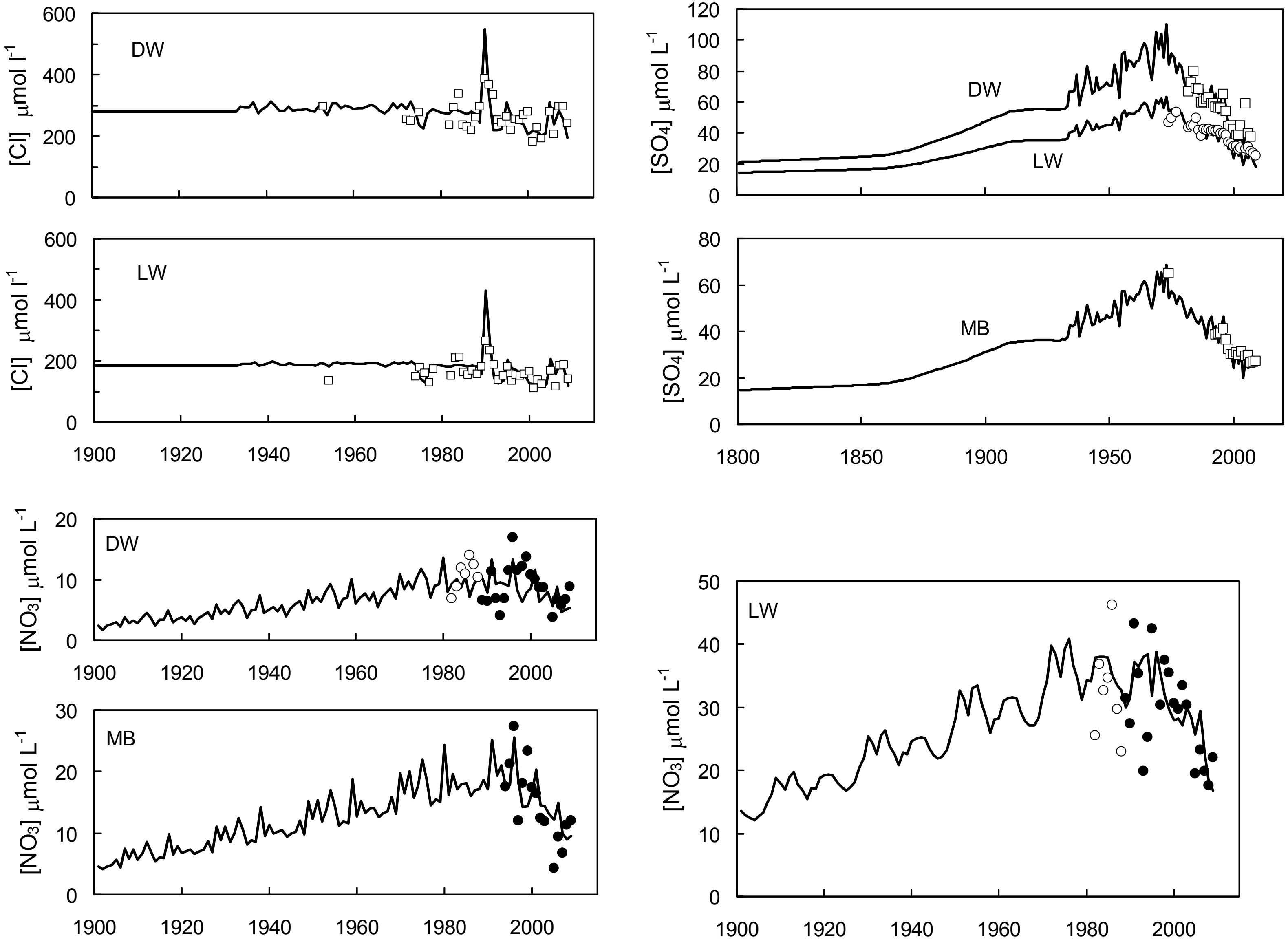
DW
[Cl] µmol l^{-1}
600
400
200
0
LW
[Cl] µmol l^{-1}
1900
1920
1940
1960
1980
2000
[SO$_4$] µmol L^{-1}
120
100
80
60
40
20
DW
LW
MB
1800
1850
1900
1950
2000
[NO$_3$] µmol L^{-1}
20
10
30
50
DW
MB
LW

Figure 5

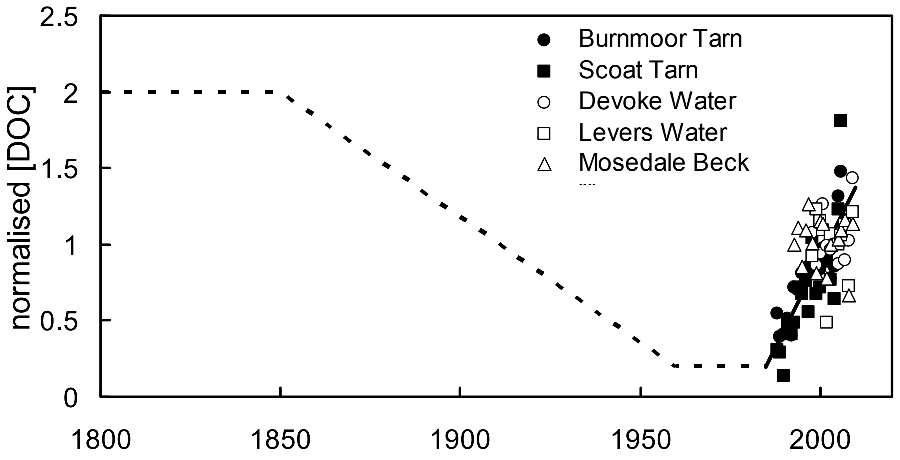
2.5
2
1.5
1
0.5
0
normalised [DOC]
1800
1850
1900
1950
2000
● Burnmoor Tarn
■ Scoat Tarn
○ Devoke Water
□ Levers Water
△ Mosedale Beck

Figure 6

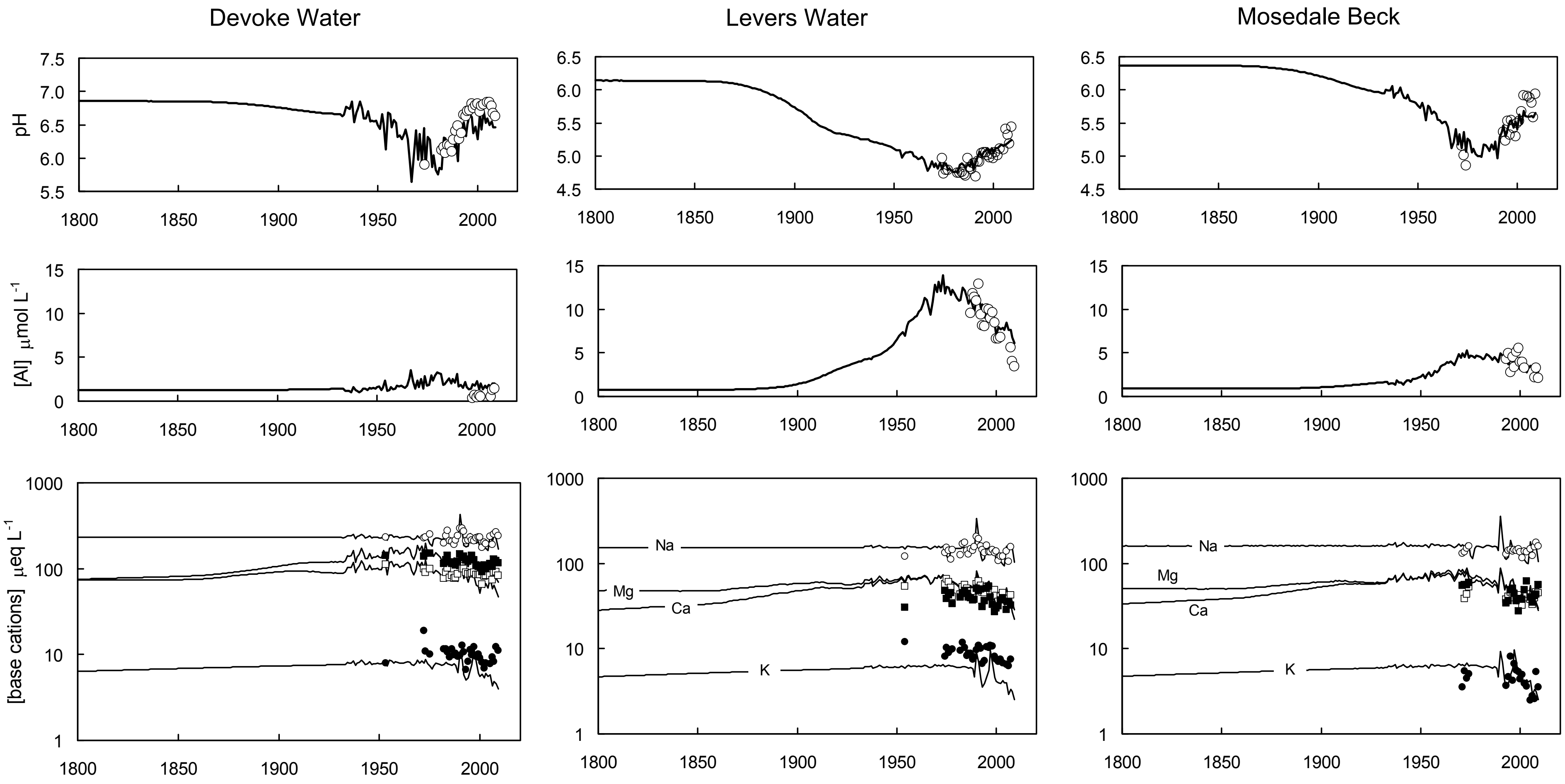
Devoke Water
Levers Water
Mosedale Beck
pH
[Al] µmol L-1
[base cations] µeq L-1
Na
Mg
Ca
K
1800
1850
1900
1950
2000

Figure 7

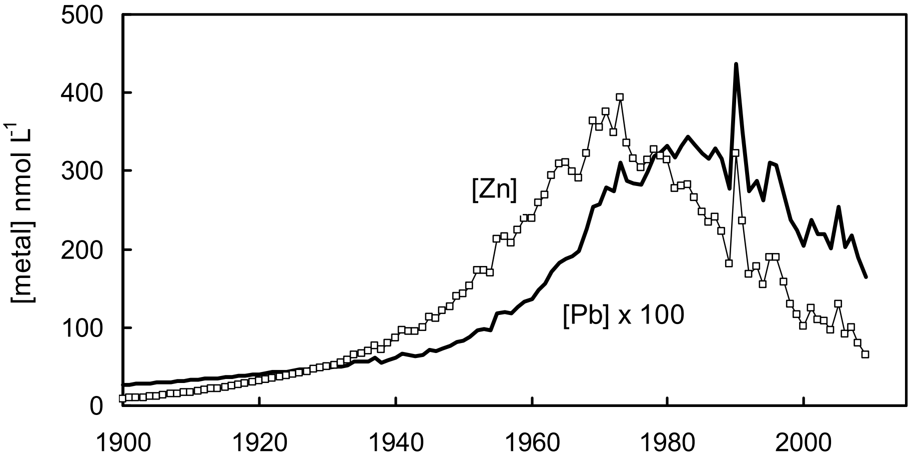
[metal] nmol L^{-1}
500
400
300
200
100
0
1900
1920
1940
1960
1980
2000
[Zn]
[Pb] x 100

Figure 8