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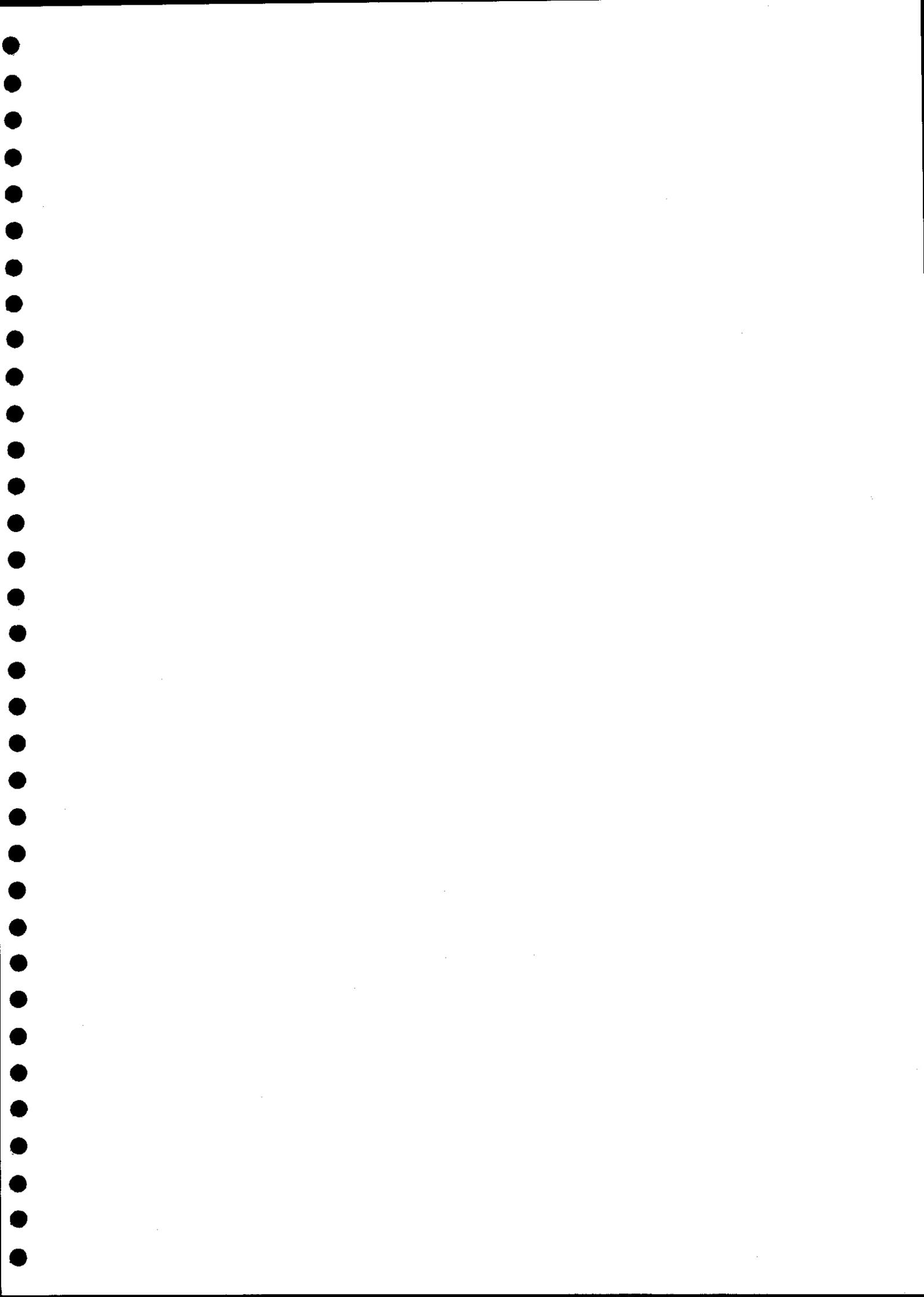
**Modelling Soil and Surface Water Acidification
at the Sor Catchment, NW Spain:**

**An Assessment of the EU Acidification Strategy
using the MAGIC Model**

Michael Renshaw & Eduardo Garcia-Rodeja



**Centre for
Ecology &
Hydrology**



Michael Renshaw
Institute of Hydrology
Crowmarsh Gifford
Wallingford
Oxfordshire
OX10 8BB

Tel: 01491 838800
Fax: 01491 692424
Telex: 849365 Hydrol G

Eduardo Garcia-Rodeja
Departamento de Edafología y Química Agrícola
Facultad de Biología
USC
15705 Santiago de Compostela
España

1 Introduction

Decades of acidic deposition of sulphur and nitrogen throughout Europe has led to the acidification of soils and surface waters and the loss of biodiversity in both aquatic and terrestrial ecosystems (Likens et al., 1979, Muniz, 1991). Evidence from such observations soon led to the hypotheses regarding the acidification process and the realisation that reduced acidic deposition would lead to the recovery in the chemical and biological status of ecosystems in severely affected areas. The implementation of monitoring programmes in the late 1970's and early 1980's, to quantify the mechanisms underlying the acidification process, soon confirmed this hypothesis, and the need to implement legislation to reduce emissions of acidic oxides throughout Europe.

The implementation of European legislation in the late 1970's, to promote reductions in emissions and deposition of acidic oxides (namely sulphur), led to the recovery of ecosystem health across Europe but was not targeted at protecting the most acidified sites. The implementation of the Second Sulphur Protocol in 1994 (UNECE, 1994) adopted modelling approaches to set limits of acidic deposition (critical loads) to protect those areas worst affected by acidic deposition; this was the first time an effects based strategy had been adopted in addressing the problem of acidification. These critical loads are based upon empirical relationships that describe the sensitivity of receptors to acidifying oxides of sulphur and nitrogen and have identified many key areas throughout Europe that are considered sensitive to acidification. Comparison with loads of acidic deposition to these areas (critical load exceedance) gives an estimate of the likely damage occurring in these systems. Under the Second Sulphur Protocol the areas of critical load exceedance are minimised in the key sensitive areas. In terms of the future acidification status of ecosystems, however, these maps are misleading and do not imply recovery.

The key questions that must be addressed in terms of recovery are; "in which areas" and "by how much" should emissions and deposition of acidifying sulphur and nitrogen be reduced to allow adequate recovery to take place. Also of equal importance is "how long" will it take for such recovery to occur given a reduction in acidic deposition; this has ramifications on the timing of the planned reductions if a given recovery is to take place within a specified time frame. In terms of recovery, these questions can only be addressed using "dynamic models"; they offer the only realistic possibility of assessing the time relationships between changing acidic deposition and changes in the acidification status of catchment soils and surface waters.

This report details the results of a study involving the application of a catchment based soil and surface water acidification model, the Model of Acidification of Groundwaters In Catchments (MAGIC, Cosby et al. 1985 a, b) to the River Sor catchment in North West Spain to assess the historical, present, and future acidification status in the region. The study concentrates on; 1) modelling the effects of the most recent plans to reduce acidic emissions, and their precursors throughout Europe, and 2) the level of acidic deposition required to achieve recovery to a pre-determined level (critical loads).

2 The Sor Catchment

The River Sor catchment is located in the Northern Spanish province of Galicia (43° 30' N, 7° 40' W). The catchment forms a 20 km² area of the upper watershed of the River Sor, 820 m above sea level, which drains North into the Bay of Biscay. The watershed has been intensively monitored for a period of two years from November 1991 until October 1993; the work is funded by a local power station (Endesa) at the nearby town of As Pontes, 20 km South West of the catchment. The primary cause for concern regarding the acidification of soils and surface waters in this area is the location of a 1400 Mw coal burning power station 20km upwind of the catchment. The power station uses local lignite coal (ca. 2.5% sulphur) which results in a high loading of anthropogenic sulphur to the Sor catchment. The site also forms part of the International Cooperative Programme on Integrated Monitoring (ICP-IM, Kleemola and Forsius, 1996), a European-wide network which is part of the effects based monitoring of the United Nations Economic Commission for Europe (UN-ECE) Convention on Long Range Transboundary Air Pollution (LRTAP).

Land-use within the catchment is dominated by heathland (60%, *Ulex* sp. and *Erica Mackaiana*), and a mixture of deciduous woodland, consisting mainly of birch (*Betula alba* L.) and oak (*Quercus robur* L., 18%), reforested areas of coniferous woodland (mainly *Pinus Sylvestris* L., 14%), the remaining 8% is managed pastureland (Table 1). Mean annual rainfall to the region is c. 1655 mm and mean monthly air temperatures range from 7°C in January to 17°C in August.

	Xantar	Sanche	Foxo
Heathland	58	63	57
Pine	22		26
Deciduous	17	33	10
Pasture	3	4	7

Table 1. Land-use within the three sub-catchments of the upper River Sor. Units in percentage of sub-catchment area.

Bedrock geology consists of metasedimentary rocks of Ordovician and Silurian age; slates, phyllites, mica-schists and quartzites. Two small syntectonic granites of Ordovician age are located in the North of the catchment. Although the region has not undergone major glaciation, as in many acidified areas of Northern Europe, periglacial deposits are evident within the catchment. Soils vary considerably in depth from 10 cm to 2-3 m depending on local variations in geology and geomorphology, but tend to be deeply weathered consisting

of varying depths of colluvium overlying humic cambisols and umbric regosols. Poorly drained areas of the catchment exhibit local development of humic gleysols and peat. In areas dominated by granitic lithologies, cambic podsol's and fibric histosol's dominate.

Four watersheds are monitored within the catchment, three of which were chosen for the application of the MAGIC model; the Xantar, Sanche and Foxo sub-catchments (Table 1).

3 Major Ion Chemistry

Monthly samples of bulk deposition, throughfall and streamwater have been analyzed for major cations and anions between the period 1991 and 1993 (Garcia-Rodeja, 1997).

Bulk deposition chemistry reflects a strong marine influence with high concentrations of both chloride and sodium. Chloride output flux from the three sub-catchments is +/-10% of measured bulk deposition input flux (Figure 1) and reflects the steady state nature of chloride within the soil system. Observed total sulphur deposition is dominated by the anthropogenic component (c. 83-87% at all sites) and reflects the high deposition loading of sulphur from the nearby Endesa power station. Sulphur output flux is consistently less than that in bulk deposition and ranges from 19% less at the Sanche to 48% less at the Foxo (Figure 1). The ability of these soils to adsorb sulphur is characteristic of highly weathered profiles rich in iron and aluminium oxides that have not undergone major glaciation (Couta et al. 1979).

Although sulphur is the dominant anthropogenic ion, both in deposition and streamwater, nitrate contribution to total anthropogenic anion load in streamwater varies from 10% at the Sanche and Xantar to 25% at the Foxo. These systems are nitrogen saturated and show similar levels of nitrate leakage to sites elsewhere in Europe (Traaen and Stoddard 1995). No ammonium currently leaks to surface waters despite moderate inputs (Figure 1).

Base cation input-output budgets strongly reflect the underlying geology of each sub-catchment. At the Foxo and Sanche, total base cation output flux exceeds the input flux by 35-39% and surface water base cation concentrations exceed those of anions, thereby imparting a strong buffering capacity on surface water pH and alkalinity (Table 2). Alternatively at the Xantar, the area is underlain by sedimentary and hydrothermal quartzites where base cation content, and weathering rate, is lower; this results in total base cation output flux being only 27% higher than the input flux and surface water base cation concentrations are lower than anion concentrations resulting in lower pH and alkalinity of surface waters (Table 2).

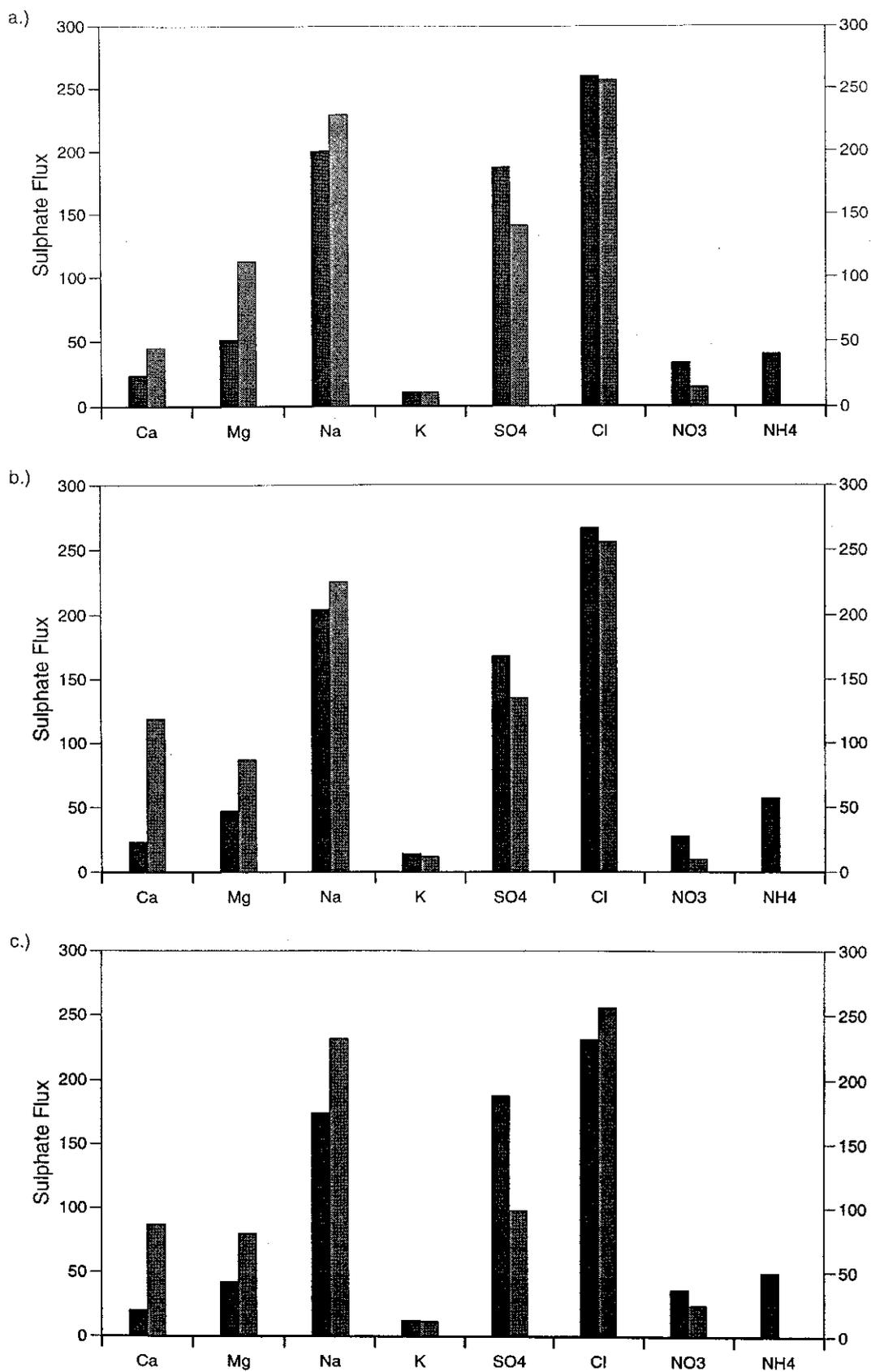


Figure 1. Measured bulk deposition input, and output fluxes (1992 mean) for major cations and anions at the three sub-catchments of the River Sor; a) Xantar, b) Sanche, and c) Foxo. Left bar = input flux, right bar = output flux. Units in $\text{meq m}^{-2} \text{yr}^{-1}$.

4 The MAGIC model

The development of dynamic models to predict the response of soil and surface water chemistry to changing acidic deposition and land-use requires a detailed knowledge of the soil processes that lead to loss of soil base status and the acidification of surface waters. The main thrust of hydrochemical modelling has focused on the development of physically based models to quantify the effects of changing acidic deposition on soil and surface water quality. Such models, however, require simplification of the complex physicochemical processes that determine ion concentrations throughout the soil column without affecting the model's ability to predict the catchment scale responses. This "averaging" or "lumped parameter approach" allows the models to be easily applied both on a catchment and a regional basis with only a limited amount of input data required to calibrate and drive the model.

MAGIC uses a lumped approach in two ways: (i) a myriad of chemical and biological processes active in catchments are aggregated into a few readily-described processes, and (ii) the spatial heterogeneity of soil properties within the catchment is lumped to one set of soil parameters. MAGIC consists of a set of equations which quantitatively describe the equilibrium soil processes and the chemical changes that occur as soil water enters the stream channel, a set of mass balance equations which quantitatively describe the catchment input-output relationships for base cations and strong acid anions in precipitation and streamwater, and a set of definitions which relate the variables in the equilibrium equations to the variables in the mass-balance equations.

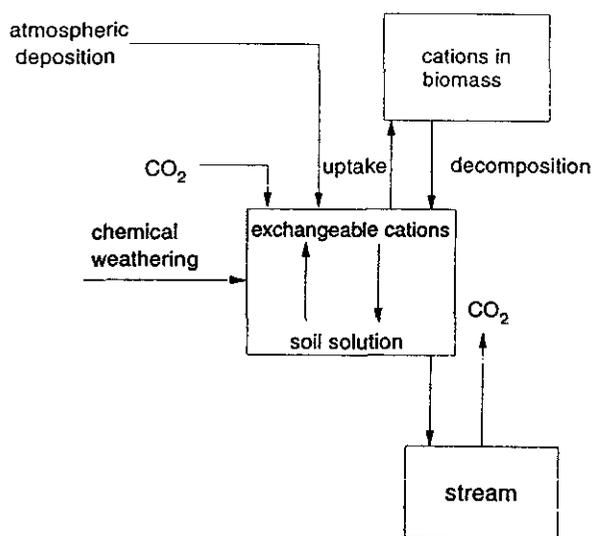


Figure 2. Schematic representation of the flows and stores in MAGIC.

Implemented in its simplest form, the model is a two compartment representation of a catchment (Figure 2). Atmospheric deposition enters the soil compartment and the equilibrium equations are used to calculate soil water chemistry. The water is then routed to the stream compartment and the appropriate equilibrium equations are reapplied to calculate streamwater chemistry.

The model has been successfully applied at site specific (Jenkins et al 1997), regional (Sefton et al 1997), and more recently national scale (Renshaw et al. In Prep.) in Europe and North America and is one of several dynamic models included in the UN-ECE Handbook on mapping Critical Loads (Henriksen et al. 1989). The model has also been extensively used within the UK Critical Loads Programme (Jenkins and Shaw, 1993).

4.1 Model Calibration Procedure

For this study deposition history for all major ions was modelled using the DAIQUIRI (Syri et al. 1997) and DEPUPT models (Alvetag et al. 1997) to match the observed bulk deposition fluxes at the Sor catchment. No distinction is made between the deposition to each of the sub-catchments given their close proximity. The modelled deposition data agree well with measured bulk deposition data and no adjustment of chloride or sulphate input flux was necessary to model the observed concentrations in streamwater.

Sulphur output flux is modelled by first using modelled bulk deposition from DEPUPT and estimating the appropriate sulphur retention capacity of the soil system. Sulphur dynamics in MAGIC are modelled by a langmuir isotherm which describes the concentration dependent adsorption of sulphur ions onto the soil exchange complex (Hornberger et al 1986); adsorption is assumed to be completely reversible. An appropriate set of parameters that describe the langmuir isotherm (the maximum adsorption capacity (E_{max}) and the half saturation constant (C), Table 2) were chosen such that the present day observed sulphate concentration was simulated in surface water.

Next, the concentrations of nitrate and ammonium are calibrated by adjusting first order uptake functions to match observed surface water concentrations.

Finally, the base cation concentrations are calibrated using an optimisation procedure based on a Rosenbrock algorithm. The base cation calibration involves fitting the results of long term model simulations to currently observed water and soil base cation data (target variables). The target variables consist of surface water concentrations of Ca, Mg, Na, K and soil exchangeable fractions of Ca, Mg, Na, K (based on the catchment weighted average). The target variables thus comprise a vector of measured values all of which must be reproduced by the model if a calibration is to be successful. The use of multiple, simultaneous targets in an optimisation procedure provides robust constraints on model calibration (Cosby et al. 1986).

Those physicochemical soil parameters measured in the field (depth, bulk density and CEC) are considered "fixed" parameters in the model (Table 2). Base cation weathering rates and

base cation selectivity coefficients for the soils are not directly measurable and are considered as "adjustable" model parameters to be optimised in the calibration procedure.

	Xantar	Sanche	Foxo
Fixed Parameters			
Depth	0.75	0.75	0.75
Bulk Density	754	726	764
CEC	47	49	47
E_{max}	36	40	65
C	400	400	400
Target Variables			
Soil			
ECa	6.5	7.0	6.4
Emg	3.4	3.4	3.3
ENa	3.2	3.0	3.3
Ek	3.3	4.1	2.7
Water			
Ca	50	110	81
Mg	78	75	74
Na	227	195	205
K	9	9	9

Table 2. MAGIC fixed parameters and target variables. Units for depth in m, bulk density in $kg\ m^{-3}$, CEC in $meq\ m^{-2}$, E_{max} in $meq\ kg^{-1}$, C in $meq\ m^{-3}$, exchangeable base cation fractions are expressed as a percentage of the CEC, and Surfacewater concentrations of base cations in $\mu eq\ l^{-1}$.

The historical deposition sequence is estimated by scaling currently observed bulk deposition to a reconstruction of sulphur emissions from the local Endesa power station from 1850 to 1993 (Figure 3) using the DAIQUIRI and DEPUPT models.

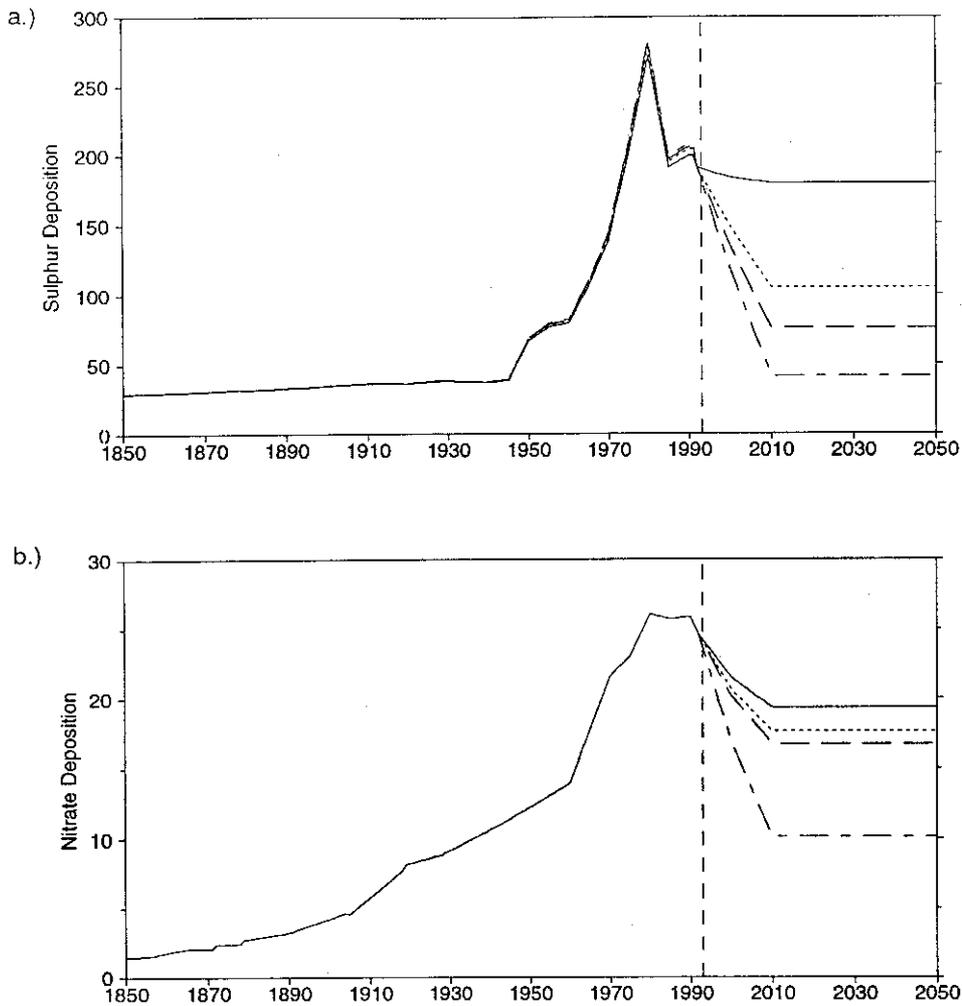


Figure 3. Historical (1850 to 1993) and future (1994 to 2050) deposition of a.) sulphur, and b.) nitrate for the Sor catchment. Data is based on modelled bulk deposition from the DAIQUIRI model. Units in $\text{meq m}^{-2} \text{yr}^{-1}$.

Land-use history has not been well documented for the Sor catchment, given that monitoring was only introduced in 1991; a conservative estimate of net base cation uptake by the forests has been simulated using the DEPUPT model. Many areas of forest have not been managed and most trees appear to have very slow growth rates and are consequently small in size. It has therefore been inferred that the forests have small base cation uptake requirements relative to the large pool of base cations present in the soil (Figure 4).

The calibrations are performed on simulations run from 1850 to 1993. After each historical

simulation, the model variables in 1993 are compared with the observed data in 1993, the adjustable parameters are modified as necessary to improve the fit and the historical simulation is re-run. The procedure is repeated until no further improvement in the fit is achieved.

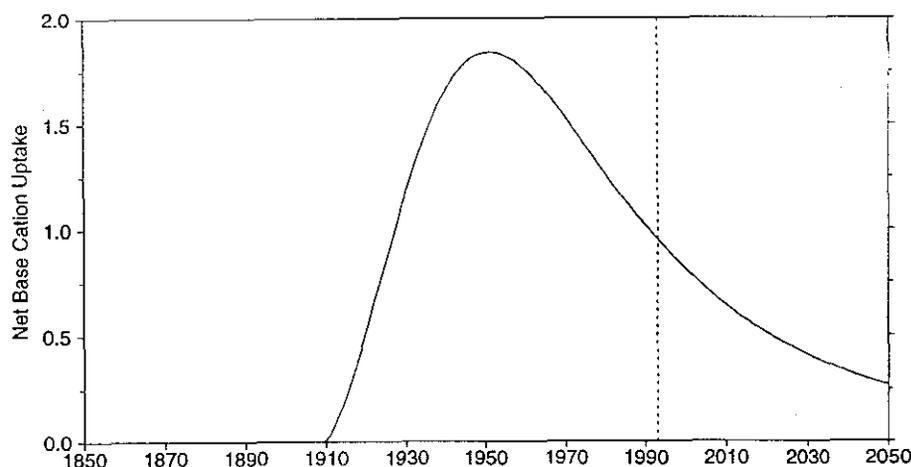


Figure 4. Historical (1850 to 1993) and future (1994 to 2050) net base cation uptake requirements by biomass at the Sor catchment. Data are based on results from the DEPUPT model. Units in $\text{meq m}^{-2} \text{yr}^{-1}$.

5 Results

5.1 Deposition and Uptake Scenarios

The historical and future deposition used in MAGIC were modelled using source-receptor emission and deposition models. Historical and future emissions scenarios for Europe were based on work undertaken at the International Institute for Applied Systems Analysis (IIASA, Amann et al. 1996) and the RAINS model (Alcamo et al. 1990). Using modelled emissions data from RAINS as an input to the DAIQUIRI model estimates of total deposition of all ions were made to the Sor catchment based on the EMEP grid. Site specific deposition was estimated using the DEPUPT model and scaled to measured bulk deposition at the Sor catchment. Figure 3 shows how sulphur and nitrogen deposition are estimated to have increased over the historical period from 1850 to 1993 from the DEPUPT model. The historical trend in deposition is assumed to follow that of the emissions from the Endesa power station very closely given its close proximity.

Base cation uptake requirements by biomass were estimated using the DEPUPT model, based on biomass density and element composition details (Garcia-Rodeja, pers. comms.). Figure

4 shows the historical and future predictions for net uptake requirement of total base cations by biomass.

Future controls on the emission of acidic oxides, and their precursors, throughout Europe has received attention recently by the European Commission (DG XI) by preparing a working document 'Draft Communication to the Council and Parliament on a : Community Strategy to combat Acidification (COM(97)88/4)'. The planned directive revises the reductions ratified under the UN-ECE protocol on further reductions in sulphur emissions. Consultation with the IIASA has resulted in the development of a number of cost-effective scenarios that aim to minimise critical load exceedance throughout all European member states. An interim target year of 2010 has been identified for these reductions. The proposed strategy has nine scenarios, of which four have been chosen to adequately represent a variety of future deposition scenarios for the MAGIC model;

- 1) CRP - Current Reduction Plan. UN-ECE Second Sulphur Protocol (UN-ECE 1995) based on officially declared national emission ceilings to be achieved by 2010,
- 2) REF - Reference scenario. Adopting the more stringent of the CRP and the CLE (Current Legislation) scenario by 2010,
- 3) B1 - One of six scenarios (B1 - B6) that attempt to achieve 50% gap closure for those areas unprotected by scenario CRP by 2010. Non-EU countries are assumed to comply with the REF scenario and no emission reduction from shipping is assumed.
- 3) MFR - Maximum Technically Feasible Reduction. Considers constraints imposed by current legislation and historically observed turnover rates of capital stock when determining the application potential of the presently available emission control options.

A 56 year forecast (1994 to 2050) was used to assess the likely response of soil and surface water chemistry to changes in acidic deposition.

	Sulphur	Nitrate
CRP	3	21
REF	43	25
B1	58	29
MFR	78	58

Table 3. Percentage reductions in sulphur and nitrate deposition (1993 relative to 2050) for four future acid deposition scenarios of the proposed EU Acidification Strategy.

5.2 Model Calibration

The MAGIC model was successfully calibrated to present day chemistry for soils and surface waters at all three sites (Table 4). At the Sanche and Foxo the historical simulation suggests that there has been little acidification (Figures 5.2 and 5.3). At the Xantar, however, there is predicted to have been a drop of one pH unit over the historical period (Figure 5.1). MAGIC predicts a loss of c. 40% in exchangeable soil cation pool over the historical period at all three sites (Figures 5).

	Xantar		Sanche		Foxo	
	Obs.	Sim.	Obs.	Sim.	Obs.	Sim.
stream pH	5.3	5.2	6.7	6.3	6.1	6.2
stream ANC	-16	-14	45	40	38	30
soil BS%	16.3	16.7	17.5	18.0	15.7	15.9

Table 4. Observed (Obs.) and MAGIC simulated (Sim.) present day (1993) streamwater pH, ANC and soil base saturation (BS%). Units are \log_{10} for pH, $\mu\text{eq l}^{-1}$ for ANC and percentage of CEC for soil BS%.

5.3 Future Responses of Soils and Surface Waters.

The response of surface waters to reductions in acidic deposition at the three sites is for a continued deterioration in pH and ANC under the CRP, REF and B1 scenarios. Sustained recovery is only initiated at the acidified Xantar sub-catchment under the most stringent scenario (MFR) where there is a large reduction in sulphur deposition (Table 4, Figure 3). At the unacidified Sanche and Foxo catchments the continued deterioration in streamwater chemistry is only stabilised; no long term recovery is predicted even under the MFR scenario.

There is a continued loss of soil cation pool under the CRP, REF and B1 scenarios at all three sites. Only under the MFR scenario is this loss of cation pool stabilised at all three sites yet with no long term recovery predicted by MAGIC.

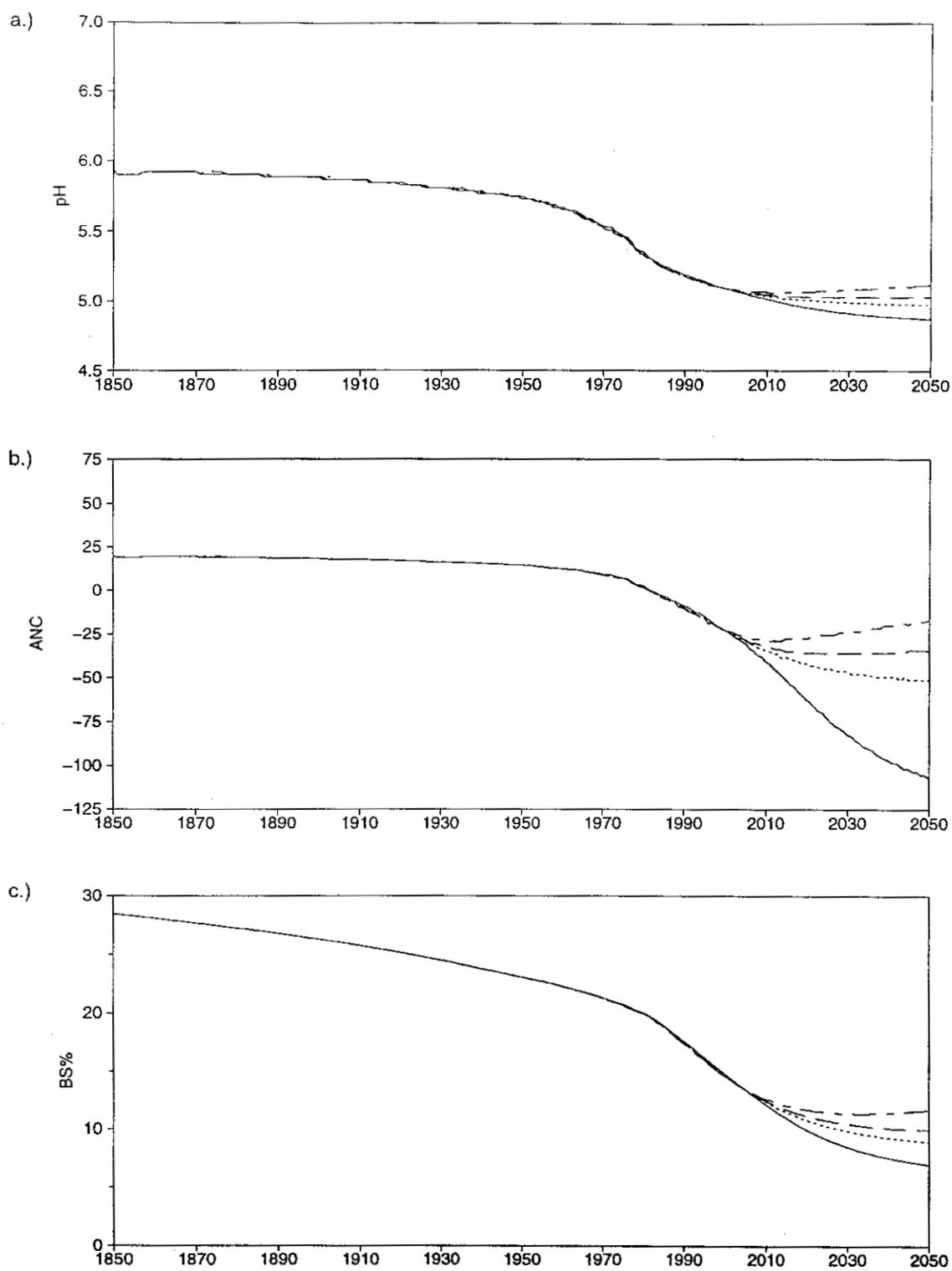


Figure 5.1. MAGIC simulated a) surface water pH, b) ANC and c) soil base saturation from 1849 to 2050 at the Xantar. Units are \log_{10} for pH, $\mu\text{eq l}^{-1}$ for ANC and percentage of CEC for soil BS%

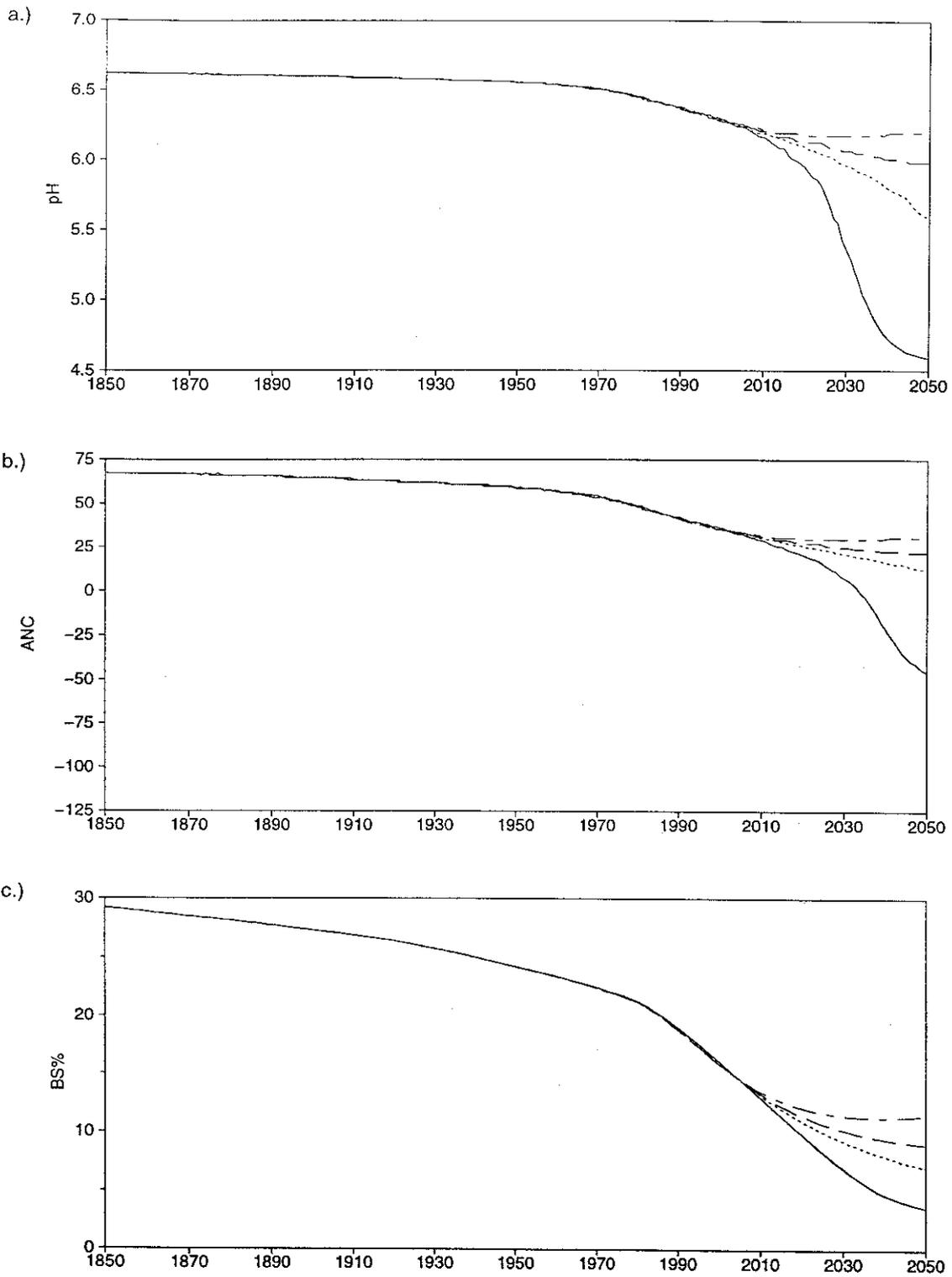


Figure 5.2. MAGIC simulated a) surface water pH, b) ANC and c) soil base saturation from 1849 to 2050 at the Sanche. Units are \log_{10} for pH, $\mu\text{eq l}^{-1}$ for ANC and percentage of CEC for soil BS%.

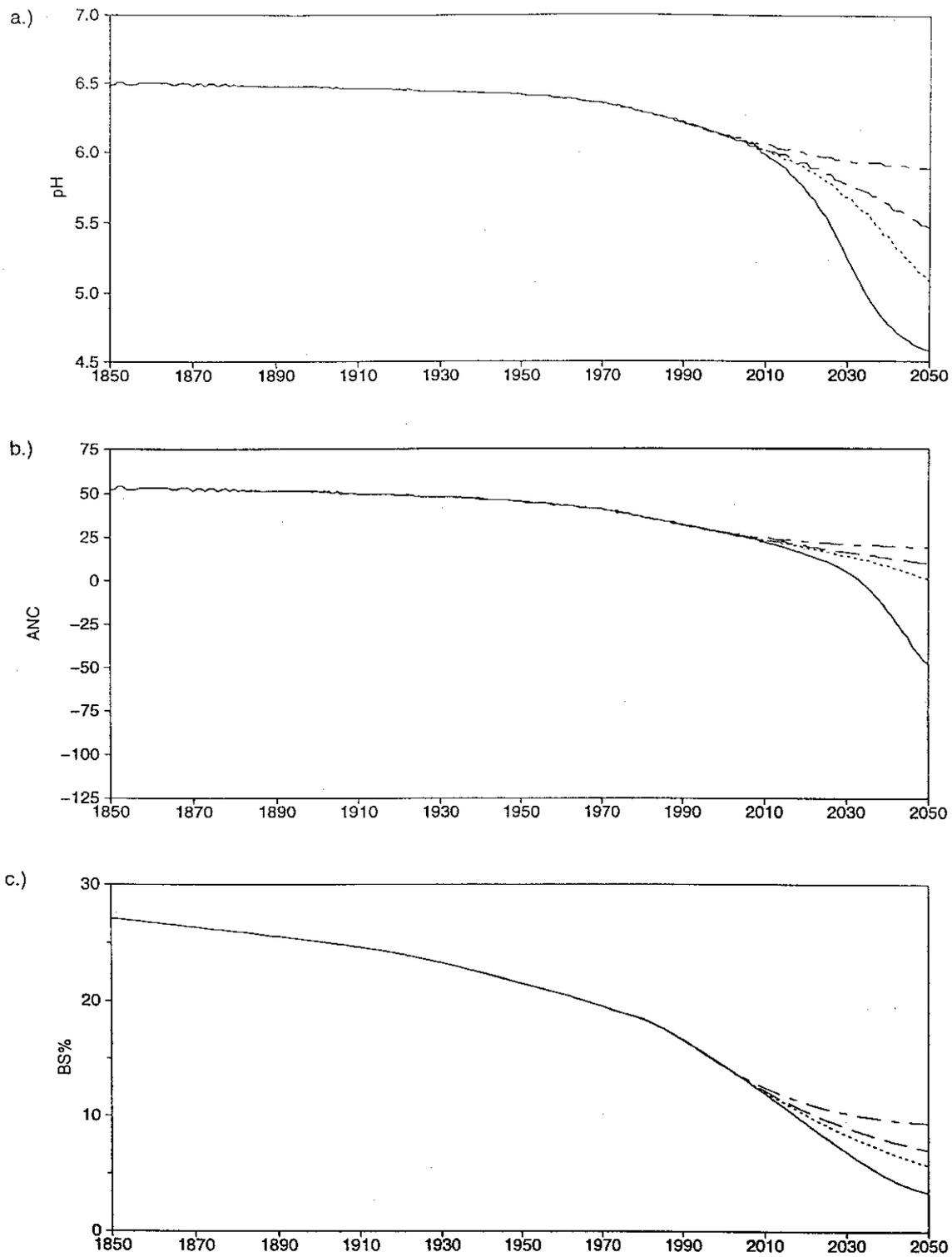


Figure 5.3. MAGIC simulated a) surface water pH, b) ANC and c) soil base saturation from 1849 to 2050 at the Foxo. Units are \log_{10} for pH, $\mu\text{eq } t^{-1}$ for ANC and percentage of CEC for soil BS%.

6 Critical Loads

Determining the level of acidic deposition (critical load) for sulphur, nitrogen or total acidity required to prevent environmental damage beyond a pre-determined level can be assessed temporally using the MAGIC model. A critical load is an intrinsic catchment property that broadly equates to the long term base cation weathering rate; it is assumed to be time independent when calculated under steady state conditions. Critical loads can be calculated for various compartments of the ecosystem, namely soils, surface waters and vegetation, although the methods of calculation differ (Sverdrup et al. 1990).

A critical load as defined by a dynamic model differs from a critical load based on steady state approaches by incorporating time dependent processes such as cation exchange, sulphur adsorption and net biomass uptake that affect soil and streamwater chemistry. The dynamic modelling approach to critical load calculation also provides a more conservative method of calculation since recovery over a pre-determined time scale is inherent in the calculation; this also leads to lower critical loads and higher critical load exceedance at more acidified sites. Dynamic modelling approaches were not adopted by the UN-ECE in the development of the protocol on further reductions in sulphur emissions but the relevance of dynamic models to the future assessment of the protocol have been emphasised (Kleemola & Forsius 1996; Jenkins et al. 1997; Forsuis et al. 1997).

MAGIC calculates a critical load, in this case for total sulphur deposition, by adjusting present day anthropogenic sulphur deposition and running the model forward in time. The deposition change, whether an increase or decrease, is assumed to be undertaken at present day as a step change and held constant for the given time period. The water quality variable, in this case surface water ANC, is then compared with the environmental target to be achieved (ANC_{lim}) in the future. ANC_{lim} is the critical ANC required to protect a biological target within the ecosystem, in this case an ANC_{lim} value of $0 \mu\text{eq l}^{-1}$ defines the 50% probability of survival of brown trout in the UK; this value has been adopted by the UK Critical Loads Programme (CLAG, 1995), although other European countries have adopted different values (Henriksen et al. 1992). The model then uses an iteration procedure to obtain the level of sulphur deposition required to maintain the ANC at the ANC_{lim} over a specified period of time. This level of sulphur deposition then becomes the critical load for sulphur. Critical loads based on a 50 year timescale are generally adopted since this represents an economically justifiable time frame over which such reductions can be achieved.

The use of dynamic models such as MAGIC for the calculation of critical loads for sulphur is of particular relevance in this region due to the strong capacity of the soils to retain sulphur on the exchange complex. The process of hysteresis has a significant effect on soil and surface water chemistry under reduced sulphur load, thereby affecting recovery and hence the determination of the critical load.

Surface water critical loads for sulphur for a critical chemistry of $ANC_{lim} = 0$ and $20 \mu\text{eq l}^{-1}$ were calculated using the MAGIC model and are presented in Figure 6. An alternative ANC_{lim} was chosen to give a more conservative estimate of the critical load based on recent evidence in the UK that suggests that an ANC_{lim} of $0 \mu\text{eq l}^{-1}$ is too low to protect fish populations (Harriman et al. 1995). These are compared with the modelled present day deposition of total

sulphur from the DEPUPT model. For the acidified Xantar catchment the critical load is zero; this implies that even if all anthropogenic sulphur were to be removed from the deposition in the first year of the forecast, surface water ANC could not recover to the $ANC_{lim} = 0$ by 2050. In fact ANC is predicted to recover to only $-8 \mu\text{eq l}^{-1}$ by 2050 under zero anthropogenic sulphur deposition. At the Sanche and Foxo the current sulphur deposition exceeds the critical load for surface water despite both sites being unacidified.

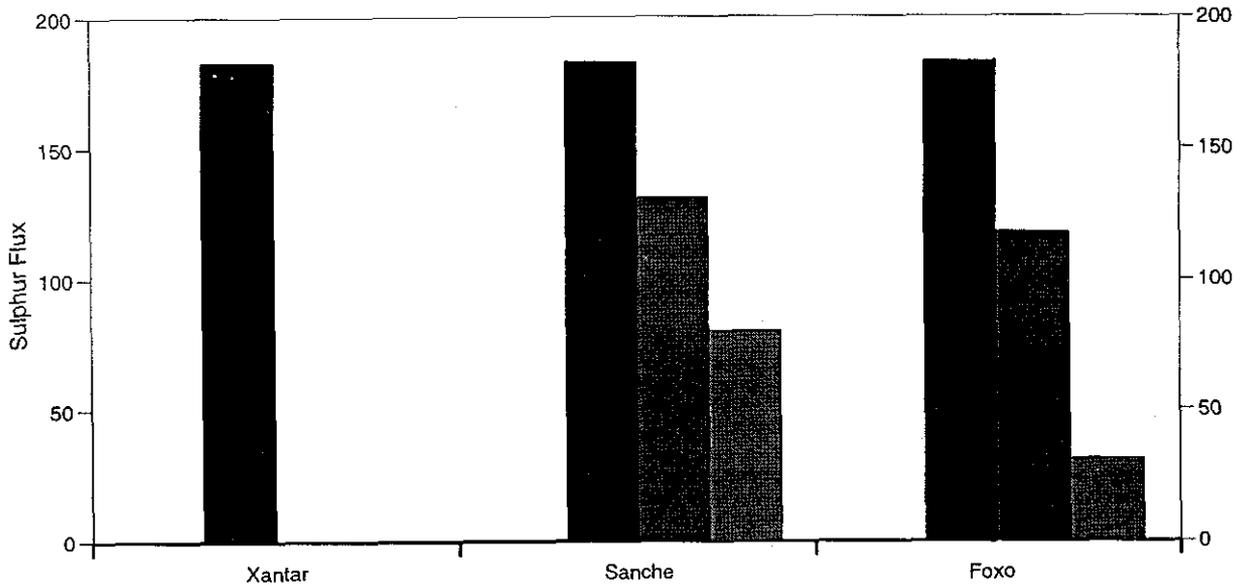


Figure 6. Modelled Sulphur deposition (from the DEPUPT model) (left bar) versus surface water critical loads for $ANC_{lim} = 0$ (middle bar) and $20 \mu\text{eq l}^{-1}$ (right bar). Units in $\text{meq m}^{-2} \text{yr}^{-1}$ of H^+ ions.

7 Discussion and Conclusions

The application of the MAGIC model to three sub-catchments of the River Sor provides insight into the effects of changing acidic deposition on catchment water quality.

The model was calibrated using detailed site specific deposition, soils and water chemistry data from the three sub-catchments. Calibration of the model to present day observed soil and water chemistry in 1993 indicates varying degrees of historical acidification which can be attributed to local variations in geology that affect the weathering rate of each sub-catchment.

Present day soil base status is similar at all three sites and historical loss of soil cation pool is also similar given that acid deposition loading to the soil is the same at the three sites.

Responses to reduced acidic deposition over the 56 year forecast period show broadly similar responses with continued deterioration in soil and surface water quality under all but the most stringent scenario (MFR), whereby sulphur deposition is reduced to a level close to background sea salt levels (Table 4). At the Xantar this lack of recovery is partly attributable to the sensitivity of the site and its low weathering rate (c. $30 \text{ meq m}^{-2} \text{ yr}^{-1}$).

The apparent lack of recovery under reduced acidic deposition is also explained by the large quantities of sulphur retained by the soil system over the historical period (Figure 7). Figure 7 shows how, under reduced sulphur deposition (B1 scenario), the output flux continues to exceed the input flux until beyond the 56 year forecast period. This reflects the non linear adsorption-desorption characteristics of sulphur implicit within the model. Given that all soil sulphur in the MAGIC model is reversibly bound, its release will continue to have a negative effect on soil and surface water quality into the future under reduced deposition scenarios. Here lies the greatest uncertainty; "is sulphur adsorption completely reversible in the soils at the Sor catchment" ?, or in fact in any catchment soils ?. There is evidence that some sulphur can be irreversibly retained by catchment soils; Harrison et al. 1989 suggested that as much as 36% of adsorbed sulphur may be irreversibly retained by forest soils in the USA. This sulphur will therefore not leach to surface waters under reduced sulphur loading thereby reducing the leaching of cations and leading to enhanced recovery. Recovery in pH and alkalinity cannot occur while sulphur is still being released from the soil exchange complex at a rate that exceeds base cation inputs from weathering and deposition. This will continue to deplete base cations from the soil system thereby delaying any recovery that may have been expected under such large reductions in acidic deposition. If this is true for the Sor catchment it would imply that the MAGIC predictions of soil and surface water quality in the future may be a worse case scenario.

The question of reduced nitrogen deposition has not been considered in detail here. Nitrate leaching is evident in all three catchments (Table 1) and contributes between 10 and 25% of acidic anion load in surface water. The linear retention of nitrogen implied within the MAGIC model does not adequately describe the complex processes that determine nitrogen leaching to surface waters. Nitrate contribution to total acid anion load is likely to increase in the future as reductions in sulphur deposition effect, although the control of nitrogen deposition is more problematic than that of sulphur given its more diffuse sources.

Models such as MAGIC have not yet been used to develop protocols for reducing emissions and deposition of acidity, although more recently these approaches have been used in consultation over the proposed EU Acidification Strategy (Jenkins and Renshaw, 1997, Forsius et al. 1997) and are likely to form an increasingly important role in developing strategy if they can be applied over wide areas.

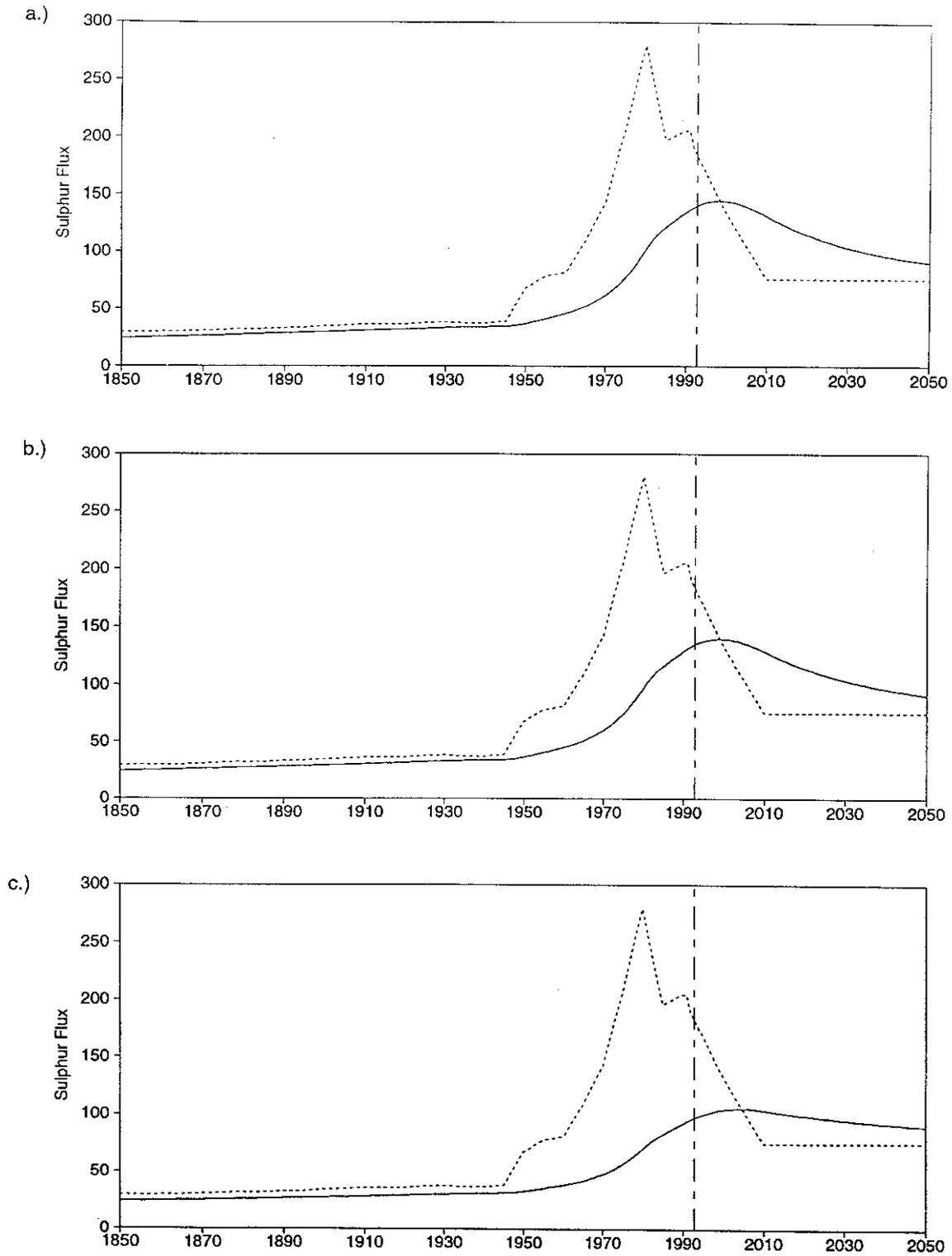


Figure 7. Modelled input (dotted line, from DEPUPT model) and output (solid line, MAGIC) fluxes from 1850 to 2050 for; a) Xantar, b) Sanche, and c) Foxo sub-catchments of the River Sor. Units in $\text{meq m}^{-2} \text{yr}^{-1}$.

8 References

- Alcamo, J., Shaw, R. and Hordijk, L. (eds.) 1990. The RAINS model of acidification: science and strategies in Europe. Kluwer Academic Publishers, Dordrecht, the Netherlands.
- Alvetag, M., Walse, C. and Warfvinge, P. 1997. A method for reconstructing historic deposition and uptake from present day values. *Water, Air and Soil Pollution* (In Press).
- Amann, M., Bertok, L., Cofala, J., Gyarfas, F., Heyes, C., Klimont, Z. and Schopp, W. 1996. Cost-effective Control of Acidification and Ground-Level Ozone. Second Interim Report to the European Commission, DG XI. IIASA, December 1996. 112 p.
- Cosby, B.J., Hornberger, G.M., Galloway, J.N. and Wright, R.F. 1985 a. Modelling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry. *Water. Res.*, 21, 51-63.
- Cosby, B.J., Hornberger, G.M., Galloway, J.N. and Wright, R.F. 1985 b. Time scales of acidification: A quantitative model for estimating freshwater acidification. *Environ. Sci. Technol.*, 19, 1144-1149.
- Cosby, B.J., Hornberger, G.M., Wright, R.F. and Galloway, J.N. 1986. Modelling the effects of acid deposition: Control of long term sulphur dynamics by soil sulphur adsorption. *Water. Res. Res.*, 22, 1283-1291.
- Couta, W., Lathwell, D.J. and Bouldin, D.R. 1979. Sulphate Sorption by two Oxisols and an Alfisol of the Tropics. *Soil Science*, 27, 108-116.
- Forsius, M., Alvetag, M., Bak, J., Guardans, R., Holmberg, M., Jenkins, A., Johansson, M., Kleemola, S., Rankinen, K., Renshaw, M., Sverdrup, H. and Syri, S. 1997. Assessment of the Effects of the EU Acidification Strategy: Dynamic Modelling on Integrated Monitoring Sites. Finnish Environment Institute, Helsinki.
- Garcia-Rodeja, E., Fernandez Sanjurjo, M.J. and Fernandez Vega, V. 1997. Input-Output Fluxes in the River Sor Catchment (Galicia, NW Spain). *Chemosphere*, 326.
- Harriman, R., Bridcut, E.E. and Anderson, H. 1995. The relationship between salmonoid fish densities and critical ANC at exceeded and non-exceeded stream sites in Scotland. *Water Air and Soil Pollution*, 85, 2455-2460.
- Harrison, R.B., Johnson, D.W. and Todd, D.E. 1989. Sulfate Adsorption and Desorption Reversibility in a Variety of Forest Soils. *J. Environ. Qual*, 18, 419-426.
- Henriksen, A., Sverdrup, H. and DeVries, W. 1989. Mapping Critical Loads: A Guidance to the Criteria, Calculations, Data Collection and Mapping of Critical Loads. Miljorapport 1990:14. Nordic Council of Ministers. Copenhagen.
- Henriksen, A., Kamari, J., Posch, M. and Wilander, A. 1992. Critical Loads of Acidity:

Nordic Surface Waters. *Ambio*, 21, 5, 356-363.

Hornberger, G.M., Cosby, B.J, and Galloway, J.N. 1986. Modelling the effects of acid deposition: uncertainty and spatial variability of long term sulphate dynamics in a region. *Wat. Res.*, 22, 1293-1302.

Jenkins, A. & Shaw, C. 1993. Comparison of empirical and dynamic model approaches for surface waters. In: (Eds.) M.Hornung & R.A.Skeffington. *Critical loads: concepts and applications*. ITE Symposium No. 28. HMSO, London.

Jenkins, A., Renshaw, M., Helliwell, R., Sefton, C., Ferrier, R. and Swingewood, P. 1997. Modelling surface water acidification in the UK. Application of the MAGIC model to the Acid Waters Monitoring Network. IH Report No. 131. Institute of Hydrology, Wallingford.

Kleemola, S. and Forsius, M. (Eds.). 1996. 5th Annual Report 1996. UN ECE Convention on Long Range Transboundary Air Pollution. International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems. *The Finnish Environment 27*. Finnish Environment Institute, Helsinki.

Likens, G.E., Wright, R.F., Galloway, J.N. & Butler, T.J. 1979. Acid Rain. *Sci. Am.*, 241, 4351.

Muniz, I.P. 1991. Freshwater acidification: its effects on species and communities of freshwater microbes, plants and animals. *Proc. Royal. Soc. Edin.*, 97b, 227-254.

Renshaw, M., Helliwell, R.C., Jenkins, A., and Ferrier, R.C. In Prep. A National Scale Application of the MAGIC Model: A Tool to Assess the Temporal and Spatial Effects of Reducing Acidic Deposition in the UK.

Sverdrup, H., de Vries, W. & Henriksen, A. 1990. Mapping critical loads - guidance to criteria, methods and examples for mapping critical loads and areas where they have been exceeded, Task force on mapping - UN-ECE, Umweltbundesamt, Berlin, Federal Republic of Germany.

Syri, S., Johansson, M. and Kangas, L. 1997. Application of Nitrogen Transfer Matrices for Integrated Assessment. *Atmospheric Environment*. (In Press).

Traaen, T.S. and Stoddard, J.L. 1995. An assessment of nitrogen leaching from watersheds included in the ICP on waters. Norwegian Institute for Water Research. ISBN 82-577-26990.

UN/ECE. 1994. Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Further Reduction of Sulphur Emissions. Document ECE/EB.AIR/40 (in English, French and Russian), New York and Geneva, 106 pp.

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