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# Application of MAGIC to Lake Redó (Central Pyrenees): an assessment of the effects of possible climate driven changes in atmospheric precipitation, base cation deposition, and weathering rates on lake water chemistry

Lluís CAMARERO*, Richard F. WRIGHT[1)], Jordi CATALAN and Marc VENTURA

Centre for Advanced Studies of Blanes (CEAB-CSIC) Accés C.S. Francesc 14. E-17300 Blanes, Spain
[1)]Norwegian Institute for Water Research (NIVA) Box 173 Kjelsås, N-0411, Norway
*e-mail of corresponding author: camarero@ceab.csic.es

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*ABSTRACT*

*The process-oriented catchment-scale model MAGIC was used to simulate water chemistry at Lake Redó, a high mountain lake in the Central Pyrenees, Spain. Data on lakewater and atmospheric deposition chemistry for the period 1984-1998 were used to calibrate the model, which was then used to reconstruct past and to provide forecasts for three hypothetical future scenarios of deposition. Forecast scenarios considered several combinations of changes in S and N deposition due to abatement strategies, and in base cation deposition due to climate-induced changes in air-mass trajectories from northern Africa. Scenario 1 assumed constant deposition of base cations at the present level plus the expected decrease in S and N deposition resulting from reduced emissions; scenario 2 (best case) assumed an increase in base cation deposition plus the same decrease in S and N deposition as in scenario 1; scenario 3 (worst case) assumed a decrease in base cation deposition plus no decrease in S and N deposition. The hindcast indicated that during the past 140-year period changes in lake water chemistry have been significant for a remote mountain catchment, although no substantial acidification has occurred. In this regard Lake Redó can be described as a "non-sensitive lake" maintaining a reference condition. The forecasts indicated changes that do not affect this status, but the trends, even if slight, were different between scenarios. A slight decline in the surface water ANC is predicted by Scenario 3. The N budget indicates an unusually low retention in the catchment, which may result in enhanced sensitivity to further increased N deposition. Some of the discrepancy between modelled and measured $Ca^{2+}$ in lake water during 1984-98 could be explained by changes in rainfall amounts and by increased weathering rates due to increases in air temperature.*

*Key words: acidification recovery, MAGIC model, base cation, deposition, weathering, climate change*

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## 1. INTRODUCTION

Acid deposition in Europe has decreased substantially during the period 1980-2000 as a result of international agreements to reduce the emissions of sulphur (S) and nitrogen (N) compounds to the atmosphere. Evaluation of the resulting effects on acidification of freshwaters has shown that chemical recovery has begun (Stoddard *et al.* 1999; Skjelkvåle *et al.* 2001; Evans *et al*. 2001), but there is hysteresis in the reversal of acidification which can vary from one system to another, and among geographic areas (Stoddard *et al*. 1999; Forsius *et al*. 2001). Hysteresis can be caused by delayed responses in catchment soils, such as replenishment of the depleted pool of base cations on the soil exchange complex and desorption of acid anions previously stored in soils, but in addition, other factors might play a role. The effect of climate change on the biogeochemistry of catchments has been identified as one such factor (Psenner & Schmidt 1992; Sommaruga-Wögrath *et al*. 1997; Devito *et al*. 1999). Changes in precipitation and temperature can affect organic matter decomposition in soils and result in enhanced leaching of inorganic N as documented by whole catchment experiments (Wright 1998), and increases in concentrations of dissolved organic carbon such as found in the U.K. (Monteith *et al*. 2001). A significant decrease in the atmospheric deposition of base cations has been observed in the northern hemisphere, partly due to changes in anthropogenic emissions and land use (Hedin *et al*. 1994), but possibly also due to changes in climate (Moulin *et al*. 1997). In parts of eastern North America the decline in base cation deposition has occurred concurrently with a decline in S deposition (Nilles & Conley 2001). In several European alpine lakes, where soils are sparse or absent, a decrease in atmospheric deposition of base cations has been measured, but an increasing trend in base cation concentrations in lakewater was observed (Mosello *et al*. 2002).

Here we explore some possible interactions of climate change and acid deposition on the chemistry of Lake Redó, an alpine lake in the Central Pyrenees, Spain. We use the MAGIC model (Cosby *et al*. 1985a, 2001) and data on lakewater and atmospheric deposition for the period 1984-1998. We first calibrate the model to 1997 and compare the hindcasted model results with measured data 1984-97. We then use the model to forecast the effects of three scenarios of future base cation and acid deposition. Although the effects of acid deposition have been low in

**Tab. 1**. Calendar of the different samplings conducted at Lake Redó along the period 1984-98 and reported in this paper.

| | | | | | | calibration year |
|---|---|---|---|---|---|---|
| Lake water | 84-85<br>(summer to summer) | | | 91-92<br>(summer to summer) | 96-97<br>(summer to summer) | 97-98<br>(summer to summer) |
| Atmos.precipitation | | 87-88<br>(summer to summer) | 90<br>(summer & autumn) | | | 97-98<br>(summer to summer) |
| Soil | | | | | 96<br>(summer) | 98<br>(summer) |

the Pyrenees (Camarero *et al*. 1995b; Camarero & Catalan 1998), the acid-sensitive catchment of Lake Redo is underlain by crystalline bedrock. It is influenced by significant deposition of base cations from the Iberian peninsula and north Africa (Camarero & Catalan 1993, 1996). Future climate change may entail changes in transport and deposition of base cations contained in Saharan dust. The effects may be of significance for surface waters in large areas of southern Europe. As for future acid deposition, we have used the 'optimistic' scenario B1 (see description below) in the RAINS model (Amman *et al*. 1996). The MAGIC application presented here aims to assess the efficacy of these emission reduction policies with variable base cation deposition scenarios on surface water quality in catchments of the characteristics that of Lake Redó.

## 2. METHODOLOGY

### 2.1. Study site

Lake Redó is situated in a high mountain catchment in the Central Pyrenees (42º38'33"N, 0º46'13"E). The catchment is a glacial cirque with rocky, steep slopes. The altitude of the catchment ranges between the lake level, at 2243 m a.s.l., and the highest peak, at 2645 m a.s.l., with an average crest altitude of 2397 m a.s.l. The bedrock of the catchment is composed of granodiorite; in the eastern part there are bedrock fractures containing calcite veins. The lake has a well-defined outlet, but no permanent inlet streams. Most of the water input to the lake comes during spring snowmelt, and briefly after the heavy rain episodes in summer and autumn. The catchment is located above the treeline, and the vegetation is alpine grassland. The dominant communities are *Carici-Festucetum eskiae* and *Ranunculo-Festucetum eskiae* meadows on south-facing slopes, and *Gentiano-Caricetum curvulae* meadows on north-facing slopes. Soils are dominated by umbric leptosol about 35 cm thick on average. About 25% of the catchment is bare rock. The lake is deep (max. 73 m), and relatively large when compared with the catchment area: it covers 16% of the total area of the catchment. The lake has no macrophytes except for a few mosses in the littoral zone.

### 2.2. MAGIC model

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry (Cosby *et al*. 1985a, 1985b, 2001). The model simulates soil solution and surface water chemistry to predict average concentrations of the major ions. MAGIC calculates for each time step (in this case year) the concentrations of major ions under the assumption of simultaneous reactions involving sulphate adsorption, cation exchange, dissolution-precipitation-speciation of aluminium and dissolution-speciation of inorganic and organic carbon. MAGIC accounts for the mass balance of major ions in the soil by bookkeeping the fluxes from atmospheric inputs, chemical weathering, net uptake in biomass and loss to runoff.

Data inputs required for calibration of MAGIC comprise lake and catchment characteristics, soil chemical and physical characteristics, input and output fluxes for water and major ions, and net uptake of base cations by vegetation.

### 2.3. Chemical data

Data on lakewater chemistry and atmospheric deposition used to calibrate MAGIC for Lake Redó catchment were obtained during 1997 and 1998. Water chemical analyses were carried out according to the methods agreed within the MOLAR and EMERGE projects (The MOLAR water chemistry group 1999). Soil physical and chemical parameters were measured according the UN-ECE ICP-IM manual (Kleemola & Søderman 1993) in 1996 and 1998. Surface lake water chemistry data for time-trend comparison were compiled from several studies carried out since 1984. The data were collected as part of several different projects (see table 1 for a sampling calendar), and therefore the record lacks continuity over the 14-year period. The series consists in practice of four periods (1984-85, 91-92, 96-97 and 97-98) in which measurements were more frequent, plus occasional measurements in the intervening periods. Time-trend precipitation data are from 1987-88, 1997-98 and a four-month period in 1990. Data from 1987-88 and 1997-98 were collected at the High Mountain Research Centre (CRAM) station. Data from 1990 were collected at three stations in the Aigüestortes National Park.

Lake Redó is a relatively large lake (24 ha), when compared to other mountain lakes. Its maximum depth is 73 m, and the mean depth is 32 m. This causes the average water turnover time to be long, c. 4-5 years. The lake is frozen during a 6-month period from mid-end of December to June. The chemical data used in the calibration correspond to average values of monthly

**Tab. 2**. Input parameters: yearly averaged chemical composition of bulk deposition, (measured and corrected by the ice-cover dilution effect), in lake retention of solutes, lakewater composition, and soil physico-chemical parameters. Bold values were used to calibrate MAGIC. The concentrations in lake water modelled after calibration are compared to the input concentrations.

| | | deposition | | in lake retention | lake outlet | | soil parameters | | |
|---|---|---|---|---|---|---|---|---|---|
| | | measured | less 30% | meq $m^{-2}$ $y^{-1}$ | measured | modelled | | | |
| $H_2O$ | mm | 1414 | **1414** | | **1273** | | depth | m | **0.35** |
| | | | | | | | bulk density | kg $m^{-3}$ | **647** |
| $Ca^{2+}$ | µeq $l^{-1}$ | 22 | **15** | **8.8** | **71** | 72 | CEC | meq $kg^{-1}$ | **82** |
| $Mg^{2+}$ | µeq $l^{-1}$ | 3 | **2** | **6.2** | **7** | 7 | ex. Ca | % | **17.7** |
| $Na^+$ | µeq $l^{-1}$ | 13 | **9** | **0** | **12** | 13 | ex. Mg | % | **3.3** |
| $K^+$ | µeq $l^{-1}$ | 3 | **1** | **9.4** | **<2** | 1 | ex. Na | % | **0.2** |
| $NH_4^+$ | µeq $l^{-1}$ | 15 | **10** | **10.9** | **2** | 1 | ex. K | % | **0.8** |
| $SO_4^{2-}$ | µeq $l^{-1}$ | 21 | **14** | **3.8** | **27** | 27 | BS | % | **22** |
| $Cl^-$ | µeq $l^{-1}$ | 11 | **8** | **0** | **10** | 9 | C | % | **8.6** |
| $NO_3^-$ | µeq $l^{-1}$ | 10 | **12** | **9.6** | **11** | 11 | N | % | **0.6** |
| | | | | | | | C | mol $m^{-2}$ | **1623** |
| SBC | µeq $l^{-1}$ | | | | **91** | 92 | N | mol $m^{-2}$ | **113** |
| SAA | µeq $l^{-1}$ | | | | **48** | 46 | C/N | mol $mol^{-1}$ | **14.2** |
| ANC | µeq $l^{-1}$ | | | | **47** | 47 | | | |
| $H^+$ | µeq $l^{-1}$ | | | | **0.4** | 0.3 | | | |
| pH | | | | | **6.43** | 6.52 | | | |
| $HCO_3^-$ | µeq $l^{-1}$ | | | | **47** | 45 | | | |
| $Al^{n+}$ | µeq $l^{-1}$ | | | | **0** | 0 | | | |
| $Org^-$ | µeq $l^{-1}$ | | | | **1** | 3 | | | |

samples taken at the outlet of the lake from July 1997 to July 1998 (Tab. 2). Runoff volume closely matched the precipitation water input to the catchment during summer, indicating that seepage is negligible; evapotranspiration is minor. The water retention time in the catchment is on the order of 3-4 days only. Based on these observations, we assumed the annual discharge to be close (*ca* 90%) to the precipitation input. Due to incomplete discharge measurements, this was also assumed to estimate monthly discharge from precipitation during the snow-free season. From January to March all precipitation is in form of snow, little melting occurs, and runoff is maintained at base levels. As for the thaw, based on field measurements we assumed that *ca* 20% of the accumulated winter precipitation melts during April, 60% during May, and the remaining 20% during June. These estimates were used to calculate volume-weighted mean concentrations of ions in runoff, which did not differ substantially from the non-weighted averages.

Volume-weighted average concentrations of ions in precipitation were obtained from measurements carried out from the beginning of July 1997 to the beginning of July 1998 (Tab. 2). The yearly precipitation volume was 1414 mm. Much of the winter precipitation runs off as snowmelt under the ice without mixing into the lake. A first peak of high concentration runoff occurs initially, followed by salt-impoverished meltwater that causes lake water dilution relative to precipitation. The monthly sampling of lake chemistry and outlet chemistry probably missed the peak runoff during snowmelt in 1997. This high concentration peak was captured by more detailed sampling at the nearby Lake Bacivèr (Catalan *et al.* 1990). As an effect, the average $Cl^-$ concentration is 30% lower in lake water than in precipitation. Consequently, the fluxes of all constituents in deposition were reduced by 30% for calibration, using $Cl^-$ as a conservative tracer of dilution

A total of 12 soil profiles were sampled to determine their physico-chemical characteristics. Soils in the catchment were then mapped according to the field observations, slope, orientation, vegetation, and physico-chemical properties. Soils cover 59% of the catchment. The rest is bare rock (25%) and the lake itself (16%). Soils had significantly different exchangeable $Ca^{2+}$ saturation in samples from the east subcatchment (where calcite veins are found) and the west subcatchment. The soils can be grouped into two main classes: mineral and organic, the main differences being lower bulk density, higher cation exchange capacity, and higher C and N contents in the organic soils. The data used to calibrate MAGIC were aggregated and weighted by soil type and percentage of cover per $m^2$ of terrestrial part of the catchment (Tab. 2).

### *2.4. MAGIC calibration*

MAGIC (version 7) was calibrated using the mean lake chemistry data and mean soil chemistry data (Tab. 2) as targets (Cosby *et al.* 2001). The calibration was set up with the terrestrial catchment (125 ha) and lake (24 ha) using one soil box and yearly time steps. In-lake retention of ions was measured (Tab. 2), with the exception of N ions, which were calibrated (see the nitrogen budget below).

First $SO_4^{2-}$ and $Cl^-$ were calibrated. The $Cl^-$ budget was balanced after reducing the deposition values by about 30%, as mentioned above. Sulphate adsorption capacity in the soil was assumed to be low (1 meq $m^{-2}$).

**Tab. 3**. Nitrogen budget (meq $m^{-2}$ $y^{-1}$) for Lake Redó in 1997-98 as simulated by MAGIC.

| **per $m^2$ land area (124 ha)** | deposition | retention | nitrification | runoff | |
|---|---|---|---|---|---|
| $NH_4^+$ | 16.1 | -3.0 | -10.9 | 2.2 | |
| $NO_3^-$ | 10.6 | -4.2 | 10.9 | 17.3 | |
| sum | 26.7 | -7.2 | 0.0 | 19.5 | |
| **per $m^2$ lake surface (25 ha)** | deposition | runoff land | retention | outlet | |
| $NH_4^+$ | 16.1 | 11.1 | -10.9 | 16.3 | |
| $NO_3^-$ | 10.6 | 85.7 | -9.6 | 86.7 | |
| sum | 26.7 | 96.8 | -20.5 | 103.0 | |
| **per $m^2$ catchment + lake (149 ha)** | deposition | soil retention | nitrification | retention lake | outlet |
| $NH_4^+$ | 16.1 | -2.5 | -9.1 | -1.8 | 2.7 |
| $NO_3^-$ | 10.6 | -3.5 | 9.1 | -1.6 | 14.5 |
| sum | 26.7 | -6.0 | 0.0 | -3.4 | 17.3 |

To balance the $SO_4^{2-}$ budget, a weathering rate of 15 meq $m^{-2}$ $y^{-1}$ was assumed. A geologic supply of $SO_4^{2-}$ has been observed in the Pyrenees (Jenkins *et al*. 2003), and the $SO_4^{2-}$ probably comes from Mg-rich carbonate minerals bearing sulphate and from pyrite (Catalan *et al*. 1993)

Next the nitrogen budgets were calibrated. The spatially weighted mean soil chemistry contains 8.6% C and 0.6% N. Total pool sizes per $m^2$ land area were thus 1620 mol C $m^{-2}$ and 113 mol N $m^{-2}$ (Tab. 2). C/N ratio was 14.3. The parameters in MAGIC were adjusted such that the N budget (Tab. 3) was reproduced by the model for the year 1997: lake retention of $NH_4^+$ and $NO_3^-$ was estimated at 10.9 and 9.6 meq $y^{-1}$ per $m^2$ lake area (Tab. 4). For N retention by the soil the active C pool was assumed to be 1/10 of the total (i.e. 162 mol C $m^{-2}$ soil). We chose this low fraction so as to exaggerate the effect of future N saturation in the soil. The actual actve C pool is probably a much larger fraction. The required retention was obtained with C/N intercept of 17.4 (100% retention) and slope of 4 C/N units (i.e. 0% retention at C/N of 13.4). Nitrification was set at 95% to obtain the correct proportion of $NH_4^+$ and $NO_3^-$ in runoff to the lake. At this point of the calibration the strong acid anions and $NH_4^+$ had been calibrated and the sum of strong acid anions in the lake agreed with the measured 48 µeq $l^{-1}$.

The next step was the calibration of base cations. This was done by a procedure in which the weathering rate and initial (i.e. 1857) base saturation were selected, the model run for 140 years iteratively, the simulations compared with 1997 measurements, and the initial parametres modified at each iteration as to obtain convergence of both simulations and measurements. The final calibrated values for weathering and initial percentage base saturation are given in table 4. At this point in the calibration the sum of base cations in the lake agreed with measured 91 µeq $l^{-1}$, and the ANC also agreed 47 µeq $l^{-1}$.

Finally the $H^+$, $Al^{n+}$ and organic anion concentrations were calibrated by adjusting the concentration of organic acids and the solubility constant for aluminium hydroxide in lakewater. The measured concentrations of these three components were very small, and the ANC was comprised almost entirely of $HCO_3^-$ (Tab. 2).

## 2.5. Simulation scenarios

Once calibrated, MAGIC was used to construct hindcast (1857-1997) of lakewater chemistry. Hindcast scenarios for deposition of sulphur (Mylona 1993) and nitrogen (Alveteg *et al*. 1998) were provided by EMEP models.

The calibrated model was then used to evaluate the impact of three forecast scenarios for the period 1997-2047 for deposition of base cations and strong acids. Variability in the chemical composition of atmospheric deposition in the Pyrenees shows two very different components according to the air mass trajectories (Camarero & Catalan 1996). Air masses of south and southeast origin bring significantly higher deposition of base cations than air masses of north and northwest origin. The characteristics of the future deposition will be conditional on the relative intensity of these two components. If future climate change entails increased drought conditions from the Iberian peninsula and north Africa, the result may increase deposition of base cations in the Pyrenees. Alternatively, if southernly air mass trajectories occur at lower frequency the transport of base cations can be diminished.

With respect to future acid deposition, we have used the 'optimistic' scenario in the RAINS model (Scenario B1 in Amman *et al*. 1996) that identifies for the year 2010 the cost-minimal allocation of emission reductions to attain in each grid cell within the EU a decrease of the area of unprotected ecosystems (i.e. with deposition above the critical load) by at least 50%. For this scenario, it is assumed that EU countries will reduce their emissions if necessary further than a reference level estimated as the more stringent outcome of the current reduction plan (based on an inventory of officially declared national emission ceilings) and the current legislation (which takes into account national and international legislation as well as commitments made within the framework of the Convention on Long-range Transboundary Air Pollution of the UNECE); it was in addition assumed that the non-EU countries will not reduce their emissions further than the reference level, and also that no measures will be taken to reduce emissions from ships on the sea.

**Tab. 4**. Calibrated MAGIC parameters for Lake Redó

| | Units | L. Redó |
|---|---|---|
| **Lake parameters** | | |
| discharge | m y$^{-1}$ | 1.273 |
| water retention time | y | 4.05 |
| relative area lake | % | 16 |
| mean depth | m | 32 |
| temperature | °C | 5 |
| $pCO_2$ | atm | 0.0007 |
| solubility $Al(OH)_3$ | log$_{10}$ | 8.2 |
| total organic acid | mmol m$^{-3}$ | 1 |
| pK1 | log$_{10}$ | 3.04 |
| pK2 | log$_{10}$ | 4.51 |
| pK3 | log$_{10}$ | 6.46 |
| **Soil parameters** | | |
| depth | m | 0.35 |
| porosity | | 0.5 |
| bulk density | kg m$^{-3}$ | 647 |
| soil mass | kg m$^{-2}$ | 226 |
| CEC | meq kg$^{-1}$ | 82 |
| $SO_4^{2-}$ half sat | | 100 |
| $SO_4^{2-}$ max cap | | 1 |
| temperature | °C | 4 |
| $pCO_2$ | atm | 0.0035 |
| solubility $Al(OH)_3$ | log$_{10}$ | 8.16 |
| total organic acid | mmol m$^{-3}$ | 200 |
| pK1 | log$_{10}$ | 3.04 |
| pK2 | log$_{10}$ | 4.51 |
| pK3 | log$_{10}$ | 6.46 |
| **Calibrated parameters** | | |
| weathering $Ca^{2+}$ | meq m$^{-2}$ y$^{-1}$ | 79.0 |
| weathering $Mg^{2+}$ | meq m$^{-2}$ y$^{-1}$ | 7.0 |
| weathering $Na^{+}$ | meq m$^{-2}$ y$^{-1}$ | 4.5 |
| weathering $K^{+}$ | meq m$^{-2}$ y$^{-1}$ | 2.0 |
| weathering $SO_4^{2-}$ | meq m$^{-2}$ y$^{-1}$ | 15.0 |
| initial saturation $Ca^{2+}$ | % | 21.2 |
| initial saturation $Mg^{2+}$ | % | 3.6 |
| initial saturation $Na^{+}$ | % | 0.2 |
| initial saturation $K^{+}$ | % | 0.9 |
| selectivity coeff. Al-Ca | -log$_{10}$ | -1.76 |
| selectivity coeff. Al-Mg | -log$_{10}$ | -2.44 |
| selectivity coeff. Al-Na | -log$_{10}$ | -2.16 |
| selectivity coeff. Al-K | -log$_{10}$ | -5.67 |
| initial C pool | mol m$^{-2}$ | 162 |
| initial N pool | mol m$^{-2}$ | 10.5 |
| initial C/N | | 15.4 |
| C/N slope $NH_4^{+}$ | | 4 |
| C/N slope $NO_3^{-}$ | | 4 |
| C/N intercept $NH_4^{+}$ | | 17.4 |
| C/N intercept $NO_3^{-}$ | | 17.4 |

The implementation of such measures would reduce in 2010 the S deposition in the Pyrenean area by 41%, and N by 16% relative to 1990 levels. The three scenarios considered are:

1) Scenario 1. This scenario assumes further reductions in emissions, causing deposition of S and N to decrease by 41 and 16 % respectively by the year 2010 relative to 1990 (Scenario B1, Amman *et al.* 1996). Furthermore, this scenario assumes that there will be no significant changes in base cation deposition.
2) Scenario 2. For this scenario we assumed a progressive increase in base cation deposition to 3-fold 1997 levels by the year 2020 and then constant, and the future acid deposition remains the same as scenario 1. These base cation levels have been measured in episodic events in the past (Camarero & Catalan 1993), and could be achieved as an annual pattern either by an increase of the southern air mass trajectories, an increase in the base cation concentrations during dust episodes, or a combination of both.
3) Scenario 3. During the 1990s a decrease in $Ca^{2+}$ deposition was measured in the central Pyrenees. According to this trend, we selected a scenario in which $Ca^{2+}$ (the most abundant base cation) deposition would decline to about half of the 1997 level by the year 2020. We combine this with acid deposition maintained at the present level during the future. Hypothetically, this situation may be due to the failure in reaching the agreed N emission reductions in Europe (Erisman *et al.* 2003), or to a future increase in acid emissions in developing countries in north Africa, which could offset the expected decreasing emissions in Europe. Scenario 3 represents the opposite extreme from scenario 2.

## 3. RESULTS AND DISCUSSION

MAGIC was used to reconstruct lake water chemistry from 1857 to 1997. The hindcast indicated changes in the water chemistry during the 140-year period that are considerable for a remote mountain catchment (Fig. 1), but minor in absolute values and indicating only slight acidification. Lake ANC decreased from 65 µeq l$^{-1}$ in 1857 to 47 µeq l$^{-1}$ in 1997 in response to the increase in $SO_4^{2-}$ of about 14 µeq l$^{-1}$ (from 13 to 27 µeq l$^{-1}$) and the increase in $NO_3^{-}$ of about 9 µeq l$^{-1}$ (from 2 to 11 µeq l$^{-1}$).

The forecasts under the three scenarios also indicated changes that were modest in absolute values, but with clear opposite trends (Fig. 1): pH was predicted to stay in the narrow range between 6.5 and 6.8 in all cases. Under scenario 1 (scenario of reduced S and N and no change in base cation deposition) only a slight increase of 3 µeq l$^{-1}$ ANC was predicted (from 47 µeq l$^{-1}$ in 1997 to 50 µeq l$^{-1}$ in 2047), whereas under scenario 2 (reduced S and N and increased base cation deposition) a clear improvement in ANC was predicted in which ANC would eventually increase above pre-acidification conditions (increase of 47 µeq l$^{-1}$ in 1997 to 87 µeq l$^{-1}$ in 2047), and scenario 3 (no change in S and N deposition and decreased base cation deposition) would give a slight further decrease of 7 µeq l$^{-1}$ (to 40 µeq l$^{-1}$ in 2047) in ANC.

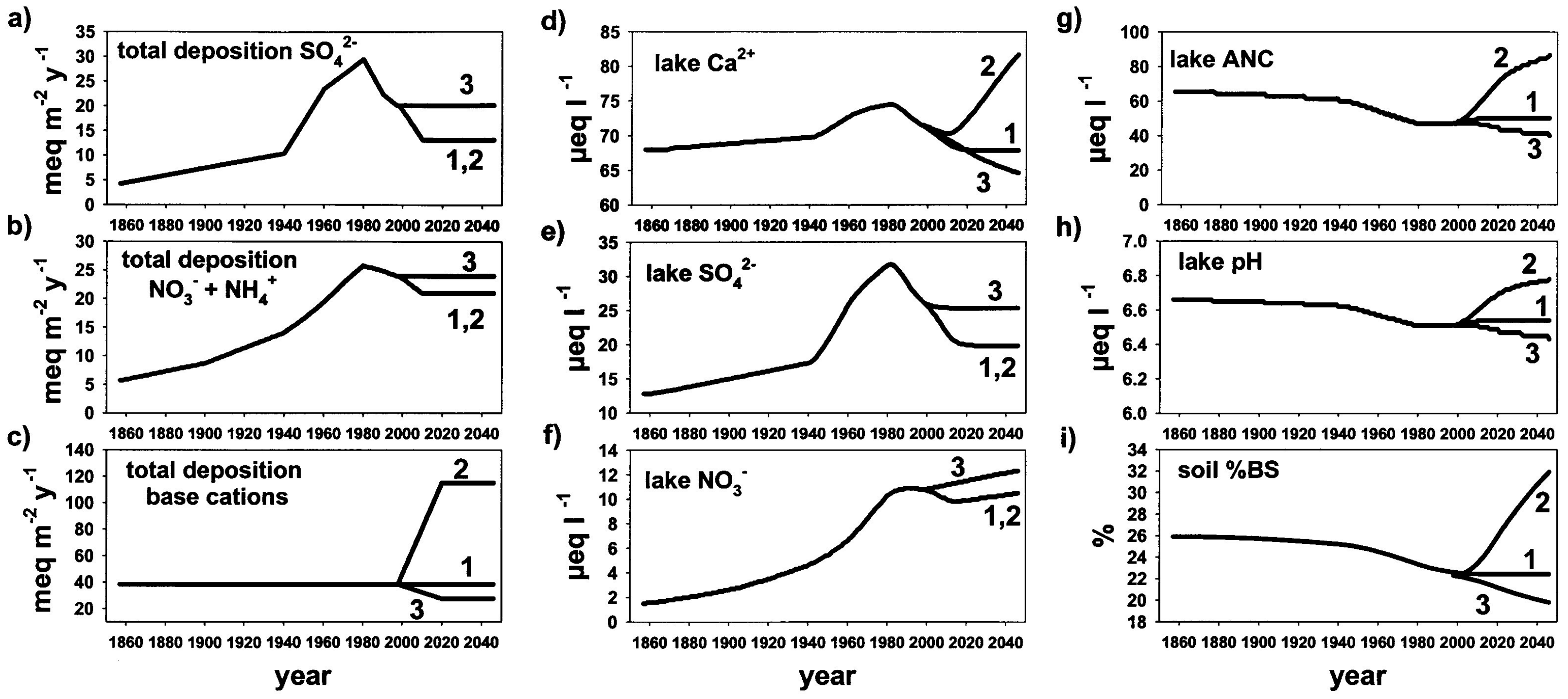

**Fig. 1**. Time series of: **a**) S; **b**) N; and **c**) base cations deposition used in MAGIC modelling. Model simulations of: **d**) Ca$^{2+}$; **e**) SO$_4^{2-}$ ; **f**) NO$_3^-$; **g**) ANC; **h**) pH in lake Redó water; and **i**) soil base saturation (%). Historical S trends produced by Mylona (1993), and N by Alteveg *et al.* (1998). Forecast scenarios: 1) reduced S and N deposition according to scenario B1 (Amman *et al.* 1996), base cations maintained at present levels; 2) B1 and three-fold increase in base cations; 3) no change in S and N deposition and decrease to one-half in Ca$^{2+}$ deposition.

The latter result is the opposite to scenario 1, recovery as a consequence of future abatement of emissions in Europe.

The changes in lake water chemistry since 1857 as simulated by MAGIC were minor because acid deposition in this region of the Pyrenees is modest relative to more heavily-impacted areas in central and northern Europe (Tarrason & Schaug 2000). In this regard Lake Redó can be described as a "non-sensitive" lake, in that acidification has been minor and the lake maintains a reference condition. Indeed there have been no reported damage to key acid-sensitive groups in the biota, such as diatom assemblages, invertebrates, and fish populations in the Pyrenees (Camarero *et al*. 1995b). It is therefore possible that none of the changes predicted under the three hypothetical scenarios can cause surface waters to deviate from this reference condition.

The increase in $NO_3^-$ concentration is one of the most significant changes in lake chemistry as reconstructed by the model. In 1997 nitrogen deposition (35 meq $m^{-2}$ $y^{-1}$) was higher than sulphate deposition (28 meq $m^{-2}$ $y^{-1}$), and the nitrogen budget indicates that the catchment retained only *ca* 22% of N deposition. A further 13% of incoming N was retained in the lake, as a possible result of in-lake processes such as N assimilation for algal growth, denitrification and nitrate reduction in the sediments (Camarero 1994) (Tab. 3). The terrestrial catchment leaks an unusually high fraction of the incoming N, probably because of the extremely sparse soil cover, cold temperatures and sparse vegetation in the catchment. Similar high percent leaching of N deposition in high mountain catchments has also been reported from the Tatra Mountains in Slovakia (Kopacek *et al*., in prep.) and the Rocky Mountains of USA (William *et al*. 1996). Such characteristics make these high elevation systems very sensitive to further increased N deposition. The simulations incorporated the nitrogen saturation concept linked to the C/N ratio of the active soil organic matter pool. The runs shown here assume that only 1/10 of the total soil carbon is active, and yet the change in future $NO_3^-$ concentrations is only 2 µeq $l^{-1}$ from 2000 to 2040. If the entire C pool were used, the change would be only 0.2 µeq $l^{-1}$. In any case the future change is predicted to be small.

The simulated and observed lake chemistry during the last 14 years are shown in figure 2. Observed values correspond to the composition of surface lakewater sampled at the centre of the lake, and are assumed to represent the water flowing out of the lake. A comparison of simulations and observations revealed that there were some discrepancies due to uncertainties in the input parameters or inadequate process representation. On the other hand, observed time-series are in practice intermittent and with detailed observations available for only four one-year-periods between 1984-98. Year-to-year variability is a significant factor that affects trends, but can not be adequately assessed with the available data. For this reason the observations are merely indications of a possible trend, and the discussion below is therefore intended to propose explanations for the disagreements between simulations and observations rather than to actually test specific hypotheses.

Most of the parameters were correctly modelled: MAGIC simulations closely matched the observed median trend of $SO_4^{2-}$ concentrations in lakewater during 1984-1998 (Fig. 2b). As a result, both the modelled and observed ANC increased, although the observed trend is steeper than the simulated trend (Fig. 2a). The most important difference was in $Ca^{2+}$, which did not decrease in the lake as foreseen by the model (Fig. 2c). Modelled base cation deposition was constant and equal to 1997-98 values over time. The modelled decreasing $Ca^{2+}$ concentration in lakewater is the result of a modelled decrease in cation exchange in the soil, as simulated by the model owing to the lower inputs of acid deposition.

The observed $Ca^{2+}$ concentrations increased, however. There are three possible explanations for this. Firstly, there could have been an increased supply of $Ca^{2+}$ in precipitation over this period. The observed $Ca^{2+}$ deposition, however, has decreased (Tab. 5).

Secondly, there is a possible dilution caused by larger precipitation volumes at the beginning of the time series. The largest volumes were indeed recorded in 1984-85, followed by a relatively dry period which continued until about 1995, thereafter relatively high precipitation was observed from 1996. The water renewal time of the lake is *ca* 4-5 years, and thus the effects of a copious amount of thaw water or a drought can span a period longer than the hydrological year – thus, the concentration of solutes in the lake may remain high immediately after the wetter period in 1996. If dilution was the cause for the observed increase in $Ca^{2+}$, the same increase should be seen in the concentrations of other ions. This was not observed for $Cl^-$ and $Na^+$. The model simulates no major change in both ions, in agreement with observations of the conservative ion $Cl^-$, both in the lake (Fig. 2e) and precipitation (Tab. 5); in contrast, $Na^+$ showed greater variability (Fig. 2d). This could indicate that there was not a previous dilution. However, $Cl^-$ and $Na^+$ have a predominantly marine origin, and their concentrations are less influenced by precipitation volume than that of elements with geological origin which are diluted by larger amounts of precipitation. Consequently the hypothesis of an hydrological control on $Ca^{2+}$ concentration can not be completely discarded.

Finally, a third explanation could be an increase in the weathering rate of $Ca^{2+}$. This is consistent with the change in Si concentration, which increases at a similar rate as $Ca^{2+}$ (Fig. 2f). Enhanced weathering rates might have been caused by the warmer climate in this area since 1984, where the mean annual air temperature has increased by about 2 ºC from the early 1970s to 2000 (Catalan *et al*. 2002). The main factor controlling the

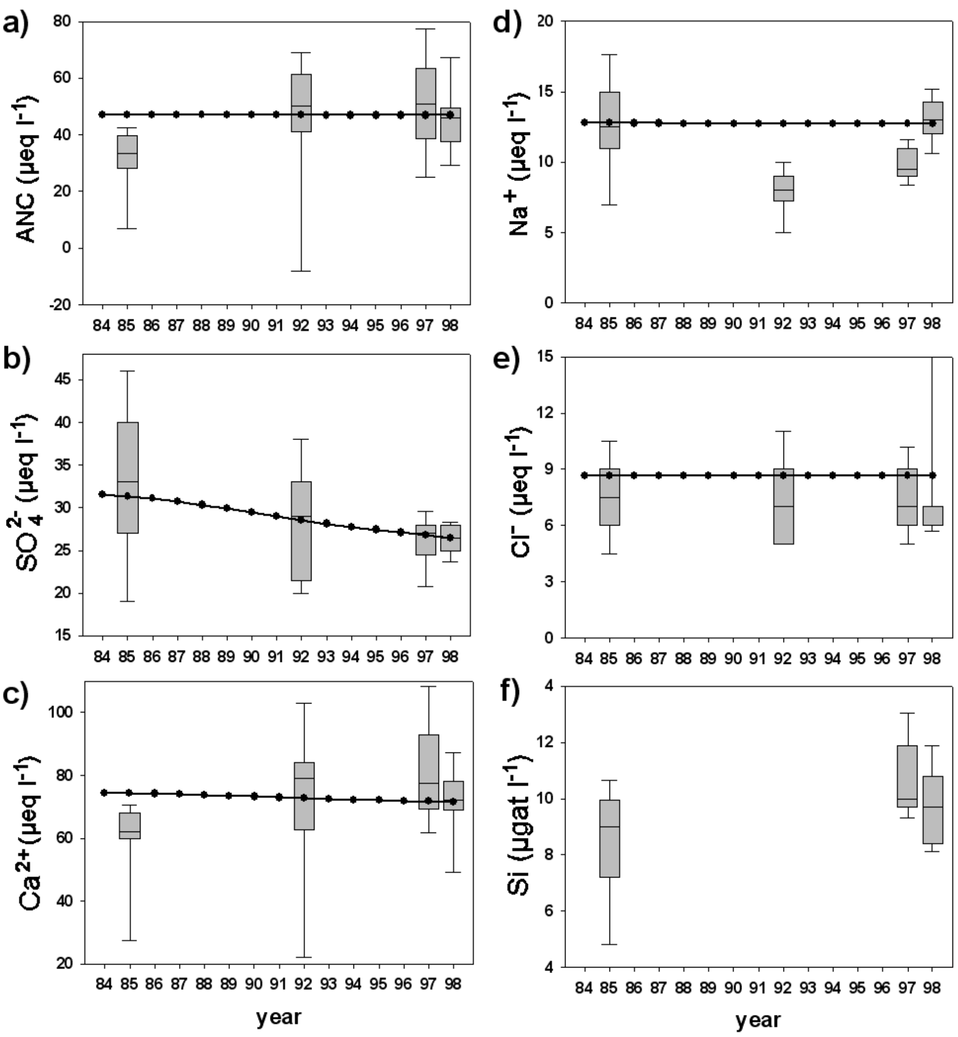

**Fig. 2**. Observed and modelled: **a**) ANC; **b**) $SO_4^{2-}$; **c**) $Ca^{2+}$; **d**) $Cl^-$; **e**) $Na^+$; and **f**) Si in lakewater during the period 1984-1998. Box-plots represent the measurements in 84-85, 91-92, 96-97 and 97-98. Bars indicate the 10th and 90th percentiles, boxes are the 25th and 75th percentiles, and the lines within the boxes are the median values. The dots crossed by a trend line are the MAGIC simulations, representing the yearly average concentration.

**Tab. 5:** Precipitation amount for of 1984, 87, and 97 (from summer to summer) and a four-month period in 1990 (late summer - early autumn). Figures within brackets correspond to equivalent four-month periods for comparison with 1990 data. Average precipitation concentration and deposition of $Ca^{2+}$, $Na^+$ and $Cl^-$ during the three sampled periods from 1987 to 1998 in Lake Redó area.

| | precipitation | $Ca^{2+}$ | | $Na^+$ | | $Cl^-$ | |
|---|---|---|---|---|---|---|---|
| | mm | µeq $l^{-1}$ | meq $m^{-2}$ | µeq $l^{-1}$ | meq $m^{-2}$ | µeq $l^{-1}$ | meq $m^{-2}$ |
| Aug 84 - Aug 85 (Aug 84 - Nov 85) | 1531 (766) | | | | | | |
| Aug 87 - Aug 88 (Aug 87 - Nov 87) | 1133 (350) | 65 (73) | 74 (25) | 18 (18) | 20 (6) | 13 (12) | 14 (4) |
| ----- (Aug 90 - Nov 90) | -- (349) | -- (52) | -- (18) | -- (21) | -- (7) | -- (13) | -- (4) |
| Jul 97-Jul 98 (Aug 97 - Nov 97) | 1414 (483) | 22 (20) | 32 (10) | 13 (5) | 18 (2) | 11 (9) | 16 (4) |

supply of cations to water over large time periods is the exchange capacity of catchment soils (Warfvinge *et al.* 1992). Soil cover in alpine environments, however, is often scarce and have small base cation pools making them sensitive to acid deposition. In addition, there are large areas of bare rock in which water flows without any contact with soils. In alpine environments such this, lake water chemistry may respond to rapid changes in chemical weathering caused by increasing air temperature over short time scales (of the order of the lake turnover time).

This third hypothesis is in good agreement with the results of Sommaruga-Wögrath *et al.* (1997) for lakes in the eastern Alps: they report a similar increase in $Ca^{2+}$

and Si in lake water correlated with increased air temperature during the same time period. A parallel increase of $SO_4^{2-}$ with a geologic origin was found in the Alps, which was not the case in the Pyrenees where trends in lake water $SO_4^{2-}$ declined in line with reductions in S emissions. Irrespective of this, the results from the Alps indicate that high mountain catchments respond with extreme sensitivity to climate warming through enhanced weathering rates, and this further supports our third explanation.

Dynamic models such as MAGIC are useful management tools to assess the efficacy of emission reduction policies and to define new emission reduction targets (Jenkins *et al*. 2002). Climate change is an important environmental driver that can potentially cause hystereris in the recovery from acidification in surface waters through different processes, and there is therefore a need to include these effects in the models. For instance, our results from scenario analysis in lake Redó show that changes in the inputs of dust due to future climate change could affect the acid-base status of the lakes: if the decreasing trend in base-cation deposition observed in the period 1987-98 continues, it may interfere with the recovery rates expected from reduced emissions of acidic pollutants; in contrast, global warming may enhance weathering rates and allow a more effective acid deposition neutralisation, as can be interpreted from our data. This indicates that the model could be refined by including this effect of climate change on weathering.

The results presented here also reinforce the importance of nitrogen deposition in high altitude catchments as an acidifying agent. The present MAGIC application is of relevance for policy because it shows that variable cation deposition and weathering rate are factors to be taken into account when designing reduced emission policies and predicting their effects in high mountain ecosystems. It is of relevance not only for the Pyrenees, but also for southern Europe in general: they are particularly relevant to other mountain ranges in this area that are influenced by Saharan dust deposition and where acidification has occurred in a higher degree than the Pyrenees (Jenkins *et al*. 2003).

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