Changes in atmospheric deposition and streamwater chemistry over 25 years in undisturbed catchments in a Mediterranean mountain environment

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Highlights:

Mediterranean baseflow streamwater chemistry shows similar temporal trends to those observed in temperate and alpine catchments in Europe and North America towards lower sulphate concentrations and higher alkalinity.

Increased silicate weathering in the current warmer climate is a likely factor underlying the alkalinity increase in streamwater.

Despite the high N deposition received the studied catchments are far from N saturation, although small increases in streamwater NO_3^- concentrations may indicate the onset of eutrophication.

Abstract

Surface water chemistry has changed in response to reduced atmospheric deposition of sulphur and acidity in many regions of Europe and North America. Most of these studies come from acidic or low-alkalinity surface waters under high acidic deposition. Mediterranean climates offer a different biogeochemical context, characterised by streamwaters of higher alkalinity and low acid inputs. In this paper, we use surveys of streamwater chemistry conducted in 1981-1984 and again in 2007 in the Montseny natural park (NE Spain) to test whether streamwaters of these well-buffered catchments respond to changes in atmospheric deposition, which has declined for S during the last decades in NE Spain while remaining about stable for nitrogen. The 23 sampled streams drained heathland, beech forests and evergreen oak forests in relatively undisturbed small catchments underlain by silicate bedrock. Bulk deposition of sulphate at Montseny decreased by 54% while nitrate bulk deposition increased (non-significantly) by 30% in this period. Total N deposition is estimated in the range 15-30 kg N ha y^{-1} for NE Spain. This is well above threshold values (e.g 10 kg N ha^{-1} y^{-1}) reported as starting nitrogen saturation symptoms in forest ecosystems in Europe. Baseflow sulphate concentrations decreased on average by 47 µeq L^{-1} or 29% of early 1980s concentrations. Baseflow mean nitrate concentrations increased significantly but only from 5.5 to 8.9 µeq L^{-1}. Thus, despite decades of high N deposition, these ecosystems appear to be still far from N saturation. Baseflow alkalinity and base cation concentrations increased substantially, probably a combined result of decreased S deposition, enhanced silicate weathering under current higher temperatures, reduced plant cation uptake as vegetation matures, and slightly drier conditions in the survey of 2007. Overall, these well-buffered catchments have shown sizable changes in baseflow chemistry in response to changed atmospheric deposition and other environmental changes.

1.Introduction

Emissions of oxidized nitrogen species from fossil fuel combustion and of reduced N from livestock raising and field fertilization have increased in Spain in the last two decades (EMEP, 2010). In Europe, N emissions also increased, peaking in the 1980s and subsequently leveling off or slightly decreasing in some European countries (Tarrasón and Schaug, 2000). To curb these and other pollutant emissions, such as SO_2, control programs have been set at national and international levels under the initiative of the Convention of Long-range Transboundary Air Pollution (Bull et al. 2001). These programs have succeeded in reducing S deposition, and this has been reflected in terrestrial and aquatic ecosystems (Kahl et al. 2004; Skjelkvale et al. 2005; Stoddard et al. 1999). However, the control on N emissions has not been as successful across Europe and many regions exhibit an absence of changes in soil and streamwater N concentrations (Skjelkvale et al. 2005; Wright et al. 2001) or even an increase (Rogora, 2007; Whitehead et al. 2002).

The sustained additions of N from the atmosphere, combined with a declining retention capacity as forests mature can lead to "nitrogen saturation", a condition that occurs when the availability of inorganic N is in excess of biological demand (Aber et al. 1989). The nitrogen saturation hypothesis postulates that under elevated atmospheric N deposition, forest ecosystems would undergo changes corresponding to varying degrees of N saturation (Skeffington and Wilson, 1988), eventually leading to NO_3^- losses to drainage waters (Aber et al. 1989; Stoddard et al. 2001). In addition, several studies in temperate and alpine catchments have shown that NO_3^- concentrations in surface waters have also been affected by climate change (Baron et al. 2009; Park et al. 2003; Rogora, 2007; Watmough et al. 2004) as increases in temperature and soil humidity affect biotic-mediated processes such as N mineralization and nitrification.

On the other hand, S deposition has clearly declined in Europe and North America leading to a recovery of lakes and streamwaters from acidification, although the rate of SO_4^{2-} decline in surface waters was smaller than in deposition for most sites in Europe and North America, indicating a lagged response of soils (Kahl et al. 2004; Skjelkvale et al. 2005).

Since the early 1970s, small catchments have been recognized as a useful tool for investigating how ecosystems respond to changes caused by natural and man-made

perturbations (Likens et al. 1977; Likens and Bormann, 1995) and much information on the biogeochemical responses to different impacts, affecting deposition, climate, and land use, has been assembled from temperate ecosystems in central and northern Europe and in North America. However, much less is known for European Mediterranean ecosystems.

In this study we tested whether changing deposition trends of S and N were reflected in the chemistry of small streams draining relatively undisturbed catchments in a span of ca. 25 years for a mountainous system in NE Spain. This was done by re-sampling in 2007 a network of streams that had been sampled in 1981 and 1984. The sampled streams drained heathland, beech forests and evergreen oak forests on silicate bedrocks in the Montseny mountains in NE Spain.

2. Study site

The Montseny mountains (longitude 2º 16' to 2º 33' E; latitude 41º 42' to 41º 52' N) are situated 40 km to the NNE from Barcelona and are formed by three massifs (Fig. 1): Turó de l'Home - Les Agudes (TH, 1700 m a.s.l), Matagalls (M, 1693 m) and La Calma elevated plateau (LCal, 1300 m). The climate is montane Mediterranean, with mean annual precipitation ranging between 800-1200 mm and mean annual air temperature ranging between 7 and 12 ºC depending on altitude and slope aspect. Since 1950 mean annual temperature has increased by 1.2-1.4ºC at Montseny (Peñuelas and Boada, 2003). Most rainfall occurs in spring and autumn, and summer drought is attenuated by summer storms. A snowpack may develop at higher altitudes but it is usually short-lived.

Most of Montseny is underlain by silicated bedrocks: Ordovicic phyllites in the west and central sectors and schists, granites and granodiorites in the north and east sectors. The relief is very steep. Soils have a high level of spatial heterogeneity because of this rugged topography. Most of the soils are colluvial and very stony. They are classified (Soil Survey Staff, 1992) as Entisols (Lithic Xerorthents) or Inceptisols (Typic, Lithic or Dystric Xerochrepts). The main pedogenetic process is the formation of a cambic horizon with moderate illuviation (Hereter, 1990). The soils are moderately acidic, acidity being buffered by silicate weathering and cation exchange. Calcium is the dominant exchangeable base cation (Hereter 1990).

Slopes are covered by closed-canopy forests of the evergreen holm oak (*Quercus ilex*) and, at higher altitudes, of European beech (*Fagus sylvatica*). Culminal areas of each massif are covered by heathlands, often dominated by *Calluna vulgaris*, and grasslands. The area has been protected as a natural park since 1977-1978.

Acidic atmospheric deposition is not a major issue at Montseny. In the period 1978 – 1988 0nly 26% of precipitation samples and 20% of the annual precipitation amount had a pH <4.5 (Rodà et al. 1993). More recent precipitation is even less acidic, and has, on average, positive alkalinity (Àvila and Rodà, 2002). Montseny lies, however, within the polluted air mass of the Barcelona conurbation, with high levels of nitrogen oxides and other pollutants (Pey et al. 2009). Though Montseny ecosystems above ca. 1000 m of altitude are often within clouds, throughfall studies in beech and fir forests at these elevations suggest that occult deposition has a minor contribution to inputs of water and pollutants (Rodà, 1983).

Streamwaters draining silicate-bedrock catchments at Montseny are characterised by medium to high alkalinity, with baseflow alkalinity ranging generally between 300 and 1000 µeq L^{-1}. This testifies to the substantial acid neutralising capacity of these ecosystems. However, first-order rivulets in the uppermost reaches of Montseny show baseflow alkalinities <200 µeq L^{-1} with a few of them under 100 µeq L^{-1}.

2.1 Basin characteristics

The sampled catchments covered the full range of altitudes within the massif above human settlements. Their mean altitude ranged between 805 and 1464 m a.s.l. (Table 1). As they were mostly first- and second-order streams draining the slopes of the main peaks in Montseny, their average slope was quite steep (21º, Table 1). Catchment area ranged from 6 to 600 ha, but the median was 23 ha. Dominant vegetation types in the sampled catchments were the same as in Montseny as a whole: evergreen holm oak forest, beech forest and heathland-grasslands. Catchment characteristics for each vegetation type are also given in Table 1.

3. Material and methods

3. 1 Atmospheric deposition

Atmospheric deposition was sampled at La Castanya Biological Station (LC) at the center of the Montseny massif (Fig. 1). Long-term biogeochemical studies have been undertaken at this site since 1978 (Rodà et al. 1999). Since 2002 this site has been instrumented as a background regional air quality site (EUSAAR network- European Supersites for Atmospheric Aerosol Research, http://www.eusaar.net), where total suspended particles (TSP), and size-fractioned particles (PM10, PM2.5 and PM1) are recorded and analyzed (Pérez et al. 2008; Pey et al. 2009). Studies at this site have documented a trend of declining S deposition (Àvila, 1996) and have evaluated the impact of African dust (Àvila et al. 1998, 2007). For precipitation, 4 bulk collector samplers of the Hubbard Brook type (Likens et al. 1977) were used from June 1983 to May 1993 and 2 collectors from June 1994 until today (with an interruption in 2001). Since 2002, a wet/dry deposition sampler (ESM Andersen instruments™, G78-1001) was added in parallel to bulk collectors. For particulate suspended matter, 24-h samples were collected once a week on quartz filters using high volume samplers (30 m^3/h) and DIGITEL™ cut-off inlets for PM10, PM2.5 and PM1. Nitrogen oxide and NO_2 were continuously sampled by chemiluminescence (MCV-984™) in a cabin deployed by the Department of Medi Ambient i Habitatge of the Generalitat de Catalunya at this site. Meteorological variables (precipitation, air temperature, relative humidity, global radiation, wind direction and speed) were measured with Campbell™ instruments in a 2-m meteorological tower.

Measuring dry deposition is less straightforward than wet deposition. Direct measurement of dry deposition is difficult since it depends on many factors, including meteorological conditions, characteristics of the pollutants being deposited (e.g. different gases and particles), and characteristics of the surface on which deposition occurs. The most accepted and common method for estimating dry deposition is the so-called "inference method." The inferential method is a combination of measurement and modeling that involves indirect estimation of dry deposition rates on the basis of routinely measured air concentrations and meteorological parameters. The method is based on an assumed steady-state relationship $F = V_d C$, where the dry deposition flux or rate (F) is a product of the dry deposition velocity (V_d) and the concentration (C) of an airborne pollutant.

Besides the inferential method, several workers have reported dry deposition measurements from collection approaches such as: 1) collection on dry-only collectors, 2) on surrogate surfaces, and 3) throughfall, a process that scavenges dry deposition from the forest canopies and represents the total input to the soil (Dise and Wright, 1995; MacDonald et al. 2002). While throughfall is a good estimator of dry deposition for ions with little interaction with the canopy (Cl^-, SO_4^{2-}, Na^+ and Ca^{2+}; Parker, 1983), for N this is not so, because N is retained by leaves and the biota in the canopy (Parker, 1983). Deposition on collector surfaces also may underestimate deposition for gaseous compounds, many of them nitrogenated such as NO_y (sum of HNO_{3g}, NO, NO_2), NH_3 and for submicron particles $(NH_4)_2SO_4$, NH_4HSO_4, and particulate NO_3^- (p-NO_3^-). For gases and fine aerosols, micrometeorological and inferential methods are recommended (Fowler et al. 2009).

For a broad picture of the range of dry N deposition in NE Spain, we have compiled several studies in this region from the literature, mostly based on throughfall and branch washing and the inferential method. For the latter we have combined information from: (1) deposition on the dry bucket of the wet/dry collector at LC, which collects coarse aerosols but underestimates NO_y, NH_3 and fine aerosol deposition; (2) p-NO_3^- and p-NH_4^+ concentration in PM10 filters at LC; (3) NO and NO_2 concentrations measured at LC; and (4) NH_3, HNO_3 and NO_x reported from EMEP stations in E-NE Spain (Cap de Creus, Els Torms, Zarra and Víznar; Fig. 2). Deposition velocities for p-NO_3^- and p-NH_4^+, NH_3, HNO_3, NO and NO_2 were taken from published values for forests ecosystems (Holland et al. 2005; Kalina et al. 2002; Krupa, 2003; Muller et al. 1993).

3.2 Streamwater chemistry

Streamwater samples were collected in three surveys in the early 1980s: 7 June 1981 (hereafter named S1), 21 December 1981 (S2) and 1 May 1984 (S4) and a more recent one in 21-26 February 2007 (S5). A further survey on 21 January 1982 (S3), undertaken after 356 mm of precipitation in the preceding 5 days was not included in this exercise to avoid the effects of highflows on streamwater chemistry.

We sampled a number of running-water streams and rivulets all over Montseny plus, for comparison, five springs and a natural seep. Sampling points were first selected on the basis of accessibility: e.g. most streams were sampled just above where they crossed main routes surrounding and crossing the Montseny mountains. Because we wanted to avoid the confounding effect of within-catchment pollution sources, aerial photographs and land use maps were screened for houses, farms, cultivated fields and major roads and all catchments harbouring any of these sources were excluded from the analyses reported here. All catchments fulfilling the above conditions, and that were sampled at least once in 1981-1984 and again in 2007, were used to assess changes in streamwater chemistry (n = 23 catchments; Fig. 1). The sampled catchments were not completely undisturbed: regulations of the natural park allow for continued use of natural resources and the main perturbations affecting the sampled areas were small-scale selection thinning in the forested catchments and burning and livestock grazing in the heathland-grassland catchments. There were not major disturbances prior to sampling. Both forest harvest and heathland burning were more prominent in the early 1980s than later on.

Two holm oak catchments in La Castanya valley have routinely been sampled for a long-term period and are used here for corroborating the multi-catchment survey results. TM9 is a 6-ha catchment entirely covered by a dense holm-oak forest; it faces N and has very steep slopes (33.5º). TM0 is a 200-ha catchment with holm oak forest covering 60% of its surface (in the lower slopes) and beech (5%) and heathlands (35%) occupying the higher reaches (from 950 to 1340 m). The catchment faces NE and has a mean slope of 15.7º. Both catchments are over phyllites. For a better comparison with the hydrological conditions of the surveys, this long-term data base was filtered so that only baseflow samples are considered here. The sampling periods were from January 1984 to December 1997 for TM9 and from January 1990 to December 1999 for TM0.

Streamwater samples were collected in high-density polyethylene 250-ml bottles that had been previously rinsed with distilled deionized water and triple-rinsed with sample water. After collection, they were stored in ice boxes until reaching the laboratory, where pH, alkalinity and conductivity were measured within 48 h in unfiltered aliquots. Alkalinity was measured by a conductimetric method (Golterman et al. 1978); the same method was used throughout the study period. Samples were filtered with 0.45 μm pore size Millipore filters and stored (at -20ºC) for further analysis. Major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) were

264 determined by atomic absorption spectrometry during the early surveys and by ion
265 chromatography equipped with CG12A - CS12A separator column and CSRS-ULTRAII
266 autosupressor for cations and NH_4^+ for the 2007 survey. In the early surveys (S1 and S2),
267 NO_3^- was determined with continuous flow injection analysis (Technicon^{TM}) and Cl^- with a
268 colorimetric method (Method 325.2; EPA, 1979) using a colour reactive (50% mercuric
269 thiocyanate +50% $FeNH_4(SO_4)_2$) and reading the colour at 480 nm. Since January 1984,
270 NO_3^-, SO_4^{2-} and Cl^- were analysed by ion chromatography equipped with anionic columns
271 (AS4A-SC) and anion self regenerating suppressor ASRS-ULTRA in the 1984 and 2007
272 surveys. Since the early analytical runs, great care has been taken to follow quality
273 assurance protocols for water analyses. Routine laboratory checks included the use of
274 synthetic samples of known concentrations to check for precision and accuracy, including
275 external references (National Bureau of Standards, reference materials 2694-I or 2694-II).
276 Differences were < 10%, except for Ca (<15%). For the surveys in which all major cations
277 and anions were analyzed (S4 and S5) data quality was also checked by a cation-anion
278 balance (based on concentrations in µeq L^{-1}) and by comparing the measured electric
279 conductivity with conductivity calculated from the concentration of all measured ions and
280 their specific conductivity. The results of these checks were (arithmetic means ± SE): 0.97
281 (± 0.006) and 1.02 (± 0.018) for the ratio sum cation/sum anion, respectively for S4 and S5,
282 and 1.06 (± 0.007) and 0.96 (± 0.027) for the ratio calculated conductivity/measured
283 conductivity, indicating good analytical quality.
284
285 Streamwater chemistry varies depending on streamflow, which was not measured in these
286 surveys. Intensive sampling of Montseny streams showed that chemical variables related to
287 silicate weathering (alkalinity, pH, Na^+, Ca^{2+} and Mg^{2+}) decreased with stormflow (Àvila et
288 al. 1992), whereas Cl^-, SO_4^{2-}, NO_3^- and K^+ tended to increase albeit with different patterns.
289 Nitrate and K presented peaks before or just at peakflow, decreasing sharply afterwards,
290 while SO_4^{2-} and Cl^- tended to have high concentrations during recession (Àvila et al. 1992).
291 The response to flow was principally linked to rainfall intensity and antecedent soil
292 moisture conditions (Àvila et al. 1992; Piñol et al. 1992a). The surveys here analyzed were
293 undertaken in winter and spring in baseflow conditions typical of the humid season at
294 Montseny. Precipitation in the previous month varied between 18 and 56 mm in the
295 different surveys, and the number of days without rain varied between 3 and 23 (Table 2).
296 The hydrological conditions during the surveys can be described with the runoff from a
297 gauging point at La Llavina, a station managed by the Agència Catalana de l'Aigua de la

298 Generalitat de Catalunya. This gauging point is only 2 km downstream of the sampled
299 catchments in La Castanya Valley (LL, Fig. 1). La Llavina catchment is underlain by the
300 predominant lithology in Montseny (phyllites and schists) and is covered by 52% holm oak
301 forest, 22% beech forest and 26% heathland and grassland. This watershed has been shown
302 to represent the hydrology of the physiographic region of the southern slopes of Montseny
303 (Piñol et al. 1992b). During the sampling surveys, La Llavina specific runoff varied only
304 between 1 and 14 L sec^{-1} km^{-2} (Table 2), i.e. around the median of daily specific runoff for
305 the period 1980-2008 that was 6.4 L sec^{-1} km^{-2}. A further test for the homogeneity of
306 hydrological conditions was undertaken by using Cl^- as a watershed-level tracer (Hedin et
307 al. 1995). Because silicate bedrocks do not produce Cl^- by weathering nor does it
308 participate in a major way in biological interactions, the ratio between Cl^- in precipitation
309 to Cl^- in streamwater is determined by evapotranspiration. Therefore, for similar
310 hydrological conditions, a similar ratio Cl rain/Cl streamwater (Cl_r /Cl_s) is expected. We
311 calculated this ratio using the Cl^- VWM concentration in precipitation at LC for the year of
312 the survey as Cl_r and the Cl^- concentration at the TM9 catchment in each survey as Cl_s.
313 TM9 is an intensively studied catchment in La Castanya Valley which was sampled in all
314 the surveys. The Cl_r /Cl_s ratios ranged between 0.22 and 0.28 (Table 2) evidencing similar
315 hydrological conditions between surveys. Therefore, based on these indicators, we interpret
316 differences between surveys as stemming mostly from causes other than solute variation
317 due to changes in hydrological conditions.
318
319 3.3 Statistical analysis
320
321 The comparison between earlier and recent streamwater chemistry was done with the
322 paired Wilcoxon test, and significance is given at $P<0.05$. For all analytes except alkalinity
323 and SO_4^{2-}, the earlier data were computed as the average of S1, S2, and S4 and compared
324 with S5. Alkalinity, pH and SO_4^{2-} were only analyzed in S4, so the comparison was
325 between S4 and S5.
326
327
328
329
330 4. Results and discussion

331

332 4.1 N and S atmospheric deposition in NE Spain

333

334 From 1983 to 2009, sulphate concentrations and deposition at La Castanya decreased
335 markedly (Figs. 3-4). At this site, SO_4^{-2}-S deposition decreased by 54% over this period, at
336 a linear rate of 0.14 kg S ha^{-1} y^{-1} (Fig. 4). This reflects a general decrease throughout
337 Catalonia as revealed by four stations of the Catalan precipitation monitoring network
338 where wet S deposition decreased on average by 26% in a shorter period (1996-2007).
339 Similar decreasing trends have been found elsewhere in Europe and North America and are
340 a result of the success of abatement measures implemented in these regions (Butler et al.
341 2001; Eimers et al. 2004). On the contrary, an increase in NO_3^- concentrations in bulk
342 precipitation has been recorded at La Castanya (Fig. 3) as well as in the Catalan monitoring
343 network (Àvila et al. 2010). These increasing NO_3^- trends have been related to the general
344 increase of Spanish NO_x emissions, though site-specific changes such as local increases in
345 population and industrial activity have also a role at certain sites (Àvila et al. 2010). By
346 contrast, NH_4^+ concentrations showed significant decreases at three of the four stations of
347 the Catalan monitoring network related to a 20-65% decrease in local farming activity
348 (Àvila et al. 2010). By contrast, at La Castanya neither concentrations nor deposition of
349 NH_4^+ showed a significant temporal trend (Figs. 3-4). Nitrogen wet deposition fluxes in the
350 Catalan network did not show significant trends partly due to the opposite variation of
351 NO_3-N and NH_4-N and partly because of a decrease (non-significant) of the amount of
352 precipitation in recent years.

353

354 For a broader view of N deposition in eastern Spain, a compilation of N bulk and wet
355 deposition values for rural/mountain sites covering a north-south transect from the
356 Pyrenees to Sierra Nevada, Andalucía (Fig. 2) along eastern Spain is given in Table 3. For
357 Catalonia, deposition values ranged between 3.5 kg N $ha^{-1}y^{-1}$ at Prades, Tarragona (though
358 this estimate is from the period 1981-1994 and it might have increased in recent years), to
359 7.7 kg N $ha^{-1}y^{-1}$ for the Pyrenees. The average wet and/or bulk deposition calculated for
360 Catalonia based on these data was 5.6 kg N $ha^{-1}y^{-1}$. For Valencia, the average was 4.2 kg N
361 $ha^{-1}y^{-1}$ with a range between 2.0 and 5.9 kg N $ha^{-1}y^{-1}$, from measurements in 1999 (Table
362 3).

363

The effect of atmospheric deposition on terrestrial ecosystems depends not only on wet fluxes but on total deposition. Therefore, dry deposition must also be taken into account. Little data on dry deposition N fluxes exist for eastern Spain, whereas in Mediterranean-type ecosystems in California N dry deposition can be especially significant (Bytnerowicz and Fenn, 1996; Fenn et al. 2003). In Tables 4 and 5, N dry deposition estimates are given based on different techniques. At the Montseny sites of LC and Riera St. Pere (which is in the massif south-eastern slopes, at a distance of 7 km from La Castanya), dry deposition was estimated by branch washing (Rodà et al. 2002; Rodrigo and Àvila, 2002). These measurements indicated that N dry deposition was the major deposition flux, accounting for 62-67% of total N deposition. A similar result (dry deposition amounting to 71% of total N deposition) was obtained at Vallcebre, north-central Catalonia, by measuring Scots pine (*Pinus sylvestris*) throughfall (Table 4). However, this result has to be taken with caution given that this site is occasionally affected by the plume of a close coal-fired power plant (Puig et al. 2008). Moreover, throughfall may not be a good indicator of dry deposition as canopy uptake is important in Mediterranean forests: e.g. *Quercus ilex* forests in Montseny and Prades mountains showed negative or near zero net throughfall values (Table 4). In Valencia, Sanz et al. (2002) estimated dry deposition for Aleppo pine (*Pinus halepensis*) forests with a leaf-washing technique following Bytnerowicz et al. (1987). The percent N dry deposition thus obtained ranged between 30-64% of total deposition except for the remote reference site of Burbàguena (Table 4).

Based on the above measurements, it can be deduced that dry deposition makes an important contribution to total N deposition in rural sites in eastern Spain. This is important to evaluate the total N deposition affecting the Montseny mountains. Using the dry/wet ratios in Catalonia for the calculation of total deposition, dry deposition would represent 10-24 kg N $ha^{-1}y^{-1}$. With an average wet deposition flux of about 5.5 kg N $ha^{-1}y^{-1}$, this would produce a total N deposition ranging between 15 and 30 kg N $ha^{-1}y^{-1}$. This is an important chronic load that may lead to measurable changes in ecosystems in NE Spain. This is assessed below for streams in the Montseny massif.

4.3 Comparison of streamwater chemistry between surveys

Streamwater chemistry of the 23 sampled streams (Table 6) is broadly representative of undisturbed small catchments on silicate bedrock in the Montseny mountains: streamwaters

are circumneutral (mean pH 7.0), with rather high alkalinity for mountain catchments on carbonate-free rocks (range 76-1000 μeq L^{-1}), and low NO_3^- .

Between the early 1980s and 2007, baseflow SO_4^{2-} concentrations decreased on average by 48 μeq L^{-1} or 29% of initial concentrations (Table 6). Sulphate decreased in 13 out of 14 catchments where it was analyzed, a highly significant result according to the Wilcoxon paired test (*P*=0.001). The only stream were sulphate did not decrease was a heathland catchment were it remained stable (105 and 106 μeq L^{-1} in 1984 and 2007, respectively). Sulphate was the only ion that decreased significantly in streamwater during the study period (Table 6). From 1983 to 2007 volume-weighted mean sulphate concentrations in bulk deposition at LC decreased by 19.4 μeq L^{-1} as assessed by the linear regression of Fig. 3. Applying a concentration factor (i.e. the ratio of annual precipitation amount to annual streamflow) of 2.5-3 typical for Montseny catchments (Piñol et al. 1999), this would translate into a decrease of 49-58 μeq SO_4^{2-} L^{-1} in streamwater, close to the observed average. Of course, other inputs such as lower S dry deposition and in-catchment S processes may be involved in the observed declines in streamwater SO_4^{2-}. Long-term monitoring of two of the 23 sampled catchments (TM0 and TM9) also reveal that baseflow SO_4^{2-} concentrations decreased substantially during their respective monitoring periods. (Table 7). The annual rate of decrease for TM9 (2.1 μeq L^{-1} y^{-1}) closely matches the rate calculated by the decrease between multi-catchment surveys (1.9 μeq L^{-1} y^{-1}), although at TM0 sulphate decreased at a higher rate (3.3 μeq L^{-1} y^{-1}).

Contrary to SO_4^{2-}, nitrate increased in 17 out of the 23 catchments where it was analyzed, an statistically significant result (Wilcoxon paired text: *P* <0,05; Table 6), Nitrate mean concentrations in the sampled streams increased only from 5.5 to 8.9 μeq L^{-1} between the early 1980s and 2007, i.e. a large proportional increase but with NO_3^- concentrations in 2007 being still fairly low. It is interesting to note these low values despite at least several decades of large total atmospheric N inputs onto these ecosystems, as discussed in the previous section. The estimated total N deposition fluxes in NE Spain (15-30 kg N ha^{-1} y^{-1}) are above the threshold values (e.g. 10 kg N ha^{-1} y^{-1}) reported as starting nitrogen saturation symptoms in forest ecosystems in Europe. Thus, despite decades of rather high N deposition, these ecosystems appear to be still far from N saturation, though the significant NO_3^- increase in streamwater suggests the onset of a more “leaky” N cycle.

Baseflow NO_3^- concentrations in TM0 and TM9 did not show any change in the 1984 to 1999 period (Table 7). Input–output budgets calculated for these catchments indicated a very tight N cycle, with nearly all inorganic N entering the catchments in bulk deposition being apparently retained within the catchment (Àvila et al. 1999). Gaseous N losses were not measured but are probably low in these well-aerated soils with moderated amount of organic matter and in the steep channels of these streams where little organic-rich sediment accumulate. Inorganic N inputs in precipitation were similar to the N amounts annually stored in the net growth of aboveground biomass in the holm oak forests of Montseny (Escarré et al. 1999). Thus, atmospheric inputs can provide nutrients for these forests, which are generally in an aggrading phase after small-scale forest harvests and still show a capacity to retain N. This is corroborated by negative N net throughfall fluxes in holm oak forests at Montseny (Table 4). By contrast, heathland ecosystems consisting in vegetation formed by shrubs, grasses and forbs should have much lower nutrient requirements. However, input – ouput budgets at two heathland catchments at La Calma in 1984 showed a retention of 6.9 and 7.7 kg N $ha^{-1}y^{-1}$ for a bulk deposition flux of 7.9 kg N $ha^{-1}y^{-1}$ (Belillas, 1989), thus retaining 87-97% of N in bulk deposition. This retention capacity might have changed later on, since heathland burning has practically ceased since the early 1980s.

Several authors have found that climate change plays a role in streamwater NO_3^- concentrations, because plant uptake and N mineralization are both enhanced in a warmer climate (Baron et al. 2000, 2009; Goodale et al. 2003). Therefore, the rates and timing of biotic responses may lead to either N retention or leaching eventually translated in a seasonal variation. At Montseny there is not indication of a seasonal component in the two intensively studied catchments; baseflow NO_3^- concentrations were always very low and detectable concentrations only occurred during stormflows. In Montseny, soil winter temperatures are probably high enough to allow some soil biological activity to go on even in winter, thus resulting in high retention of incoming NO_3^- at all seasons.

Because of the streamwater decrease in SO_4^{2-} and increase in NO_3^-, the comparison between the early 1980s and 2007 stream chemistry indicate that these catchments are undergoing a shift towards a more prominent role of NO_3^- in the acid anion balance, reflecting the increased N/S ratio in atmospheric deposition.

Conductivity, alkalinity and Ca^{2+} concentrations in streamwater increased substantially between the early 1980s and 2007, the changes being statistically significant for the three variables (Wilcoxon paired test: $P<0.013$ in all cases). Thus, streamwaters were generally more mineralised in the 2007 survey than in the average of the three surveys in 1981-1984. These increases were higher at low altitudes (Fig. 5), with catchments at mean altitudes lower than 1000 m, covered by holm oak forests, showing increases of alkalinity of ca. 350 µeq L^{-1}, while the three highest altitude catchments, covered by beech forests, showing either no change or a slight decrease in alkalinity. In part the increase in mineralization of streamwaters between the early 1980s and 2007 may be apparent, resulting from drier antecedent hydrological conditions in the 2007 survey than in the 1984 survey (the only of the three 1980s surveys where alkalinity was measured), as shown by the lower specific runoff at La Llavina gauging station in February 2007 (Table 2). However, there is also strong evidence that not all the increase in alkalinity was due to varying hydrological conditions between surveys. First, a permanent spring in the La Castanya area, that was known from biweekly monitoring in the early 1980s to have a very constant chemistry, also increased its alkalinity from 588 µeq L^{-1} in 1984 to 639 µeq L^{-1} in 2007. Second, the long-term record of streamwater chemistry TM0 and TM9 also showed a sustained, multi-year increase in baseflow alkalinity (Fig. 6, Table 7). From the respective linear regressions of streamwater alkalinity on sampling date, alkalinity increased by 11.0 (SE 1.9) µeq L^{-1} y^{1} in TM9 during 1984-1997, and by 20.8 (SE 3.6) µeq L^{-1} y^{1} in TM0 during 1990-1999 (Table 7). Should these rates of increase hold for the whole period between the 1984 and 2007 surveys, streamwater alkalinity of these streams would have increased by 253-478 µeq L^{-1} in TM9 and TM0, respectively, i.e. the same order of magnitude of the observed increases that were 406 and 263 µeq L^{-1}, respectively. This substantiates that the marked increase in alkalinity found by comparing two specific sampling dates (the 1984 and 2007 surveys) is not merely a result of different antecedent hydrological conditions but is consistent with long-term increases observed in the area.

In the Montseny mountains, several environmental changes are taking place resulting in higher alkalinity in streamwaters. From the long-term record, it is deduced that most of this increase is accounted by an increase of base cations (43 and 72% respectively for TM9 and TM0) while the reduction of sulphate deposition would account for around 17 % of the alkalinity change. Silicate weathering may have been enhanced under current higher temperatures: at La Castanya (700 m asl), mean air temperature increased by 0.081 ºC per

year in the period January 1993 to December 2009 (unpublished results), and at the summit of Montseny mean air temperature increased by 0.065 ºC per year in the period January 1978 to December 1995 (data from the Meteorological Observatory of Turó de l'Home, 1700m asl; Fig. 1).

Overall, these well-buffered catchments have shown sizable changes in baseflow chemistry. These changes in ion concentrations between surveys did not appear to be caused by differences in streamflow, since Cl^- did not show significant differences between them (Table 6); rather, they suggest a strong response to changed atmospheric deposition and to climate warming during the last 25 years in the Montseny massif.

Conclusions

Montseny streamwaters sampled over a 25-year span showed a decrease in sulphate concentrations that paralleled the decline in S atmospheric deposition, indicating a direct and rapid response of these undisturbed catchments to atmospheric drivers. Because sulphate is an acid anion, its reduction favoured an increase in alkalinity. However, this alkalinisation was also fostered by a temperature-mediated increase of silicate weathering that produced an increase of base cations in streamwater. This increase in base cations and alkalinity was more pronounced at low altitude catchments covered with holm oak, suggesting differential effects of atmospheric deposition and climate change, and indicating the need for further studies to better understand the observed patterns.

Despite the high N deposition received, catchments in Montseny were far from N saturation, and most of the deposited N was retained within the systems, even in high elevation heathlands with poor vegetation development. However, small increases in streamwater NO_3^- concentrations indicated the onset of eutrophication.

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762 Table 1. Physical characteristics of sampled catchments at Montseny.
763 Lithology Or= Ordovicic phyllites; Mec = Metamorphic schists; Gr= Granite and
764 Granodiorite
765

All catchments (n=23)	Mean	Std. Dev	Median	Min	Max
Sampling elevation (m)	1029	191	1057	670	1235
Mean elevation (m)	1213	195	1255	805	1464
Maximum elevation (m)	1397	235	1360	900	1703
Catchment area (ha)	66	123	23	6.3	600
Average slope (º)	21.0	6.0	20.0	6.7	34
Forest cover (%)	60	39	75	0	100
Holm oak (n=7)					
Sampling elevation (m)	781	115	740	670	950
Average elevation (m)	959	109	965	805	1112
Maximum elevation (m)	1136	154	1170	900	1343
Area (ha)	54	68	24	6.4	200
Average slope (º)	21.9	6.2	20.0	15.5	33.5
Forest cover (%)	83.1	19.1	90	50	100
Lithology	100% basins Ordovicic phyllites				
Beech (n=9)					
Sampling elevation (m)	1164	54	1150	1057	1225
Average elevation (m)	1349	99	1298	1244	1464
Maximum elevation (m)	1533	158	1457	1350	1703
Area (ha)	96	194	17	6.3	600
Average slope (º)	21.9	5.3	21.6	15.0	33.2
Forest cover (%)	90	10	90.0	75	100
Lithology	67% basins Mec; 22% basins Gr; 11% basins Gr+Mec				
Heathland (n=7)					
Sampling elevation (m)	1103	106	1045	1000	1235
Average elevation (m)	1292	63	1288	1180	1362
Maximum elevation (m)	1481	174	1480	1270	1695
Area (ha)	41	37	32	10.1	114
Average slope (º)	19	7	20	6.7	26.0
Forest cover (%)	6.4	11.1	0.0	0.0	25.0
Lithology	43% basins Or; 57% basins Mec				

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Table 2. Hydrology indicators in the different surveys. The ratio of Cl^- in rain to Cl^- in stream (Cl_r /Cl_s) is a rough indicator of the amount of evapotranspiration, and has been calculated as the ratio between volume weighted mean Cl^- concentrations in bulk deposition in the year corresponding to the survey as the numerator (Cl_r) and Cl^- concentration at the TM9 stream for the date of the corresponding survey in the denominator (Cl_s).

	S1 6 June 1981	S2 21 Dec 1981	S4 1 May 1984	S5 22-26 Feb 2007
Rainfall previous month (mm)	56.0	26.0	17.8	31.8
Number previous days without rain	12	3	23	4
La Llavina Specific runoff ($L\ sec^{-1}\ km^{-2}$)	7.53	1.06	13.8	2.38
TM9 and TM0 Specific runoff ($L\ sec^{-1}\ km^{-2}$)	--	--	5.0	1.3
Cl_r / Cl_s	--	0.23	0.28	0.22

780 Table 3. Compilation of bulk or wet N deposition values (in kg N $ha^{-1}y^{-1}$) in localities
781 along north-eastern (Catalonia) and eastern (Valencia) Spain. Sites are displayed in
782 Figure 2. Wet (w) or bulk (b) method of sampling is indicated.
783
784

Map id.	Site	NH_4^+-N	NO_3-N	Sum N	Wet bulk	period	Ref.
		kg N $ha^{-1}y^{-1}$					
	Catalonia						
1	Aiguestortes (Pyrenees)	4.18	3.50	7.69	b	1997-2007	Camarero and Aniz 2010
2	Sort	2.41	3.25	5.66	w	1996-2007	Àvila et al. 2010
3	Begur	1.58	2.61	4.19	w	1996-2007	"
4	Palautordera	3.34	3.39	6.73	w	1995-2007	"
5	La Castanya	3.02	2.89	5.91	b	1983-2007	"
6	Garraf	1.63	3.33	4.96	b	2003-2004	Àvila (unpublished)
7	La Sènia	2.35	2.31	4.66	w	1996-2007[a]	Àvila et al. 2010
8	Vallcebre	3.60	3.00	6.60	b	2000-2001	Puig et al. 2008
9	Prades	1.80	1.70	3.50	b	1981-1994	Escarré et al. 1999
	Valencia						
10	Morella	2.93	1.81	4.74	w	1999	Sanz et al. 2002
11	Burbágena	2.94	1.16	4.10	w	"	"
12	Benicarló	3.54	2.36	5.90	w	"	"
13	Vallliviana	3.07	2.48	5.55	w	"	"
14	El Saler	2.14	2.47	4.61	w	"	"
15	La Peira	1.72	2.31	4.03	w	"	"
16	Gandía	1.46	1.49	2.95	w	"	"
17	Alcoi	1.35	0.69	2.04	w	"	"

785 [a] (no 2003-2004)
786

787 Table 4. Dry N deposition estimates (in kg ha^{-1} y^{-1}) along eastern Spain, with different
788 methods. See detailed calculations for the inferential method in Table 5.
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790

Site	NH_4^+-N	NO_3^--N	Sum N	Method	period	Ref.
La Castanya	4.12	5.04	9.16	Branch washing (*Quercus ilex*)	1996	Rodà et al. 2002
Riera St. Pere	8.08	6.48	14.6	"	"	"
Burbágena	0.31	0.48	0.79	Branch washing (*Pinus halepensis*)	1999	Sanz et al. 2002
Morella	0.53	3.01	3.54	"	"	"
Benicarló	0.32	2.89	3.21	"	"	"
Vallliviana	0.29	2.09	2.38	"	"	"
El Saler	0.26	1.97	2.23	"	"	"
La Peira	0.61	3.28	3.89	"	"	"
Gandía	0.40	4.81	5.21	"	"	"
Alcoi	0.33	1.49	1.82	"	"	"
La Castanya	-1.7	-0.65	-3.4	Net throughfall (*Quercus ilex*)	1995-1996	Bellot et al. 1999
Prades	0.6	0.5	1.1	"	1981-83 1991-92	"
Vallcebre	8.7	7.6	16.3	Net throughfall (*Pinus sylvestris*)	2000-2001 [b]	Puig et al. 2008
	Sum reduced N	Sum oxidized N	Sum N			
Cap Creus	9.32	4.03	13.3	Inferential (gas and aerosol)	1999-2008	EMEP
Els Torms	19.7	4.81	24.5	"	2000-2008	"
Zarra	11.8	4.10	15.9	"	1999-2008	"
Víznar	8.26	4.22	12.5	"	1995-2008	"

791
792

Table 5. N dry deposition (in kg ha^{-1} y^{-1}) calculated with the inferential method from gas and particle air concentrations in EMEP stations along the NE coast of Spain (Figure 2) and Vd from the literature: for NH_3 and HNO_3, 2.0 cm s^{-1}; for NO and NO_2, 0.1 cm s^{-1}, based on published values in forest ecosystems from Holland et al. (2005), Kalina et al. (2002), Krupa (2003) and Muller et al. (1993).

Map id.	Site	pNH_4^+-N	NH_3-N	pNO_3^--N	HNO_3-N	NO_x-N	Total N[a]	period
	EMEP stations							
A	Cap Creus	--	8.68	--	2.80	0.52	13.3	1999-2008
B	Els Torms	--	19.2	--	3.49	0.61	24.5	2000-2008
C	Zarra	--	11.3	--	2.99	0.40	15.9	1999-2008
D	Víznar	--	7.8	--	2.51	1.00	12.5	1995-2008
	Montseny							
5	La Castanya	0.73	--	0.62	--	--		2003-2004
5	La Castanya	0.18	--	0.79	--	0.52		2008-2010

[a] for the total N sum, missing pNH_4^+-N and pNO_3^--N are estimated with the average values obtained at La Castanya, e.g. 0.455 and 0.705 kg N ha^{-1} y^{-1} respectively.

Table 6. Mean (with standard deviation in parenthesis) streamwater chemistry in 23 catchments sampled in the early 1980s and in 2007. Number of streams (n) with available data differs depending on analyte. Highlighted are significant differences (P<0.05) from the Wilcoxon paired test. Conductivity in μS cm^{-1}. Alkalinity and ion concentrations in μeq L^{-1}.

	1981-1984	2007	n
Conductivity	55.9 (23.2)	84.3 (40.1)	23
pH	7.0 (0.4)	7.1 (0.6)	14
Alkalinity	308 (181)	472 (353)	15
Na^+	190 (65)	196 (97)	23
K^+	11.2 (7.6)	11.1 (7.9)	23
Ca^{2+}	228 (151)	306 (229)	22
Mg^{2+}	136 (78)	154 (99)	22
NO_3^-	5.5 (7.5)	8.9 (7.7)	23
SO_4^{2-}	162 (67)	115 (36)	14
Cl^-	99 (36)	90 (26)	20

Table 7. Least-squares linear regressions (y = a + bx) of streamwater baseflow concentrations against time (years) for the two long-term studied streams of TM9 and TM0; x = time in years since 1984; y = analyte in μeq L^{-1}; r = correlation coefficient, *P* = probability level. Periods of study: for TM9, January 1984 – December 1997; for TM0, January 1990 – December 1999.

	a	b	r	*P*
TM9				
Alkalinity	471	11.0	0.22	<0.00001
Base cations	805	4.67	0.103	0.0047
SO_4^{2-}	200	-2.10	-0.28	<0.00001
NO_3^-	0.52	-0.001	-0.052	0.14
TM0				
Alkalinity	377	20.8	0.27	<0.00001
Base cations	640	14.9	0.23	<0.00001
SO_4^{2-}	174	-3.34	-0.37	<0.00001
NO_3^-	1.67	-0.0003	-0.0003	0.99

Figure captions

Fig. 1. Map of the streamwater sampling localities (open dots) in the Montseny mountains. Indicated are the main peaks of Turó de l'Home (TH), Matagalls (M) and La Calma (LCal), the intensively studied site of La Castanya (LC) and the gauging station of La Llavina (LL).

Fig. 2. Map of the Iberian Peninsula showing the measurement stations of atmospheric deposition. Identification numbers as in Table 3. Montseny corresponds to number 5. EMEP stations are indicated by squares: A= Cap de Creus, B= Els Torms, C= Zarra and D= Víznar.

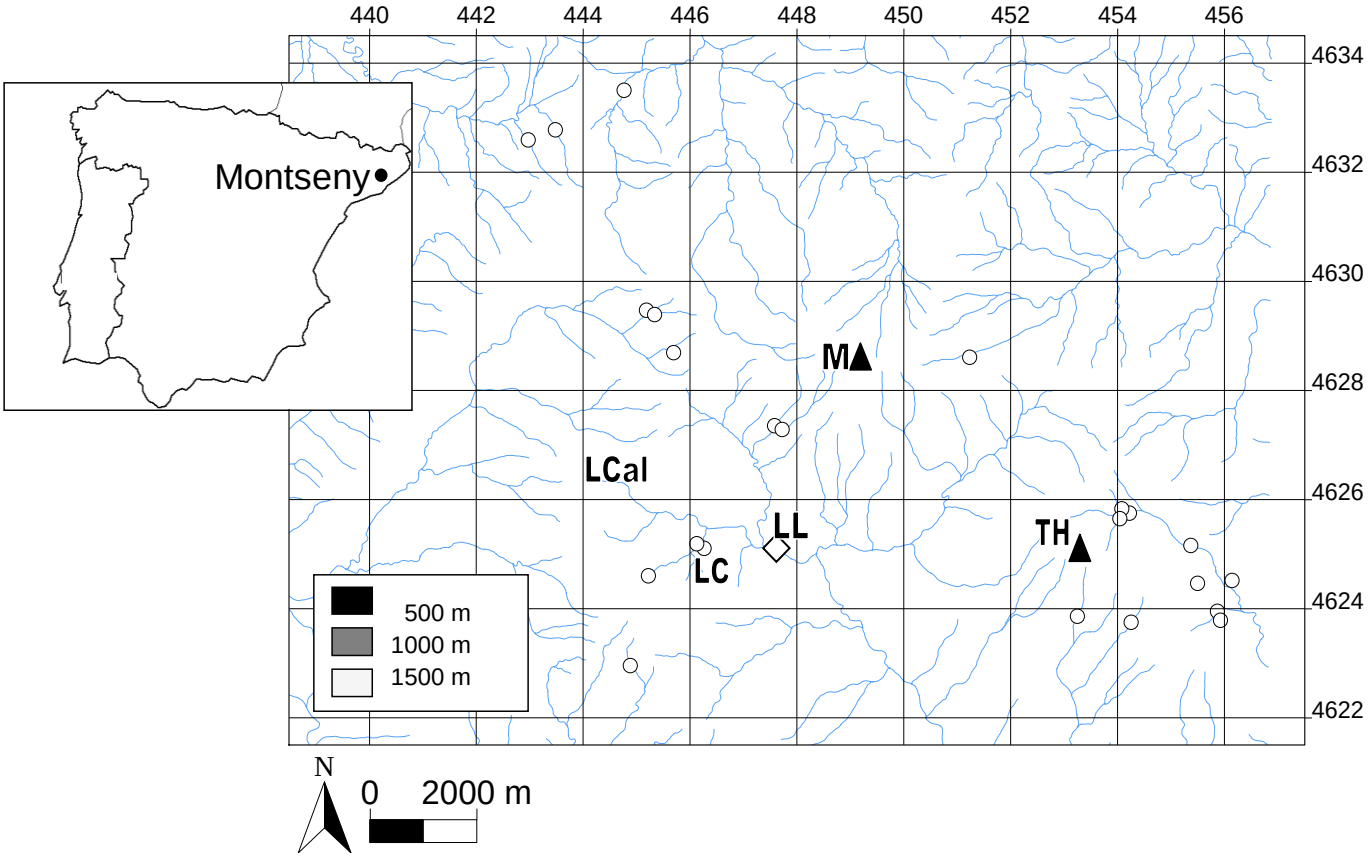
Fig. 3. Concentration time trends for SO_4^{2-}, NO_3^- and NH_4^+ in bulk deposition at La Castanya (Montseny). Least-squares linear regression equations against time (in years since 1982) are also indicated.

Fig. 4. Deposition time trends for SO_4^{2-}-S, NO_3^--N and NH_4^+-N in bulk deposition at La Castanya (Montseny). Least-squares linear regression equations against time (in years since 1982) are also indicated.

Fig. 5. Difference in streamwater concentrations between early and recent surveys at Montseny plotted against mean catchment altitude for: a) alkalinity (comparison between the 1984 and 2007 surveys); b) calcium; and c) nitrate. For calcium and nitrate the comparison is between the average of 3 early surveys (in 1981 and 1984) and the 2007 survey.

Fig. 6. Variation in baseflow alkalinity at two intensively studied streams in La Castanya: a) TM9 for the period January 1984 to December 1997, and b) TM0 for the period January 1990 to December 1999. Least-squares linear regression equations are indicated, with time in years since 1984.

Fig 1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4630
4628
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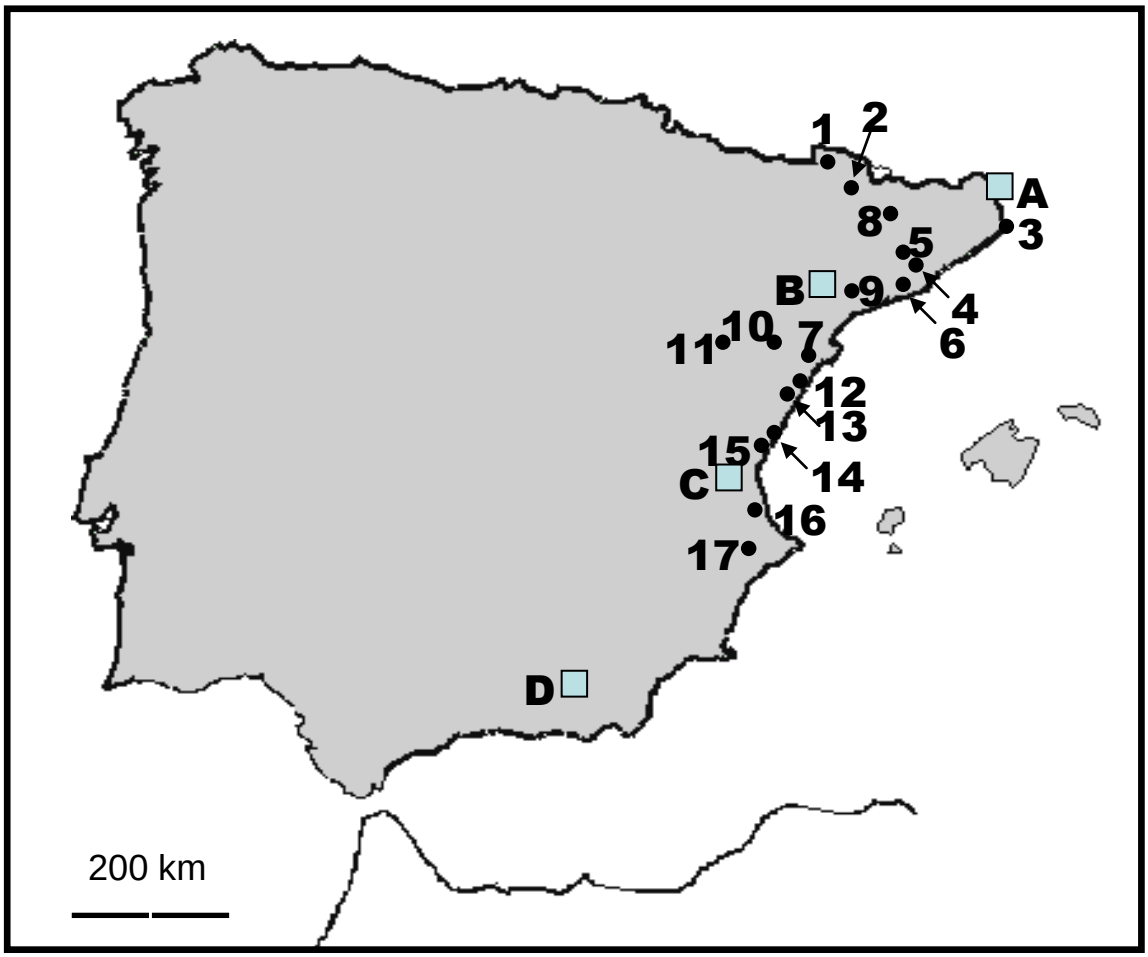
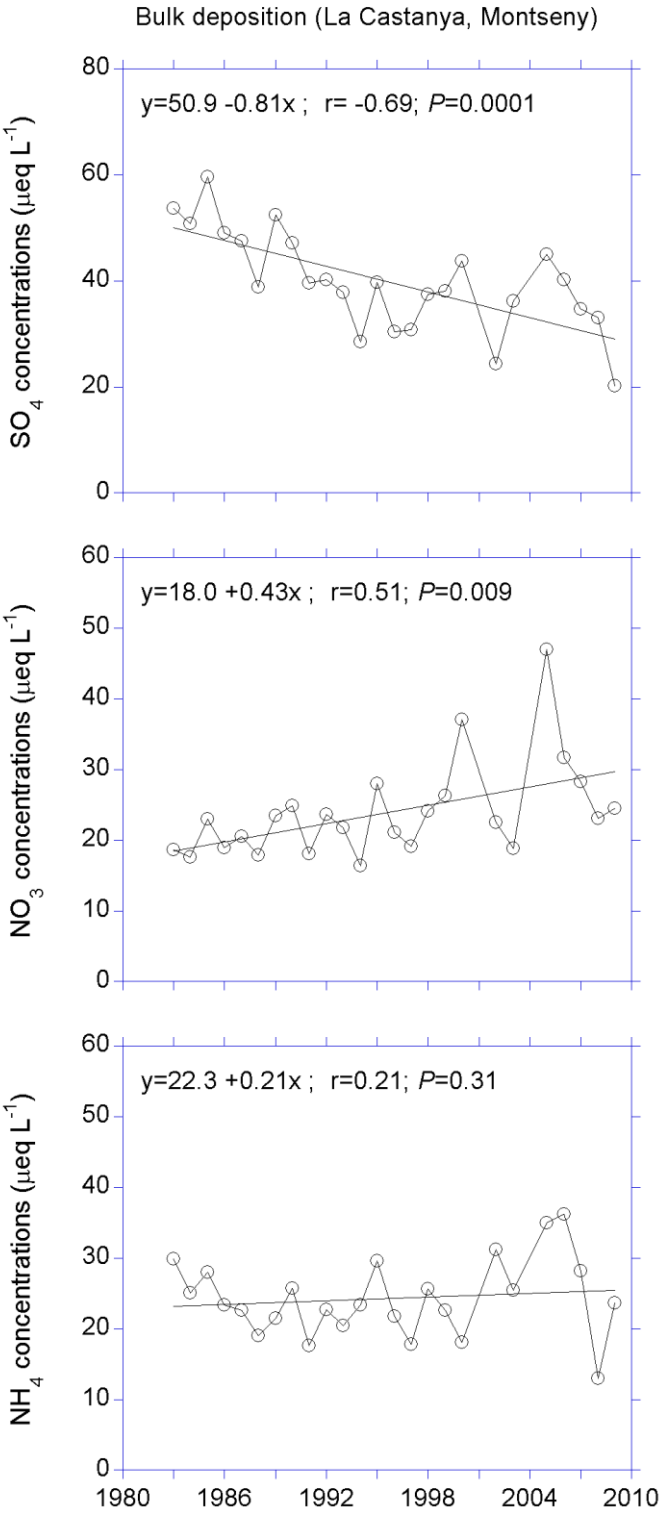
Montseny
M
LCal
LL
LC
TH
500 m
1000 m
1500 m
N
0
2000 m

Fig 2



900 Fig. 3



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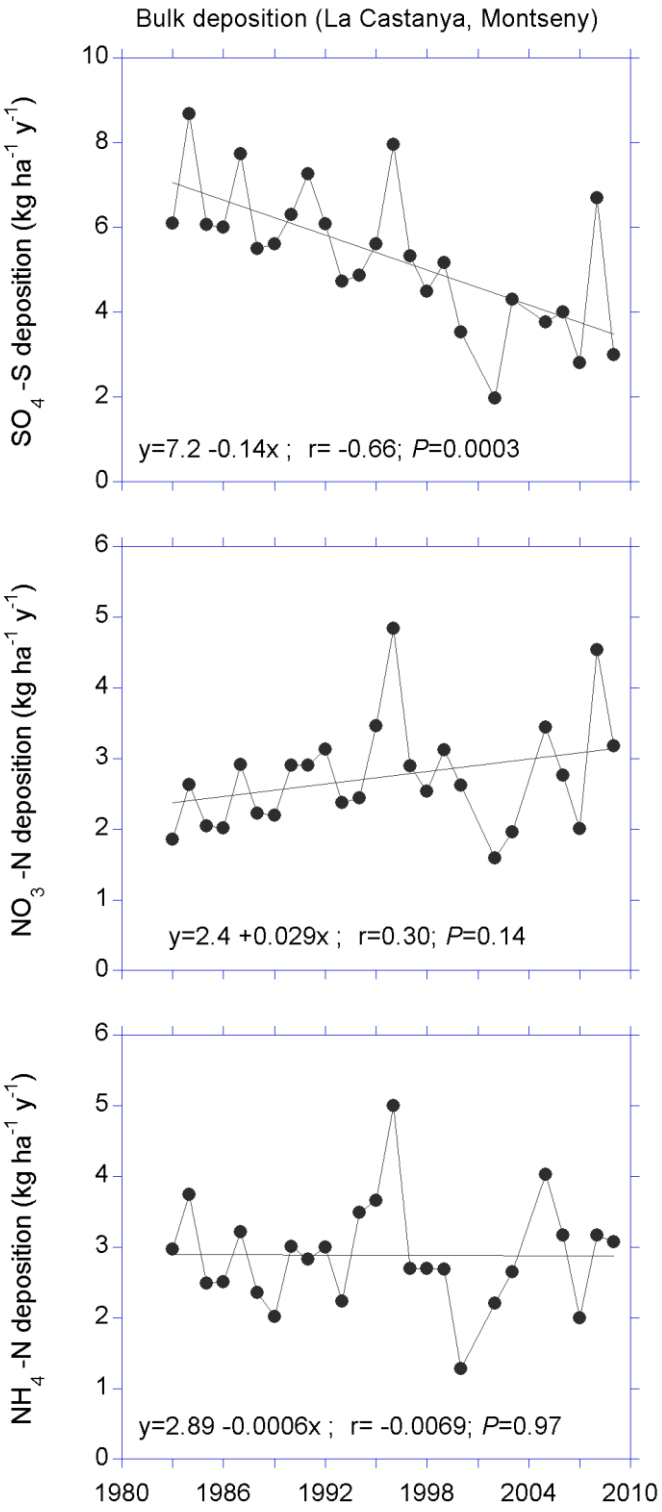
903 Fig 4



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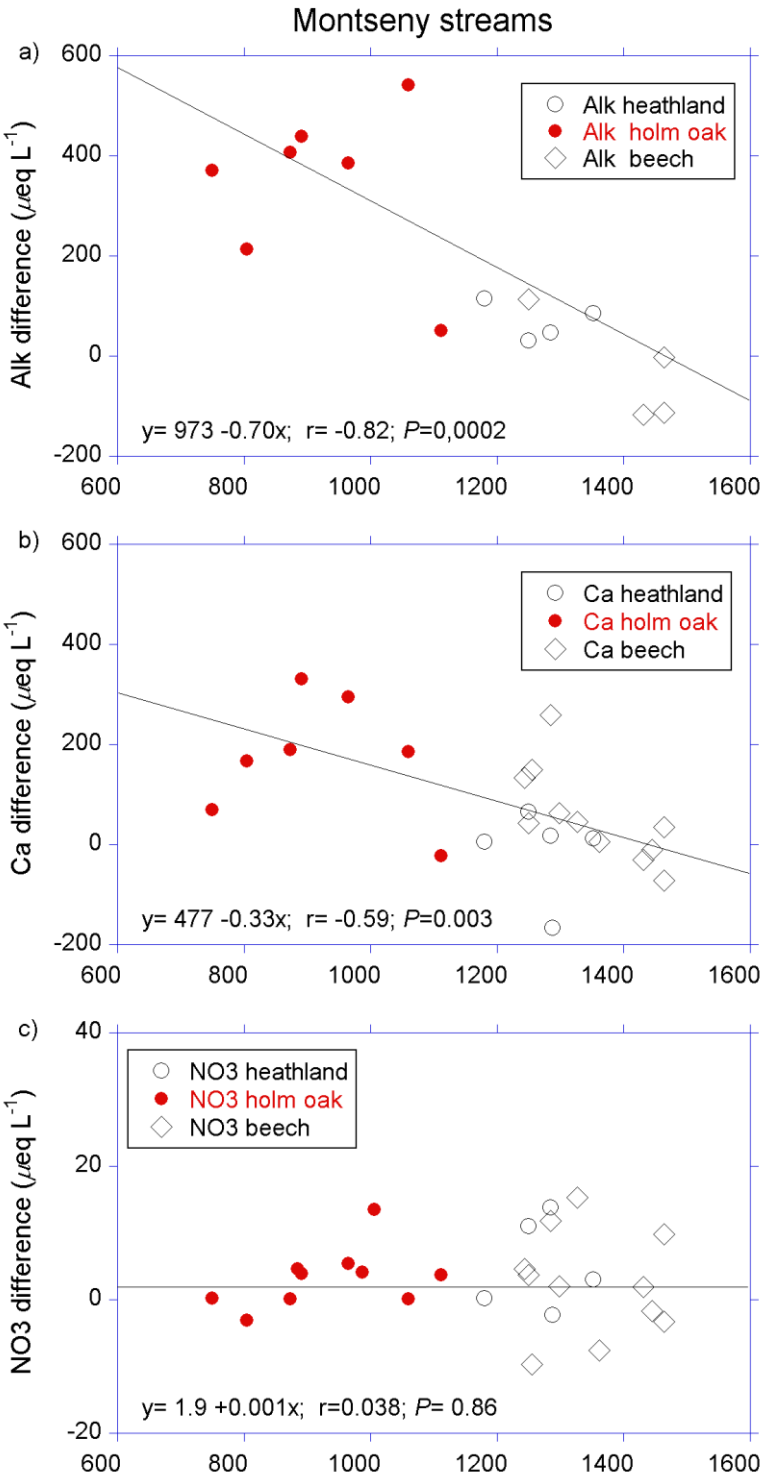
907 Fig 5



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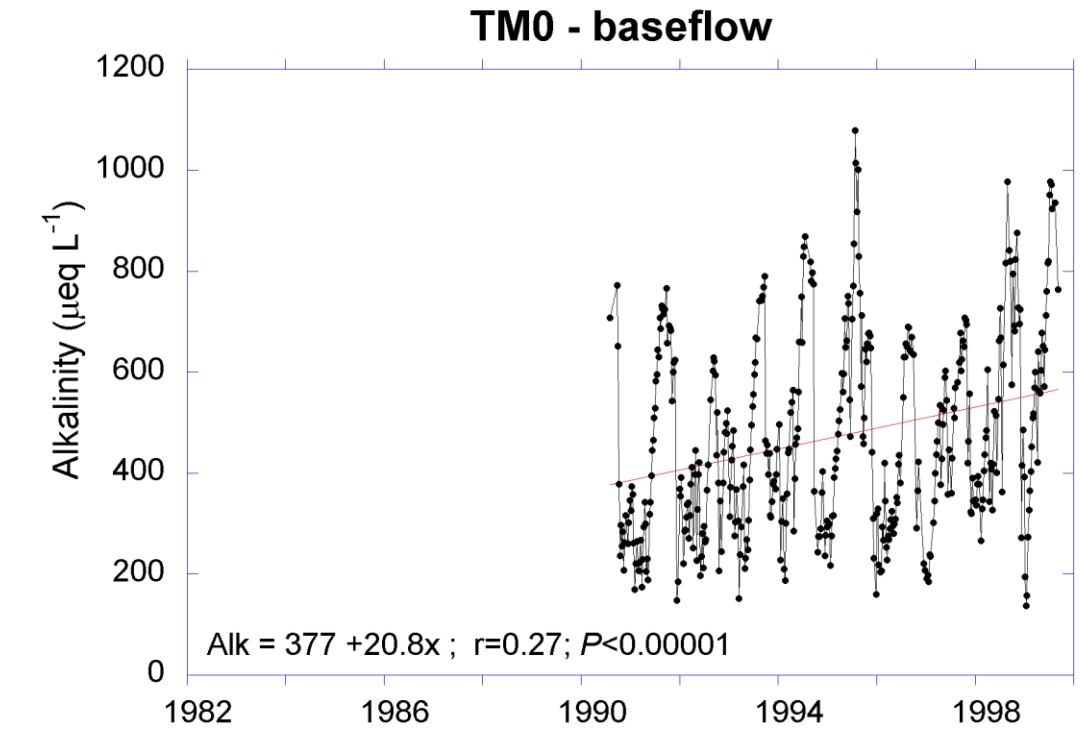
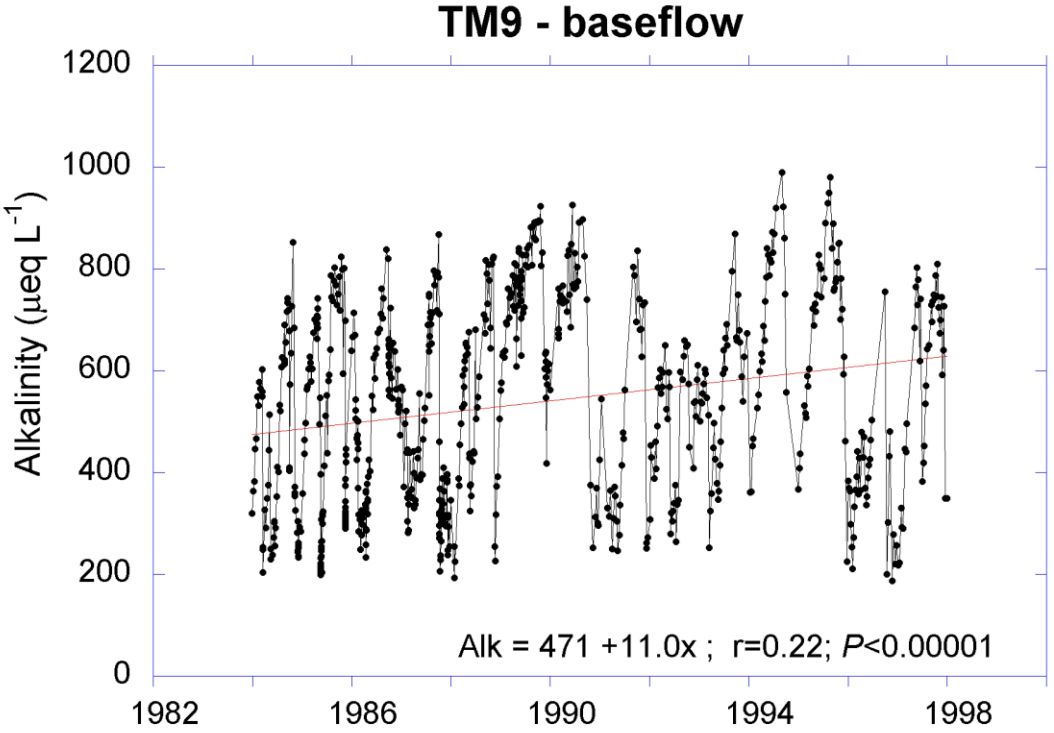
912 Fig 6


TM0 - baseflow
Alkalinity (µeq L-1)
1200
1000
800
600
400
200
0
1982
1986
1990
1994
1998
Alk = 377 +20.8x ; r=0.27; P<0.00001


TM9 - baseflow
Alkalinity (µeq L-1)
1200
1000
800
600
400
200
0
1982
1986
1990
1994
1998
Alk = 471 +11.0x ; r=0.22; P<0.00001

913