

1 **Long-term effects of changing atmospheric pollution on throughfall, bulk deposition**
2 **and streamwaters in a Mediterranean forest**

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25 **Abstract**

26 The abatement programs implanted in Europe to reduce SO₂, NO₂ and NH₃ emissions
27 are here evaluated by analysing the relationships between emissions in Spain and
28 neighbouring countries and atmospheric deposition in a Mediterranean forest in the
29 Montseny Mountains (NE Spain) for the last 3 decades. A canopy budget model was
30 applied to throughfall data measured during a period of high emissions (1995-1996) and
31 a period of lower emissions (2011-2013) to estimate the changes in dry deposition over
32 this time span.

33 Emissions of SO₂ in Spain strongly decreased (77%) and that was reflected in reductions
34 for nssSO₄²⁻ in precipitation (65% for concentrations and 62% for SO₄²⁻-S deposition). A
35 lower decline was found for dry deposition (29%).

36 Spanish NO₂ emissions increased from 1980 to 1991, remained constant until 2005, and
37 decreased thereafter, a pattern that was paralleled by NO₃⁻ concentrations in bulk
38 precipitation at Montseny. This pattern seems to be related to a higher share of
39 renewable energies in electricity generation in Spain in recent years. However, dry
40 deposition increased markedly between 1995 and 2012, from 1.3 to 6.7 kg ha⁻¹yr⁻¹.
41 Differences in meteorology between periods may have had a role, since the recent
42 period was drier thus probably favouring dry deposition.

43 Spanish NH₃ emissions increased by 13% between 1980 and 2012 in Spain but NH₄⁺
44 concentrations in precipitation and NH₄⁺-N deposition showed a decreasing trend (15%
45 reduction) at Montseny, probably linked to the reduction ammonium sulphate and
46 nitrate aerosols to be scavenged by rainfall. NH₄⁺-N dry deposition was similar between
47 the compared periods.

48 The N load at Montseny (15-17 kg ha⁻¹yr⁻¹) was within the critical load range proposed
49 for Mediterranean sclerophyllous forests (15-17.5 kg ha⁻¹yr⁻¹). The onset of N saturation
50 is suggested by the observed increasing N export in streamwaters.

51

52 **Key-words:** Emission reductions, Atmospheric deposition, Nitrogen, Sulfate, Throughfall,
53 Canopy.

54 **1. Introduction**

55 High atmospheric deposition of sulphur (S) and nitrogen (N) in the last century has lead
56 to the acidification and eutrophication of many terrestrial ecosystems in Europe and
57 North America, peaking in the 1970-1980 (Aber et al., 1998; EC, 2001; Reuss and
58 Johnson, 1986). To counteract these adverse effects, transboundary amendment
59 programs were launched by the Convention on Long-Range Transboundary Air Pollution
60 (CLRTAP) in the frame of the United Nations Economic Commission for Europe (UNECE,
61 2011). Upon the implementation of national emission limits, significant declines were
62 observed since the mid 1980s in SO₂ emissions and S in precipitation in Europe (Tørseth
63 et al., 2012). Nitrogen emissions were also significantly reduced in many European
64 countries, although higher variability was found among regions and the changes were
65 different for oxidized or reduced N (Fagerli and Aas, 2008; Konovalov et al., 2008;
66 Lövblad et al., 2004). A summary of the major results following the implementation of
67 pollution control measures can be found in Grennfelt and Hov (2005). Concerning Spain,
68 SO₂ emissions were readily cut, but the country still exceeded in 2012 the NO_x and NH₃
69 emissions ceilings for 2010, established at 847 and 353 Gg respectively (EC, 2001). The
70 link between emissions, air concentrations and deposition is complex because of the
71 interplay of the meteorological conditions, the chemical interaction between pollutants
72 in the atmosphere and the spatial scale of the region of influence. In this sense non-
73 linearities have been found between emission reductions and the decline in rainwater
74 concentration (Fowler et al., 2007).

75

76 Dry deposition of airborne pollutants makes also a significant contribution to the
77 atmospheric load of most ecosystems. However, long time records of changes in dry
78 deposition for the last decades are scarce. Changes in dry deposition have also been
79 found to change non-linearly with emissions (Fowler et al. 2005). This has been
80 attributed to the fact that for SO₂, the deposition velocity (V_d) is controlled by the
81 NH₃/SO₂ ratio, where SO₂ deposition increases as leaf pH raises in response to NH₃
82 deposition (Erisman et al., 1998; Fowler et al., 2001). Thus, dry deposition will not only
83 depend on SO₂ concentrations, but also on its relative abundance respect to NH₃. Also,
84 declining air SO₂ concentrations will affect the partitioning of gaseous NH₃ and

85 particulate NH_4^+ , which in turn will affect the spatial range affecting deposition, since
86 NH_3 will tend to be locally deposited while fine-sized NH_4^+ -sulfate aerosols have a longer
87 residence time in the atmosphere and will be mostly transported to longer distances
88 (van Jaarsveld et al., 2000).

89

90 Throughfall (TF), the water flux collected under the forest canopy, has been widely used
91 to provide an estimation of dry deposition (De Vries et al., 2003; Lindberg and Lovett,
92 1992). However, throughfall does not truly represent total deposition, since it also is
93 affected by chemical exchanges at the canopy level (Parker, 1983). When using
94 throughfall measurements to derive dry deposition fluxes, a distinction has to be made
95 between dry deposition and canopy exchange processes. These include the leaching of
96 elements from internal plant pools and/or the uptake by the canopy of gases or
97 dissolved solutes (Lovett and Lindberg, 1984; Schaefer and Reiners, 1990). To sort this
98 out, a canopy budget model has been widely used (Draaijers and Erisman, 1995;
99 Staelens et al., 2008) and will be here applied to estimate dry deposition from
100 throughfall measurements.

101 The Iberian Peninsula, in the south-western corner of the European continent, is
102 influenced by air masses from contrasting provenances. Five main air mass movements
103 have been established based on the frequency of back trajectories: 1) European or
104 continental, 2) from the Atlantic Ocean, 3) from North Africa, 4) from the
105 Mediterranean, 5) from shorter pathways, as recirculating air masses over the Iberian
106 Peninsula (Calvo et al., 2012; Escudero et al., 2007; Izquierdo et al., 2012). A cluster
107 classification of daily back-trajectories for the periods 1984-1993 and 1998-2009
108 indicated that the most frequent air flows at the Montseny mountains in NE Spain were
109 from the Atlantic Ocean (39 and 31% for the two study periods) and the Peninsular
110 recirculation (27-25%). Thus, the major air pollution influence at the north-east coast of
111 Spain may be from emissions from the Iberian Peninsula itself. However, during winter,
112 a good correlation was observed between air masses from the Mediterranean and NO_3^-
113 deposition (Izquierdo et al., 2014). Also, source receptor models indicated the influence
114 of emissions from eastern provenances on the rain chemical composition in NE Spain
115 (Izquierdo et al., 2012).

116

117 The aim of this work is to examine the relationships between S and N emissions in Spain
118 and neighbouring countries from the early 1980s to 2014 and rain concentrations and
119 deposition at a site in the NE of the Iberian Peninsula, in order to check whether the
120 abatement measures implemented by CLRTAP protocols are reflected in reduced
121 deposition. This has been undertaken by comparing the evolution of bulk deposition
122 trends at a rural forested site (La Castanya, Montseny) in NE Spain and the evolution of
123 emissions in the Iberian Peninsula, France, Italy and the totals for the European Union
124 (EU28) for this period. Previous studies have documented a SO_4^{2-} decrease in bulk
125 deposition in NE Spain (Avila, 1996; Avila and Rodà, 2002); here we expand these
126 studies for a longer time series and incorporate the examination of changes in dry
127 deposition. Changes in dry deposition along the last 3 decades cannot be traced in NE
128 Spain because of the lack of a continuous monitoring scheme for dry deposition.
129 However, throughfall measurements in two contrasting periods over this time span (in
130 1995-1996, a period of high emissions and in 2011-2013, a period of lower emissions)
131 can provide an insight on dry deposition changes, particularly for S.

132

133 Several studies have reported changes in surface stream water chemistry after
134 reduction of pollutant emissions in temperate forests in central and north Europe and
135 North America (Driscoll et al., 1998; Evans et al., 2007; Skjelkvåle et al., 2005). This
136 paper also tackles this issue by exploring the response at the ecosystem level of
137 emissions reductions, by studying changes in streamwater chemistry for a stream
138 draining an undisturbed forested catchment representing a typical Mediterranean
139 forest.

140

141 **2. Material and methods**

142 **2.1. Study site**

143 The study site was located in La Castanya valley (LC, 41°46'N, 2°21'E, 700 m.a.s.l), within
144 the Montseny mountains (Fig.1) about 40km NNE from Barcelona and 25km from the
145 Mediterranean coast. Dominant vegetation is a closed-canopy forest of holm-oak

146 (*Quercus ilex* L.). Forests at La Castanya valley were exploited in the past for charcoal
147 production, but these activities were abandoned about 60 years ago and the forest is
148 increasing in biomass (Rodà et al., 1999). The upper part of La Castanya valley comprises
149 a belt of beech forest at 1100-1200m, while heathlands and grasslands extend above this
150 altitude up to 1350m. Dominant lithology is metamorphic schist and phyllite. Soils are
151 shallow with an organic layer 0-5cm deep and an average total depth of 60 cm (Hereter
152 and Sánchez, 1999). Soils are classified as Entisols or Inceptisols (Soil Survey Staff 1992).

153 Climate is meso-Mediterranean sub-humid, with a clear seasonal cycle of higher
154 precipitation in spring and summer. Variability among years is very high (Fig. 2). At the
155 LC station, mean precipitation from 1983 to 2014 was 862mm y^{-1} (range from 518 to
156 1601 mm y^{-1} ; Fig. 2) and mean air temperature 9.5°C.

157 This site is considered as a rural background station that is topographically sheltered to
158 some extent from air pollution from the Barcelona metropolitan area. However, during
159 the warm half of the year diurnal sea-land breezes carry pollution from the coast and
160 lowland plains to the upper Montseny slopes, where LC lies, by midday (Pérez et al.,
161 2008). Besides, long-range pollutant transport also influences atmospheric deposition at
162 this site (Izquierdo et al., 2012).

163 Stream discharge was recorded in a stream named Torrent de la Mina (TM0) which is
164 gauged with a 120° V-notch weir. This catchment has a surface of 205 ha and comprises
165 two distinct zones: an upper plateau with grassland and heathlands (30% of the
166 catchment) and holm-oak forests covering the steep slopes that conform the rest of the
167 catchment (Fig 1).

168

169 **2.2. Field sampling**

170 *Open field measurements*

171 Weekly bulk deposition samples were obtained from August 1983 to August 2014
172 (interrupted from September 2000 to March 2002). Wet-only deposition (ESM
173 Andersen instruments) was sampled in parallel to bulk deposition during 2008-2013 but
174 because of the longer bulk deposition record, we will deal here with bulk deposition

175 data for the comparison of emissions and deposition trends. Bulk/wet deposition
176 collectors, a rain tipping bucket gauge and a meteorological station (Campbell with
177 CR1000 data logger) were located at a clearing in the forest close to the throughfall
178 plots (Open field sites, Fig. 1). The open field measurements were located at site LC1
179 since August 1983 to September 2000. Since March 2002, they were located at site LC2
180 (Fig. 1), about 850 m distant from the first site. Bulk collectors consisted on 19-cm-
181 diameter funnels connected by a looping tygon tube to a 10-L polyethylene bottle for
182 the period 1983-2010. In 2011, NILU-type (Norwegian Institute for Air Research) funnels
183 were used and a plastic membrane was fitted in the funnels neck which connected to a
184 2-L polyethylene bottle. Funnels were directly connected to the bottles, which were
185 kept in the dark to avoid the growth of microorganisms. Four (1983-1996) and two
186 (1997-2014) replicate collectors were used.

187 *Throughfall measurements*

188 The throughfall chemistry was sampled in two periods separated by a 15-year span: the
189 first one, in 1995-1996, took place during a period of still high emissions in Spain while
190 the second one, in 2011-2013, corresponded to a period of much lower emissions. To
191 characterize the throughfall chemistry in the first period we used throughfall data
192 measured in two plots in Montseny from June 1995 to June 1996 (Table 1). One plot was
193 located at La Castanya valley facing to the north (LC1, Fig 1). The second plot was at
194 Riera de Sant Pere (RP1) 8 km apart from La Castanya, in the Montseny slopes that face
195 to SW and had a similar aspect to that of the LC2 throughfall plot. It was considered that
196 the averaged throughfall composition of RP1 and LC1 better represented the canopy
197 changes on incident precipitation in the early period. Throughfall collectors in this
198 period consisted of a 10-cm funnel connected to a 2-L bottle, kept in the dark (Rodrigo
199 et al., 2003). Throughfall in the period March 2011-March 2013, was sampled in location
200 LC2, using 12 collectors of NILU-funnel type. Details on the forest structure of the 3
201 throughfall sampling sites are given in Table 1. Although differences in location will
202 introduce uncontrolled spatial variation in throughfall measurements, the plots had a
203 similar forest structure: they formed a continuous closed monospecific canopy of holm-
204 oak submitted to similar climate, although the difference in aspect may have some
205 effect. A review of the rainfall partitioning by vegetation in Mediterranean conditions

206 has shown that the forest structural parameters that mostly influence throughfall are
207 age, height, diameter at breast height (DBH) and basal area (Llorens and Domingo,
208 2007). Differences in some of these variables between the plots were small (Table 1)
209 and probably within the error of regressions provided by Llorens and Domingo (2007).
210 Further details on throughfall field sampling can be found in Rodrigo et al. (2003) and
211 Aguilleaume (2015).

212 For bulk deposition and throughfall, volume weighted mean (VWM) concentrations
213 were calculated based on weekly samples weighted by weekly precipitation volume. The
214 corresponding fluxes were obtained by multiplying annual VWMs by annual
215 precipitation/throughfall volume and are expressed as $\text{kg ha}^{-1} \text{y}^{-1}$, except for H^+ and
216 alkalinity, in $\text{eq ha}^{-1} \text{y}^{-1}$.

217 Non sea salt sulphate (nss SO_4^{2-}) concentrations in bulk deposition (BD) were calculated
218 as:

$$219 \text{ nss SO}_4^{2-}{}_{\text{BD}} = \text{SO}_4^{2-}{}_{\text{BD}} - (\text{Na}^+{}_{\text{BD}} * 0.12),$$

$$220 \text{ where } \text{SO}_4^{2-}{}_{\text{sea salt}} / \text{Na}^+{}_{\text{sea salt}} = 0.12 \text{ (Drever, 1982)}$$

221 *Streamwater measurements*

222 Streamwater was collected from a stream draining a 200 ha catchment named Torrent
223 de la Mina (TM0) within the La Castanya valley (Fig. 1). The recording period for
224 discharge and streamwater chemistry comprised an initial (1990 to 1999) and a recent
225 period (2010 to 2014). Water level was measured with an OTT™ water level recorder in
226 the initial period and with a pressure probe (Schlumberger Water Services) in the recent
227 one. Annual discharge ranged between 150 and 888 mm y^{-1} (Fig. 2).

228 Grab samples of stream water were collected with an approximate weekly schedule
229 from a sampling point upstream from the stilling pond. They were collected in high-
230 density polyethylene 250-mL bottles after a previous triple rinse with stream water.

231 We calculated annual VWM for bulk precipitation and stream waters, expressed in μeq
232 L^{-1} for hydrological water years defined from 1 September. For throughfall, a more

233 restricted data record obliged to consider different annual periods (June 1995 to June
234 1996 in the initial and March 2011 to March 2013 for the recent period).

235 For the stream waters, we first calculated annual fluxes (F , in $\text{kg ha}^{-1} \text{y}^{-1}$) by:

$$236 \quad F = \sum_{i=1}^N C(t_i) * Q[T_i] \quad (1)$$

237 Where $C(t_i)$ is the instantaneous concentration of the studied elements at time t_i (in mg
238 L^{-1}) and $Q[T_i]$ is the discharge (in L) for the period $T_i = (\tau_i - \tau_{i-1})$, with $\tau_{i-1} < t_i < \tau_i$, and N
239 is the number of samples taken during the whole year. To give the annual VWM
240 concentrations, fluxes were divided by the accumulated stream discharge for the year.

241 Several works have attempted to determine the best unbiased estimate of flow-
242 weighted solute concentrations and fluxes, since the appropriateness of the estimate
243 depends on the frequency of sampling related to the duration of stormflows
244 (Rekolainen et al., 1991; Stone et al., 2000; Swistock et al., 1997). Calculations based on
245 weekly sampling and the water flow corresponding to each one of the samples, the
246 procedure used here, have been recommended as a compromise between the effort of
247 sampling and the accuracy of the estimate. The accuracy of estimates with this
248 procedure has been found to lie within 10% of expected values (Rekolainen et al., 1991;
249 Stone et al., 2000; Swistock et al., 1997).

250

251 **2.3. Chemical analyses**

252 Samples were taken to the laboratory and were analyzed for pH, conductivity and
253 alkalinity within 24–48 h from sampling. Samples were filtered with $0.45\mu\text{m}$ size pore
254 acetate cellulose membrane filters and 60-mL aliquots were frozen until analysis.
255 Concentrations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , Cl^- , NO_3^- and SO_4^{2-} were measured by ion
256 chromatography (Dionex, Sunnyvale, USA). Data quality was checked with the inclusion of
257 synthetic samples of known ionic concentrations during analytical runs. The quality of
258 the analytical data was checked by a: 1) conductivity index (ratio of measured
259 conductivity to conductivity calculated from the concentration of all measured ions and
260 their specific conductivities), 2) an ionic index (ratio of the sum of cations to the sum of

261 anions). For bulk and wet deposition, a 20% variation about the central index value
262 (1.00) was accepted, according to the ICP-Forest manual (ICP-Forest Manual, 1998).
263 Because TF contains weak acids that may not have been included in our alkalinity
264 measurements, we did not impose the 20% restriction about the central value to
265 throughfall ionic index checks. Further analytical checks were undertaken by
266 participating in international comparisons (AQUACON Med-Bas, Mosello et al., 1998),
267 with highly satisfactory results.

268 **2.4. Canopy budget method**

269 To separate canopy exchange from dry deposition, a Canopy Budget Model (CBM) has
270 been generally used (Draaijers and Erisman, 1995; Staelens et al., 2008; Adriaenssens et
271 al., 2012). The CBM is based on the following balance between fluxes above and below
272 the canopy: $TF+SF = PD + DD + CE$, where TF stands for throughfall, SF for stemflow, PD
273 for Precipitation Deposition, DD for Dry Deposition and CE for Canopy Exchange. Canopy
274 exchange, if positive, indicates the leaching of ions from the canopy (CL), and if negative,
275 the uptake of ions (CU). Stemflow at the LC site contributed only 3% of total rainfall
276 (Rodrigo et al., 2003) and because of its small contribution, SF fluxes have not been
277 considered here. Then,

$$278 \quad TF-PD = \text{net TF} = DD+CE$$

279 In this procedure, dry deposition is estimated based on a tracer ion that is assumed not
280 to be influenced by canopy exchange processes and assuming that aerosols containing
281 the other ions of interest have a similar deposition behaviour than the ion chosen as
282 reference (Ulrich, 1983). Here Na^+ was used as an inert tracer as recommended in
283 several studies (Staelens et al., 2008) to derive DD for base cations, SO_4^{2-} and Cl^- . To
284 characterise PD, either wet or bulk deposition can be used, but using wet deposition will
285 result in the estimation of fine plus coarse aerosol dry deposition, while bulk deposition
286 would mostly indicate dry deposition of fine aerosols (Balestrini et al., 2007); thus wet
287 deposition is used here.

288 Nitrogen compounds can be taken up in the canopy (Boyce et al., 1996; Ignatova and
289 Dambrine, 2000) and there is a need to estimate this flux in order to derive dry

290 deposition. To estimate nitrogen canopy uptake (CU), we considered that NH_4^+ uptake
291 can be equated to the net leaching of base cations, and NO_3^- is considered to be
292 retained at a fixed efficiency rate related to NH_4^+ . To balance the charges, NO_3^- uptake is
293 then equated to H^+ uptake (Staelens et al., 2008; Adriaenssens et al., 2012). It is well
294 known that NH_4^+ is preferentially retained by leaves relative to NO_3^- and an efficiency
295 factor of 6 for NH_4^+ vs NO_3^- uptake has been proposed for forests in Europe (de Vries et
296 al., 2003; Schmitt et al., 2005; Thimonier et al., 2005; Zhang et al., 2006) and will be also
297 applied here:

$$CU(\text{NH}_4 + \text{NO}_3) = \left(\frac{x\text{NH}_4 * (TF)\text{NH}_4 + (TF)\text{NO}_3}{x\text{NH}_4 * (TF)\text{NH}_4} \right) * CU(\text{NH}_4)$$

298 with $x=6$.

299 2.5. Statistical analysis

300 Air pollution emissions per country were obtained from the EMEP database site:
301 http://www.ceip.at/ms/ceip_home1/ceip_home/webdab_emepdatabase/reported_emissiondata/.

302 Local urban NO_x air concentration data was obtained from the Catalan Air Quality
303 network for Barcelona (Gràcia station; Direcció General de Qualitat Ambiental,
304 Generalitat de Catalunya). Data from electricity generation in Spain were downloaded
305 from Red Eléctrica Española (<http://ree.es/es/publicaciones>).

306 Mann-Kendall test were used to analyze trends in emissions for the years reported by
307 EMEP (1980-2012), and for bulk deposition measured at Montseny (1983-2014). Sen's
308 slope estimator was used to indicate the rate of change, a robust method for estimating
309 the true slope of a linear trend (Gilbert, 1987). Stream water concentration and fluxes
310 presented a non-continuous record which prevented using the Mann-Kendall tests, thus
311 differences between an initial (1990-1999) and recent period (2010-2014) were tested
312 with ANOVA tests. Percent changes for emissions and bulk deposition were also
313 recalculated for the same years of streamwater data for a more accurate comparison.
314 Stepwise regressions were used to determine principal contributors to N and S rain
315 concentrations and deposition at Montseny.

316

317 3. Results

318 3.1. Changes in emissions

319 The evolution of emissions in Spain and its neighbouring countries can be seen in Fig. 3.
320 The significance of the trends was checked with the Mann-Kendall test and percent
321 reductions or increases were calculated comparing 5-year averages at the beginning and
322 the end of the reported periods. The significance of the Mann-Kendall Tau, and the %
323 difference between the 5-yr initial and recent period are shown in Table 2.

324 Sulfur dioxide reductions were similar in all countries, decreasing between 75 and 85%.
325 For NO₂, Italy and France accomplished higher reductions (51 and 42% respectively)
326 than Spain and Portugal (34 and 32%). In all countries except Spain, the Mann-Kendall
327 Tau was significant for NO₂ (Table 2). The evolution of emissions in France and Italy
328 showed a change of trend in the early 1990s with a clear declining evolution thereafter
329 (Fig 2). For Spain, there was an increasing trend until the early 1990s, emissions
330 remained stable at high levels until around 2005, and since 2006 a sharp declining trend
331 was initiated (Fig 3).

332

333 For NH₃, Spain and France increased emissions by 13% and 1%, respectively, while NH₃
334 emission declined in Italy and Portugal (Table 2).

335

336 3.2. Relationship of rain and throughfall chemistry with emissions

337 Rain concentrations are strongly influenced by precipitation amounts. The time trend of
338 annual precipitation did not show a significant pattern during the study period (Fig. 2).
339 Hence, trends in element concentrations in precipitation, though partly influenced by
340 the variability of the rainfall amount, were probably more influenced by atmospheric
341 emission and transport processes.

342 The temporal evolution of SO₄²⁻, NO₃⁻, and NH₄⁺ VWM concentrations in bulk deposition
343 at Montseny are compared to SO₂, NO₂, and NH₃, Spanish emissions in Figs. 4a, b and c,
344 respectively. Pearson regression analysis indicated that SO₄²⁻ VWM concentrations were
345 strongly correlated with the Iberian Peninsula (sum of Portuguese and Spanish) SO₂
346 emissions (Pearson R=0.85; p<0.0001), with France and Italy emissions (both R=0.82

347 $p < 0.0001$) and with the EU28 emissions as a whole ($R = 0.65$; $p = 0.0002$). SO_4^{2-} -S
348 deposition fluxes at Montseny were also highly correlated with emissions (Pearson R
349 significant to $p < 0.001$ for the Iberian Peninsula, France, Italy and the EU28). Thus, the
350 effective widespread measures undertaken in Europe since the early 1980 to reduce SO_2
351 emissions have been translated into a reduction in precipitation SO_4^{2-} concentrations and
352 S deposition fluxes. However, the rate of reduction was not proportional: while SO_2
353 emissions were reduced around 80% (Table 2), SO_4^{2-} concentrations and S fluxes were
354 only reduced by 55-63% when comparing the values in 1995-1996 to those in 2011-2013
355 (Tables 3 and 4).

356 The evolution of NO_2 Spanish emissions from 1980 to 2014 showed different phases: an
357 increase from 1980 to 1991, a plateau around 1400 Gg NO_2 from 1992 to 2005, and a
358 decrease thereafter (Fig 4b). However, when breaking the series considering 2005 as a
359 tipping year, a significant increase occurred in the first period ($p < 0.001$; Sen slope = 17.9
360 Gg y^{-1}), and a significant decrease from 2005 on ($p = 0.003$, Sen slope = -78 Gg y^{-1}).
361 Similarly, nitrate VWM in bulk precipitation at Montseny increased until 2005 and
362 decreased thereafter, being significantly correlated with the Iberian Peninsula NO_2
363 emissions (Pearson $R = 0.66$; $p < 0.0001$), but not correlated to France, Italy or the EU28
364 NO_2 emissions ($p > 0.05$). Mann-Kendall trend test indicated a significant increasing trend
365 until 2005 ($p = 0.001$, Sen slope = $0.51 \mu\text{eq L}^{-1} \text{y}^{-1}$), and a decrease for the second period
366 ($p = 0.019$) at a rate of $-1.65 \mu\text{eq L}^{-1} \text{y}^{-1}$ (Fig. 4b). When considering emissions for the
367 whole EMEP record (1980 to 2012), neither NO_2 emissions nor NO_3^- concentrations
368 showed a significant pattern ($p = 0.26$ and 0.18 , respectively).

369 No significant correlation was found between NO_3^- -N fluxes at Montseny and emissions,
370 except for Spanish NO_2 emissions ($p = 0.014$).

371 The relevance of the different contributions to NO_3^- VWM concentrations was tested
372 with a stepwise regression considering NO_2 emission data from EMEP (France, Italy, the
373 Iberian Peninsula and the EU28) and a proxy of local emissions (near-ground NO_x air
374 concentrations in the center of Barcelona from the Catalan Air Quality network) as
375 independent variables. Precipitation amount was also included due to the marked
376 dilution effect of rain on N concentrations (Prado-Fiedler, 1990). The model included

377 precipitation (standardized coefficient $B=-0.31$; $p=0.012$); NO_x Barcelona emissions ($B=$
378 0.42 ; $p=0.005$) and Iberian Peninsula emissions ($B=0.43$; $p=0.011$). Correlation
379 coefficient for this model was $r=0.92$. Thus, both local and national emissions strongly
380 affect NO_3^- deposition in Montseny.

381 Spanish NH_3 emissions significantly increased between 1980 and 2012 (Table 2), but
382 NH_4^+ concentrations in bulk deposition did not show a significant temporal trend in this
383 period ($p=0.26$). From Fig. 4c it can be seen that emissions increased steadily until the
384 early 2000s and thereafter remained approximately stable. The correlation between
385 Spanish NH_3 emissions and NH_4^+ concentrations in bulk deposition was marginally
386 significant ($R= 0.32$; $p=0.056$), but the correlation increased when considering the
387 Iberian Peninsula emissions ($R=0.36$; $p= 0.027$). No correlations were found between
388 NH_4^+ VWM concentrations in bulk deposition and Italian and France or the EU 28 NH_3
389 emissions, nor for NH_4^+ -N fluxes and emissions of all the above considered countries.

390

391 Throughfall was sampled at two moments in this time series: the first (1995-1996) can
392 be taken to represent the period of high N emissions. The more recent one (2011-2013)
393 can be taken to represent the current situation, where SO_2 and NO_x emissions have been
394 reduced but NH_3 emissions still increase. Bulk deposition and throughfall VWM
395 concentrations for these two periods are presented in Table 3. Non sea salt- SO_4^{2-}
396 concentrations in bulk deposition and throughfall declined between the two studied
397 periods (with reductions of 63 and 60% for bulk deposition and throughfall,
398 respectively). Changes in Spanish and the Iberian Peninsula SO_2 emissions during this
399 time span decreased by 72 and 76%, respectively.

400 Nitrate concentrations decreased in bulk deposition between periods but increased by
401 23% in throughfall (Table 3). Ammonium concentrations in bulk deposition and
402 throughfall decreased between periods, with reductions of 46 and 72% for bulk
403 deposition and throughfall (Table 3) while Spanish NH_3 emissions increased by 8% in this
404 period. Since atmospheric ammonia is principally involved in neutralizing SO_2 to form
405 ammonium sulfate aerosols, the strong decrease of SO_2 may have resulted in a reduced
406 formation of ammonium aerosols and may have facilitated NH_3 dry deposition close to

407 sources. However, the N changes in throughfall do not directly show the changes in dry
408 deposition, since N can be taken up at the canopy level (Ignatova and Dambrine, 2000;
409 Staelens et al., 2008). To deduce N dry deposition a canopy budget model was applied
410 which is commented below.

411

412 **3.3. Dry deposition fluxes derived from a canopy budget model**

413 The methodology used here has been recommended in ICP-Forest manual even though
414 some uncertainties remain for the estimation of NO_3^- -N exchanges and dry deposition
415 (Adriaenssens et al., 2012; Staelens et al., 2008). Since the assumptions included in the
416 model were identical for the two study periods, results may be comparable between
417 periods. Bulk and wet deposition were recalculated to coincide with the throughfall
418 periods (Table 4).

419 The changes for the element fluxes in wet deposition for the years of throughfall data
420 also indicated strong declines for SO_4^{2-} -S (59%), NH_4^+ -N (54%) and NO_3^- -N (42%, Table 4).
421 However, based on the CBM estimations, dry deposition decreased for SO_4^{2-} -S (28%) and
422 NH_4^+ -N (5%) while it strongly increased for NO_3^- -N from 1.26 to 6.76 kg NO_3^- -N $\text{ha}^{-1} \text{y}^{-1}$
423 (Table 4). Thus, while in the first period, NH_4^+ -N accounted for most of total inorganic N
424 dry deposition (94%), in the second it only accounted for 47%. Changes in meteorology
425 between periods may explain part of these differences, as discussed below.

426 **3.4. Changes in streamwater chemistry**

427 We hypothesized that the described changes in N atmospheric deposition will be
428 transferred to the stream water, given the low residence time of water within this
429 catchment which makes it highly responsive to inputs (Bernal et al., 2013). Streamwater
430 SO_4^{2-} concentrations decreased by 22% between an initial (1990-99) and a more recent
431 period (2010-2014, Table 5), a lower decline than that of deposition that suggests soil
432 sulphate retention. NO_3^- concentrations in streamwater more than doubled (significant
433 to $p < 0.1$) but the change in NO_3^- -N export was smaller due to the fact that fluxes result
434 from the product of concentrations by water export which was lower in the second
435 period. In Fig. 5, a clear change in the ecosystem response relative to N inputs is shown:

436 for similar dissolved inorganic N, ($\text{DIN} = \text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) deposition, higher exports were
437 found in the more recent period (2010-2014), suggesting the onset of N saturation.

438 **4. Discussion**

439 Large changes in the emission of acidifying pollutants have been achieved in Europe
440 following the implementation of abatement measures in the 1980s. These measures are
441 costly and there is an interest in contrasting their long-term effectiveness regarding
442 changes in air quality, precipitation chemistry, atmospheric deposition and the response
443 of ecosystems. However, the link between emissions, concentrations and deposition is
444 complex and non-linearities between emission reductions and precipitation
445 concentrations have been described (Fowler et al., 2005; 2007). Part of the lack of
446 correlation may be due to the influence of meteorological conditions, which may impose
447 a high variability to the rain chemistry and deposition series, especially in the
448 Mediterranean because of its very high precipitation variability. However, long time
449 series may reveal trends robust enough to describe the relationships between emissions
450 and deposition. Here, we compared a simultaneous record of 30 years of emissions and
451 precipitation chemistry and deposition at a site in NE Spain for a period encompassing
452 marked changes in S and N emissions (Figs. 2 and 3).

453 In this study we observed similar declines in SO_2 emissions in Spain (77%) than in
454 neighbouring countries and the EU28 (75-85%, Table 3). However, the decline in
455 nssSO_4^{2-} concentrations in precipitation and $\text{SO}_4^{2-}\text{-S}$ deposition was lower (65% and 62%,
456 respectively) than emissions. A similar pattern was found in a study of emission and
457 deposition changes for 5 defined source regions in Europe for the period 1980-2000, in
458 which the regions to which Spain belonged presented a 80% reduction in SO_2 emissions
459 and 40-50% reduction in $\text{SO}_4^{2-}\text{-S}$ deposition (Fowler et al., 2007).

460 For the period of common measures of wet deposition and throughfall, while S wet
461 deposition decreased by *ca.* 60%, the estimated change in dry deposition between
462 1995-96 and 2011-13 was only 28% (Table 4), indicating a shift towards a higher
463 contribution of dry deposition to total deposition (from 25 to 40%) at this site as SO_2
464 emissions are reduced. This may be explained by a drier meteorology in the second

465 period (30% less precipitation) but is also consistent with an increase in the SO₂
466 deposition velocity as ambient SO₂ concentrations are reduced (Fowler et al., 2001).

467 When considering total deposition amounts (wet + dry), a 55% decline was found. This
468 decline in S deposition can translate through soils to drainage waters. A previous study
469 of small headwater streams in the Montseny mountains indicated a 30% decrease of
470 SO₄²⁻ concentration in streamwaters from 1980 to 2007 (Avila and Rodà, 2012). The
471 results of the present work corroborate this trend by showing significant differences in
472 streamwater SO₄²⁻ concentrations in the TMO stream, and about half S exports from the
473 catchment in the recent period (Table 5).

474 The emissions of oxidized N declined by 32% in Spain, a higher reduction than model
475 estimates for the regions that include Spain in Fowler et al. (2007) which ranged
476 between a small 2% reduction and a 6% increase. Overall, from 1983 to 2014, NO₃⁻
477 concentrations in precipitation and NO₃⁻-N deposition slightly increased (3-4%). Nitrate
478 concentrations in precipitation were explained (R²= 0.92) by a model that included
479 variations in precipitation amount, local NO_x emissions in Barcelona, and emissions at a
480 Peninsular scale. Spanish NO₂ emissions from 1980 to 2013 showed a clear increasing
481 trend until 2005 and a steep decline thereafter and NO₃⁻ concentrations closely tracked
482 these changes (Fig. 3b). Main contributors to NO_x emissions in Spain are road transport
483 (33%) and energy use + electricity supply for transport (60%; EEA 2012). Electricity
484 generation has shifted in recent years in Spain from coal and natural gas to a higher role
485 of renewable energies. NO₂ Spanish emissions closely tracked this change (linear
486 correlation coefficient r= 0.94, p<0.001), suggesting the important role of electricity
487 generation on NO_x emissions and eventually in NO₃⁻ deposition.

488 Ammonia emissions increased by 13% in Spain between 1980 and 2012 (Table 2).
489 However, NH₄⁺ in precipitation and NH₄⁺-N deposition at the Montseny site showed a
490 decreasing trend (15% reduction). This can be due to several processes and the
491 interaction between them. Opposite time trends are involved in the formation of NH₄⁺
492 aerosols (increasing NH₃ and decreasing SO₂ and NO_x emissions): with declining SO₂ and
493 NO₂ emissions in recent years there is a decreasing formation of ammonium sulphate
494 and nitrate aerosols, thus lower NH₄⁺ is available to be scavenged by precipitation and

495 lower NH_4^+ in precipitation is expected. However, due to the reduced formation of
496 aerosols, there are changes in the partitioning between $\text{NH}_3/\text{NH}_4^+$ and this may affect
497 the residence time of NH_4^+ in the atmosphere and thus the spatial scale of $\text{NH}_3/\text{NH}_4^+$
498 deposition. Fine NH_4^+ aerosols are long-range transported so that decreasing SO_2 and
499 NO_x emissions will tend to decrease NH_4^+ wet deposition at sites remote from sources,
500 but enhance local dry deposition of NH_3 .

501 Dry deposition changes for N were estimated from throughfall measurements by
502 applying a canopy budget model that indicated increasing NO_3^- -N dry deposition (Table
503 4). A reason for this increase may be the very low initial throughfall NO_3^- -N values in the
504 year 1995-1996, a period that was 30% rainier than usual, thus restraining the dry spells
505 for dry deposition. As a further check of the validity of the N dry deposition estimates,
506 we calculated dry deposition with the inferential method using a record of aerosol
507 concentrations and gases (HNO_3 , NO_2 , NH_3) at the La Castanya plot and taking their
508 deposition velocity (V_d) from reported values for forests. This estimation was only done
509 for the 2012 period because of lack of gas measurements in the 1995 period. The
510 calculation produced a dry deposition estimate of $6.22 \text{ kg ha}^{-1} \text{ yr}^{-1}$ for N-oxidized and
511 $4.04 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of N-reduced forms which compared well with the dry deposition
512 estimate of NO_3^- -N calculated with the CBM ($6.76 \text{ kg ha}^{-1} \text{ yr}^{-1}$) but underestimated
513 NH_4^+ -N deposition by 50%. However, as a first approach, we can frame the dry
514 deposition in 2011-2013 for NO_3^- -N and NH_4^+ -N in $6\text{-}7 \text{ kg ha}^{-1} \text{ yr}^{-1}$ and $4\text{-}6 \text{ kg ha}^{-1} \text{ yr}^{-1}$,
515 respectively. Total N deposition in both periods was similar ($16\text{-}17 \text{ kg ha}^{-1} \text{ yr}^{-1}$, Table 4),
516 but the contribution of the dry and wet modes varied between periods: while in 1995
517 dry and wet deposition fluxes were similar (around 50%), in the recent period dry
518 deposition dominated (75%).

519 Chronic addition of N amounts in the range of $15\text{-}17 \text{ kg ha}^{-1} \text{ yr}^{-1}$ are within the critical
520 loads proposed for Mediterranean sclerophyllous forests ($15\text{-}17.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$; (Bobbink et
521 al., 2010). Thus, the holm oak forests in the NE Iberian Peninsula may be at the brink of
522 experiencing adverse effects. One way to explore the N status of an ecosystem is to
523 monitor the changes in the drainage waters of unperturbed catchments. At present, a
524 shift is observed towards higher N export.

525 **5. Conclusions**

526 Emissions of S in Spain, as in other European countries, have strongly decreased (77%)
527 and that was reflected in reductions for nssSO_4^{2-} concentrations in precipitation and
528 SO_4^{2-} -S deposition (around 60%) during the period from 1980 to 2012. The observed
529 lower decline (29%) in dry deposition was consistent with reports of lower SO_2
530 deposition velocity as ambient SO_2 is reduced.

531 NO_2 emissions in Spain increased from 1980 to 1991, remained constant until 2005, and
532 decreased thereafter, a pattern that was paralleled by NO_3^- in bulk precipitation at
533 Montseny. This pattern seems to be related to a shift in electricity generation from coal
534 and natural gas to a higher role of renewable energies in Spain. However, dry deposition
535 increased markedly in the recent period, from 1.3 to 6.7 $\text{kg ha}^{-1} \text{yr}^{-1}$. Differences between
536 the 2 periods were probably related to differences in rainfall amount, since the latter
537 period was drier and the contribution from dry deposition was higher.

538 NH_3 emissions have increased by a 13% between 1980 and 2014 in Spain but NH_4^+
539 concentrations in precipitation and NH_4^+ -N deposition at the Montseny site showed a
540 decreasing trend (15% reduction). We suggest that the reduction of SO_2 and NO_x
541 emissions precludes the formation of ammonium sulphate and nitrate aerosols to be
542 scavenged by rainfall. The estimations with a canopy budget model showed similar
543 NH_4^+ -N dry deposition between the compared periods.

544 The N loads at Montseny were in the range of 15-17 $\text{kg ha}^{-1} \text{yr}^{-1}$, within the critical loads
545 proposed for Mediterranean sclerophyllous forests (15-17.5 $\text{kg ha}^{-1} \text{yr}^{-1}$; (Bobbink et al.,
546 2010). The onset of N saturation at this Mediterranean holm oak forests is suggested
547 since higher DIN export during the more recent period sampled was registered under
548 similar DIN loads.

549

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Table 1. Study site characteristics.

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	1995-96	1995-96	2011-13
	LC1	RP1	LC2
Altitude (m)	731	535	765
Orientation	N	SW	SW
Diameter at breast high (cm)	11.3 ± 4.8	12.0 ± 4.2	13.0 ± 4.1
Trees·ha ⁻¹	2127	1753	2571
Basal area (m ²)	26.5	22.3	29.0

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725 Table 2. Emission trends for Spain and surrounding countries between 1980 and 2012
726 (Portugal, between 1992 and 2012). Negative percent change indicates reduction and
727 positive percent, increase between 5-yr initial and final periods. Man-Kendall p value is
728 also indicated.

Emission		Mann-Kendall p value	5-year initial Gg	SD	5-year final Gg	SD	%change
SO ₂	Portugal	<0.0001	305	31	48	5	-84
	Spain	<0.0001	1870	233	430	26	-77
	France	<0.0001	1004	220	255	29	-75
	Italy	<0.0001	1302	262	195	18	-85
	Iberian P.	<0.0002	2175	249	479	28	-78
NO ₂	Portugal	0.003	257	7	170	8	-34
	Spain	0.265	1391	28	942	19	-32
	France	<0.0001	1746	107	1017	44	-42
	Italy	<0.0001	1863	201	904	53	-51
	Iberian P.	0.245	1648	31	1112	26	-33
NH ₃	Portugal	<0.0001	61	2	47	1	-22
	Spain	<0.0001	339	26	384	6	13
	France	0.049	688	9	697	22	1
	Italy	<0.0001	455	10	388	14	-15
	Iberian P.	<0.0001	339	25	437	7	8

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Table 3. Water volume (mm y⁻¹) and ion VWM concentrations (in ueq L⁻¹) in bulk deposition (BD) and throughfall (TF) and their percent change between an initial (6 June 1995 to 25 June 1996) and final period (1 March 2011 to 1 March 2013) at Montseny. Negative percent change indicates reduction and positive percent, increase, between the two periods.

	Water vol.	pH ¹	H	Alk	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻	nssSO ₄ ²⁻	Cl ⁻
1995-1996													
BD	1161.5	5.28	8.7	19.1	21	3.78	36.9	7.88	32.7	29.5	41.1	38.6	26.6
TF	858.5	6.11	1.25	76.2	32	64.1	79.5	26.2	41.9	33.6	71.2	67.4	55.5
2011-2013													
BD	860	6.06	1.9	41.5	20.3	3.2	53.3	11.1	17.6	18	16.6	14.2	21.2
TF	694	5.93	1.4	75.7	44.4	60.8	108	43	11.8	41.3	32	26.7	63.7
%change													
BD	-26.0	14.8	78.2	117.3	-3.3	-15.3	44.4	40.9	-46.2	-39.0	-59.6	-63.3	-20.3
%change													
TF	-19.2	-2.9	12.0	-0.7	38.8	-5.1	35.8	64.1	-71.8	22.9	-55.1	-60.4	14.8

746 ¹ Median pH
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756 Table 4. Fluxes in wet deposition (WD), net throughfall (nTF) and Total deposition (TD).
757 Dry deposition (DD) and canopy exchange (CE) fluxes have been derived from a
758 throughfall canopy budget model for an initial (1995-1996) and a recent period (2011-
759 2013). Units in $\text{kg ha}^{-1} \text{y}^{-1}$.

	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+-N	NO_3^--N	sum N	$\text{SO}_4^{2-}-\text{S}$	Cl^-
1995-1996									
WD	4.10	1.13	6.29	0.74	5.13	3.51	8.64	6.17	7.23
nTF	2.08	19.5	7.11	1.95	-0.29	0.37	0.08	3.37	9.27
DD	2.08	0.58	3.12	0.37	6.36	1.26	7.62	2.31	3.75
CE	0.00	18.9	3.99	1.58	-6.65	-0.89	-7.54	0.59	5.52
TD	6.18	1.72	9.41	1.11	11.5	4.77	16.3	9.34	11.0
2011-2013									
WD	4.59	0.98	9.78	1.17	2.36	2.03	4.39	2.52	6.44
nTF	3.02	18.4	8.02	3.10	-1.04	2.60	1.56	1.53	11.5
DD	3.02	0.65	6.40	0.77	6.07	6.76	12.8	1.66	4.24
CE	0.00	17.8	1.58	2.33	-7.12	-4.16	-11.3	-0.13	7.23
TD	7.61	1.63	16.2	1.94	8.43	8.79	17.2	4.18	10.7
WD %change	12.0	-13.3	55.5	58.1	-54.0	-42.2	-49.2	-59.2	-10.9
DD %change	45.2	12.1	105.1	108.1	-4.6	436.5	68.4	-28.1	13.1
TD %change	23.1	-5.2	72.4	74.8	-26.7	84.3	5.8	-55.2	-2.7

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765 Table 5. Comparison of stream conductivity, ion VWM concentrations (in $\mu\text{eq L}^{-1}$), water
 766 drainage (mm y^{-1}) and fluxes in streamwater (in $\text{kg ha}^{-1} \text{y}^{-1}$) from the TMO catchment.
 767 Differences between periods were tested with ANOVA (initial period=1990-1994. recent
 768 period =2010-2014) and significant differences are highlighted in bold. Percent
 769 differences between periods are also indicated.

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	Water	Cond.	Alk	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NO ₃ ⁻	SO ₄ ²⁻	Cl ⁻
VWM										
1990-1999	-	53.6	291	197	8.2	203	192	4.5	157	90.7
2010-2014	-	63.7	383	219	7.2	253	145	11.2	123	95.4
p-value	-	0.001	0.012	0.053	0.36	0.002	0.064	0.081	0.005	0.47
%change		19	32	11	-12	25	-24	250	-22	5
Export flux								NO ₃ ⁻ N	SO ₄ ⁻ S	
1990-1999	403		1105	17.7	1.29	15.9	6.1	0.33	10.1	12.9
2010-2014	283		1043	14	0.84	14.4	4.9	0.49	5.65	9.6
p-value	0.35		0.83	0.47	0.3	0.68	0.47	0.55	0.15	0.4
%change	-30		-6	-21	-35	-9	-20	48	-44	-26

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782 Figure captions

783 Fig. 1 Study site at La Castanya (Montseny mountains, NE Spain). LC1 corresponds to
784 1983-2000 bulk deposition and 1995-1996 throughfall measurements. LC2 corresponds
785 to 2002-2014 bulk deposition and 2011-2013 throughfall measurements. The Torrent
786 de la Mina catchment (TMO) is also indicated.

787 Fig 2. Precipitation and drainage from the Torrent de la Mina stream for the period
788 1983-2014. Units are mm y^{-1} . Hydrologic years defined from 1 September.

789 Fig 3. Temporal evolution of emissions reported to EMEP (in Gg) for Spain and
790 neighbouring countries. a) SO_2 , b) NO_2 , c) NH_3 .

791 Fig 4. Temporal evolution of annual VWM concentrations in bulk deposition at la
792 Castanya (Montseny) and annual Spanish emissions. a) SO_4 mean concentrations in bulk
793 deposition and SO_2 emissions, b) NO_3 mean concentrations in bulk deposition and NO_2
794 emissions, c) NH_4 mean concentrations in bulk deposition and NH_3 emissions.

795 Fig 5. Dissolved inorganic nitrogen ($\text{DIN} = \text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) annual fluxes in the
796 streamwaters draining the TMO catchment vs. annual DIN bulk deposition fluxes at the
797 site, for two recording periods.

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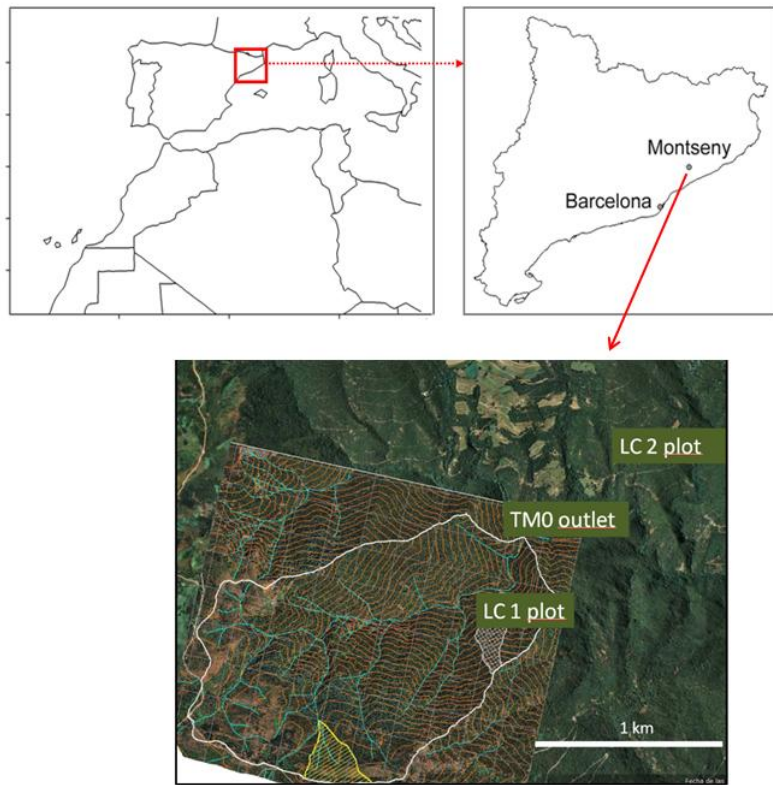
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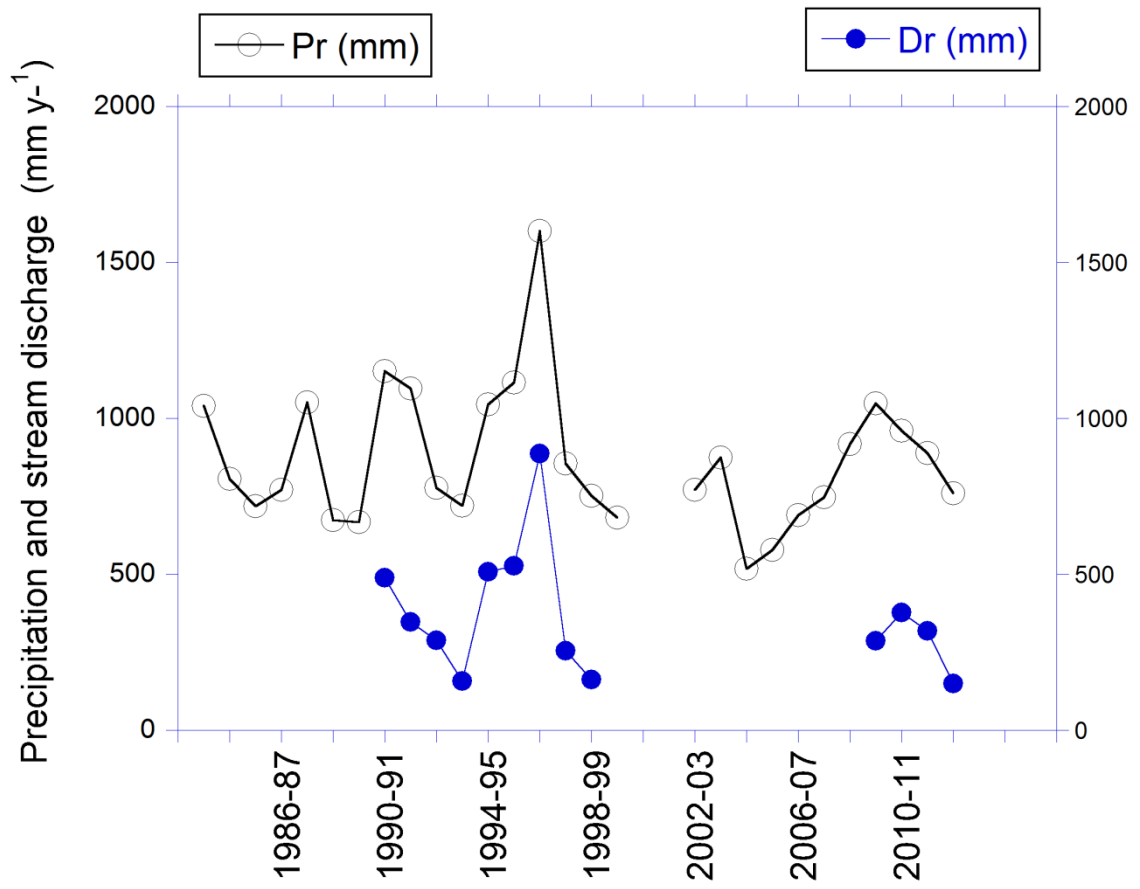
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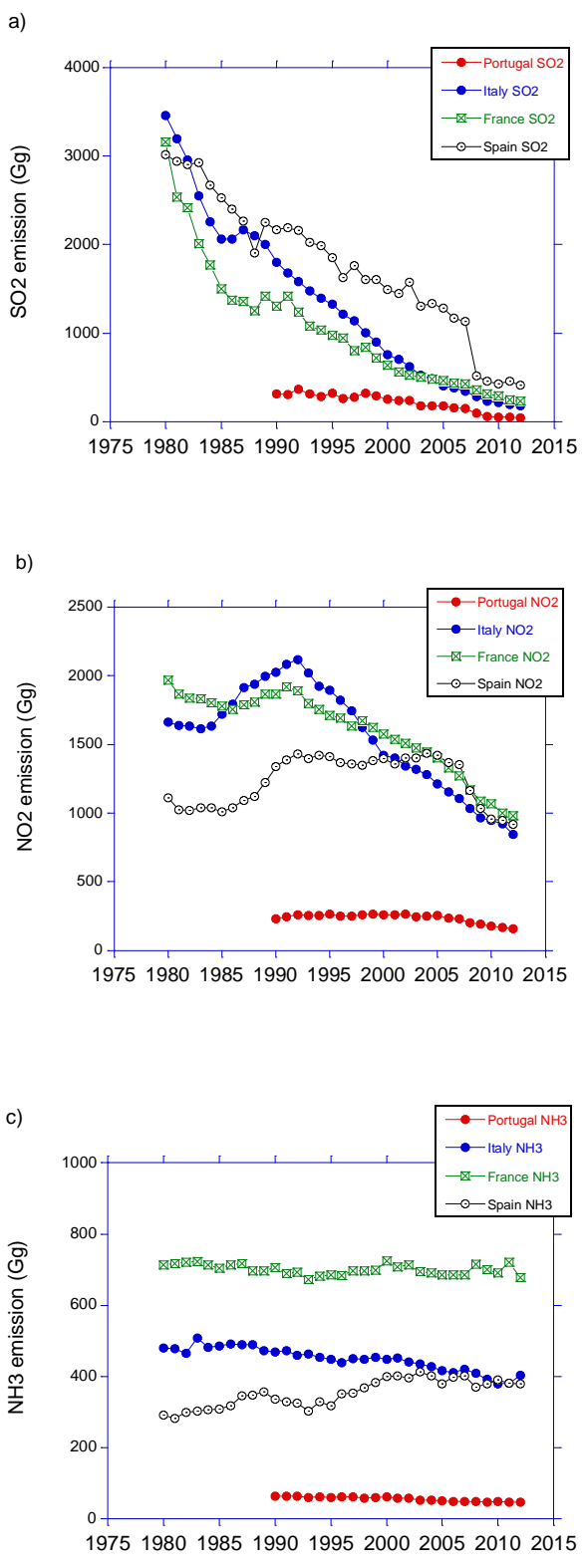
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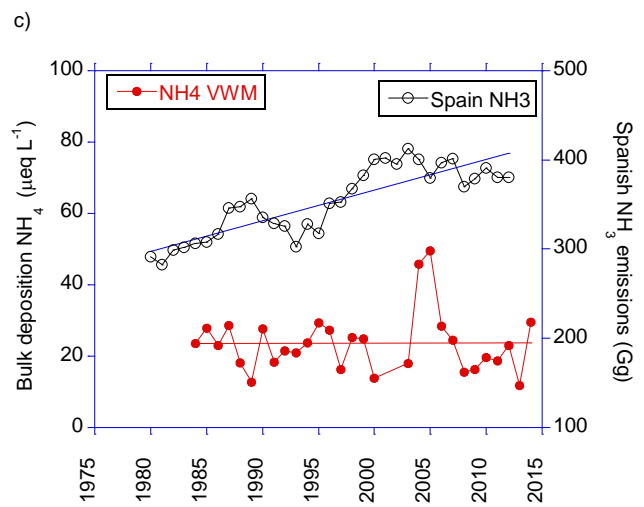
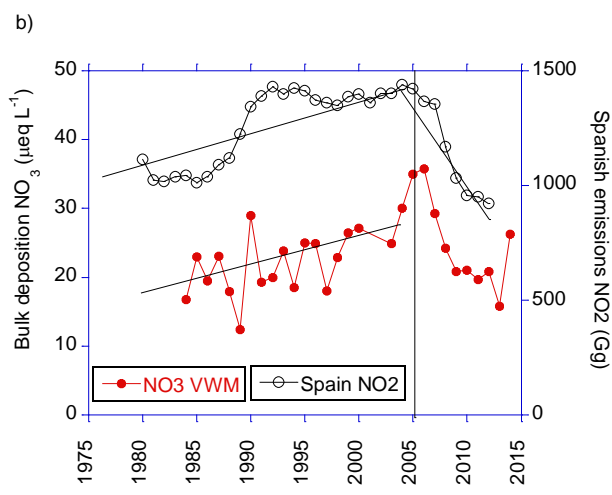
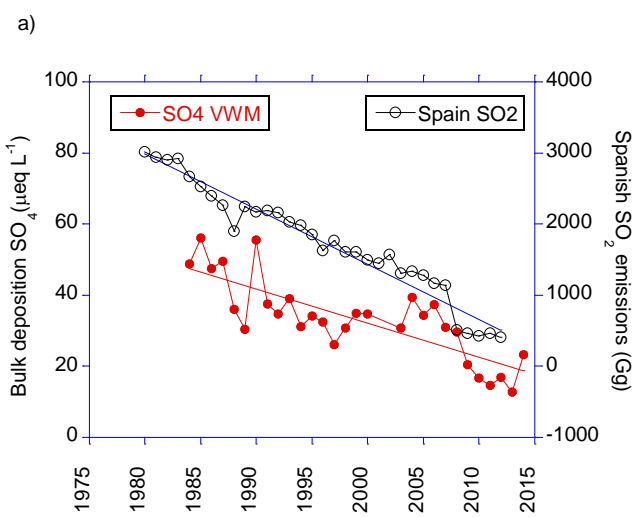
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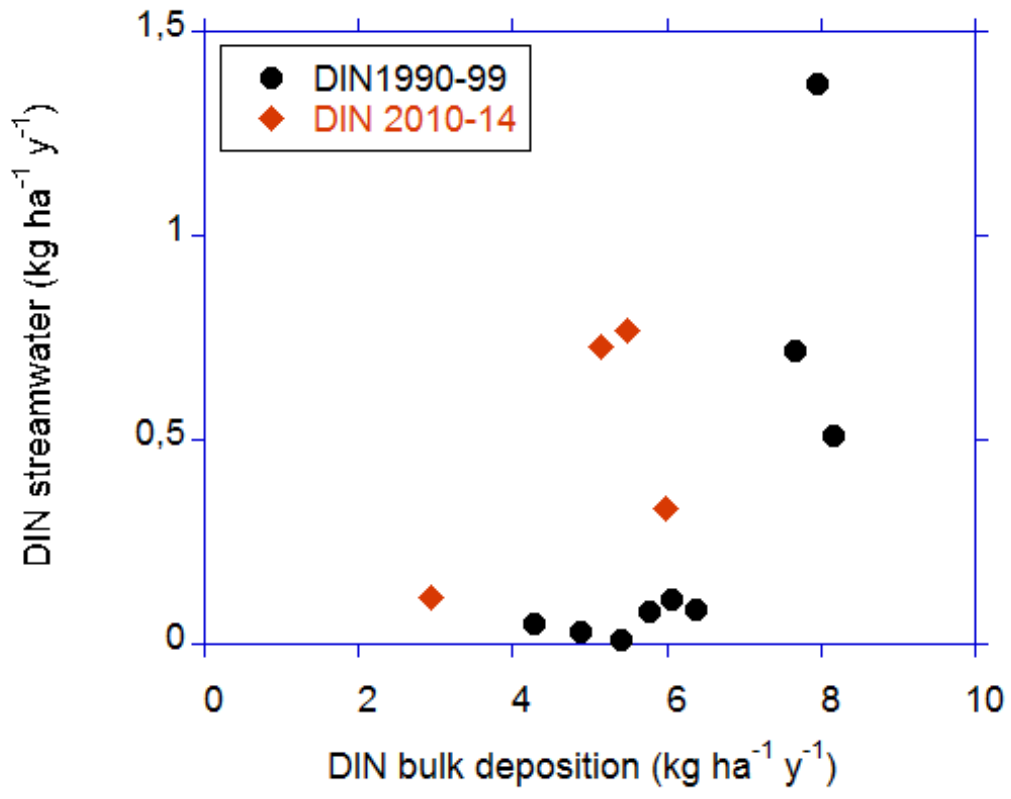
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