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 SO_2, NO_2 and NH_3 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 SO_2 in Spain strongly decreased (77%) and that was reflected in reductions

34   for $nssSO_4^{2-}$ in precipitation (65% for concentrations and 62% for SO_4^2-S deposition). A

35   lower decline was found for dry deposition (29%).

36   Spanish NO_2 emissions increased from 1980 to 1991, remained constant until 2005, and

37   decreased thereafter, a pattern that was paralleled by NO_3^- 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 $ha^{-1}y^{-1}$.

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 NH_3 emissions increased by 13% between 1980 and 2012 in Spain but NH_4^+

44   concentrations in precipitation and NH_4^+-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. NH_4^+-N dry deposition was similar between

47   the compared periods.

48   The N load at Montseny (15-17 kg $ha^{-1}yr^{-1}$) was within the critical load range proposed

49   for Mediterranean sclerophyllous forests (15-17.5 kg $ha^{-1}yr^{-1}$). The onset of N saturation

50   is suggested by the observed increasing N export in streamwaters.

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

53   Canopy.

1. Introduction

High atmospheric deposition of sulphur (S) and nitrogen (N) in the last century has lead to the acidification and eutrophication of many terrestrial ecosystems in Europe and North America, peaking in the 1970-1980 (Aber et al., 1998; EC, 2001; Reuss and Johnson, 1986). To counteract these adverse effects, transboundary amendment programs were launched by the Convention on Long-Range Transboundary Air Pollution (CLRTAP) in the frame of the United Nations Economic Commission for Europe (UNECE, 2011). Upon the implementation of national emission limits, significant declines were observed since the mid 1980s in SO_2 emissions and S in precipitation in Europe (Tørseth et al., 2012). Nitrogen emissions were also significantly reduced in many European countries, although higher variability was found among regions and the changes were different for oxidized or reduced N (Fagerli and Aas, 2008; Konovalov et al., 2008; Lövblad et al., 2004). A summary of the major results following the implementation of pollution control measures can be found in Grennfelt and Hov (2005). Concerning Spain, SO_2 emissions were readily cut, but the country still exceeded in 2012 the NO_x and NH_3 emissions ceilings for 2010, established at 847 and 353 Gg respectively (EC, 2001). The link between emissions, air concentrations and deposition is complex because of the interplay of the meteorological conditions, the chemical interaction between pollutants in the atmosphere and the spatial scale of the region of influence. In this sense non-linearities have been found between emission reductions and the decline in rainwater concentration (Fowler et al., 2007).

Dry deposition of airborne pollutants makes also a significant contribution to the atmospheric load of most ecosystems. However, long time records of changes in dry deposition for the last decades are scarce. Changes in dry deposition have also been found to change non-linearly with emissions (Fowler et al. 2005). This has been attributed to the fact that for SO_2, the deposition velocity (V_d) is controlled by the NH_3/SO_2 ratio, where SO_2 deposition increases as leaf pH raises in response to NH_3 deposition (Erisman et al., 1998; Fowler et al., 2001). Thus, dry deposition will not only depend on SO_2 concentrations, but also on its relative abundance respect to NH_3. Also, declining air SO_2 concentrations will affect the partitioning of gaseous NH_3 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).

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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 and 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, 41º46'N, 2º21'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 9.5ºC.

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 120º 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 Aguillaume (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 kg ha^{-1} y^{-1}, except for H$^+$ and

216 alkalinity, in eq ha^{-1} y^{-1}.

217 Non sea salt sulphate (nss SO$_4^{2-}$) concentrations in bulk deposition (BD) were calculated

218 as:

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

220 where SO$_4^{2-}{}_{sea\ salt}$/ Na$^+{}_{sea\ salt}$ = 0.12   (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 (Schlumburger 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 kg ha^{-1} y^{-1}) by:

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

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 0.45µm 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 TF-PD = 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:

$$CU(\text{NH4} + \text{NO3}) = \left(\frac{x\text{NH4} * (TF)\text{NH4} + (TF)\text{NO3}}{x\text{NH4} * (TF)\text{NH4}} \right) * CU(\text{NH4})$$

298 with x=6.

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 QualitatAmbiental,

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 NO_2, 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 NO_2 (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 NH_3, Spain and France increased emissions by 13% and 1%, respectively, while NH_3

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 SO_4^{2-}, NO_3^-, and NH_4^+ VWM concentrations in bulk deposition

343   at Montseny are compared to SO_2, NO_2, and NH_3, Spanish emissions in Figs. 4a, b and c,

344   respectively. Pearson regression analysis indicated that SO_4^{2-} VWM concentrations were

345   strongly correlated with the Iberian Peninsula (sum of Portuguese and Spanish) SO_2

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 µeq L^{-1} y^{-1}), and a decrease for the second period

366 (p=0.019) at a rate of -1.65 µeq L^{-1} 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 (2011-1013)

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 $ha^{-1}y^{-1}$

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, (DIN = NO_3-N + NH_4-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 SO_4^{2-}-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 SO_4^2-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 SO_2

466   deposition velocity as ambient SO_2 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   SO_4^{2-} 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 SO_4^{2-} concentrations in the TM0 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, NO_3^-

477   concentrations in precipitation and NO_3^--N deposition slightly increased (3-4%). Nitrate

478   concentrations in precipitation were explained (R^2= 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 NO_2 emissions from 1980 to 2013 showed a clear increasing

481   trend until 2005 and a steep decline thereafter and NO_3^- 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. NO_2 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 NO_3^- deposition.

488   Ammonia emissions increased by 13% in Spain between 1980 and 2012 (Table 2).

489   However, NH_4^+ in precipitation and NH_4^+-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 NH_4^+

492   aerosols (increasing NH_3 and decreasing SO_2 and NOx emissions): with declining SO_2 and

493   NO_2 emissions in recent years there is a decreasing formation of ammonium sulphate

494   and nitrate aerosols, thus lower NH_4^+ 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 NH_3/NH_4^+ and this may affect

497   the residence time of NH_4^+ in the atmosphere and thus the spatial scale of NH_3/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 kg ha^{-1} yr^{-1} for N-oxidized and

511   4.04 kg $ha^{-1}yr^{-1}$ of N-reduced forms which compared well with the dry deposition

512   estimate of NO_3^--N calculated with the CBM (6.76 kg ha^{-1} 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 6-7 kg $ha^{-1}yr^{-1}$ and 4-6 kg $ha^{-1}yr^{-1}$,

515   respectively. Total N deposition in both periods was similar (16-17 kg $ha^{-1}yr^{-1}$, 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 15-17 kg $ha^{-1}yr^{-1}$ are within the critical

520   loads proposed for Mediterranean sclerophyllous forests (15-17.5 kg$ha^{-1}yr^{-1}$; (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.

5. Conclusions

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

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

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

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

References

556 Aber J, McDowell W, Nadelhoffer K, Magill A, Berntson G, Kamakea M, et al. Nitrogen saturation
557   in temperate forest ecosystems. BioScience 1998: 921-934.
558 Adriaenssens S, Staelens J, Wuyts K, Samson R, Verheyen K, Boeckx P. Retention of dissolved
559   inorganic nitrogen by foliage and twigs of four temperate tree species. Ecosystems
560   2012; 15: 1093-1107.
561 Avila A. Time trends in the precipitation chemistry at a mountain site in northeastern Spain for
562   the period 1983–1994. Atmospheric environment 1996; 30: 1363-1373.
563 Avila A, Rodà F. Assessing decadal changes in rainwater alkalinity at a rural Mediterranean site in
564   the Montseny Mountains (NE Spain). Atmospheric environment 2002; 36: 2881-2890.
565 Avila A, Rodà F. Changes in atmospheric deposition and streamwater chemistry over 25years in
566   undisturbed catchments in a Mediterranean mountain environment. Science of the
567   Total Environment 2012; 434: 18-27.

568 Balestrini R, Arisci S, Brizzio MC, Mosello R, Rogora M, Tagliaferri A. Dry deposition of particles
569   and canopy exchange: Comparison of wet, bulk and throughfall deposition at five forest
570   sites in Italy. Atmospheric Environment 2007; 41: 745-756.
571 Bernal S, Belillas C, Ibáñez J, Àvila A. Exploring the long-term response of undisturbed
572   Mediterranean catchments to changes in atmospheric inputs through time series
573   analysis. Science of the Total Environment 2013; 458: 535-545.
574 Bobbink R, Hicks K, Galloway J, Spranger T, Alkemade R, Ashmore M, et al. Global assessment of
575   nitrogen deposition effects on terrestrial plant diversity: a synthesis. Ecological
576   applications 2010; 20: 30-59.
577 Boyce RL, Friedland AJ, Chamberlain CP, Poulson SR. Direct canopy nitrogen uptake from 15N-
578   labeled wet deposition by mature red spruce. Canadian Journal of Forest Research 1996;
579   26: 1539-1547.
580 Calvo A, Pont V, Olmo F, Castro A, Alados-Arboledas L, Vicente A, et al. Air masses and weather
581   types: a useful tool for characterizing precipitation chemistry and wet deposition.
582   Aerosol and Air Quality Research 2012; 12: 856-878.
583 De Vries W, Vel E, Reinds G, Deelstra H, Klap J, Leeters E, et al. Intensive monitoring of forest
584   ecosystems in Europe: 1. Objectives, set-up and evaluation strategy. Forest Ecology and
585   Management 2003; 174: 77-95.
586 Draaijers G, Erisman J. A canopy budget model to assess atmospheric deposition from
587   throughfall measurements. Water, Air, and Soil Pollution 1995; 85: 2253-2258.
588 Drever JI. The geochemistry of natural waters. 126-128. Prentice-Hall, Inc., Englewood Cliffs. N.
589   Jersey, 1982.
590 Driscoll C, Likens G, Church M. Recovery of surface waters in the northeastern US from
591   decreases in atmospheric deposition of sulfur. Water, Air, and Soil Pollution 1998; 105:
592   319-329.
593 EC. Directive 2001/81/EC, OJ L 309, 22–30, 27 November, 2001.
594 EEA. Air Quality in Europe-2012 Report. 2012
595 Erisman J, Mennen M, Fowler D, Flechard C, Spindler G, Grüner A, et al. Deposition monitoring in
596   Europe. Environmental Monitoring and Assessment 1998; 53: 279-295.
597 Escudero M, Querol X, Avila A, Cuevas E. Origin of the exceedances of the European daily PM
598   limit value in regional background areas of Spain. Atmospheric Environment 2007; 41:
599   730-744.
600 Evans C, Reynolds B, Hinton C, Hughes S, Norris D, Grant S, et al. Effects of decreasing acid
601   deposition and climate change on acid extremes in an upland stream. Hydrology and
602   Earth System Sciences Discussions Discussions 2007; 4: 2901-2944.

603   Fagerli H, Aas W. Trends of nitrogen in air and precipitation: Model results and observations at
604   EMEP sites in Europe, 1980–2003. Environmental Pollution 2008; 154: 448-461.
605   Fowler D, Smith R, Muller J, Cape JN, Sutton M, Erisman JW, et al. Long term trends in sulphur
606   and nitrogen deposition in Europe and the cause of non-linearities. Water, Air, & Soil
607   Pollution: Focus 2007; 7: 41-47.
608   Fowler D, Smith R, Muller J, Hayman G, Vincent K. Changes in the atmospheric deposition of
609   acidifying compounds in the UK between 1986 and 2001. Environmental Pollution 2005;
610   137: 15-25.
611   Fowler D, Sutton M, Flechard C, Cape J, Storeton-West R, Coyle M, et al. The control of SO2 dry
612   deposition on to natural surfaces by NH3 and its effects on regional deposition. Water,
613   Air and Soil Pollution: Focus 2001; 1: 39-48.
614   Gilbert RO. Statistical Methods for Environmental Pollution Monitoring 1987. Van Nostrand
615   Reinhold. New York.
616   Grennfelt P, Hov Ø. Regional air pollution at a turning point. AMBIO: A Journal of the Human
617   Environment 2005; 34: 2-10.
618   Hereter A, Sánchez JR. Experimental areas of Prades and Montseny. Ecology of Mediterranean
619   evergreen oak forests. Springer, 1999, pp. 15-27.
620   Ignatova N, Dambrine É. Canopy uptake of N deposition in spruce (Picea abies L. Karst) stands.
621   Annals of forest science 2000; 57: 113-120.
622   Izquierdo R, Alarcón M, Aguillaume L, Avila A. Effects of teleconnection patterns on the
623   atmospheric routes, precipitation and deposition amounts in the north-eastern Iberian
624   Peninsula. Atmospheric Environment 2014; 89: 482-490.
625   Izquierdo R, Benítez-Nelson CR, Masqué P, Castillo S, Alastuey A, Àvila A. Atmospheric
626   phosphorus deposition in a near-coastal rural site in the NE Iberian Peninsula and its
627   role in marine productivity. Atmospheric Environment 2012; 49: 361-370.
628   Konovalov I, Beekmann M, Burrows J, Richter A. Satellite measurement based estimates of
629   decadal changes in European nitrogen oxides emissions. Atmospheric Chemistry and
630   Physics 2008; 8: 2623-2641.
631   Lindberg S, Lovett G. Deposition and forest canopy interactions of airborne sulfur: results from
632   the integrated forest study. Atmospheric Environment. Part A. General Topics 1992; 26:
633   1477-1492.
634   Llorens P, Domingo F. Rainfall partitioning by vegetation under Mediterranean conditions. A
635   review of studies in Europe. Journal of Hydrology 2007; 335: 37-54.
636   Lovett G, Lindberg S. Dry deposition and canopy exchange in a mixed oak forest as determined
637   by analysis of throughfall. Journal of Applied Ecology 1984: 1013-1027.
638   Lövblad G, Tarrasón L, Tørseth K, Dutchak S. emeP assessment Part i: european Perspective.
639   Norwegian Meteorological Institute, PO Box 2004; 43.
640   Manual ICP-Forest. Manual on methods and criteria for harmonized sampling, assessment,
641   monitoring and analysis of the effects of air pollution on forests. UN-ECE, Fed. Res.
642   Centre for Forestry and Forest Products (BFH) 1998.
643   Mosello R, Bianchi M, Geiss H, Marchetto A, Morselli L, Muntau H, et al. Italian Network for the
644   Chemistry of Atmospheric Deposition. Intercomparison 1/98. Consiglio Nazionale delle
645   Ricerche. Istituto Italiano di Idrobiologia. Verbania Pallanza. 81 pp, 1998.
646   Parker G. Throughfall and stemflow in the forest nutrient cycle. Advances in ecological research
647   1983; 13: 57-133.
648   Prado-Fiedler R. On the relationship between precipitation amount and wet deposition of
649   nitrate and ammonium. Atmospheric Environment. Part A. General Topics 1990; 24:
650   3061-3065.
651   Pérez N, Pey J, Castillo S, Viana M, Alastuey A, Querol X. Interpretation of the variability of levels
652   of regional background aerosols in the Western Mediterranean. Science of the total
653   environment 2008; 407: 527-540.

654   Rekolainen S, Posch M, Kämäri J, Ekholm P. Evaluation of the accuracy and precision of annual
655   phosphorus load estimates from two agricultural basins in Finland. Journal of Hydrology
656   1991; 128: 237-255.
657   Reuss J, Johnson D. Ecological studies 59. Springer-Verlag, New York, 1986.
658   Rodrigo A, Avila A, Roda F. The chemistry of precipitation, throughfall and stemflow in two holm
659   oak (Quercus ilex L.) forests under a contrasted pollution environment in NE Spain.
660   Science of the Total Environment 2003; 305: 195-205.
661   Rodà F, Retana J, Gracia CA, Bellot J Ecology of Mediterranean evergreen oak forests. Vol 37:
662   Springer Publ, 1999.
663   Schaefer DA, Reiners WA. Throughfall chemistry and canopy processing mechanisms. Acidic
664   precipitation. Springer, 1990, pp. 241-284.
665   Schmitt M, Thöni L, Waldner P, Thimonier A. Total deposition of nitrogen on Swiss long-term
666   forest ecosystem research (LWF) plots: comparison of the throughfall and the inferential
667   method. Atmospheric Environment 2005; 39: 1079-1091.
668   Skjelkvåle B, Stoddard J, Jeffries D, Tørseth K, Høgåsen T, Bowman J, et al. Regional scale
669   evidence for improvements in surface water chemistry 1990–2001. Environmental
670   Pollution 2005; 137: 165-176.
671   Staelens J, Houle D, De Schrijver A, Neirynck J, Verheyen K. Calculating dry deposition and
672   canopy exchange with the canopy budget model: review of assumptions and application
673   to two deciduous forests. Water, Air, and Soil Pollution 2008; 191: 149-169.
674   Stone K, Hunt P, Novak J, Johnson M, Watts D. Flow-proportional, time-composited, and grab
675   sample estimation of nitrogen export from an eastern Coastal Plain watershed.
676   Transactions of the ASAE 2000; 43: 281-290.
677   Swistock BR, Edwards PJ, Wood F, Dewalle DR. Comparison of methods for calculating annual
678   solute exports from six forested Appalachian watersheds. Hydrological Processes 1997;
679   11: 655-669.
680   Thimonier A, Schmitt, Waldner P, Rihm B. Atmospheric deposition on Swiss long-term forest
681   ecosystem research (LWF) plots. Environmental Monitoring and Assessment 2004; 30: 1-
682   38.
683   Tørseth K, Aas W, Breivik K, Fjæraa A, Fiebig M, Hjellbrekke A, et al. Introduction to the
684   European Monitoring and Evaluation Programme (EMEP) and observed atmospheric
685   composition change during 1972–2009. Atmospheric Chemistry and Physics 2012; 12:
686   5447-5481.
687   Ulrich B. Interaction of forest canopies with atmospheric constituents: SO2, alkali and earth
688   alkali cations and chloride. Effects of accumulation of air pollutants in forest ecosystems.
689   Springer, 1983, pp. 33-45.
690   UNECE. Protocols to the Convention on Long-Range Transboundary Air Pollution 2011,,
691   http://www.unece.org/env/lrtap/status/lrtap_s.htm [accessed 8 May 2011]. 2011.
692   van Jaarsveld BC, Krijnen P, Pieterman H, Derkx FH, Deinum J, Postma CT, et al. The effect of
693   balloon angioplasty on hypertension in atherosclerotic renal-artery stenosis. New
694   England Journal of Medicine 2000; 342: 1007-1014.
695   Zhang G, Zeng GM, Jiang YM, Yao JM, Huang GH, Jiang XY, Tan W, Zhang XL, Zeng M. Effects of
696   weak acids on canopy leaching and uptake precesses in a coniferous-decideous mixed
697   evergreen forest in central-south China. Water, Air and Soil Pollution 2006; 172: 39-55.
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703   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		5-year final Gg		
			Mean	SD	Mean	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 kg ha^{-1} y^{-1}.

	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+-N	NO_3^--N	sum N	SO_4^{2-}-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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	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 (TM0) 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 (DIN = NO3-N + NH4-N) annual fluxes in the
796 streamwaters draining the TM0 catchment *vs.* annual DIN bulk deposition fluxes at the
797 site, for two recording periods.

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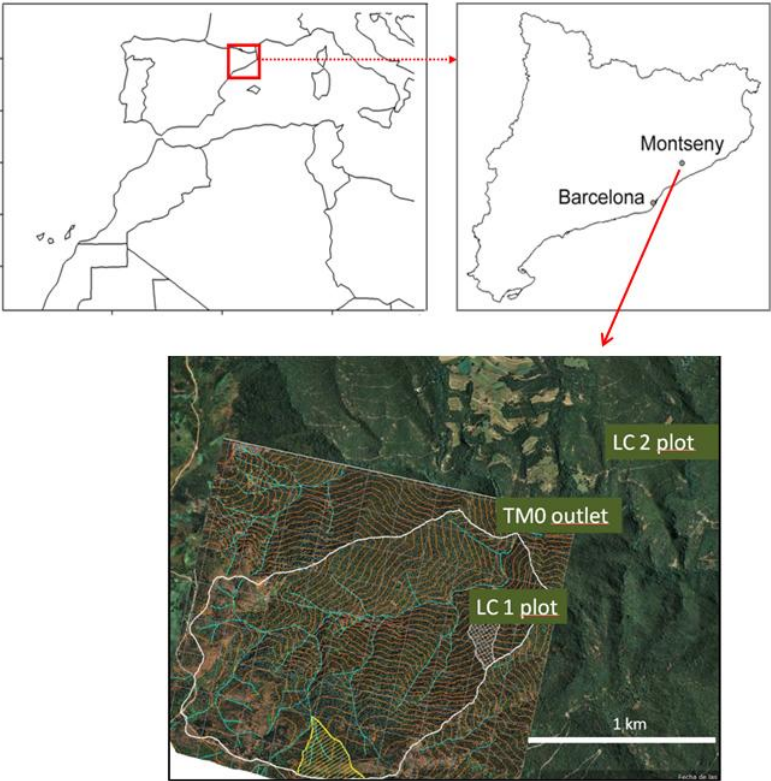799

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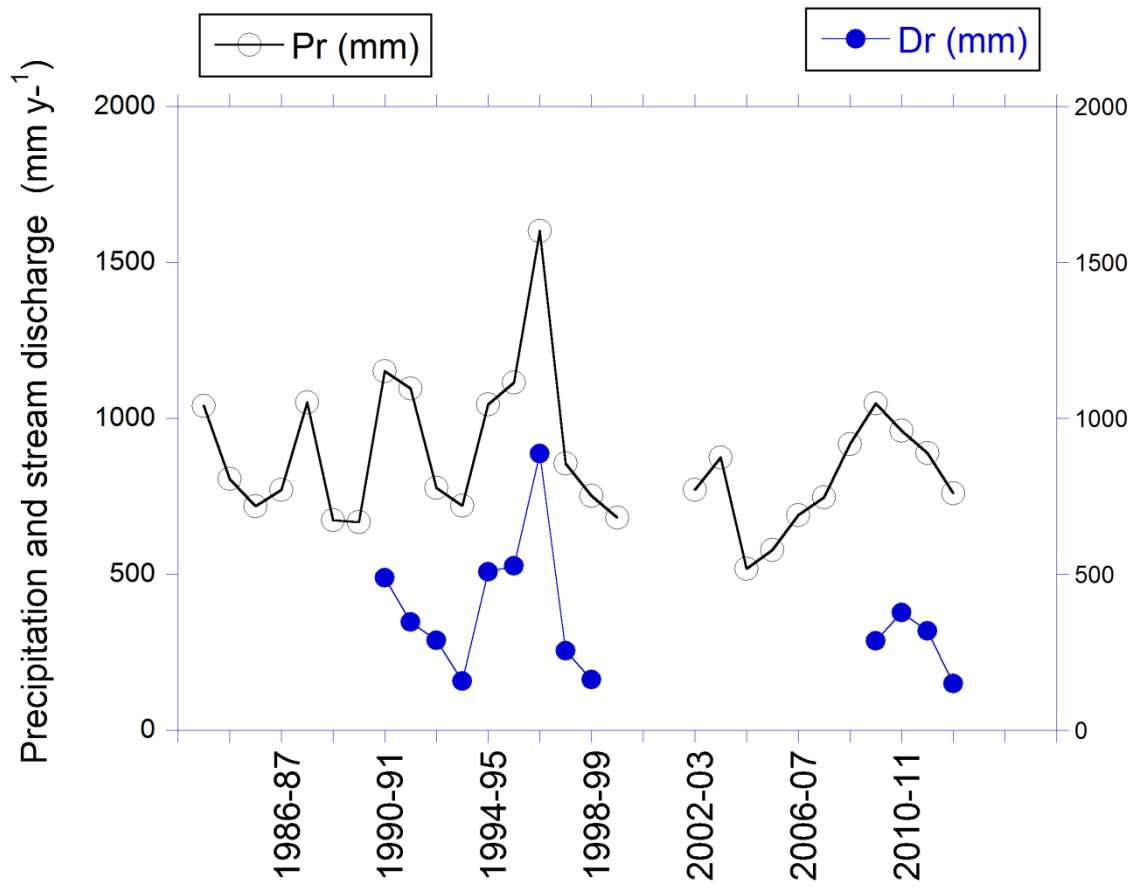811

812   Fig 1

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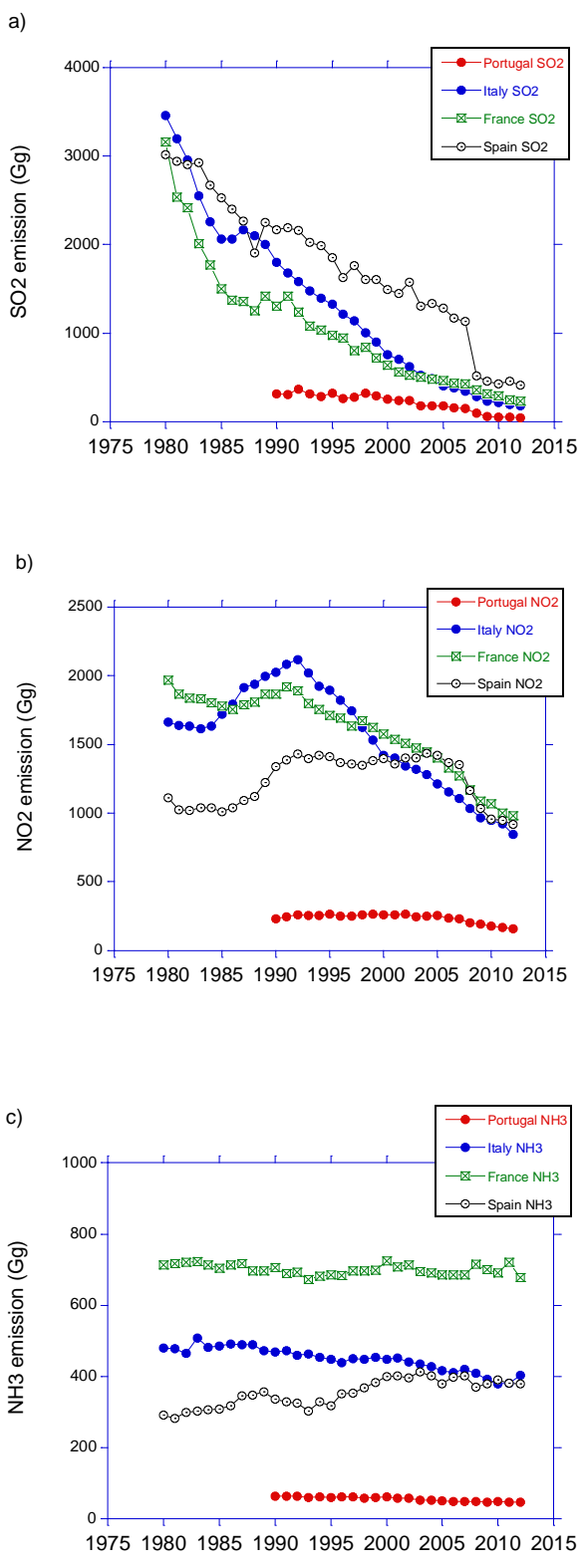
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824   Fig 2

836   Fig 3

a)

b)

c)

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839   Fig 4

a)

b)

c)

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842   Fig 5

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