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3 **Exploring the long-term response of undisturbed Mediterranean catchments to changes in**
4 **atmospheric inputs through time series analysis.**

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25 **Abstract**

26 The aim of this study was to gain insights on the potential hydrological and biogeochemical
27 mechanisms controlling the response of two nested Mediterranean catchments to long-term
28 changes in atmospheric inorganic nitrogen and sulphate deposition. One catchment was steep and
29 fully forested (TM9, 5.9 ha) and the other one had gentler slopes and heathlands in the upper part
30 while side slopes were steep and forested (TM0, 205 ha). Both catchments were highly
31 responsive to the 45% decline in sulphate concentration measured in atmospheric deposition
32 during the 1980's and 1990's, with stream concentrations decreasing by 1.4 to 3.4 $\mu\text{eq L}^{-1} \text{y}^{-1}$.
33 Long-term changes in inorganic nitrogen in both, atmospheric deposition and stream water were
34 small compared to sulphate. The quick response to changes in atmospheric inputs could be
35 explained by the small residence time of water (4-5 months) in these catchments (inferred from
36 chloride time series variance analysis), which was attributed to steep slopes and the role of
37 macropore flow bypassing the soil matrix during wet periods. The estimated residence time for
38 sulphate (1.5-3 months) was substantially lower than for chloride suggesting unaccounted sources
39 of sulphate (i.e., dry deposition, or depletion of soil adsorbed sulphate). In both catchments,
40 inorganic nitrogen concentration in stream water was strongly damped compared to precipitation
41 and its residence time was of the order of decades, indicating that this essential nutrient was
42 strongly retained in these catchments. Inorganic nitrogen concentration tended to be higher at
43 TM0 than at TM9 which was attributed to the presence of nitrogen fixing species in the
44 heathlands. Our results indicate that these Mediterranean catchments react rapidly to
45 environmental changes, which make them especially vulnerable to changes in atmospheric
46 deposition.

47 **Keywords:** long-term trends, atmospheric deposition, stream water chemistry, water
48 residence time, Mediterranean catchment, heathlands.

49 1. Introduction

50 Increased atmospheric deposition of nitrogen (N) and specially sulphur (S) during the
51 twentieth century lead to the acidification of many terrestrial and aquatic ecosystems in Europe
52 and North America (Aber et al., 1998; Reuss and Johnson, 1986; Shannon, 1999). After the
53 implementation of transboundary amendment programs in the 1990s, significant declines in
54 atmospheric deposition, especially S, were observed all over the North Hemisphere (Sickles and
55 Shadwick, 2007; Skjelkvale et al., 2005; Stoddard et al., 1999).

56 Long-term monitoring studies showed that some catchments respond quickly to changes
57 in atmospheric deposition with declines in nitrate (NO_3^-) and sulphate (SO_4^{2-}) export in
58 agreement with those observed in precipitation (Kothawala et al., 2011; Mattson et al., 1997;
59 Prechtel et al., 2001). However, in other cases the catchments' biogeochemical response to
60 atmospheric changes was small (Alewell et al., 2000; Kothawala et al., 2011). Several factors
61 have been invoked for explaining this different behaviour between catchments, from climate
62 (Eimers and Dillon, 2002; Mitchell et al., 2011) to catchment-specific characteristics that can
63 influence N and S cycling such as type of soil (Alewell et al., 2000, 2001; Eimers and Dillon,
64 2002), presence of S-minerals (Driscoll et al., 1998; Shanley et al., 2005), presence of wetlands
65 (Björkvald et al., 2009), or type of vegetation (De Schrijver et al., 2007, 2008). Few studies have
66 explored, however, how catchment hydrology affects the response of surface waters to changes in
67 atmospheric deposition. Recently, Mitchell et al. (2011) reported a strong hydrological control on
68 the net losses of SO_4^{2-} from catchments across eastern North America, while Kothawala et al.
69 (2011) concluded that fast drainage from soil to groundwater prevented N processing by soil
70 biota, and thus promoted a rapid response to decreasing nitrate deposition in steep slope
71 catchments in Canada. Furthermore, the residence time of water within catchments is related to
72 topography (McGlynn et al., 2003; McGuire et al., 2005). These influences of topography on

73 catchment hydrology may affect runoff solute concentrations, and ultimately, the response of
74 surface waters to changes in atmospheric deposition.

75 Most of the studies evaluating the effect of changes in atmospheric inputs on stream water
76 chemistry have been undertaken in temperate regions of Europe and North America, yet research
77 on how catchments respond to changing deposition in drier regions is scarce. In Mediterranean
78 catchments, high water demand by vegetation and low rainfall in summer result in a marked
79 seasonality of hydrological and biogeochemical processes (Holloway and Dahlgren, 2001), which
80 affects the temporal pattern of solutes and thus, it could influence the response of catchments to
81 environmental changes. Here, we focused on Montseny catchments studied since the early 1980s,
82 which represent Mediterranean forests and heathlands in sub-humid landscapes of the Iberian
83 Peninsula (Rodà et al., 1999). The studied catchments receive abundant precipitation in spring
84 and autumn and experience strong evaporative demand in summer. Annual precipitation (~900
85 mm/year), however, is sufficient to provide a perennial streamflow, though water yield is very
86 low in summer. Previous work at Montseny suggested the existence of preferential flow paths
87 that bypass the soil and rooting zone and directly connect surface water flows with deep
88 subsurface flows that feed groundwater, mostly during wet conditions (Àvila et al., 1995), which
89 could contribute to reduce the mean residence time of water in these catchments.

90 Atmospheric deposition to these catchments is characterized by relatively high
91 concentration of strong mineral anions and low acidity due to neutralization by mineral dust
92 (Àvila, 1996; Àvila and Rodà, 2002). Starting in the early 1980s, a declining trend for SO_4^{2-}
93 concentrations in bulk deposition has been observed which has been accompanied by a decrease
94 in SO_4^{2-} baseflow stream concentrations (Àvila, 1996; Àvila and Rodà, 2012). In contrast, NO_3^-
95 concentration in bulk deposition and stream water has increased, though baseflow stream
96 concentrations are still low ($< 10 \mu\text{eq L}^{-1}$), an indication that the catchments are far from N

97 saturation (Àvila et al., 2010; Àvila and Rodà, 2012). In this study, we elaborate on these
98 temporal patterns in atmospheric N and S concentration in precipitation and stream water to
99 investigate the mechanisms underlying the observed changes at the catchment level.

100 We performed variance and trend analysis in precipitation (17-years record) and stream
101 water time series (>10-year record) in two nested catchments with different topographic
102 characteristics and vegetation cover. The smaller one was fully covered by holm oak (*Quercus*
103 *ilex* L.) while the larger one, besides holm oak, also had heathlands with N-fixing species. We
104 also used stream water data from a third nested catchment fully covered with heathland (only 3-
105 year record) for complimentary analysis. We focused on SO_4^{2-} and inorganic N, and used Cl^- as a
106 conservative solute little affected by biogeochemical processes that is an excellent tracer of
107 hydrological processes through catchments (Jones et al., 2006; Kirchner et al., 2000). The mean
108 travel time of water and solutes was inferred through time series analysis, a statistical approach
109 based on the idea that catchments not only do modify the magnitude of solute concentrations
110 coming from atmospheric inputs, but also their variability (Kirchner et al., 2000; Kirchner et al.,
111 2010; Zhang and Schilling, 2005). Highly variable solute concentrations in precipitation are
112 damped as water from many precipitation events is stored and mixed in the catchment, so that the
113 overall variance of solute concentration in precipitation is higher than in runoff time series, which
114 typically show long-term correlations. We considered both the time lag up to which time series
115 had some degree of correlation and the ratio between the variance of precipitation and runoff time
116 series as proxies of the mean residence time of water and solutes within the catchment (Frank,
117 2009; Kirchner et al., 2010).

118 Our goal was to gain insights on the potential hydrological and biogeochemical
119 mechanisms controlling the response of these two montane catchments to atmospheric changes,
120 and to compare their response to that reported for catchments from other geographical regions.

121 Very few studies have been conducted in Mediterranean environments addressing these issues on
122 water and solute residence time in catchments and here we provide the first results aiming at
123 elucidating the hydrochemical processes controlling them. We hypothesized that the existence of
124 preferential flow paths in these catchments will limit the contact time between solutes and biota
125 in the soil-root zone, fastening the response of stream water chemistry to changes in atmospheric
126 nutrient inputs. Thus, we expected that mean travel time of non-limiting nutrients, such as SO_4^{2-} ,
127 will approach that of conservative solutes (Cl^-), while the mean travel time of N will be strongly
128 controlled by biota. Further, we expected that the catchment with heathlands, a community that
129 includes N-fixing species, will be enriched in N, and thus more N saturated (*sensu* Aber et al.,
130 1998), compared to the oak catchment. Consequently, we hypothesized that the oak catchment,
131 more N limited, will retain N more efficiently and thus, its streamwater chemistry would be less
132 responsive to changes in atmospheric N inputs than the catchment with heathlands.

133 2. Study Sites

134 The precipitation sampling site and the studied catchments belong to the experimental
135 study site of La Castanya Biological Station (LC, 41° 46'N, 2°21'E) located in the Montseny
136 massif, 40 km NNE from Barcelona (Fig. 1). Most of Montseny is forested, and 75% of its surface
137 is protected as a natural park and biosphere reserve. Forests of evergreen holm oak cover about
138 50% of the Montseny natural park, while beech (*Fagus sylvatica*) forests cover 14%. Heathlands
139 and grasslands dominate at higher altitudes and represent 9% of the Montseny surface (Catalan
140 Land Cover Map, MCSC, www.creaf.uab.es/mcsc/). Heathlands are dominated by *Calluna*
141 *vulgaris*, *Cytisus scoparius* (a N_2 -fixing shrub), *Juniperus communis*, *Erica arborea*, *Erica*
142 *scoparia*, and *Pteridium aquilinum*.

143 The Torrent de la Mina stream is gauged at several places producing the two studied
144 nested catchments TM9 (and TM5, only used for complimentary analysis) within a larger one,

145 TM0 (Fig. 1 and Table 1). The TM9 stream drains a steep slope small catchment (5.9 ha, mean
146 slope 35°) totally covered by holm oak forest with a 5- to 9-m high closed canopy. The TM5
147 stream drains heathlands in the upper part of TM0, which has gentler slopes (mean slope 11°; Fig.
148 1 and Table 1). TM0 is the largest catchment (205 ha, mean slope 26°) and it is conformed by two
149 distinct physiographic units: holm oak and beech forests on very steep slopes and heathlands in
150 the upper part with gentler slopes (Fig. 1 and Table 1). Holm oak forests in these catchments were
151 heavily exploited for charcoal production until ca. 1955 and later on they have remained
152 undisturbed. Fire has not occurred in the forested parts of the catchment in the last century, but
153 burning was periodically applied in some parts of the heathlands and grasslands until the late
154 1980s to improve the land for pasture though not affecting TM5 (Belillas and Rodà, 1991).

155 The climate is subhumid meso-Mediterranean. The mean annual air temperature varies
156 with altitude and aspect, from 9.5°C on the north-facing slope at 1250 m a.s.l. to 13°C on the
157 lower reaches of the west-facing slope (data from May 1993 to December 2002). Annual
158 precipitation averaged 868 mm year⁻¹ for the period 1983-2010 at the LC meteorological station.
159 Summer drought is attenuated by frequent orographic, short-lived storms. Snowfall accounts on
160 average for only 3% of annual precipitation and snowpacks are sporadical and short-lived. During
161 the study period, there was a large interannual variability of annual precipitation (623-1529 mm
162 year⁻¹) and runoff (average TM0 and TM9: 95-882 mm year⁻¹), as expected for Mediterranean
163 climate (Latron et al., 2009). There was no significant temporal trend, over the study period, for
164 precipitation, runoff, or for the runoff/precipitation ratio at the annual scale (in all cases,
165 correlation coefficient (r) <0.26 and p >0.05). No significant trend over time was observed either
166 for monthly precipitation, annual maximum daily precipitation or the 90th percentile of annual
167 precipitation (in all cases, r <0.2 and p >0.05). The lack of temporal trends in water inputs and
168 outputs for the study period supports that temporal changes in stream water chemistry during this

169 period of study were related to changes in precipitation chemistry rather than to changes in
170 rainfall, evapotranspiration, or runoff temporal patterns.

171 The bedrock at LC is a metamorphic phyllite, with quartz, chlorite, albite, and muscovite
172 as major minerals. The relief of the side slopes of the catchment is rugged with rock outcrops
173 breaking the forest canopy continuum. Soils on the steep slopes of the Torrent de la Mina
174 catchment are shallow with an organic layer 0-5-cm deep and an average total depth of 60 cm
175 (based on 10 soil profiles excavated until the bedrock; Hereter and Sánchez, 1999). Spatial
176 heterogeneity is high because of the rugged topography. Most of the soils in the slopes are
177 colluvial with discontinuities in the distribution of the very abundant stones and little vertical
178 distinction in morphological features. They are classified as Entisols (Lithic Xerorthents) or
179 Inceptisols (Typic, Lithic or Dystric Xerochrepts; Soil Survey Staff, 1992). The main pedogenetic
180 process is the formation of a cambic horizon, with moderate illuviation (Hereter, 1990). Soils at
181 the rolling slopes of the upland plateau have a 3-cm depth organic layer and a 19-cm depth A-
182 horizon (averaged from 29 soil profiles). The soil organic carbon content is higher at the upland
183 plateau than at the steep slopes in both the O-horizon (13.1% vs. 9.6%) and the A-horizon (6.2%
184 vs. 2.3%). The soils in the slopes are acidic (pH in water from 4.6 to 5.3), acidity being buffered
185 mainly by silicate weathering and cation exchange. Calcium is the dominant exchangeable base
186 cation, and it is especially abundant in the upper organic soil ($9.5 \text{ cmol}_c \text{ kg}^{-1}$) for a cation
187 exchange capacity (CEC) of $16.4 \text{ cmol}_c \text{ kg}^{-1}$. In the mineral soil, base saturation is low (37%),
188 with Ca and Mg amounting to 1.5 and $1.4 \text{ cmol}_c \text{ kg}^{-1}$ respectively for a CEC of $10.9 \text{ cmol}_c \text{ kg}^{-1}$.
189 There is a significant positive relationship between CEC and the content of soil organic matter
190 (Hereter, 1990).

191 **3. Material and Methods**

192 *3.1. Field sampling and chemical analysis*

193 Atmospheric bulk deposition was sampled weekly with four (July 1983-June 1996) or two
194 (July 1996-Dec2000) replicate funnel-type collectors. These collectors consisted of a 19-cm
195 diameter polyethylene funnel connected by a looping tygon tubing to a 10-L bucket placed 1.5 m
196 above the ground. To gauge stream discharge, the TM0 catchment was equipped with a 120° V-
197 notch weir and both TM9 and TM5 with a 60° V-notch weir each. Water level was continuously
198 measured with a stage recorder (Weather Measure™ at TM9 and TM5, OTT™ at TM0).

199 The recording period for discharge and stream water chemistry was different for each
200 catchment, but coincident in some part of the record: from 8/10/1983 to 11/19/1985 for TM0,
201 10/22/1982 to 11/14/1985 for TM5; and from 8/10/1983 to 12/31/1997 for TM9. The sampling of
202 TM0 was restarted later, from 9/10/1990 to 12/20/1999. No more recent data are available for
203 TM5. Grab samples of stream water were collected weekly several meters upstream from the
204 stilling pond with an approximately weekly schedule. They were collected in high-density
205 polyethylene 250-ml bottles previously rinsed with distilled deionized water and triple-rinsed with
206 sample water. More frequent samples (15-60 min depending on stormflow shape) were obtained
207 during storms at TM9 with an automatic sampler from 1983 to 1989.

208 Stream solute concentration can vary substantially during storms when superficial overland
209 flow and shallow subsurface flow can contribute significantly to runoff generation (Àvila et al.
210 1992; Bernal et al., 2005). This variation in solute concentration affects the total variance of the
211 chemical time series, thus modifying the results obtained through variance analysis. Some authors
212 have already cautioned about results obtained from data series that combine high-frequency
213 sampling during storms with low-frequency sampling during baseflow conditions (Feng et al.,
214 2004), as is the case for the TM9 catchment. In order to make the variance of solute

215 concentrations and the mean travel time estimates comparable between TM0 and TM9
216 catchments, we excluded stormflow samples from TM9. This was accomplished through the
217 separation of quickflow (here equated to stormflow) and delayed flow (here baseflow) based in
218 Hewlett and Hibbert (1967) proposal with the partition calculated from the beginning of the
219 hydrograph using a constant incremental value of $0.537 \text{ L s}^{-1} \text{ km}^{-2} \text{ h}^{-1}$. Only samples below this
220 threshold value were considered baseflow samples, and thus, retained for data series analysis.
221 These baseflow samples accounted for ~ 70% of total flow, which consistently matched with the
222 groundwater contribution estimated for these catchments (Neal et al., 1995). Streamwater samples
223 from TM5 covered a too short period for time trend analysis and were used as complimentary
224 data.

225 Bulk deposition and streamwater samples were retrieved to the laboratory the same day of
226 collection and measured for conductivity, pH and alkalinity. Then they were filtered with $0.45 \mu\text{m}$
227 pore-size cellulose acetate filters and aliquots were stored ($-20 \text{ }^\circ\text{C}$) until analysis. Major ions
228 (NH_4^+ , NO_3^- , SO_4^{2-} and Cl^-) were analysed by ion chromatography. Analytical precision and
229 accuracy were checked routinely using external references (National Bureau of Standards,
230 reference materials 2694-I and 2694-II) and by participating in European intercalibrations
231 (AQUACON MEDWAS, Mosello et al. 1998) with excellent results.

232 3.2. Data analysis

233 3.2.1. Basic statistical analysis and two-component mixing model

234 We calculated the arithmetic average (AA), standard deviation (SD), and volume-
235 weighted average (VWA) of solute concentrations for bulk precipitation and baseflow stream
236 water for the whole period of study. Moreover, VWA was calculated for each water year, defined
237 from 08/01 to 07/31. For precipitation time series, VWA was calculated by multiplying weekly
238 solute concentration (in $\mu\text{eq L}^{-1}$) by weekly volume of precipitation (in L m^{-2}), summing up the

239 obtained values for the period of interest and dividing it by the total volume of precipitation
240 recorded for the same period. For stream water time series, VWA was calculated by multiplying
241 instantaneous solute concentration (x_i , in $\mu\text{eq L}^{-1}$) by stream discharge between successive time
242 steps corresponding to the sample x_i (D_i , in L). For each time step, D_i was calculated as:

$$243 \quad D_i = q_i(t_i - t_{i-1}) - \frac{(t_i - t_{i-1})(q_i - q_{i-1})}{2} \quad (1)$$

244 being q instantaneous stream discharge (in L s^{-1}). We summed up the obtained values for the
245 period of interest ($\sum x_i D_i$) and divided it by the accumulated stream discharge for the same
246 period ($\sum D_i$).

247 Linear regression analysis was used to analyze annual long-term trends of VWA solute
248 concentration in precipitation and baseflow stream water. To analyze differences in baseflow
249 solute concentration between streams, we applied the Wilcoxon rank sum test (Helsel and Hirsch,
250 1992).

251 We developed a simple two-component mixing model to infer whether stream water
252 chemistry at TM0 was influenced by the presence of heathlands at the upper plateau. We used
253 VWA concentrations from the TM9 (period 1983-1997) and TM5 (period 1983-1985) streams as
254 a proxy of the chemical signature of the forest (67.3% of the area) and heathland (30.5% of the
255 area) units comprised in TM0, respectively. Then, we calculated the expected stream solute
256 concentration for Cl^- , SO_4^{2-} , and DIN based solely on mixing processes. We had to assume that
257 the chemical signature of the heathland unit (only available for a 3-years period) did no change
258 over time. To ensure that differences between expected and measured VWA concentration at
259 TM0 did not result from changes over time not captured by the available TM5 data, we
260 recalculated expected VWA concentrations for the three solutes using data for the period 1983-
261 1985 only.

262 3.2.2. Analysis of variance and variography

263 For each chemical time series, we calculated the total variance (σ^2) that includes the
264 variation from long-time scales (seasonal, year-to-year variation, long-term trends) to short-time
265 scales (monthly, weekly variation). To analyze only the short-term variability but not the
266 variability due to long-term correlations, we calculated the variance between adjacent data points
267 or lag-1 semivariance (γ_{lag-1}):

268
$$\gamma_{lag-1} = \frac{1}{2(n-1)} \sum_{i=1}^{n-1} (x_{i+1} - x_i)^2. \quad (2)$$

269 In our case, γ_{lag-1} included the variability arising from correlations at time-scales of weeks
270 because the mean frequency of the samples in the data set was 6 days. Time series without long-
271 term correlations show $\gamma_{lag-1} \sim \sigma^2$, while time series with strong long-term correlations show γ_{lag-1}
272 $\ll \sigma^2$ (Shröder, 1991). Long-term correlations are typically stronger in stream runoff than in
273 precipitation time series because water inputs are stored and mixed within the catchment. Thus,
274 γ_{lag-1} of stream runoff is lower and differs more from σ^2 than γ_{lag-1} of precipitation (Kirchner et al.,
275 2010). The damping ratio between γ_{lag-1} in precipitation and γ_{lag-1} in runoff (γ_P/γ_R) can be
276 interpreted as a roughly measure of the mean travel time of water or the mean residence time of
277 solutes in catchments (Frank, 2009; Kirchner et al., 2010). We used γ_{lag-1} instead of σ^2 to calculate
278 γ_P/γ_R because the former is robust against long-term correlations (Kirchner et al., 2010).

279 We extended the variance analysis by performing a semivariogram analysis or
280 variography to explore the structure of the variance of solute concentrations not only between
281 adjacent points in the time series (lag-1), but also across different time lags. We chose
282 semivariogram analysis because our chemical time series were not evenly spaced which
283 complicates the application of other statistical techniques such as spectral analysis or
284 autocorrelation analysis (Chatfield, 2004). Semivariograms plot the semivariance at different lag

285 times ($\gamma(h)$), that is the average dissimilarity between data values separated by a lag time h
286 (Chatfield, 2004; Rossi et al., 1992), and they are useful to explore the degree of autocorrelation
287 of environmental variables across time scales (Fortin and Dale, 2005; Legaard and Thomas,
288 2007).

289 Flat semivariograms are indicative of time series with neither short-term nor long-term
290 correlations, and they are best fitted with a random model (Fig. 2, pure nugget model). Time
291 series with some degree of temporal correlation are characterized by a small $\gamma(h)$ at short time
292 lags, which then increases with h until reaching a plateau or sill once the data points become
293 independent from each other. Three key parameters are estimated by fitting a theoretical spherical
294 model to the empirical semivariogram: the nugget effect (C_o), the range (A_o), and the sill (C_l)
295 (Fig. 2, spherical model). The C_o is the *unstructured* variation that accounts for both the variance
296 at time scales shorter than sampled and any random effect or measurement error included in the
297 time series (Li and Reynolds, 1995). The A_o indicates the time lag up to which the time series has
298 some degree of correlation or memory in the concentration time series due to the mixing
299 processes in the catchment, and it is a proxy of the mean residence time (Kirchner et al., 2010). In
300 our study, the mean residence time estimate was biased towards baseflow conditions because
301 solute concentrations during stormflow were excluded from the data analysis. The difference
302 between C_o and C_l , the value of $\gamma(h)$ at the plateau, is the partial sill C that accounts for the
303 *structured* variation or the amount of variance due to the temporal dependence (Li and Reynolds,
304 1995). The stronger the autocorrelation in a time series, the larger is the C/C_l ratio. When the
305 long-term correlations of the time series extend for longer time lags than the duration of the study
306 period, the $\gamma(h)$ does not level off and it keeps rising with increasing h for the whole range of
307 available time scales (Fig. 2, linear model).

308 We used ordinary least squares to fit $\gamma(h)$ to theoretical models, and we used R^2 as a
309 measure of the goodness of fit. If the linear and spherical models resulted in similar R^2 , we
310 choose the linear one (Diggle and Ribeiro, 2007). Statistical analyses were performed with R
311 (spline and geoR packages).

312 **4. Results**

313 *4.1. Precipitation and streamwater solute concentrations*

314 Solute concentration in precipitation ranged over two orders of magnitude for Cl^- , SO_4^{2-}
315 and NO_3^- from 1983 to 1999 (Table 2; Fig. 3 grey lines). Ammonium exhibited the highest range
316 of variation (Table 2). The contribution of NH_4^+ and NO_3^- to atmospheric N deposition was
317 similar (Table 2).

318 Chloride and SO_4^{2-} concentrations in baseflow stream water were less variable than in
319 precipitation with maximum values being 2-3-fold higher than minimum concentrations at TM0
320 and TM9 (Table 2; Fig. 3a and b). Mean Cl^- and SO_4^{2-} concentrations in stream water (either AA
321 or VWA) tripled and quadrupled those in precipitation at TM5, TM0 and TM9 (Table 2). Annual
322 VWA concentrations at TM9 were significantly higher than at TM0 for Cl^- and SO_4^{2-}
323 (Wilcoxon/Kruskal Wallis Rank Sum test; Cl^- : $z = -2.7$, $p = 0.0067$; SO_4^{2-} : $z = -2.7$, $p = 0.0062$)
324 (Fig. 4a and b).

325 Ammonium concentration in stream water was always below the analytical detection limit
326 ($0.5 \mu\text{eq L}^{-1}$), therefore dissolved inorganic N (DIN) data in stream water refer only to NO_3^-
327 (Table 2). DIN concentration (VWA) in stream water was 5-, 8-, and 50-fold lower than DIN
328 concentration in atmospheric deposition at TM5, TM0, and TM9, respectively (Table 2). DIN
329 concentration (VWA) in stream water was lower at TM9 than at TM0 (Table 2). However, there
330 were no significant differences in annual VWA concentration of DIN between TM9 and TM0
331 (Wilcoxon/Kruskal Wallis Rank Sum test; $z = 1.67$, $p = 0.09$).

332 The two-component mixing model used to infer the influence of the forest and heathland
333 units on TM0 stream water chemistry indicated that the expected and observed Cl^- mean
334 concentrations differed by $< 10\%$ (93.9 vs. 87.4 $\mu\text{eq L}^{-1}$, respectively). For SO_4^{2-} , the expected
335 concentration (182.8 $\mu\text{eq L}^{-1}$) was 16% higher than the measured concentration (157 $\mu\text{eq L}^{-1}$).
336 The expected concentration of DIN for TM0 (6.9 $\mu\text{eq L}^{-1}$) was 27% higher than the observed one
337 (5.5 $\mu\text{eq L}^{-1}$). We obtained a similar result for Cl^- when we recalculated expected concentrations
338 for the period 1983-1985. For SO_4^{2-} , the expected and measured concentrations for the period
339 1983-1985 were similar (188.8 vs. 182.2 $\mu\text{eq L}^{-1}$). For DIN, the expected DIN concentration for
340 TM0 (6.7 $\mu\text{eq L}^{-1}$) was similar for the period 1983-1985 to that obtained for the whole period,
341 however, during those years DIN concentration at TM0 was very much lower (0.5 $\mu\text{eq L}^{-1}$).

342 *4.2. Long-term trends of solute concentrations*

343 The interannual precipitation trend of SO_4^{2-} concentration (VWA) from 1983 to 1999
344 showed a significant decrease of 45% at a rate of 1.4 ± 0.3 (mean \pm std. error) $\mu\text{eq L}^{-1} \text{y}^{-1}$, as
345 estimated by the linear regression slope ($r^2 = 0.64$, $p < 0.001$, $df = 16$; Fig. 4b). Nitrate
346 concentration in atmospheric deposition increased slightly during this period, but the trend was
347 not statistically significant ($r^2 = 0.18$, $p = 0.085$, $df = 16$). Considering the sum of NH_4^+ and NO_3^- ,
348 there was no trend in annual DIN concentration in precipitation from 1983 to 1999 (Fig. 4c).

349 Annual Cl^- concentration at both streams, TM9 and TM0, did not show any significant
350 trend from 1983 to 1999 (Fig. 4a). In contrast, annual SO_4^{2-} concentration declined at TM9 and
351 TM0 at a rate of 1.4 ± 0.8 and 3.4 ± 1 $\mu\text{eq L}^{-1} \text{y}^{-1}$, respectively. However, this temporal trend was
352 only significant for TM0 ($r^2 = 0.62$, $n = 11$, $p = 0.0039$).

353 The TM0 stream showed no significant trend in NO_3^- concentration over time (Fig. 4c).
354 Nitrate concentration at the TM9 stream tripled between 1983 and 1997, increasing at a rate of

355 0.09 $\mu\text{eq L}^{-1} \text{y}^{-1}$ though this trend was only marginally significant ($r^2 = 0.27$, $n = 14$, $p = 0.06$;
356 Fig. 4c).

357 4.3. Variance analysis of solute concentrations

358 The σ^2 of Cl^- and SO_4^{2-} concentration in stream water was damped compared to
359 atmospheric inputs (5 and 7 times for Cl^- , 3 and 4 times for SO_4^{2-} at TM9 and TM0 respectively;
360 Table 2). The σ^2 of DIN in stream water was two orders of magnitude lower than in precipitation
361 for both streams (Table 2). At the TM5, the σ^2 of stream Cl^- concentration was similar to
362 precipitation whereas the σ^2 of DIN in stream water was 4 times lower than in atmospheric
363 deposition (Table 2).

364 The γ_{lag-1} of solute concentration in precipitation time series was lower than its σ^2 , by 8%
365 (Cl^-) and 20% (SO_4^{2-} and DIN). In stream water, differences between the γ_{lag-1} and σ^2 were more
366 pronounced: at least 40% for both, Cl^- and SO_4^{2-} . The smallest difference between σ^2 and γ_{lag-1} for
367 stream water time series was shown by DIN at TM0 (Table 2).

368 At the TM0 and TM9 streams, the γ_P/γ_R ratio for Cl^- ranged between 15 and 18 which
369 mean that the fluctuations in Cl^- precipitation time series were averaged in 15-18 stream water
370 samples (so, weeks). The SO_4^{2-} γ_P/γ_R ratio was lower than for Cl^- , and it was 2-fold lower at TM9
371 than at TM0 (Table 2), suggesting less damping of SO_4^{2-} concentrations at TM9. The γ_P/γ_R ratio
372 for DIN at the TM0 and TM9 streams was between one and two orders of magnitude larger than
373 for Cl^- and SO_4^{2-} (Table 2). The TM5 stream showed the smallest γ_P/γ_R ratios for the three solutes
374 (Table 2).

375 The empirical semivariograms $\gamma(h)$ calculated from solute concentration time series
376 showed contrasting patterns between precipitation and stream water. For the three studied solutes,
377 the $\gamma(h)$ s obtained from the precipitation time series were flat and did not show any clear trend
378 with increasing h as expected for a pure nugget model (Fig. 5). Consequently, the linear and

379 spherical models did not fit the empirical data. In contrast to precipitation, the $\gamma(h)$ s obtained from
380 the stream water chemical time series showed that the fluctuations of solute concentration were
381 consistently structured for Cl^- and SO_4^{2-} . The $\gamma(h)$ increased gradually over the first ~ 18-20 weeks
382 for Cl^- until reaching a plateau (Fig. 5a). The $\gamma(h)$ for SO_4^{2-} increased more abruptly than for Cl^- ,
383 levelling off after the first ~ 9-12 weeks (Fig. 5b). For both Cl^- and SO_4^{2-} , the goodness of fit was
384 higher for the spherical model than for the linear model (Table 3). The structured variation was
385 larger at TM0 than TM9 as indicated by the C/C_I index (Table 3). The $\gamma(h)$ for stream water
386 concentrations of both, Cl^- and SO_4^{2-} , fluctuated around the sill following a clear 52-weeks annual
387 cycle. This pattern was especially noticeable for the TM0 stream (Fig. 5a and b).

388 The $\gamma(h)$ for DIN did not level off but increased gradually with h at the TM0 stream (Fig.
389 5c). In this case, the linear model was a good predictor of the structure of DIN fluctuations (Table
390 3). At the TM9 stream, the $\gamma(h)$ obtained from the DIN time series was flat as expected from a
391 pure nugget model, and did not show any seasonal pattern (Fig. 5c). The fact that stream NO_3^-
392 concentration at TM9 was under the detection limit most of the time may affect the
393 semivariogram analysis, thus limiting its interpretation.

394 **5. Discussion**

395 *5.1. Differences in the catchment response to long-term changes in atmospheric deposition.*

396 Atmospheric deposition of S all over Europe and North America started decreasing in the
397 late 1980s as a result of the implementation of transboundary amendment programs to deal with
398 ecosystem acidification (Aber et al., 1998; Reuss and Johnson, 1986; Shannon, 1999). At the
399 Montseny Mountains, sulphate in precipitation started decreasing as soon as the amendment
400 protocols were established, and it decreased by 45% ($1.4 \mu\text{eq L}^{-1} \text{y}^{-1}$) between 1983 and 1999, an
401 amount similar to that reported in other parts of Europe and North America for the same period
402 (Stoddard et al., 1999; Watmough et al., 2005). Both streams, TM0 and TM9, were highly

403 responsive to this change in atmospheric deposition as indicated by the decreasing trend in
404 streamwater SO_4^{2-} concentration between 1983 and 1999. The magnitude of such decline over
405 time was similar to that observed in precipitation and it was on the range of values reported for
406 other streams in Europe and North America (from 0 to $5.9 \mu\text{eq L}^{-1} \text{y}^{-1}$; Stoddard et al., 1999;
407 Watmough et al., 2005). These findings indicate that catchments in the Mediterranean region
408 experience sizable changes in response to changed atmospheric deposition similar to those
409 described in more polluted environments in central and north Europe.

410 Changes in atmospheric deposition of DIN concentration over the period 1983-1999 were
411 not as marked as for SO_4^{2-} since there was a significant increase for NO_3^- but no significant trend
412 for NH_4^+ (Àvila et al., 2010). Similarly, no clear trend in the atmospheric deposition of DIN has
413 been reported across Europe and North America (Oulehle et al., 2011; Stoddard et al., 1999).
414 However, stream DIN concentrations increased significantly (by 3-fold) at the TM9 stream for
415 the period 1983-1997 suggesting that ecosystem retention was declining. These findings were
416 supported by a recent study showing that, for 23 headwater streams draining comparable small
417 catchments in the Montseny Mountains, nitrate concentrations in 2007 were significantly higher
418 than in the early 1980s (Àvila and Rodà, 2012). These results suggest that these forests may be
419 responding to the chronic atmospheric N deposition of $15\text{-}30 \text{ kg N ha}^{-1} \text{y}^{-1}$ experienced at least
420 since the early 1980s (Àvila et al., 2010). However, low stream DIN concentrations all year
421 around indicated that the ecosystem is still far from N saturation.

422 In contrast to TM9, stream DIN concentration did not significantly increase over time at
423 the TM0 and thus, it appears not to be as affected by chronic N deposition as TM9. Yet, this
424 stream showed significantly higher DIN concentration than TM9, which supports the expectation
425 that TM0, with heathland N-fixing species in its upper part, was more enriched in N than TM9,
426 fully covered by holm oak. The mixing model based on stream solute concentrations from TM5

427 (heathland) and TM9 (holm-oak, taken to represent the forested part of the catchment) indicated a
428 proportional contribution of the different vegetation units of the TM0 catchment (67% forest and
429 30% heathland) to its stream water chemistry for Cl^- and SO_4^{2-} . This result was corroborated
430 when we recalculated expected concentrations for the period with data from TM5 only (1982-
431 1985). Instead, DIN concentration predicted for TM0 by the mixing model tended to be
432 substantially higher than measured empirically. We acknowledge that our model predictions are
433 limited because stream water chemistry for TM5 was available only for a 3-year period.
434 However, the estimated difference between expected and observed DIN concentration could have
435 been even higher if DIN at the TM5 stream would have increased over time as observed for TM9.
436 Overall, our results indicated that the drainage of the heathlands resulted in increased DIN
437 concentration at TM0, yet this vegetation unit had a disproportionately lower influence on stream
438 water chemistry at the TM0 outlet than expected solely by mixing processes. This result could be
439 explained by assimilation of DIN by biota along the 1.8 km of stream channel and riparian zone
440 separating the outlet of TM5 and the TM0 weir station as reported for other temperate and
441 Mediterranean catchments (Bernal and Sabater, 2012; Mulholland, 2004).

442 *5.2. Differences in the residence time of water and solutes between catchments.*

443 Chloride is considered as a natural tracer, whose inputs from precipitation circulate
444 conservatively within a catchment and thus this solute has been broadly used in hydrologic studies
445 to trace transport, storage and mixing of water compartments (e.g., Kirchner et al., 2001; Neal and
446 Kirchner, 2000; Neal and Rosier, 1990). In the Montseny catchments, Cl^- was about three times
447 higher in stream water than in precipitation, as expected for catchments with high evaporative
448 demand. This increase reflected mostly the concentrating effect of evapotranspiration because
449 annual input-output catchment budgets for Cl^- (including both base and stormflow samples)

450 showed a net balance close to zero for a similar period of study (1983-1994; Àvila et al., 1999),
451 thus discounting any substantial contribution from unmeasured dry or occult Cl⁻ deposition.

452 The variability of Cl⁻ concentrations in stream water was strongly damped relative to that
453 in precipitation indicating that new water inputs from precipitation mixed with old ones already
454 stored in groundwater, a consistent result with previous studies from isotope analysis (Neal et al.
455 1992). We analyzed the variance of the Cl⁻ time series with two different approaches and we used
456 both, the Cl⁻ damping ratio γ_p/γ_s , and the range ($A\sigma$) of the semivariogram for Cl⁻ streamwater time
457 series as a proxy of the mean residence time of water in the Montseny catchments. Both analyses
458 suggested that the groundwater compartment may be small in both catchments as indicated by a
459 mean residence time of water of around 15-20 weeks (4-5 months), in spite of TM0 being 33-fold
460 larger in catchment area than TM9. Our results are concordant with previous studies showing that
461 there is no relationship between mean residence time of water and the size of headwater
462 catchments (McGlynn et al., 2003; McGuire et al., 2005; Soulsby and Tetzlaff, 2008).

463 In contrast to catchment size, topography has been identified as a key factor determining
464 water transport, and thus, mean travel times through catchments. Simple topographic indices such
465 as mean catchment slope have been shown as good proxies of mean residence time of water in
466 catchments (McGuire et al., 2005; Soulsby and Tetzlaff, 2008). However, we found only a slight
467 difference in the residence time of water between the studied catchments (2-3 weeks lower at
468 TM9 than at TM0), though the slope at TM9 was substantially higher than at TM0 (mean slope
469 35° vs. 26°). Thus, our results suggest that differences in topography between these two nested
470 catchments were not large enough to result in substantial differences in their water mean residence
471 time.

472 The mean residence time of water in the Montseny catchments (4-5 months) was low when
473 compared to that reported for montane catchments at the H.J. Andrews forests in north-western

474 United States (1-3 years, McGuire et al., 2005), the only published study that we are aware
475 reporting mean residence time estimates for catchments as steep as ours (between 26°-35° and 15°-
476 30° for the Montseny and the H.J. Andrews forests, respectively). This difference suggests that
477 some other factors in combination with steep slopes must come into play when explaining the
478 rapid movement of water through the Montseny catchments. In addition to topography, major
479 water flow paths in catchments strongly depend on soil hydrological properties (infiltration
480 capacity, porosity), with high responsive soils favouring low water residence times. Tetzlaff et al.
481 (2009) showed that residence time of water was better explained by soil hydrological properties
482 than by topography in catchments at the Cairngorm Mountains of Scotland, where residence time
483 was lower in catchments dominated by overland flow and shallow subsurface storm flow than in
484 catchments with deep subsurface flows. Our estimates are on the low range of those reported for
485 the Scottish catchments (from 2-15 months) and thus, the low residence time of water estimated
486 for the Montseny catchments could result from a low groundwater contribution which could be
487 favoured by the extremely shallow and stony soils at the study site. However, previous work has
488 shown that groundwater dominates the baseflow stream runoff (that is what was analyzed here)
489 and accounts for the major part (~70%) of the annual stream runoff in these catchments (Neal et
490 al., 1995). Therefore, our results suggest the existence of a quick transmission path connecting
491 precipitation inputs to subsoil major flow paths toward the stream channel.

492 Previous studies on soilwater chemistry at Montseny suggested the existence of
493 preferential flow paths connecting soil superficial flows with subsurface flows, especially during
494 wet periods when baseflow stream water was a mixture of groundwater and soil subsurface flow
495 (Àvila et al., 1995). In contrast, during dry periods subsurface areas were reduced and soils were
496 likely disconnected from the stream, which was mainly fed by groundwater (Àvila et al., 1995).
497 This marked seasonality in the groundwater level between dry and wet periods, which is

498 accentuated in catchments with high evaporative demand, could have profound implications in
499 the travel time of water and solutes through catchments because water is stored for shorter periods
500 in shallow than in deep groundwater (Asano et al., 2002; Soulsby et al., 2000). The seasonality of
501 stream water chemistry is related to such temporal pattern in hydrological flow paths, with
502 increased concentration of atmospherically derived compounds in winter when the water table is
503 high and shallow groundwater contributes to baseflow stream runoff (Rice and Bricker, 1995).
504 The marked annual seasonality of atmospheric derived compounds, Cl^- and SO_4^{2-} , exhibited by
505 both study catchments supports that hydrological flow paths were strongly seasonal at the
506 Montseny Mountains. This seasonality in groundwater level in combination with the steep slopes
507 and the role of macropore flow bypassing the soil matrix during wet periods could explain the
508 small residence time of water in the Montseny catchments compared to other catchments reported
509 in the literature.

510 The hydrological processes governing the fast drainage of water toward the stream channel
511 in these Mediterranean catchments may facilitate the circulation of atmospheric inputs through the
512 catchment and thus, one might expect a high responsiveness of these catchments to changes in
513 atmospheric deposition. We analyzed the mean residence time of SO_4^{2-} and DIN, two solutes that
514 in contrast to Cl^- are subject to strong biogeochemical processing and can be stored in the plant
515 and soil pools (particularly DIN), which in principle may increase their mean residence time in the
516 catchment. Yet, we expected small differences between the mean residence time of these solutes
517 and Cl^- because water circulated quickly through the catchment toward the stream. As observed
518 for Cl^- , SO_4^{2-} concentration was several times higher in stream water than in precipitation, and its
519 semivariance exhibited a seasonal pattern, especially for TM0. Yet, both the damping ratio γ_p/γ_s
520 and the A_0 were substantially lower for SO_4^{2-} than for Cl^- , suggesting a mean residence time of
521 SO_4^{2-} between 1.5 and 3 months at the TM9 and TM0 catchments. Such unexpected low mean

522 residence time of SO_4^{2-} could be explained by the release of S previously adsorbed in the soil
523 during periods of high S deposition in the past, a catchment internal source that has been
524 documented in many forested catchments of North America and Europe (Mitchell and Likens,
525 2011; Mitchell et al., 2011). Previous average input-output budgets showed that, in contrast to Cl^- ,
526 there was a net loss of S of $\sim 3 \text{ kg ha}^{-1} \text{ y}^{-1}$ (balance between 6.3 and 9.3 $\text{kg S ha}^{-1} \text{ y}^{-1}$ in inputs and
527 outputs; Àvila et al., 1999), which probably corresponded to dry deposition since a net throughfall
528 flux of $1.2 \text{ kg S ha}^{-1} \text{ y}^{-1}$ ($\sim 17\%$ of input fluxes) was measured in TM0 holm oak plots during the
529 1990s (Bellot et al., 1999). Net throughfall Cl^- fluxes were related to lixiviation of internal Cl^-
530 pools in oak leaves rather than to dry deposition (Bellot et al., 1999). Nutrients deposited over soil
531 and plant surfaces during dry periods are washed during rainfalls, becoming available to soil biota
532 in high concentration pulses that could exceed nutrient demand, especially for non-limiting
533 nutrients such as sulphate. We propose that this excess of nutrients could pass through the
534 biological active soil with minimal interaction escaping from soil and vegetation storage, which
535 could potentially reduce the residence time of nutrients in the catchment. This feature is probably
536 more accentuated in Mediterranean catchments compared to humid ones where dry deposition is
537 more continually incorporated into soils by a more constant precipitation. Future studies reporting
538 mean residence time for conservative vs. non-conservative solutes in different regions of the
539 world are needed to test this hypothesis.

540 Finally, the variography of stream water time series of DIN, the most bioreactive solute
541 included in this study, exhibited a dramatic distinct behaviour related to Cl^- and SO_4^{2-} . First, its
542 concentration in stream water was damped by two orders of magnitude compared to precipitation.
543 Second, the semivariogram of NO_3^- concentration time series did not level off until reaching time
544 lags of decades for the TM0 stream, and did not shown any clear seasonal pattern. These results
545 bear the idea that these catchments are still N limited and thus, nitrate is highly retained by biota

546 and it remains stored in the ecosystem pools for long time, even if water circulates rapidly through
547 preferential pathways and has low contact time with the rooting zone and soil biota.

548 Our study indicates that fairly undisturbed catchments in this Mediterranean region had a
549 quick response (in the scale of months) to the decreasing trend in SO_4^{2-} atmospheric deposition
550 during the 1980s and 1990s. This responsiveness could be explained by the residence time of
551 water in these catchments which was low compared to values available in the literature from other
552 geographical regions. A steep topography and a quick transmission path connecting precipitation
553 inputs to subsoil major flow paths toward the stream could favour the fast drainage of water
554 through these catchments, while suggesting a small groundwater reservoir. We pose that a large
555 contribution of dry deposition to total atmospheric inputs and the strong seasonality of
556 hydrological flow paths could contribute to reduce the mean residence time of water and solutes in
557 these Mediterranean catchments. However, the impact of different hydrological flow paths during
558 dry and wet periods on water mean residence time may depend on the geologic configuration of
559 the soil-bedrock profile, information that generally is not easy to obtain from catchments. Our
560 results suggest that the resilience of Mediterranean montane ecosystems to environmental changes
561 may be low compared to more humid ecosystems, and thus, changes in management strategies
562 and/or abrupt climatic changes could have dramatic effects of their biogeochemistry. In contrast to
563 S, there was no clear temporal trend in atmospheric N deposition and thus, the catchment response
564 to changing N inputs could not be evaluated. Nevertheless, our results suggest that despite chronic
565 N deposition, this essential nutrient is still highly retained by these ecosystems as indicated by low
566 stream concentrations with no seasonal pattern and the high mean retention time of DIN within
567 the catchment (in the scale of decades). Moreover, we found that heathlands with N-fixing species
568 located at the catchment plateau affected downstream water chemistry significantly, even though
569 they only covered a small area of the catchment (~30%). Recent studies have reported a

570 progressive replacement of heathlands by oak forests (Peñuelas and Boada, 2003). According to
571 our results, this biome shift could result in a substantial decrease in nitrate concentration in stream
572 water, which would counterbalance, at least in part, the expected future increase in stream N
573 export in response to chronic N deposition. This study contributes to illustrate that Mediterranean
574 montane catchments are highly sensitive to environmental changes, and that their vulnerability to
575 anthropogenic pressure can only be assessed with well-designed long-term monitoring
576 programmes covering decades of hydrological and chemical data (Lovett et al., 2007).

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584

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752

753 **Tables**

754 **Table 1.** Geographic characteristics, lithology and vegetation cover of the three monitored
755 subcatchments at the Torrent de la Mina catchment (Montseny Mountains, NE Spain).

Catchment characteristics	TM9	TM0	TM5
Area (ha)	5.9	205	6.8
Altitude Range (m a.s.l.)	710-1036	650-1343	1240-1335
Mean slope (°)	35	25.8	10.8
Orientation	N	NE	NW
Lithology	Metamorphic phyllite	Metamorphic phyllite	Metamorphic phyllite
Vegetation (%)			
Holm Oak	100	52.2	—
Beech	—	15.1	—
Heathland	—	30.5	100

756

Table 2. Statistical descriptors of solute concentration time series in precipitation and the studied streams (TM9, TM0, and TM5).

Solute	Sample type	Min	Max	AA	SD	VWA	σ^2	γ_{lag-1}	γ_P/γ_R	n
		$\mu\text{eq L}^{-1}$						$(\mu\text{eq L}^{-1})^2$		
Cl ⁻	Prec ^a	1.5	234	30.6	34.2	27.6	1169	1080	—	510
	TM9 ^a	60.2	166	96.6	14.7	101	215	74	15	766
	TM0 ^a	64.5	156	96.1	12.6	87.4	159	61	18	474
	TM5 ^a	34.9	268	85.1	43.2	84.9	1232	309	4	128
SO ₄ ²⁻	Prec	4.9	424	59.6	44	41.4	1916	1506	—	510
	TM9	103	288	181	26.2	189	686	243	6	765
	TM0	91.1	246	164.2	21.8	157	477	135	11	469
	TM5	100	127	181.6	25	182.3	496	292	5	127
DIN	Prec NH ₄ ⁺	0.75	242	32.1	30	23.2	886	751	—	509
	Prec NO ₃ ⁻	1.3	228	33	26.9	21.4	722	612	—	510
	Prec DIN ^c	3.3	470	65.1	53.6	44.4	2869	2386	—	509
	TM9 ^b	0.3	40.8	1.1	3.1	0.9	9	4	594	766
	TM0 ^b	0.5	53	1.7	3.5	5.5	12	9	265	484
	TM5 ^b	0.2	162	21.9	33.8	20.9	657	257	9	128

Prec: precipitation, AM: arithmetic average, SD: standard deviation, VWA: volume weighted average, n: number of samples.

σ^2 : variance, γ_{lag-1} : lag-1 semivariance.

γ_P/γ_R : ratio between γ_{lag-1} in precipitation and stream runoff. This ratio is a proxy of the mean residence time of water in weeks.

^a Study periods: 1983-1999 (prec), 1983-1997 (TM9), 1983-1985 and 1990-1999 (TM0), 1982-1985 (TM5).

^b only NO₃⁻, ^c DIN (NH₄⁺ + NO₃⁻).

Table 3. Best-fit parameters and R^2 values obtained by ordinary least squares with the linear and spherical models fitted to the $\gamma(h)$ of TM9 and TM0 solute concentration.

Stream	Solute	Linear model ^a			Spherical model ^a				
		C_0 ($\mu\text{eq L}^{-1}$) ²	Slope	R^2 (%)	C_0	C	A_0 (weeks)	C/C_1	R^2 (%)
					$(\mu\text{eq L}^{-1})^2$				
TM9	Cl ⁻	200.7	0.05	32	129.9	102.2	17.8	0.4	38.6
	SO ₄ ²⁻	642.8	0.07	8.2	401.6	281.9	9.2	0.4	38.6
	DIN	7.5	—	—	7.5	—	—	—	—
TM0	Cl ⁻	137.5	0.03	11.7	61.7	96.7	20.4	0.6	40.6
	SO ₄ ²⁻	315.3	0.07	11.7	90.9	263.7	12.5	0.5	36.3
	DIN	9.8	0.01	55	9.8	59.5	1183	>1	55

C_0 : nugget, C: partial sill or structured variation; A_0 : range, C/C_1 : structured variation index.

^aNeither model fitted either DIN concentration at TM9 or precipitation solute concentration time series.

Figure captions

Fig. 1. Vegetation map (corresponding to year 1993) showing the location of the three study catchments: TM9 (5,9 ha), TM0 (205 ha) and TM5 (6,8 ha). The position of stream gauges and deposition and meteorological measurement sites as well as topographic lines are also indicated. Coordinates are UTM 31 (ED50).

Fig. 2. Schematic representation of the theoretical models (pure nugget, linear and spherical) fitted to the empirical semivariograms $\gamma(h)$. The different fitted parameters are showed: C_0 nugget, C_1 sill, and A_0 range. The proportion of structured variation was calculated with C/C_1 , where C is the partial sill calculated as $C_1 - C_0$ (Li and Reynolds, 1995).

Fig. 3. Solute concentration in precipitation (gray) and stream water (black) at TM9 (left panels) and TM0 (right panels) for the period 1983-2000. (a) Cl^- , (b) SO_4^{2-} , and (c) inorganic N ($\text{NO}_3^- + \text{NH}_4^+$ for precipitation, only NO_3^- for stream water).

Fig. 4. Annual VWA stream water concentration in precipitation (squares), baseflow TM9 (white circles) and baseflow TM0 (black circles) for (a) Cl^- , (b) SO_4^{2-} and (c) inorganic N ($\text{NO}_3^- + \text{NH}_4^+$ for precipitation, only NO_3^- for stream water) at the Torrent de la Mina catchment. The linear trend of solute concentration across years is shown with a line only when significant ($p < 0.05$). Arrows indicate the year of implementation of the amendment protocols for sulphur (1985) and nitrogen oxides (1988) emissions (<http://www.bafu.admin.ch/luft/11640/11641/>).

Fig. 5. Semivariogram of the fluctuations in solute concentration for precipitation (dark gray), TM9 (gray) and TM0 (black) streams at the Torrent de la Mina catchment. (a) Cl^- , (b) SO_4^{2-} and (c) inorganic N ($\text{NO}_3^- + \text{NH}_4^+$ for precipitation, only NO_3^- for stream water). Dashed lines show the best fitted model in each case.

Fig. 1

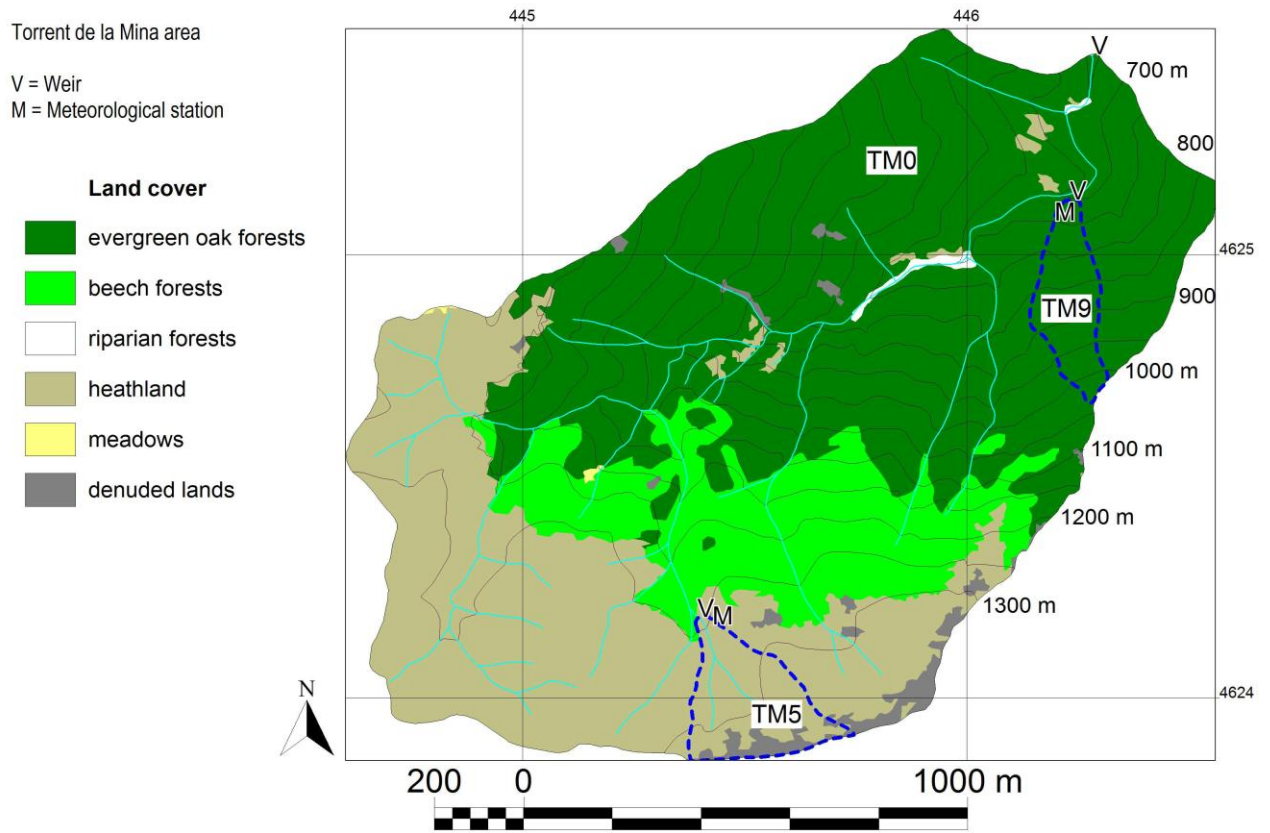


Fig. 2

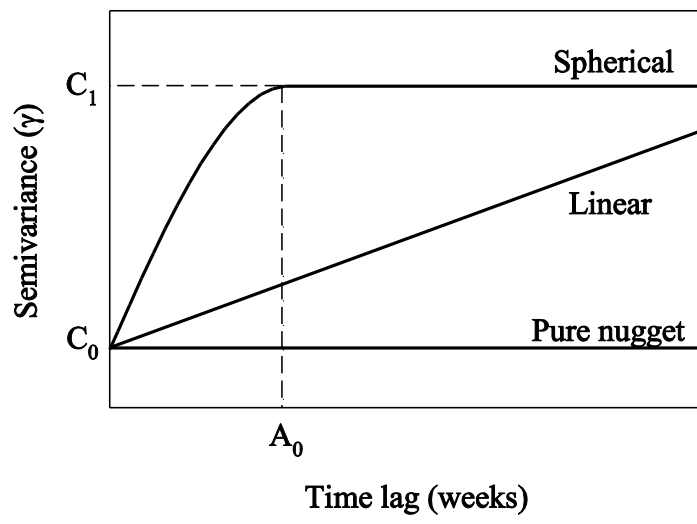


Fig. 3

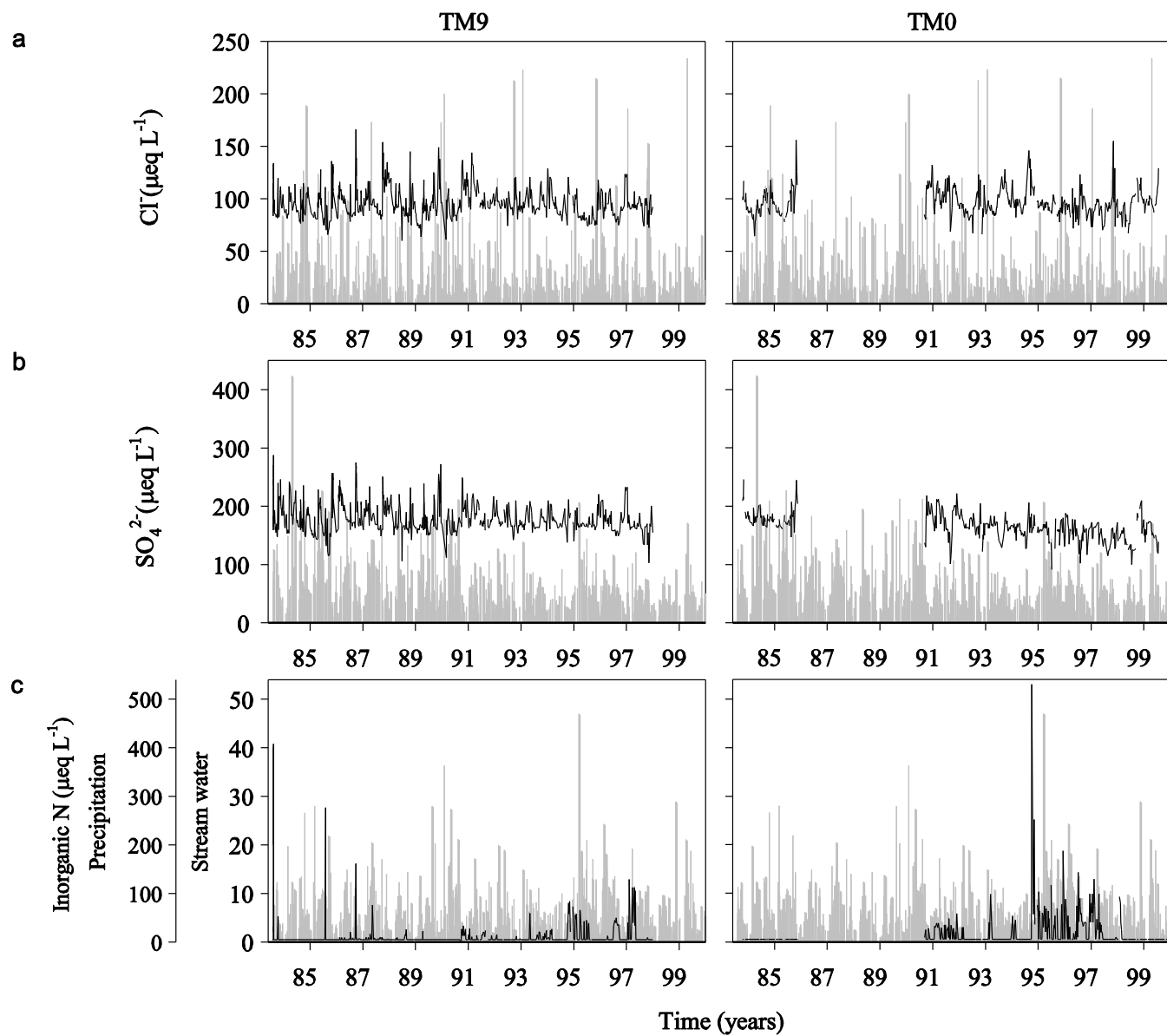


Fig. 4

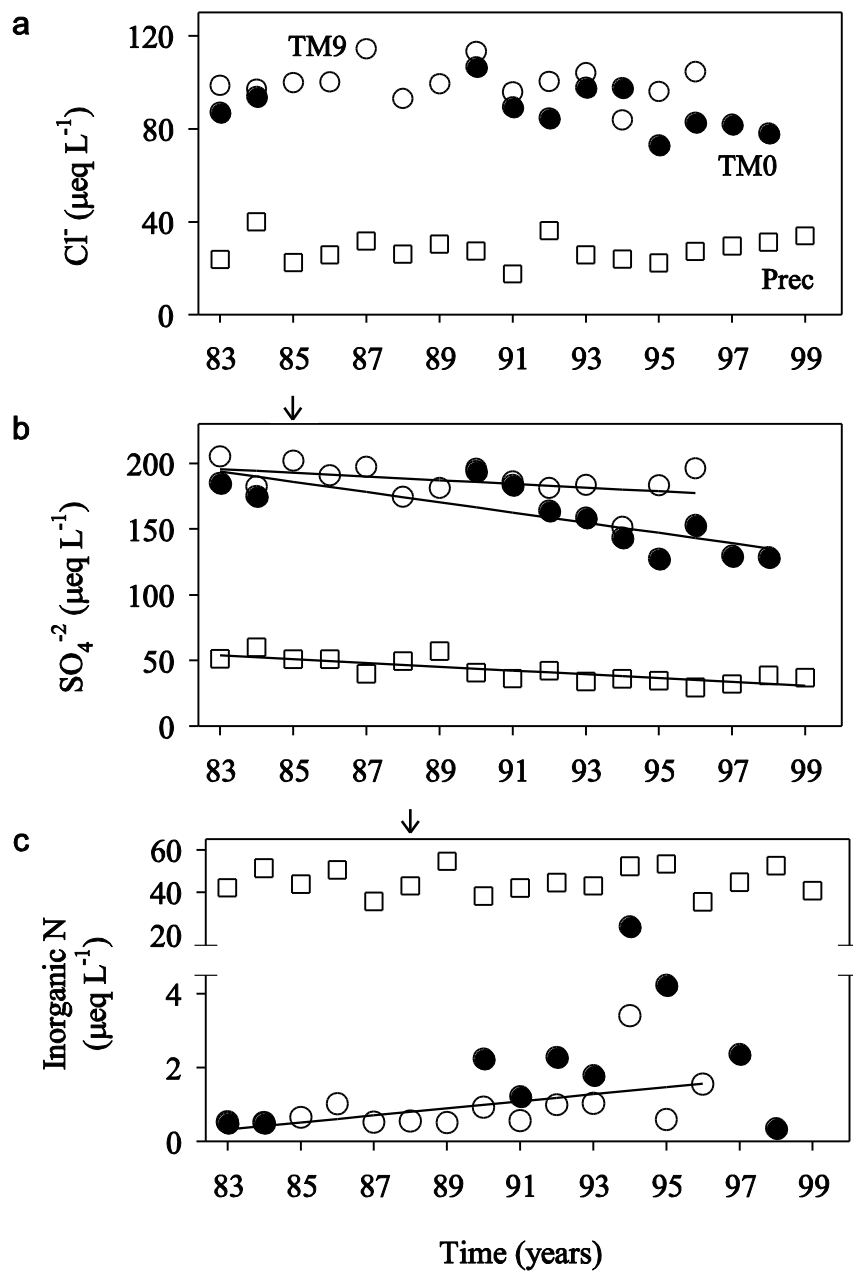


Fig. 5

