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

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**Abstract**

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

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

## 1. Introduction

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

Long-term monitoring studies showed that some catchments respond quickly to changes in atmospheric deposition with declines in nitrate ($NO_3^-$) and sulphate ($SO_4^{2-}$) export in agreement with those observed in precipitation (Kothawala et al., 2011; Mattson et al., 1997; Prechtel et al., 2001). However, in other cases the catchments' biogeochemical response to atmospheric changes was small (Alewell et al., 2000; Kothawala et al., 2011). Several factors have been invoked for explaining this different behaviour between catchments, from climate (Eimers and Dillon, 2002; Mitchell et al., 2011) to catchment-specific characteristics that can influence N and S cycling such as type of soil (Alewell et al., 2000, 2001; Eimers and Dillon, 2002), presence of S-minerals (Driscoll et al., 1998; Shanley et al., 2005), presence of wetlands (Björkvald et al., 2009), or type of vegetation (De Schrijver et al., 2007, 2008). Few studies have explored, however, how catchment hydrology affects the response of surface waters to changes in atmospheric deposition. Recently, Mitchell et al. (2011) reported a strong hydrological control on the net losses of $SO_4^{2-}$ from catchments across eastern North America, while Kothawala et al. (2011) concluded that fast drainage from soil to groundwater prevented N processing by soil biota, and thus promoted a rapid response to decreasing nitrate deposition in steep slope catchments in Canada. Furthermore, the residence time of water within catchments is related to 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 μeq $L^{-1}$), 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.

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

## 2. Study Sites

The precipitation sampling site and the studied catchments belong to the experimental study site of La Castanya Biological Station (LC, 41º 46'N, 2º21'E) located in the Montseny massif, 40 km NNE from Barcelona (Fig. 1). Most of Montseny is forested, and 75% of its surface is protected as a natural park and biosphere reserve. Forests of evergreen holm oak cover about 50% of the Montseny natural park, while beech (*Fagus sylvatica*) forests cover 14%. Heathlands and grasslands dominate at higher altitudes and represent 9% of the Montseny surface (Catalan Land Cover Map, MCSC, www.creaf.uab.es/mcsc/). Heathlands are dominated by *Calluna vulgaris*, *Cytisus scoparius* (a $N_2$-fixing shrub), *Juniperus communis*, *Erica arborea*, *Erica scoparia*, and *Pteridium aquilinum*.

The Torrent de la Mina stream is gauged at several places producing the two studied 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 35º) 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 11º; Fig.
148 1 and Table 1). TM0 is the largest catchment (205 ha, mean slope 26º) 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 $90^{th}$ 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 $cmol_c\ kg^{-1}$) for a cation
187 exchange capacity (CEC) of 16.4 $cmol_c\ kg^{-1}$. In the mineral soil, base saturation is low (37%),
188 with Ca and Mg amounting to 1.5 and 1.4 $cmol_c\ kg^{-1}$ respectively for a CEC of 10.9 $cmol_c\ kg^{-1}$.
189 There is a significant positive relationship between CEC and the content of soil organic matter
190 (Hereter, 1990).

## 3. Material and Methods

### *3.1. Field sampling and chemical analysis*

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

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

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

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

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

### *3.2. Data analysis*

#### *3.2.1. Basic statistical analysis and two-component mixing model*

We calculated the arithmetic average (AA), standard deviation (SD), and volume-weighted average (VWA) of solute concentrations for bulk precipitation and baseflow stream water for the whole period of study. Moreover, VWA was calculated for each water year, defined from 08/01 to 07/31. For precipitation time series, VWA was calculated by multiplying weekly solute concentration (in μeq $L^{-1}$) 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 μeq $L^{-1}$) 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 $$D_i = q_i(t_i - t_{i-1}) - \frac{(t_i - t_{i-1})(q_i - q_{i-1})}{2} \quad (1)$$

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.

*3.2.2. Analysis of variance and variography*

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

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

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

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

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

Flat semivariograms are indicative of time series with neither short-term nor long-term correlations, and they are best fitted with a random model (Fig. 2, pure nugget model). Time series with some degree of temporal correlation are characterized by a small $\gamma(h)$ at short time lags, which then increases with $h$ until reaching a plateau or sill once the data points become independent from each other. Three key parameters are estimated by fitting a theoretical spherical model to the empirical semivariogram: the nugget effect ($C_o$), the range ($A_o$), and the sill ($C_1$) (Fig. 2, spherical model). The $C_o$ is the *unstructured* variation that accounts for both the variance at time scales shorter than sampled and any random effect or measurement error included in the time series (Li and Reynolds, 1995). The $A_o$ indicates the time lag up to which the time series has some degree of correlation or memory in the concentration time series due to the mixing processes in the catchment, and it is a proxy of the mean residence time (Kirchner et al., 2010). In our study, the mean residence time estimate was biased towards baseflow conditions because solute concentrations during stormflow were excluded from the data analysis. The difference between $C_o$ and $C_1$, the value of $\gamma(h)$ at the plateau, is the partial sill $C$ that accounts for the *structured* variation or the amount of variance due to the temporal dependence (Li and Reynolds, 1995). The stronger the autocorrelation in a time series, the larger is the $C/C_1$ ratio. When the long-term correlations of the time series extend for longer time lags than the duration of the study period, the $\gamma(h)$ does not level off and it keeps rising with increasing $h$ for the whole range of available time scales (Fig. 2, linear model).

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

## 4. Results

### *4.1. Precipitation and streamwater solute concentrations*

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

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

Ammonium concentration in stream water was always below the analytical detection limit (0.5 $\mu eq\ L^{-1}$), therefore dissolved inorganic N (DIN) data in stream water refer only to $NO_3^-$ (Table 2). DIN concentration (VWA) in stream water was 5-, 8-, and 50-fold lower than DIN concentration in atmospheric deposition at TM5, TM0, and TM9, respectively (Table 2). DIN concentration (VWA) in stream water was lower at TM9 than at TM0 (Table 2). However, there were no significant differences in annual VWA concentration of DIN between TM9 and TM0 (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 μeq $L^{-1}$, respectively). For $SO_4^{2-}$, the expected
335 concentration (182.8 μeq $L^{-1}$) was 16% higher than the measured concentration (157 μeq $L^{-1}$).
336 The expected concentration of DIN for TM0 (6.9 μeq $L^{-1}$) was 27% higher than the observed one
337 (5.5 μeq $L^{-1}$). 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 μeq $L^{-1}$). For DIN, the expected DIN concentration for
340 TM0 (6.7 μeq $L^{-1}$) 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 μeq $L^{-1}$).
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 ± std. error) μeq $L^{-1}$ $y^{-1}$ , 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 μeq $L^{-1}$ $y^{-1}$, 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 μeq $L^{-1}$ $y^{-1}$ 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 $\sigma^2$ 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 $\sigma^2$ of DIN in stream water was two orders of magnitude lower than in precipitation
361 for both streams (Table 2). At the TM5, the $\sigma^2$ of stream $Cl^-$ concentration was similar to
362 precipitation whereas the $\sigma^2$ of DIN in stream water was 4 times lower than in atmospheric
363 deposition (Table 2).

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

368 At the TM0 and TM9 streams, the $\gamma_P/\gamma_R$ 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 $SO_4^{2-}$ $\gamma_P/\gamma_R$ 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 $\gamma_P/\gamma_R$ 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 $\gamma_P/\gamma_R$ 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 *γ(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 *γ(h)* increased gradually over the first ~ 18-20 weeks
382 for $Cl^-$ until reaching a plateau (Fig. 5a). The *γ(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 $C/C_1$ index (Table 3). The *γ(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 *γ(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 *γ(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 μeq $L^{-1}$ $y^{-1}$) 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 μeq $L^{-1}$ $y^{-1}$; 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 15-30 kg N $ha^{-1}$ $y^{-1}$ 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 disproportionally 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)

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

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

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

The mean residence time of water in the Montseny catchments (4-5 months) was low when 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 26º-35º and 15º-
476 30º 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 $\gamma_p/\gamma_s$
520 and the *Ao* 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 ~ 3 kg $ha^{-1}$ $y^{-1}$ (balance between 6.3 and 9.3 kg S $ha^{-1}$ $y^{-1}$ in inputs and
527 outputs; Àvila et al., 1999), which probably corresponded to dry deposition since a net throughfall
528 flux of 1.2 kg S $ha^{-1}$ $y^{-1}$ (~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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585 **References**

586 Aber JD, McDowell W, Nadelhoffer KJ, Magill A, Berntson G, Kamakea M, et al. Nitrogen
587 saturation in temperate forests-hypothesis revisited. Bioscience 1998; 48: 921-934.
588 Alewell C, Armbruster M, Bittersohl J, Evans CD, Meesenburg H, Moritz K, Prechtel A. Are
589 there signs of acidification reversal in freshwaters of the low mountain range in Germany?
590 Hydrol. Earth Syst. Sci. 2001; 5: 367-378.
591 Alewell D, Manderscheid B, Meesenburg H, Bittersohl J. Environmental chemistry - Is
592 acidification still an ecological threat? Nature 2000; 407: 856-857.
593 Asano Y, Uchida T, Ohte N. Residence times and flow paths of water in steep unchannelled
594 catchments, Tanakami, Japan. J. Hydrol. 2002; 261: 173-192.
595 Àvila A. Time trends in the precipitation chemistry at a montane site in north-eastern Spain for the
596 period 1983-1994. Atmos. Environ. 1996; 30: 1363-1373.
597 Àvila A, Bellot J, Piñol J. Element budgets in catchments. In: Rodà F, Retana J, Gracia CA, Bellot
598 J, editors. Ecology of Mediterranean Evergreen Oak Forests. Berlin: Springer; 1999. p. 283-
599 296.
600 Àvila A, Bonilla D, Rodà F, Piñol J, Neal C. Soilwater chemistry on a holm-oak (*Quercus ilex*)
601 forest: inferences on biogeochemical processes for a montane-Mediterranean area. J. Hydrol.
602 1995; 166: 15-35.
603 Àvila A, Molowny-Horas R, Gimeno BS, Peñuelas J. Analysis of decadal time series in wet N
604 concentrations at five rural sites in NE Spain. Water Air Soil Pollut. 2010; 207: 123-138. doi:
605 10.1007/s11270-009-0124-7.
606 Àvila A, Piñol J, Rodà F, Neal C. Storm solute behavior in a montane Mediterranean forested
607 catchment. J. Hydrol. 1992; 140: 143-161.

608 Àvila A, Rodà F. Assessing decadal changes in rainwater alkalinity at a rural Mediterranean site
609 in the Montseny Mountains (NE Spain). Atmos. Environ. 2002; 36: 2881-2890.
610 Àvila A, Rodà F. Changes in atmospheric deposition and streamwater chemistry over 25 years in
611 undisturbed catchments in a Mediterranean mountain environment. Sci. Total Environ. 2012;
612 434: 18-27. doi:10.106/j.scitotenv.2011.11.062.
613 Belillas C, Rodà F. Nutrient budgets in a dry heathland watershed in northeast Spain.
614 Biogeochemistry 1991; 13: 137-157.
615 Bellot J, Àvila A, Rodrigo A. Throughall and stemflow. In: Rodà F, Retana J, Gracia CA, Bellot J,
616 editors. Ecology of Mediterranean Evergreen Oak Forests. Berlin: Springer; 1999. p. 209-222.
617 Bernal S, Butturini A, Sabater F, Seasonal variations of dissolved nitrogen and DOC:DON ratios
618 in an intermittent stream. Biogeochemistry 2005; 75: 351-372.
619 Bernal S, Sabater F. Changes in discharge and solute dynamics between hillslope and valley-
620 bottom intermittent streams. Hydrol. Earth Syst. Sci. 2012; 16: 1595-1605. doi:10.5194/hess-
621 16-1-2012.
622 Björkvald L, Giesler R, Laudon H, Humborg C, Mörth CM. Landscape variation in stream water
623 $SO_4^{2-}$ and $\delta^{34}S_{SO4}$ in a boreal stream network. Geochim.Cosmochim. Acta 2009; 73: 4648-
624 4660. doi: 10.1016/j.gca.2009.05.052.
625 Chatfield, C. An Analysis of Time Series. Texts in Statistical Science. Boca Ratón: Chapman &
626 Hall; 2004.
627 Diggle PJ, Ribeiro Jr PJ. Model-Based Geostatistics. Springer Series in Statistics. Berlin:
628 Springer; 2007.
629 De Schrijver A, Geudens G, Augusto L, Staelens J, Mertens J, Wuyts K, et al. The effect of forest
630 type on throughfall deposition and seepage flux: a review. Oecologia 2007; 153: 663-674.
631 doi:10.1007/s00442-007-0776-1.

De Schrijver A, Staelens J, Wuyts K, Van Hoydonck G, Janssen N, Mertens J, et al. Effect of vegetation type on throughfall deposition and seepage flux. Environ. Pollut. 2008; 153: 295-303.doi:10.1016/j.envpol.2007.08.025.

Driscoll CT, Likens GE, Church MR. Recovery of surface waters in the northeastern US from decreases in atmospheric deposition of sulfur. Water Air Soil Pollut. 1998; 105: 319-329.

Eimers C, Dillon PJ. Climate effects on sulphate flux from forested catchments in south-central Ontario. Biogeochemistry 2002; 61: 337-355.

Feng X, Kirchner JW, Neal C. Spectral analysis of chemical time series from long-term catchment monitoring studies: hydrochemical insights and data requirements. Water Air Soil Poll. 2004; 4: 221-235.

Fortin MJ, Dale M. Spatial Analysis. A Guide for Ecologists. New York: Cambridge University Press; 2005.

Frank SA. The common patterns of nature. J. Evol. Biol. 2009; 22: 1563-1585. doi:10.1111/j.1420-9101.2009.01775.

Gallart F, Llorens P, Latron J, Regüés D. Hydrological processes and their seasonal controls in a small Mediterranean mountain catchment in the Pyrenees. Hydrol. Earth Syst. Sci. 2002; 6: 527-537.

Helsel DR, Hirsch RM. Statistical Methods in Water Resources. Amsterdam: Elsevier; 1992.

Hereter A. Els sòls forestals del massís del Montseny. PhD Thesis, Barcelona: University of Barcelona; 1990.

Hewlett JD, Hibbert AR. Factors affecting the response of small watersheds to precipitation in humid areas. In: Sopper WE, Lull HW, editors. International Symposium on Forest Hydrology. New York: Pergamon Press; 1967. p. 275-290.

655 Holloway JM, Dahlgren RA. Seasonal and event-scale variations in solute chemistry for four
656 Sierra Nevada catchments. J. Hydrol. 2001; 250: 106-121.
657 Jones JP, Sudicky EA, Brookfield AE, Park YJ. An assessment of the tracer based approach to
658 quantifying ground-water contribution to streamflow. Water Resour. Res. 2006; 42, W02407.
659 Kirchner JW, Feng X, Neal C, Fractal stream chemistry and its implications for contaminant
660 transport in catchments. Nature 2000; 403: 524-527.
661 Kirchner JW, Feng X, Neal C. Catchment-scale advection and dispersion as a mechanism for
662 fractal scaling in stream tracer concentrations. J. Hydrol. 2001; 254: 82-101.
663 Kirchner JW, Tetzlaff D, Soulsby C. Comparing chloride and water isotopes as hydrological
664 tracers in two Scottish catchments. Hydrol. Process. 2010; 24: 1631-1645.doi:
665 10.1002/hyp.7676.
666 Kothawala DN, Watmough SA, Futter MN, Zhang L, Dillon PJ. Stream nitrate responds rapidly
667 to decreasing nitrate deposition. Ecosystems 2011; 14: 274-286. doi: 10.1007/s10021-011-
668 9422-1.
669 Latron J, Llorens P, Gallart F. The Hydrology of Mediterranean Mountain Areas. Geography
670 Compass 2009; 3: 2045-2064. Doi: 10.1111/j.1749-8198.2009.00287.x.
671 Legaard KR, Thomas AC. Spatial patterns of intraseasonal variability of chlorophyll and sea
672 surface temperature in the California Current. J. Geophys. Res. 2007; 112: C09006.doi:
673 10.1029/2007JC004097.
674 Li H, Reynolds JF. On definition and quantification of heterogeneity. Oikos 1995; 73: 280-284.
675 Lovett GM, Burns DA, Driscoll CT, Jenkins JC, Mitchell MJ. et al. Who needs environmental
676 monitoring? Front. Ecol. Environ. 2007; 5: 253-260.
677 Mattson MD, Godfrey PJ, Walk MF, Kerr PA, Zajicek OT. Evidence of recovery from
678 acidification in Massachusetts streams. Water Air Soil Pollut. 1997; 96: 211-232.

679 McGuire KJ, McDonnell JJ, Weiler M, Kendall C, McGlynn BL, Weiker JM, Seibert J. The role
680 of topography on catchment-scale water residence time. Water Resour. Res. 2005; 41:
681 W05002.doi:10.1029/2004WR003657.
682 McGlynn B, McDonnell J, Stewart M, Seibert J. On the relationships between catchment scale
683 and streamwater mean residence time. Hydrol. Process. 2003; 17: 175-181.
684 Mitchell MJ, Likens GE. Watershed sulfur biogeochemistry: shift from atmospheric deposition
685 dominance to climatic regulation. Environ. Sci. Technol. 2011; 45: 5267-5271.doi:
686 dx.doi.org/10.1021/es200844n.
687 Mitchell MJ, Lovett G, Bailey S, Beall F, Burns D, Buso D. et al. Comparisons of watershed
688 sulphur budgets n southeast Canada and northeast US: new approaches and implications.
689 Biogeochemistry 2011; 103: 181-207.
690 Mosello R, Bianchi M, Geiss H, Marchetto A, Morselli L, Muntau H. Italian Network for the
691 Chemistry of Atmospheric Deposition. Intercomparison 1/98. Consiglio Nazionale delle
692 Ricerche. Verbania Pallanza: Instituto Italiano di Idrobiologia; 1998.
693 Mulholland PJ. The importance on in-stream uptake for regulating stream concentrations and
694 outputs of N and P from a forested watershed: evidence from long-term chemistry records for
695 Walker Branch watershed. Biogeochemistry 2004; 70: 403-426.
696 Neal C, Àvila A, Rodà F. Modelling the long-term impacts of atmospheric pollution deposition
697 and repeated forestry cycles on stream water chemistry for a holm oak forest in northeastern
698 Spain. J.Hydrol. 1995; 168: 51-71.
699 Neal C, Kirchner JW. Sodium and chloride levels in rainfall, mist, streamwater and groundwater
700 at the Phynlimon catchments, mid-Wales: inferences on hydrological and chemical controls.
701 Hydrol. Earth System Sci. 2000; 4: 295-310.

Neal C, Neal M, Warrington A, Àvila A, Piñol J, Rodà F. Stable hydrogen and oxygen isotopes studies of rainfall and streamwaters for two contrasting holm oak areas of catalonia, northeastern Spain. J. Hydrol. 1992; 140: 163-178.

Neal C, Rosier PTW. Chemical studies of chloride and stable oxygen isotopes in two conifer afforested and moorland sites in the British Isles. J. Hydrol. 1990; 115: 269- 283.

Oulehle F, Evans CD, Hofmeister J, Krejci R, Tahovska K, Persson T. et al. Major changes in forest carbon and nitrogen cycling caused by declining sulphur deposition. Global Change Biol. 2011; 17: 3115-3129.doi: 10.1111/j.1365-2486.2011.02468x.

Peñuelas J, Boada M. A global change-induced biome shift in the Montseny mountains (NE Spain). Global Change Biol. 2003; 9: 131-140.

Prechtel A, Alewell C, Armbruster M, Bittersohl J, Cullen JM, Evans CD, et al. Response of sulphur in European catchments to decreasing sulphate deposition. Hydrol. Earth Sys. Sci. 2001; 5: 311-325.

Reuss JO, Johnson DW. Acid Deposition and Acidification of Soils and Waters. New York: Springer; 1986.

Rice KC, Bricker OP. Seasonal cycles of dissolved constituents in streamwater in two forested catchments in the mid-Atlantic regions of the eastern USA. J. Hydrol. 1995; 170: 137-158.

Rodà F, Retana J, Gracia CA, Bellot J. (eds.) Ecology of Mediterranean Evergreen Oak Forests. Berlin: Springer; 1999.

Rossi RE, Mulla DJ, Franz EH. Geostatistical tools for modelling and interpreting ecological spatial dependence. Ecol. Monogr. 1992; 62: 277-314.

Shanley JB. Mayer B, Mitchell MJ, Michel RL, Bailey SW, Kendall K. Tracing sources of streamwater sulphate during snowmelt using S and O isotope ratios of sulphate and $^{35}S$ activity. Biogeochemistry 2005; 76: 161-185.

726 Shannon JD. Regional trends in wet deposition of surface in the United States and $SO_2$ emissions
727 from 1980 through 1995. Atmos. Environ. 1999; 33: 807-816.
728 Shröeder M. Fractals, Chaos and Power Laws. New York: WH Freeman; 1991.
729 Sickles JE, Shadwick DS. Changes in air quality and atmospheric deposition in the eastern
730 United States: 1990-2004. J. Geophys. Res. 2007; 112, D17301.doi: 10.1029/2006JD007843.
731 Skjelkvale BL, Stoddard JL, Jeffries DS, Torseth K, Hogasen T, Bowman J, Mannio J, Monteith
732 DT, Mosello R, Rogora M, Rzychon D, Vesely J, Wieting J, Wilander A, Worsztynowicz A.
733 Regional scale evidence for improvements in surface water chemistry 1990-2001. Environ.
734 Pollution 2005; 137: 165-176.
735 Soil Survey Staff, Keys to Soil Taxonomy, fifth ed. SMSS Technical Monograph No 19.
736 Blacksburg, Virginia: Pocahontas Press; 1992.
737 Soulsby C, Malcolm R, Helliwell R, Ferrier RC, Jenkins A. Isotope hydrology of the Allt
738 a'Mharcaidh catchment, Cairngorms, Scotland: implications for hydrological pathways and
739 residence times. Hydrol. Process. 2000; 14: 747-762.
740 Soulsby C, Tetzlaff D. Towards simple approaches for mean residence time estimation in
741 ungauged basins using tracers and soil distributions. J. Hydrol. 2008; 363: 60-74.
742 Stoddard JL, Jeffries DS, Lükewille A, Clair TA, Dillon PJ, Dillon CT. et al. Regional trends in
743 aquatic recovery from acidification in North America and Europe. Nature1999; 401: 575-578.
744 Tetzlaff D, Seibert J, Soulsby C. Inter-catchment comparison to assess the influence of
745 topography and soils on catchment transit times in a geomorphic province, the Cairngorm
746 mountains, Scotland. Hydrol. Process. 2009; 23: 1874-1886.
747 Watmough SA, Aherne J, Alewell C, Arp P, Bailey S, Clair T, et al. Sulphate, nitrogen and base
748 cation budgets at 21 forested catchments in Canada, the United States and Europe. Environ.
749 Monit. Assess. 2005; 109: 1-36.doi: 10.1007/s10661-005-4336-z.

750 Zhang YK, Schilling K. Temporal variations and scaling of streamflow and baseflow and their
751 nitrate-nitrogen concentrations and loads. Adv. Water. Resour. 2005; 28: 701-710.

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 (º) | 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 | $\sigma^2$ | $\gamma_{lag-1}$ | $\gamma_P/\gamma_R$ | n |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $\mu eq\ L^{-1}$ | | | $(\mu eq\ L^{-1})^2$ | | | |
| $Cl^-$ | 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.

$\sigma^2$: variance, $\gamma_{lag-1}$: lag-1 semivariance.

$\gamma_P/\gamma_R$: ratio between $\gamma_{lag-1}$ 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 $NO_3^-$, [c] DIN ($NH_4^+$ + $NO_3^-$).

**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] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $C_0$ ($\mu$eq $L^{-1}$)$^2$ | Slope | $R^2$ (%) | $C_0$ | C | $A_0$ (weeks) | $C/C_1$ | $R^2$ (%) |
| | | | | | ($\mu$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.

[a] Neither 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 $C_1 - C_o$ (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 ($NO_3^-$+ $NH_4^+$ 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 ($NO_3^-$+ $NH_4^+$ 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 ($NO_3^-$+ $NH_4^+$ for precipitation, only $NO_3^-$ for stream water). Dashed lines show the best fitted model in each case.

Fig. 1

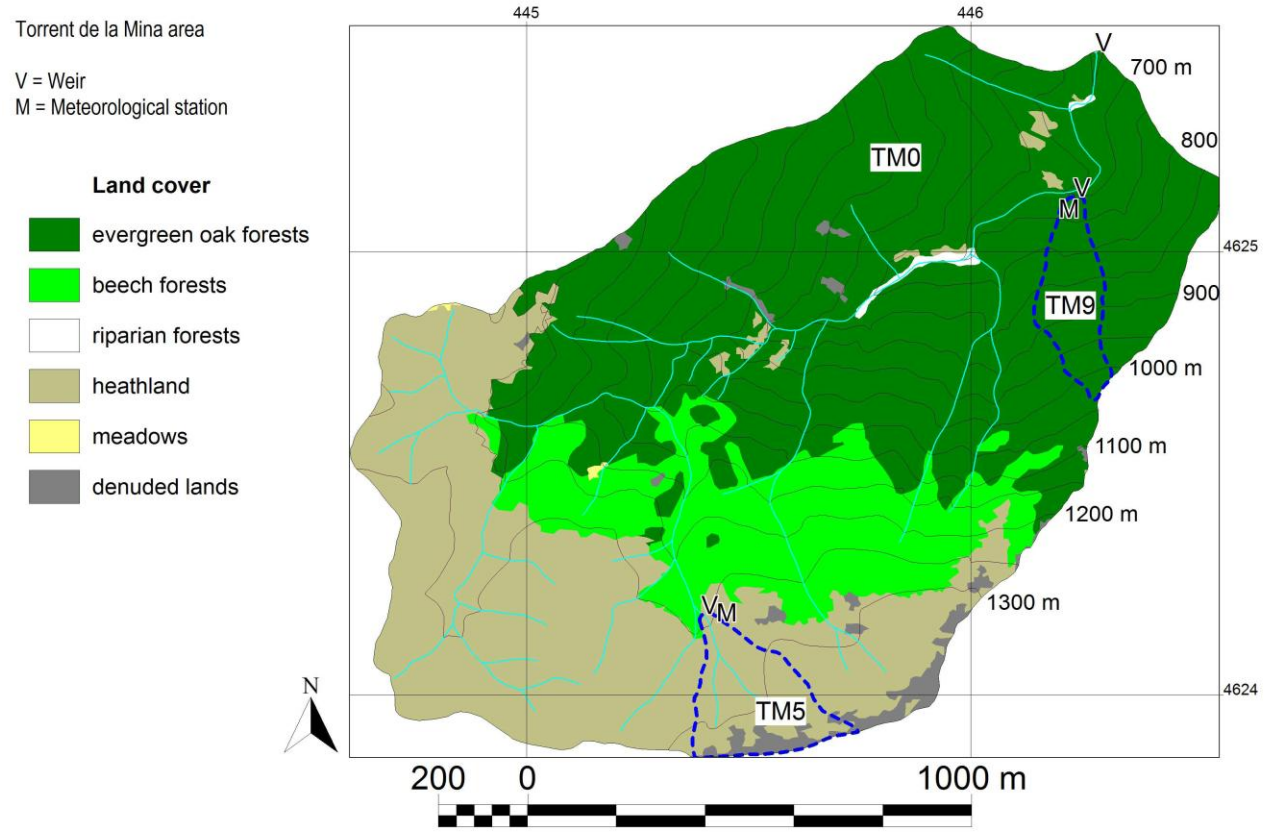

Torrent de la Mina area
V = Weir
M = Meteorological station
Land cover
evergreen oak forests
beech forests
riparian forests
heathland
meadows
denuded lands
445
446
4625
4624
700 m
800
900
1000 m
1100 m
1200 m
1300 m
TM0
TM9
TM5
V
M
N
200
0
1000 m

Fig. 2

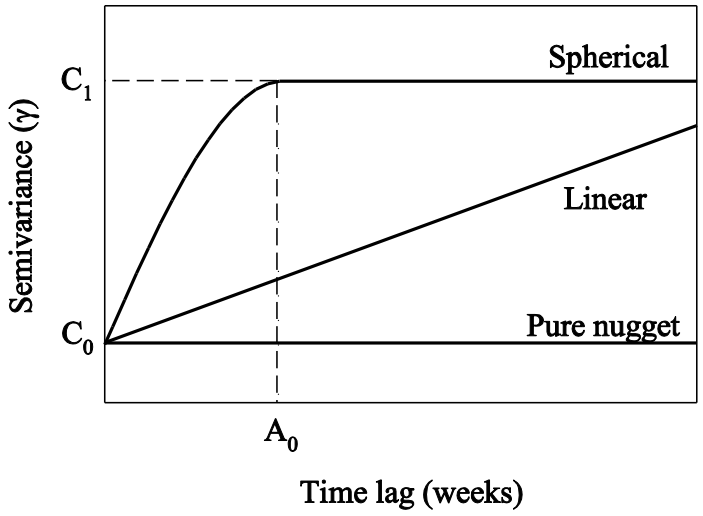

Spherical
C1
Semivariance (γ)
Linear
Pure nugget
C0
A0
Time lag (weeks)

Fig. 3

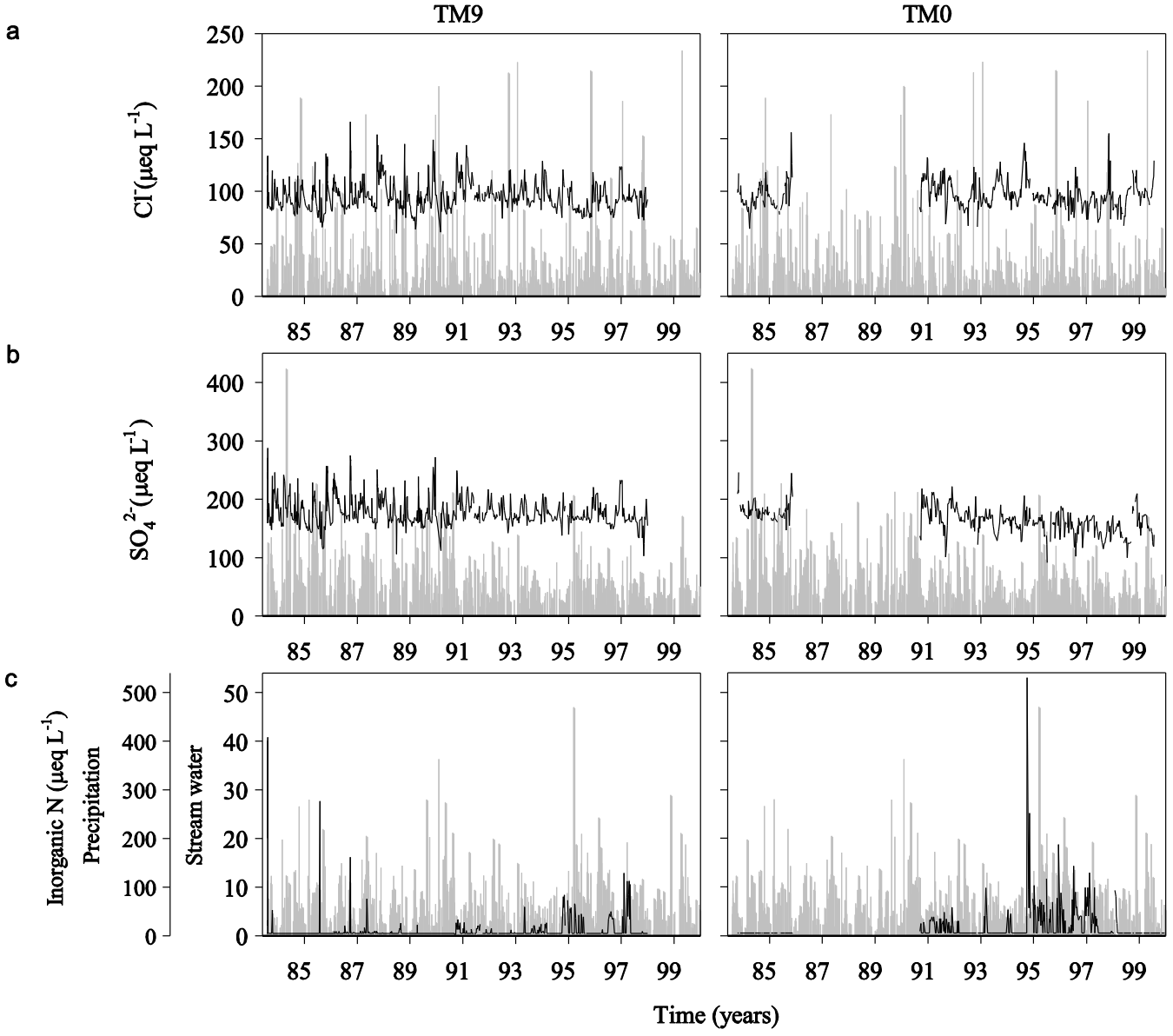

a
b
c
TM9
TM0
Cl⁻(μeq L⁻¹)
SO4 2-(μeq L⁻¹)
Inorganic N (μeq L⁻¹)
Precipitation
Stream water
Time (years)
85
87
89
91
93
95
97
99

Fig. 4

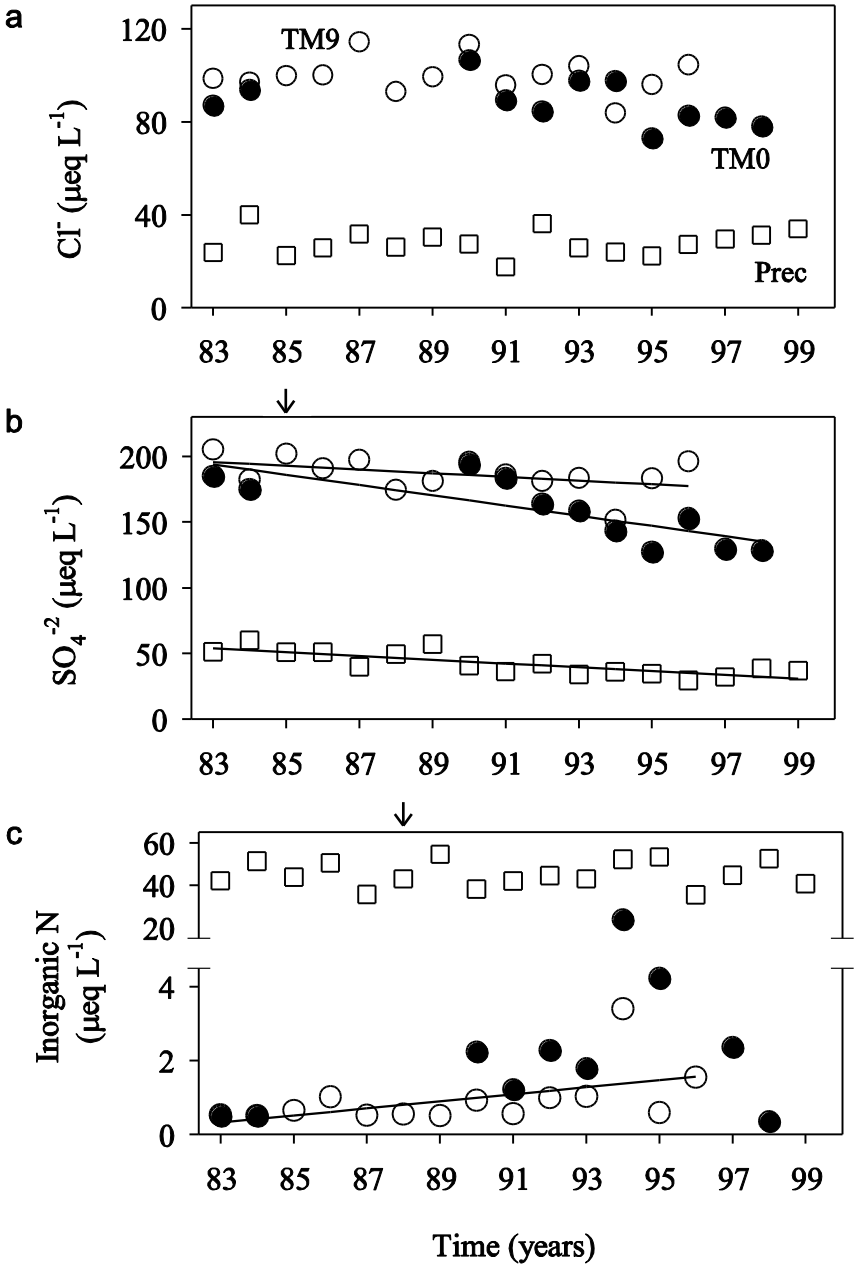
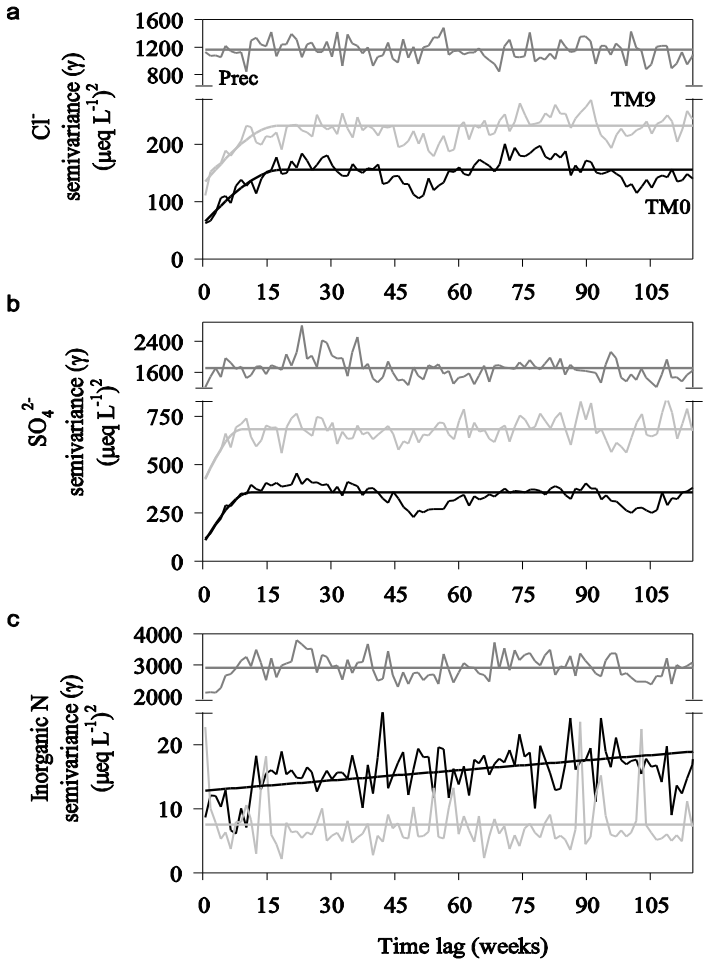

a
b
c
TM9
TM0
Prec
Cl⁻ (μeq L⁻¹)
SO4⁻² (μeq L⁻¹)
Inorganic N (μeq L⁻¹)
Time (years)
0
40
80
120
50
100
150
200
20
60
2
4
83
85
87
89
91
93
95
97
99

Fig. 5


a
b
c
Cl⁻ semivariance (γ) (µeq L⁻¹)²
SO4 2- semivariance (γ) (µeq L⁻¹)²
Inorganic N semivariance (γ) (µeq L⁻¹)²
Prec
TM9
TM0
1600
1200
800
200
100
0
2400
750
500
250
4000
3000
2000
20
10
0 15 30 45 60 75 90 105
Time lag (weeks)