Long-term hydrological and biogeochemical datasets from a Mediterranean forest site (Montseny, NE Spain)

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Abstract

In humid regions, the chemical flux and cycling of elements is intimately linked to the hydrologic cycle. This insight opened in the late s. XX a worldwide avenue for the use of small watersheds as ecological units to study the hydrological and biogeochemical functioning of ecosystems at the small catchment scale. The Montseny catchment research, starting in 1978, initially addressed the forest response to acid rain. But continuous recording for about 4 decades in two small catchments allowed to describe the changes in streamwater chemistry related to changes in atmospheric deposition (with particular emphasis to S, N and P deposition), to climate change and to the inputs of African dust. Further research and new hypothesis testing may take advantage of the collected data series in these long-term study sites at a Mediterranean site. This is the motivation for the publication of the quality-checked original stream and atmospheric deposition chemistry files whose links accompany this paper.

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Introduction and antecedents

Hydrological and biogeochemical studies in the Montseny holm oak (*Quercus ilex*) forests started in 1978 with funding from a Hispano-American project that allowed the onset of terrestrial ecology studies in Spain. Later funding was provided by a suite of projects from the Spanish Government and the European Commission. This research followed the small catchment approach developed at Hubbard Brook (Bormann et al. 1979) and, sustained over several decades, has been instrumental in showing the responsiveness of forested ecosystems to atmospheric deposition changes (Avila and Rodà 2012; Bernal et al. 2013; Avila et al. 2020) and the uniqueness of stream N response to deposition in Mediterranean forests as compared to temperate forests (Templer et al. 2022). The effects of forest management on (1) stream chemistry has been modelled (Neal et al. 1995) and that of climate change on stream chemistry (Avila et al. 1996) and on the habitat suitability for an endangered amphibian species as well (Ledesma et al. 2019). Mineral dust, originated in North Africa (Avila et al. 2007) has been shown to be an important contributor of nutrients and alkalinity to these forest ecosystems (Avila et al. 1997, 1998). Further research and new hypothesis testing may take advance of the collected data series in these long-term study sites. This is the motivation for the publication of the quality-checked original stream and atmospheric deposition chemistry files of well curated small catchments at Montseny whose links accompany this paper.

Site description

Two catchments, named TM9 and TM0, were instrumented in La Castanya valley (Montseny mountains; 41,774853 °N / 2,351109 °E) in the early 1980s within a broad-scope study on forest ecosystem functioning (Rodà et al. 1999). A gauging station was built at each site, consisting of a stilling pond and a V-notch weir. At TM0 the V-notch had a 120° angle, while the smaller TM9 weir had a 60° opening.

La Castanya valley is 40 km to the NNE of Barcelona and 27 km from the Mediterranean coast. Climate is subhumid mesomediterranean: annual precipitation is around 900 mm with a typical summer drought, but interannual variability is very high. The bedrock is a metamorphic phyllite, with quartz, chlorite, albite and muscovite as major minerals. Two catchments were instrumented in Torrent de la Mina stream, a major stream draining La Castanya valley: TM0, the main catchment and TM9, a small tributary (Fig. 1, Table 1). Relief is steep and there are some rock outcrops in the upper slopes of TM0 and in the TM0 stream channel. TM9 is located in the lower slopes of TM0 and is totally covered by holm oak. In TM0, two distinct physiographic units can be distinguished: holm-oak and beech forests on very steep slopes and heathlands and grasslands in the upland plateau (Fig. 1). Soils in the slopes of TM0 are colluvial, stony, well drained, and spatially heterogeneous due to the rugged topography. Typically, they are shallow with a 0-5-cm organic layer and depths varying between 0.25 to 1.5 m (Hereter, 1990, Hereter and Sánchez 1999). They are classified as Entisols (Lithic Xerorthents) or Inceptisols (Typic, Lithic or Dystric Xerochrepts; Soil Survey Staff 1992).

Table 1. Site characteristics

Catchment	Area (ha)	Min. altitude (m)	Max. altitude (m)	Mean slope of main stream (°)	Prevailing direction of main stream	Vegetation	Vegetation
TM9	5,9	710	1036	35	N	100% holm oak	100% holm oak
TM0	200,4	650	1343	26	NE	52% holm oak 15% beech 30%heath-land and grassland 3% rock outcrops	

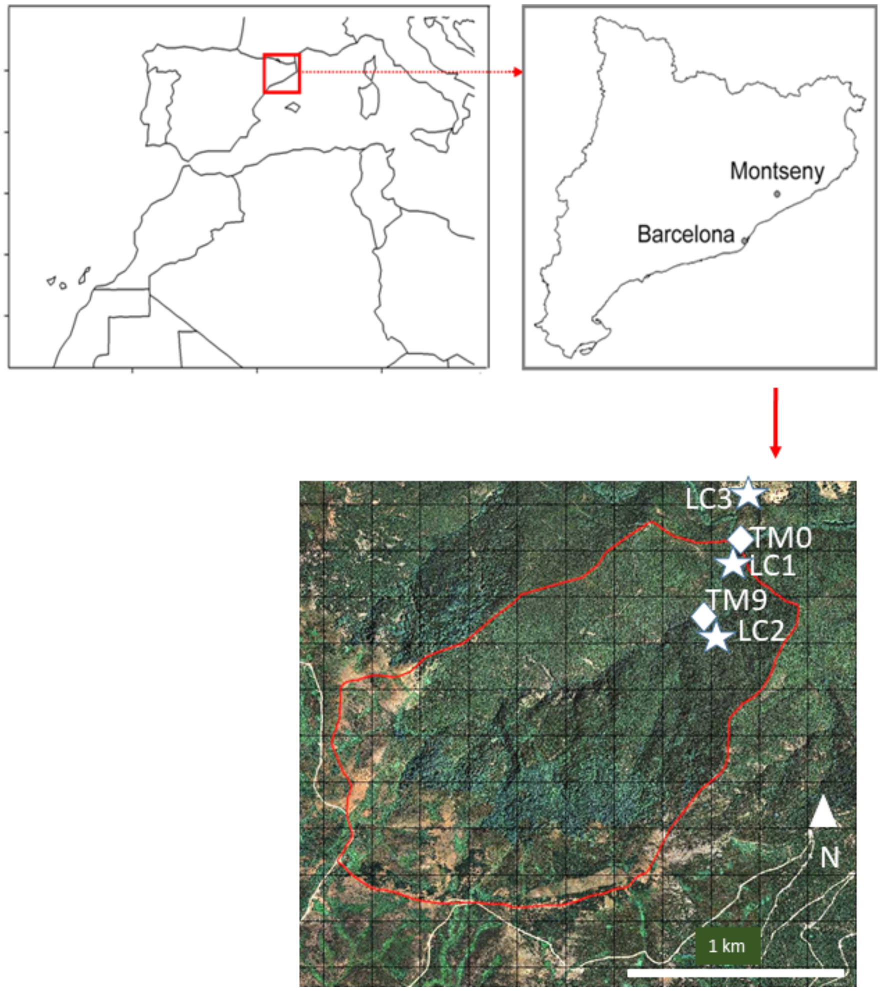

Fig 1. Site characteristics of the gaged catchments (TM9 and TM0, diamonds). LC1, LC2 and LC3 (stars) indicate the location of the atmospheric deposition collectors for different periods: LC1 equipped with bulk deposition and throughfall collectors for the period 1978-1980; LC2 with bulk deposition from 1983 to 2000 and throughfall for 1996-1997; LC3 with bulk and wet only deposition for the period 2002-2019 (see Table 2) and with throughfall in 2011-2013.

Methods

3.1 Stream water flow and chemical data

Hydrological and stream chemistry data (which includes water temperature) were monitored in the two catchments for a non-continuous record in the period 1983-2019 (Table 2).

Table 2. Time periods and instrumentation used for hydrological recording and sampling.

Catchment	Period	Instrument	recording method
TM9 (60° V notch)	1983-1997	WeatherMeasure stage level	continuous recording on paper
TM0 (120° V notch)	1990-2002	OTTstage level record	continuous recording on paper
TM0 (120° V notch)	2007-2010	OTTstage level record	continuous recording on paper
TM0 (120° V notch)	2010-2018	Schlumberger pressure probe	data logger 15 min data
Streamwater chemistry			

TM9	1983-1997	grab sample	chemical analysis
TM0	1983-2019	grab sample	

In each field visit, manual reads of the limnimetric scale located at the weir were taken and were used to calibrate the instrument flow recordings. Discharge (D_i, in L) was calculated for successive small steps tracking the variation of the hydrographs (Fig. 2).

$D_i = q_i*(t_{i+1}-t_i) + [(q_{i+1}-q_i)*(t_{i+1}-t_i)/2]$,

being q_i the instantaneous stream flow (in L/s at TM9 and in m3/s at TM0) and q_{i+1} , the stream flow for the next reading.

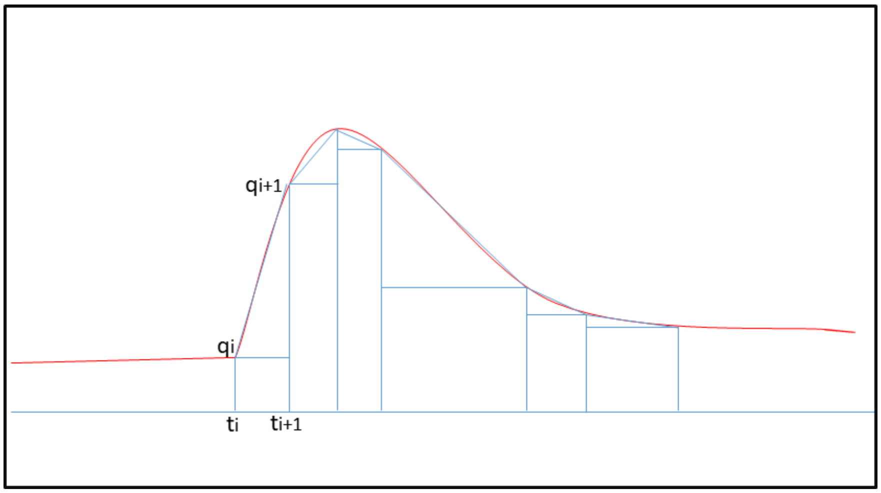

Figure 2. Hydrograph decomposition tracking flow variation.

Grab samples of stream water were collected at each visit (approximately weekly) several meters upstream from the respective stilling ponds in high-density polyethylene 250 mL bottles. More frequent samples were obtained during storms from 1983 to 1990 at TM9, collected with an automatic sampler (Avila et al. 1992).

3.2 Atmospheric deposition data

Atmospheric deposition was monitored from 1978 through 2019 with some interruptions. The location and the mode of sampling collection varied in this period as described in Figure 1. Parallel bulk and wet deposition sampling allowed comparison between the two methods: high correlation between them was found for the different ions, BD exceeding WD by around 37% for base cations (Izquierdo and Avila 2012).

3.3 Analytical methods

Stream water and atmospheric deposition samples were taken to the laboratory the same day of collection. Sample processing and analysis are described in Avila (1996), Rodà et al. (1993) and Avila et al. (2020).

Annual mean concentrations were volume-weighted for all ions except for H^+. At Montseny, with weekly rainwater pH values varying between 4.0 and 8.0, alkalinity/acidity is the conservative property to average. Volume-weighted mean alkalinity was then transformed to mean pH with the equation: pH = log (alk) + 5.2 (units in µeq L-1) which is derived from the equilibrium equations of the CO_2 -carbonate system (Stumm and Morgan, 1981).

Deposition samples with African dust were filtered and chemical (ICP-MS and ICP-AOE), mineralogical (X-Ray diffraction; Avila et al. 1997) and genomic analysis of the particulates in the filters was later performed.

DNA was extracted using the Mobio PowerSoil DNA Isolation Kit (Mobio Laboratories). PCR and high-speed multiplexed SSU rRNA gene Illumina MiSeq sequencing were carried out for 16S and 18S rRNA genes (https:// rtsf.natsci.msu.edu/).

Element input or export from the catchment was calculated as the sum of the element inputs or exports for each sample in the period of interest (e.g. month, year). Inputs are calculated as the product of bulk or wet deposition concentrations by precipitation. Export for a sample S_i is calculated as the product of the element concentration in the sample (S_i concentrations in µeq/L) by the water drained in the period starting at the point midway from S_i to the previous sample S_{i-1} and ending at the point midway from S_i to the next sample S_{i+1} (water yield in mm = L/m2). This mode of calculation has been found adequate for weekly or biweekly stream sampling frequencies, as is here the case (Rekolainen et al. 1991, Swistock et al. 1997). Drainage is also expressed per unit catchment area (drainage in mm) in the hydrology files.

Principal results

4.1 Streamwater chemistry

The Torrent de la Mina streamwaters are well buffered, with Na^+ and Ca^{2+} co-dominating as main cations and alkalinity as the main counterpart, both in TM0 and TM9. Mean pH was 7,47 and 7,54 for TM0 and TM9 respectively. Solute variation at TM9 was explained as the mixing of groundwater and deep-soilwater components, contributing 70 and 30% of annual runoff, respectively (Piñol et al. 1992, Avila et al. 1996). Both catchments responded rapidly to changes in atmospheric deposition: an alkalinity increase was found associated to declining sulfate deposition (Avila and Rodà 2012). This responsiveness may be explained by a low residence time of water in these catchments compared to other geographical areas (Bernal et al. 2013). Nitrogen was strongly retained in the catchments, with only 2% of total N deposition being exported as inorganic N in streamwater. However, higher nitrate export occurred during the wettest months (November and March). Moreover, this pattern showed an increasing trend in time, suggesting the onset of N saturation in the catchments (Avila et al. 2020).

Torrent de la Mina data have been used for modelling the stream chemistry response to forestry practices (Neal et al. 1995) and to climate change (Avila et al. 1996). More recently, the stream hydrological response to climate change scenarios from IPCC and to land use changes was modeled in the context of LIFE-Tritó project. The aim was to predict the vulnerability of the critically endangered Montseny newt (*Calotriton arnoldi*) to expected habitat changes in future scenarios (Ledesma et al. 2019). In this work, the combination of hydrological modelling, climatology and species ecology knowledge provides an example of the use of data gathering to help in the management of an endangered species.

Atmospheric deposition

Rainwater in Montseny is rarely acidic, since sulfate and nitrate acid anions are largely neutralized by base cations and ammonium (Rodà et al. 1993). Annual mean pH values ranged from 4,92 to 7,18 with a median of 6,79. All annual mean pH values below 5,50 occurred before 1990. Frequent episodes of African dust transport (Avila and Peñuelas 1999) are important contributors of alkalinity and of dissolved and particulate elements to this site (Avila et al. 1997, 1998; Castillo et al. 2017). Back trajectory analysis has revealed that the main atmospheric transport pathway to Montseny is from the Atlantic Ocean, delivering dilute and circumneutral rainwaters while acid episodes predominated in local and European trajectories (Izquierdo et al. 2012a). Nitrogen deposition was higher with air masses coming from Mediterranean/ south-east European provenances (Izquierdo et al. 2014). Significant declining trends of S deposition (since the 1980s; Avila and Rodà 2002) and N deposition (starting in the mid-2000s) have been found (Aguillaume et al. 2016; Avila et al. 2020).

The role of African episodes as contributors of phosphorus deposition in Montseny and in the near Mediterranean coast has been analysed by Izquierdo et al. (2012b) and Longo et al. (2014). Because of concern on the negative eutrophying effects of N deposition, particular attention has been devoted to characterise the N inputs to Montseny (Rodà et al. 2002, Avila et al. 2002, García-Gómez et al. 2018). Throughfall sampling and leaf washing experiments were undertaken at different times along the recording period to distinguish dry deposition from canopy exchange at the canopy level (Rodrigo et al. 2003, Avila et al. 2017). Lately, the role of the leaf microbiome was assessed using a multiple isotope approach (involving $\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$ in NO_3^- in wet deposition and throughfall) and quantification of amoA genes: microbial nitrification contributed but the NO3 dominant flux in throughfall was atmospheric (Guerrieri et al. 2020).

The Montseny catchments have shown distinctive characteristics compared to more temperate catchments, such as: **(1)** the hydrology is strongly controlled by evapotranspiration, which accounts for 2/3 of the incoming precipitation (Piñol et al. 1999), **(2)** nevertheless, there is a quick hydrologic response, as residence time of water in the catchment is estimated around 4-5 months (Bernal et al. 2013),**(3)** inorganic N is strongly retained in the system, with nitrate being the only inorganic nitrogen form detected in stream waters (detection limit = 0,5 µeq/L) mostly during stormflows; as a consequence, 98% of DIN deposition is retained in the catchments (Avila et al. 2020). The lack of relationship between DIN inputs and outputs in the Montseny catchments contrasts with the finding that N deposition is a strong driver of stream N export in temperate catchments (Templer et al. 2022). On the other hand, similarly to other catchments worldwide and corresponding to a general declining sulfate deposition trend, sulfate concentrations in Montseny stream waters have decreased, while alkalinity has increased (Avila and Rodà 2012) providing well buffered waters for these catchments lying on silicate bedrock.

Data sets and availability

We provide two datasets of open data for further exploration and hypothesis testing. Files are provided for: (1) stream water flow and stream water chemistry, doi:10.5281/zenodo.7228249; and (2) atmospheric deposition, doi: 10.5281/zenodo.7228266.

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