

NOTE

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

Anna Avila¹  | Ferran Rodà^{1,2}

¹CREAF, Campus Universitat Autònoma de Barcelona, Catalonia, Spain

²Department of Animal and Plant Biology and Ecology, Universitat Autònoma de Barcelona, Catalonia, Spain

Correspondence

Avila Anna, CREAM, Campus Universitat Autònoma de Barcelona, E08193 (Cerdanyola del Vallès), Catalonia, Spain.
Email: anna.avila@uab.cat

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Abstract

We present here, and make freely available, two long-term datasets on the hydrology and hydrochemistry of two small catchments totally or partially covered by holm oak (*Quercus ilex*) forests. Data have been collected over four decades of research on the ecology of Mediterranean evergreen forests. The datasets contain data on water fluxes in precipitation and runoff, and on the ion concentrations and fluxes in precipitation, throughfall and streamwater. Among other applications, these data have been used to obtain catchment budgets of water and elements, to document decadal changes in atmospheric deposition and streamwater chemistry, to assess the role of Saharo-Saharan dust on forest nutrient cycling, and to model habitat suitability for an endangered amphibian under future climates. To encourage their further use by the scientific community, in this paper we summarize the data context and methods, and give a nutshell of obtained results. We provide the links to these datasets on the Zenodo platform.

KEYWORDS

atmospheric deposition, forest ecosystem functioning, holm oak, La Castanya, long-term trends, Mediterranean catchment, Montseny, *Quercus ilex*, streamwater chemistry, terrestrial ecology

1 | INTRODUCTION AND ANTECEDENTS

The chemistry of streamwater draining undisturbed catchments is determined by the biogeochemical processes that occur within the catchment such as weathering of minerals, ion exchange in soils and plant uptake, by the climate of the area and by the nature of the atmospheric inputs. By analysing the patterns of solute variation and input–output budgets of elements, inferences can be made regarding the hydrological and ecological processes occurring at the scale of the small basin. With this in mind, hydrological and biogeochemical studies in the Montseny holm oak (*Quercus ilex*) forests started in 1978 supported by funds from a Hispano-American project, later followed by a suite of projects from the European Commission and the Spanish and Catalan Governments. The objective was to study the biogeochemistry of small Mediterranean catchments based in the small

catchment approach developed at Hubbard Brook, New Hampshire, USA (Likens et al., 1977). This approach, combined with information from element cycling in adjoining plots allowed to characterize for the first time in Spain the circulation of water and elements in Mediterranean holm oak forests (Escarré et al., 1984; Rodà et al., 1999).

Later on, in the mid 1980s, evidence of relevant environmental changes in atmospheric deposition and climate warming prompted interest in developing a long-term record at this site. Long-term data series are needed to understand the magnitude and direction of environmental changes, since patterns may not be obvious at short-term scales. The Montseny catchments (Catalonia, NE Spain) provide one of the longest records for a Mediterranean site and participates in the International Long term Ecological Research Network (ILTER) established to address the global response of ecosystems to environmental changes.

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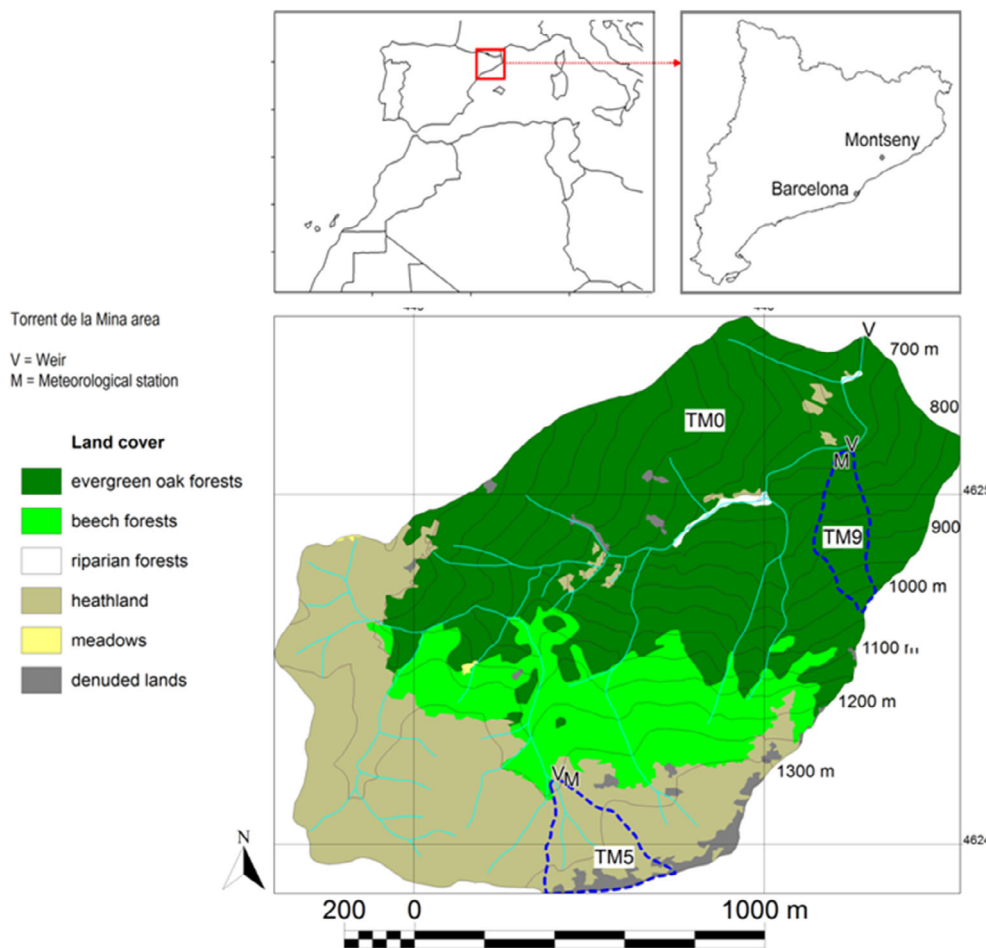


FIGURE 1 Topography and vegetation map of the Torrent de la Mina catchment. TM0 is the main catchment and nested within it are TM9 and TM5. The location of the weirs (V) and meteorological stations (M) is shown.

Further research and new hypothesis testing may take advantage 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.

2 | SITE DESCRIPTION

La Castanya valley is 40 km to the NNE of Barcelona and 27 km from the Mediterranean coast (41.775°N/2 353°E). 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.

In Torrent de la Mina stream, a major stream draining La Castanya valley, three catchments were instrumented: the main catchment (named TM0), and two small tributaries nested within TM0 (TM9 in the lower slopes of TM0 and TM5 in the upland plateau; Figure 1). However, in this data note concerning long-term data, only data from TM0 and TM9 will be presented, as TM5 only operated from 1982 to 1985.

A gauging station was built in each stream, consisting of a water stilling pond and a V-notch weir. V-notch angle varied according to

the size and water flow of each catchment: 120° at TM0 and 60° at TM9. TM9, located in the lower slopes of TM0, has a steeper relief and is totally covered by holm oak (Table 1). In TM0, two distinct physiographic units can be distinguished: (1) holm-oak and beech forests on the steep side slopes, and (2) heathlands and grasslands on the upland rolling plateau (Figure 1). Soils in the steep slopes of TM0 and TM9 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 and 1.5 m (Hereter, 1990; Hereter & Sánchez, 1999; Rodà et al., 1999). They are classified as Entisols (Lithic Xerorthents) or Inceptisols (Typic, Lithic or Dystric Xerochrepts; Soil Survey Staff, 1992). Soils at the rolling slopes of the upland plateau of TM0 have a 3-cm deep organic layer and a 19-cm deep A horizon. The soil organic carbon content in the slopes is lower than at the upland plateau (Hereter, 1990).

3 | METHODS

3.1 | Water fluxes and chemical data

Hydrological and chemistry data were monitored for different periods at the two catchments: from 1983 to 1997 at TM9, and for a non-continuous record in the period 1990–2018 at TM0.

TABLE 1 Site characteristics

Catchment	Area (ha)	Min. Altitude (m)	Max. Altitude (m)	Mean slope of main stream (°)	Prevailing direction of main stream	Vegetation
TM9	5.9	710	1036	35	N	100% holm oak
TM0	200.4	650	1343	26	NE	52% holm oak 15% beech 30% heathland and grassland 3% rock outcrops

TABLE 2 Time periods and instrumentation used for hydrological recording

Catchment	Period	Instrument	Recording method
TM9 (60° V notch)	1983–1997	WeatherMeasure limnograph	continuous record of water level on paper
TM0 (120° V notch)	1990–2002/2007–2010	OTT limnograph	continuous record of water level on paper
	2010–2018	Schlumberger diver	pressure probe; 15 min data

Water level measurements were initially recorded on paper, using WeatherMeasure (TM9) and OTT (TM0) limnographs with float-type devices installed in the respective stilling wells. In 1997, measurements at TM9 were discontinued. After 2010, TM0 was equipped with automatic pressure sensors recording water level at 15 min intervals (Table 2).

In each field visit (weekly or biweekly), water stage was manually read from the limnometric scale (LS) located in each weir; these water stage readings were used to calibrate the relationship between the water level in the weirs and the record of the limnograph or the water level sensor data. Digitalization of the limnograph curves obtained before 2010 was done manually by taking into account representative points of water level variation (Figure 2). After 2010, 15-min water levels were downloaded from the diver data logger.

Stream flow (q) was determined using rating curves. At TM9 the rating curve was empirically calibrated with discharge measurements obtained with a bucket, resulting in the following equation:

q (L/s) = $10^{(-1.61353 + 1.62225 * (\text{Log LS}) + 0.45808 * (\text{Log LS})^2)}$, where LS is limnometric scale in cm.

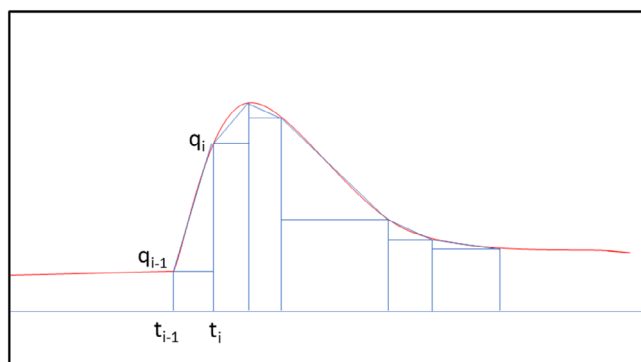
At TM0 we used the theoretical calibration for a 120° V notch weir taken from Gregory and Walling (1973):

$$q \text{ (m}^3\text{/s)} = 2.47 * \text{LS}^{2.5}, \text{ with LS in meters.}$$

Before 2010, drainage values (D_i) were obtained by integrating stream flow at uneven readings at times t_i and t_{i-1} (Figure 2), which tracked the variation of the hydrographs:

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

being q_i the instantaneous water flow and q_{i-1} that for the previous reading. After 2010, it was obtained by integrating flow at the regular 15 min steps (units of water flow were L/s at TM9 and $\text{m}^3\text{/s}$ at TM0). Annual drainage was obtained by summing the partial readings up to the year. Using the methodology described above and owing to our careful calibrations of both water level and water flow, we estimate that the maximum uncertainty associated to our drainage data may be lower than 10% on average.

**FIGURE 2** Hydrograph decomposition tracking flow variation.

Weekly or biweekly grab samples of streamwater were collected several meters upstream from the respective stilling ponds in distilled water-cleaned 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). The hydrological and biogeochemical variables which are provided in the Zenodo datasets are listed in Table 3.

3.2 | Atmospheric deposition data

Atmospheric deposition was monitored from 1978 through 2019 with some interruptions and small changes in location because measurements were undertaken for different research projects. In the period 1978–1980 bulk deposition (BD) and throughfall (TF) were collected near the TM0 weir. In 1983, BD and TF deposition collectors were located near the TM9 weir (BD collected from 1983 to 2000, TF from 1995 to 1997), and in 2002 they were moved 700 m to the NE to be included in the Montseny EUSAAR station (European Supersites for

TABLE 3 List of hydrological and biogeochemical variables measured. Conductivity and ion concentrations were measured for atmospheric deposition (bulk deposition, BD or wet deposition, WD), throughfall (TF), and streamwater

Variable (units)
Limnometric scale (cm)
Stream flow (L/s for TM9, m ³ /s for TM0)
Water output flux (L m ⁻²)
Precipitation (L m ⁻²)
Throughfall volume (L m ⁻²)
Conductivity (µS cm ⁻¹)
pH
H ⁺ conc (µeq L ⁻¹)
Alk conc (µeq L ⁻¹)
Na ⁺ conc (µeq L ⁻¹)
K ⁺ conc (µeq L ⁻¹)
Ca ²⁺ conc (µeq L ⁻¹)
Mg ²⁺ conc (µeq L ⁻¹)
NO ₃ ⁻ conc (µeq L ⁻¹)
NH ₄ ⁺ conc (µeq L ⁻¹)
SO ₄ ²⁻ conc (µeq L ⁻¹)
Cl ⁻ conc (µeq L ⁻¹)
Dust particulate matter (mg m ⁻²)
temp_water (°C)
temp_air_max (°C)
temp_air_min (°C)
temp_air_current (°C)
temp_air_mean (°C)
temp_air (°C)
temp_soil_max (°C)
temp_soil_min (°C)
temp_soil_current (°C)

Atmospheric Aerosol Research; www.eusaar.net) that runs the Environmental Geochemistry and Atmospheric Research team from IDAEA-CSIC (Pey et al., 2010). At this location, BD was measured for the period 2002–2019, wet deposition (WD) for 2002–2007 and 2014–2019 and TF for 2011–2013. Bulk deposition and throughfall collectors consisted of 19-cm diameter polyethylene funnels connected to polyethylene bottles (10 L for BD; 2 L for TF). Wet deposition was sampled with an Anderson instrument (ESM Andersen, G78-1001). Despite the location changes, we deem that the atmospheric deposition data series is robust since deposition instruments stood <1 km distance between the different locations and there were neither inhabited houses nor roads (except the track to reach the site) in the neighbourhood. In the EUSAAR site, parallel BD and WD sampling allowed comparison between the two methods: very high correlation between them was found for the different ions, BD exceeding WD by around 37% for base cations (Izquierdo & Avila, 2012).

3.3 | Analytical methods

Streamwater and atmospheric deposition samples were taken to the laboratory the same day of collection. Within 48 h of sampling, pH was measured in unfiltered samples with an Orion pH meter and alkalinity was determined by a conductometric titration (Golterman et al., 1978). Water aliquots (60 mL) were filtered through a 0.45 µm pore-size membrane filter and stored frozen for later analysis. Ion chromatography (Dionex, Sunnyvale, USA) was used for Cl⁻, NO₃⁻ and SO₄²⁻ throughout the study period. Base cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) were analysed by atomic absorption/emission spectroscopy and NH₄⁺ by colorimetry (FIA Tecator) from 1983 to 2002. From 2002 on, all ions were analysed by ion chromatography using specific columns for cations (Dionex ACG4) and for anions (Dionex AS4). Data quality was evaluated with (1) synthetic solutions prepared in the laboratory with known ionic concentrations, accepting a 10% deviation of theoretical values, and (2) an ionic ratio (cation sum/anion sum) accepting a 20% variation respect the expected value (= 1.00). More details on 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⁺. Mean H⁺ required to be derived from acidity/alkalinity mean values, since pH is not a conservative variable when pH values in a period alternate from acidic to alkaline values (Liljestrand, 1985), as is here the case for precipitation. Annual volume-weighted mean alkalinity (alk) was transformed to mean pH with the equation: $\text{pH} = \log(\text{alk}) + 5.2$ (units in µeq L⁻¹), a relationship derived from the equilibrium equations of the CO₂ - carbonate system (Stumm and Morgan, 2012).

Some rain events during African-dust intrusions left a visible particulate residue on funnel walls. Such samples were filtered, particulate matter (PM) deposition was determined and chemical (ICP-MS and ICP-AOE), mineralogical (X-Ray diffraction) analyses were performed on PM (Avila et al., 1997).

Element input or output from the catchment was calculated as the sum of the element inputs or outputs for each sample in the period of interest (e.g. month, year). For a given precipitation or streamwater sample (S_i), ion input or output fluxes were calculated as the product of its ion concentrations by the water flux corresponding to S_i:

Ion input flux S_i = Concentration in bulk deposition S_i * Precipitation S_i.

Ion output flux S_i = Concentration in streamwater S_i * Drainage S_i.

With S_i concentrations in µeq L⁻¹ and water fluxes in L m⁻².

To calculate outputs, drainage for S_i is considered corresponding to 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}. 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). The comparison of input and output fluxes allowed to calculate element budgets for the catchments.

3.4 | Streamwater characterization

The Torrent de la Mina streamwaters were well buffered, with Na^+ and Ca^{2+} co-dominating as main cations and alkalinity as the main counterpart, both in TM0 and TM9 (Avila et al., 1995, 1999). Mean pH was 7.44 and 7.53 for TM0 and TM9 (Avila et al., 1999). Solute variation at TM9 was explained as the mixing of groundwater and deep-soilwater components, contributing 70 and 30% of annual run-off, respectively (Avila et al., 1996; Piñol et al., 1992). The two catchments responded rapidly to changes in atmospheric deposition: an alkalinity increase was found associated to declining sulfate deposition (Avila & 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

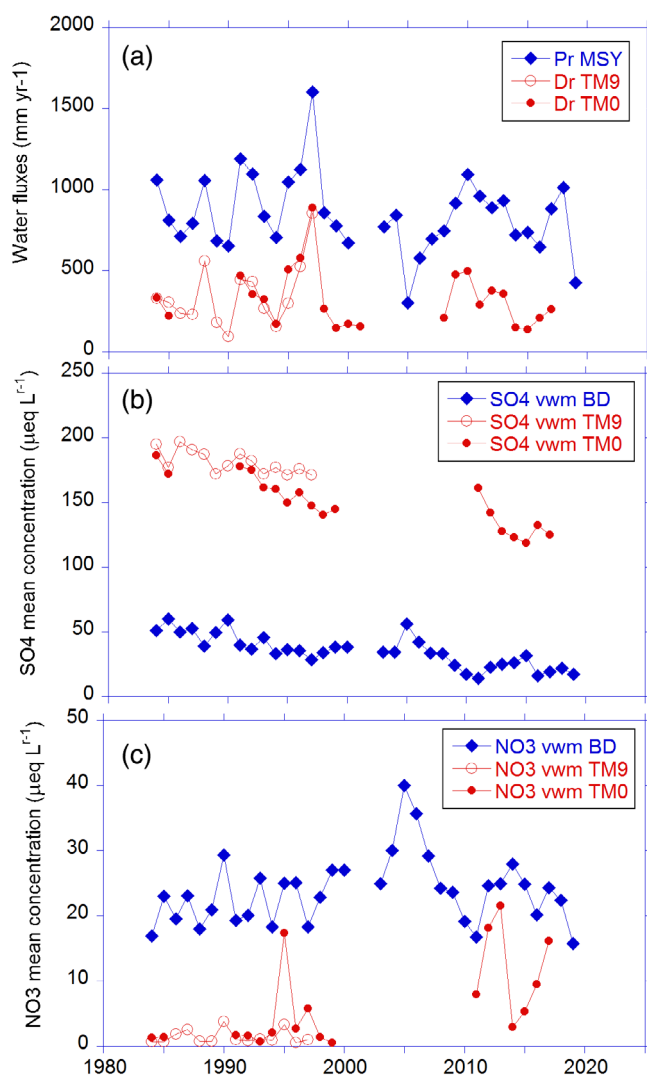


FIGURE 3 Temporal variation in: (a) hydrological fluxes, (b) sulfate: volume-weighted mean annual concentrations in bulk deposition (BD) and in TM0 and TM9 streamwater, and (c) nitrate: volume-weighted mean annual concentrations in bulk deposition (BD) and TM0 and TM9 streamwater.

exported as inorganic N in streamwater. However, higher nitrate concentrations in the stream and N 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 (Figure 3; Avila et al., 2020).

3.5 | Atmospheric deposition characterization

Rainwater in Montseny was rarely acidic, since sulfate and nitrate acid anions in precipitation were 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 only occurred before 1990.

4 | MAIN BIOGEOCHEMICAL RESULTS

Biogeochemical research at Montseny has shown the responsiveness of forested ecosystems to changes in atmospheric deposition (Avila et al., 2020; Avila & Rodà, 2012; Bernal et al., 2013). Models have been applied to predict the effects of forest management (Neal et al., 1995) and climate change on stream chemistry (Avila et al., 1996). Mineral dust, originated in North Africa (Avila et al., 2007) has been found to be an important contributor of nutrients and alkalinity to these forest ecosystems (Avila et al., 1997, 1998). Also, the specific response to nitrogen deposition of streams draining Mediterranean forests, as compared to other forest types, was demonstrated (Templer et al., 2022). Recently, the stream hydrological response to climate change scenarios from IPCC and to land use changes was modelled 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 knowledge of the species ecology provided an example of the use of data gathering and processing to help in the management of an endangered species.

Frequent episodes of African dust transport (Avila & Peñuelas, 1999) were 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 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, Avila et al., 2012). 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 & 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 was analysed by Izquierdo, Benítez-Nelson, et al. (2012) and Longo et al. (2014).

Because of concern on the negative eutrophying effects of N deposition, particular attention was devoted to characterize the N inputs to Montseny (Avila et al., 2002; García-Gómez et al., 2018; Rodà et al., 2002). 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 (Avila et al., 2017; Rodrigo et al., 2003). Lately, the role of the leaf microbiome was assessed using a multiple isotope approach (involving $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ in NO_3^- in wet deposition and throughfall) and quantification of *amoA* genes: microbial nitrification contributed but the dominant flux for nitrate in throughfall was atmospheric (Guerrieri et al., 2020).

In summary, 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 TMO 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 $\mu\text{eq/L}$) mostly during stormflows; as a consequence, 98% of dissolved inorganic deposition is retained in the catchments (Avila et al., 2020). The lack of relationship between inorganic N 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 & Rodà, 2012) providing more alkaline waters in these already well buffered streams, a striking fact for waters draining on silicate bedrock.

5 | DATASETS AND AVAILABILITY

We provide two datasets of open data for further exploration, syntheses and hypothesis testing. Files are provided for: (1) stream water flow and streamwater chemistry, doi:10.5281/zenodo.7228249; and (2) atmospheric deposition, doi: 10.5281/zenodo.7228266. They are freely available and no embargo applies to them.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available at <https://zenodo.org>, reference number 10.5281/zenodo.7228249 10.5281/zenodo.7228266.

ORCID

Anna Avila  <https://orcid.org/0000-0002-4137-0839>

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