

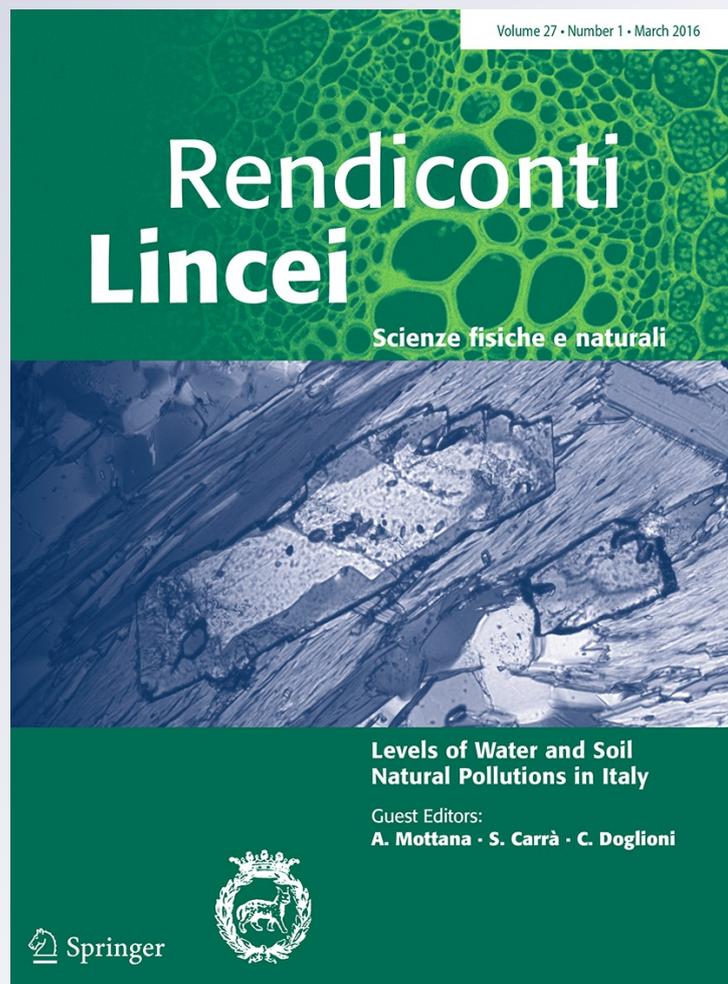
# *Release of nutrients into a forested catchment of southern Italy*

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## Release of nutrients into a forested catchment of southern Italy

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**Abstract** This work aims to improve the knowledge of nutrient exchanges between soil and atmosphere through a comparative analysis of the contribution coming from atmospheric depositions and their release in water runoff. The study has been realized on a mountain catchment, crossed by Bonis stream, tributary of Cino river and located in Sila Greca plateau (Calabria, Southern Italy). This experimental basin, laying on a basement formed by inclusive and plutonic rocks, extends for an area of 139 hectares, spreading from 975 to 1301 m a.s.l. The catchment is forested for about 95 % of its surface area with the main presence of *Pinus laricio* Poiret populations differentiated for age, density, tree canopy cover and stand characteristics within an area without human settlements and pollution sources. The basin has been instrumented, since 1986, to measure the main abiotic features in inflow and outflow discharges. These chemical and physical parameters, as N-NH<sub>4</sub>, N-NO<sub>2</sub>, N-NO<sub>3</sub>, P-PO<sub>4</sub>, S-SO<sub>4</sub>, Cl, pH and conductivity, have been analyzed on a fortnightly basis. From

collected data, it has been estimated, for each nutrient, its annual and monthly mean weighed concentrations to value the basin resilience after external inputs and its rolling action after some events, as acid depositions. In conclusion, the monitoring of mountain catchments could supply useful data about the global changes of atmospheric chemistry and, as a consequence, on the variability in quality control of surface waters, considering that mountain catchments supply most of water resources of a good-quality level for mankind.

**Keywords** Forested catchment · Hydrological processes · Solute transport · Nutrients · Calabrian pine

### 1 Introduction

The mountain catchments are the main source of a good-quality water supply. A correct water management suggests policies aimed to the planning, the optimization and, above all, the protection of this valuable natural resource. To date, there are some models, more or less compound, used in the management of water resources, fit to pretend the flow of waters and the loading of some solutes (Stoker and Seager 1974; Mosello et al. 1987; Frega and Infusino 1993; Viviani 2006). Some of these models disregard the extent of a bottom pollution owed to site features and, above all, to atmospheric deposition (Porto et al. 2011, 2013) affecting the fixation, volatilization, absorption and release of biogenic substances. Really, the atmospheric depositions affect directly biogeochemical loops and, therefore, the quality of water runoff caused by the interactions between soil, water and vegetation (van Dijk et al. 1992; Berger and Glatzel 1994). Since 1970s, in the United States of America (USA), some events of variations on chemical deposition, caused by human activities, were reported (Perkins 1974; Allegrini 1990;

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Paci 1997). Afterwards, some Swedish researchers related the depletion of aquatic environments and, in particular, the deterioration of some oligotrophic lakes, with the variations in chemical composition of daily rainfalls (Jorgensen 1974). In 1975, in Ohio State (USA), the “First International Conference on acid precipitation and on forest ecosystems” was held to study the progressive appearance of cytological and physiological effects of acid rain on forest vegetation (Gärtner 1986; Bäck and Huttunen 1992; McLoughlin and Tjolker 1992). Different ecosystems and, in particular, those of water bodies, are characterized, each one, by loops of biological elements able to reduce the negative effects of pollution through self-depuration processes (Duvigneaud and Denaeyer De-Smet 1973; Callegari and Infusino 2003; Callegari et al. 2005, 2006).

This work aims to improve the knowledge of the relationships between soil and atmosphere, through the comparative analysis of atmospheric deposition by nutrients and their following release in water outflows in a small experimental catchment into the Cosenza district of Sila Greca (39°25'15"N, 16°12'38"W, Calabria, Southern Italy), extending for an area without human settlements, of about 139 hectares. The study, indeed, wants to confirm the positive role performed by vegetation in the process of nutrient absorption, and in particular by nitrates, dissolved in atmospheric depositions reducing the pollution levels and the risk of contaminations in surface and deep waters. Besides, the study highlights that this catchment with its watercourse, by stream feature, shows some of the characteristics suggested by the EU Water Framework Direction (WFD) 2000/60/EC, requesting member states to point out their reference sites at high naturalness, without stating the guidelines to identify them.

## 2 Materials and methods

The study area (Fig. 1), of about 1.39 km<sup>2</sup> in surface area, extends from 975 to 1301 m a.s.l. and consists of a crystalline basement formed by intrusive and plutonic rocks generally fractured except some cutting valleys. The soils, largely on plutonic rocks, belong to the “Typic Xerumbrepts” association and, in small way, to the “Ultic Haploxeralfs” one in the surface layers of pleistocenic sediments in stream terraces. The catchment is forested for about 95 % of its surface area, whose 80 % is covered by Calabrian Pine (*Pinus laricio*, Poiret) populations, differentiated for age, density, tree canopy cover and stand characteristics (Table 1). Just small areas are interested by chestnut (*Castanea sativa*, Miller) reforestation (5.7 %), by catchment ditches (8.1 %) and other lands (1.2 %), colonized by black alder (*Alnus glutinosa*, Linnaeus) and aspen (*Populus tremula*, Linnaeus). The remaining basin surface is formed by clearings (2.0 %), sowable lands (1.4 %) and areas run by fire (1.6 %). The climate data, concerning the rainfall regime and

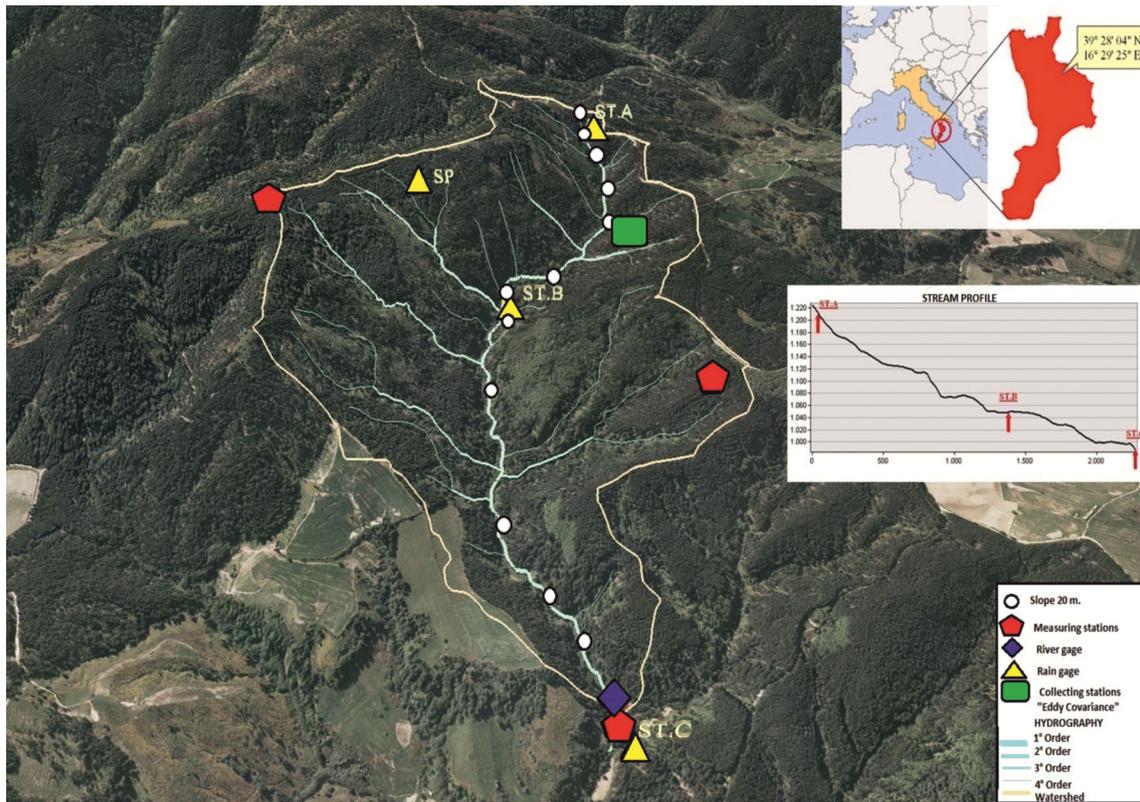
related to Lake Cecita Station, located at 1100 m a.s.l. and ongoing from 1924 to 2010 years, highlight a typical Mediterranean one with an average value of 1046.6 mm distributed in 99 rainy days. On a monthly basis, the higher rainfall data have been recorded in the months of October and November while the lowest ones have been recorded in June, July and August with the month of July lacking in rainfall events during many years of the tested time. The average monthly temperature is 9.9 °C with a mean monthly value of 2.0 °C in the coldest month and a mean monthly value of 18.6 °C in the hottest month.

The experimental catchment is supplied with three instrumented stations, located at Petrarella (1258 m a.s.l.), on the left side of Cino river, at Don Bruno (1175 m a.s.l.), on its right side, and at Bonis resort (975 m a.s.l.), at the closing section of the basin (Fig. 2), to measure the main climatic features as temperature, air relative humidity, wind speed and direction, solar radiation and pH depositions. Besides, in this last position, is located a lock chamber used for hydrological measures as highlighted, for instance, in the measures of the mean monthly rainfalls estimated in 1994 (Fig. 3). Indeed, the variations of hydrometric level have been measured by horizontal hydrometer (Iovino and Puglisi 1989; Callegari et al. 1994; Callegari and Veltri 1995). The assessment of atmospheric depositions has been realized in the three different stations. In particular, the Don Bruno station has been supplied with a tower, located at an elevation of 1100 m a.s.l., for the measurements of CO<sub>2</sub> and H<sub>2</sub>O exchanges on plant range, in a *P. laricio* reforestation plot carried out from 1960 to 1995 years. The mean annual value of the discharge rate, as average of all the analyzed stations, is 0.18 m<sup>3</sup>/s until 1993 year, reaching 0.35 m<sup>3</sup>/s in the following period after silvicultural practices that removed about 50 % of the total number of trees (30 % of the basal area) and interesting the whole basin. So, this behavior is, directly, related to the variations of interception and transpiration processes. To value the water standard grades, four measuring and collecting stations have been set up for the atmospheric deposition at different heights (min, med, max), three stations located in riverbed and one corresponding to Petrarella spring. In particular, for the sampling year 2004, the riverbed stations show the following features:

Station A (St. A): subtended surface 1.82 ha; annual flow 6070 m<sup>3</sup>, cleared in summer months (from June to August) and maximum in December; discharge coefficient 0.269; mean flow 0.20 L/s (Fig. 4).

Station B (St. B): subtended surface 12.73 ha; annual flow 42,449 m<sup>3</sup>, cleared in summer months and maximum in December; discharge coefficient 0.269; mean flow 1.37 L/s (Fig. 4).

Station C (St. C): subtended surface 139 ha corresponding to the closing section; annual flow 504,000 m<sup>3</sup> with



**Fig. 1** 3-D image of experimental area with instrumental and sampling site locations

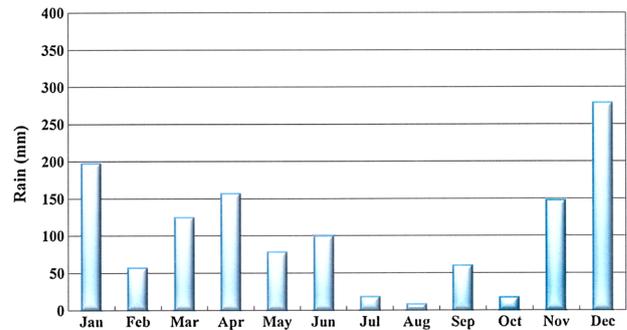
**Table 1** Morphological features of the experimental catchment

Surface area	139 ha	Basin mean slope	43.4 %
Basin perimeter	5.7 km	Stream channel slope	12.5 %
Stream channel length	2.2 km	Drainage mean slope	24.5 %
Mean elevation	1131 m a.s.l.	Stream channel slope	275 m
Maximum elevation	1301 m a.s.l.	Drainage density	7.43 km/km <sup>2</sup>
Outlet elevation	975 m a.s.l.	Gravelius coefficient	1.37



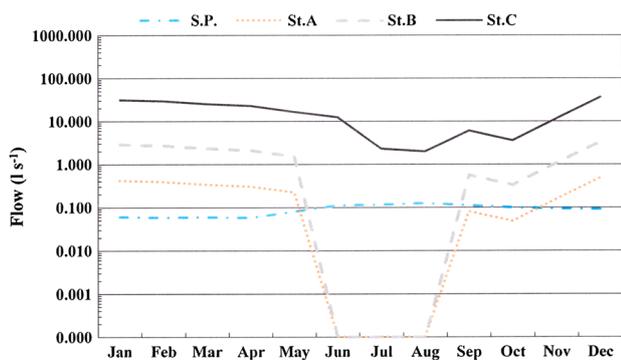
**Fig. 2** Hydro-weather instrumentation at the closing station

summer minimum values (2 L/s) and winter maximum values (36 L/s); discharge coefficient 0.294; mean flow 17.96 L/s (Fig. 4). The main temperature has been 10.1 °C with a minimum value of 6.8 °C in January and a maximum value of 14.0 °C in August.



**Fig. 3** Monthly mean flows measured in the three instrumental station in 1994

Petrarella spring station (S.P.): subtended surface 2.70 ha; discharge coefficient 0.797 highlighting an apparent feeding basin different from the real catchment, wider and deeper than the apparent one (Fig. 4). This



**Fig. 4** Monthly mean flows measured in A, B, C and Petrarella spring (S.P.) stations in 2004

last supposition is confirmed by the low variability of the recorded temperatures. Really, the mean temperature has been 9.4 °C with a minimum value of 8.6 °C in January and a maximum value of 11.3 °C in August. Finally, the storage coefficient of the basin is 24,805 m<sup>3</sup>, while the variability one is equivalent to 75 % of its discharge.

On 2004 year, for all the fluvial stations (St. A, St. B, St. C and S.P.), the following measures have been carried out.

1. The outflow measures have been lasted 24 h using a mechanical cooling sampler equipped with a flowmeter for outflow measures. 24 samplings have been realized on a fortnightly basis.
2. The atmospheric depositions have been collected with a mechanical cooling sampler. The samplings have been realized on a fortnightly basis.

In all the stations, collections of water samples have been performed and, afterwards, the main chemical and physical parameters have been measured such as nitrates, ammonia, phosphates, chlorides, sulfates, pH and conductivity estimated in the Laboratory of Water Cycle of UNICAL (University of Calabria). All the samplings and the following analysis have been conducted according to the handbook no. 64 and following updates edited by CNR-IRSA. Finally, the knowledge of atmospheric depositions and outflow discharges has permitted the assessment of their weighed averages that is:

$$C_p = \frac{\sum_{i=1}^{12} C_i \cdot X_i}{X_t} \tag{1}$$

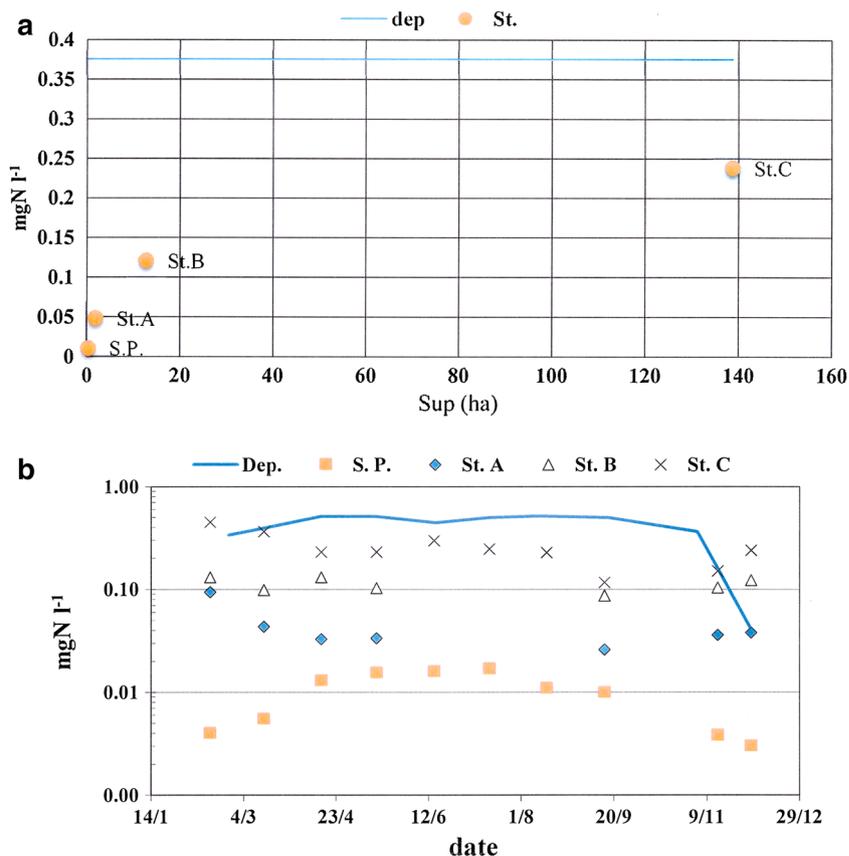
where  $C_p$  is mean weighed concentration;  $C_i$  mean monthly concentration;  $X_i$  monthly hydrological quantity (depositions, discharges),  $X_t$  annual hydrological quantity.

### 3 Results and discussion

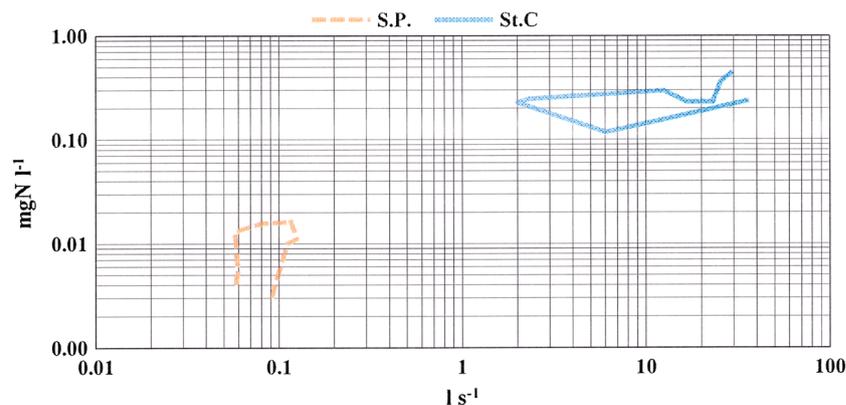
The results have highlighted mean weighed concentrations of nitrogen, in its own three forms (N-NH<sub>4</sub>, N-NO<sub>2</sub> AND N-NO<sub>3</sub>, for the three different stations, equal to: St.

A = 0.0485 mg N/L, St. B = 0.1210 mg N/L and St. C = 0.2384 mg N/L but, especially, nitrogen is present in its nitric form (St. A = 0.0454 mg N/L, St. B = 0.1119 mg N/L and St. C = 0.2316 mg N/L), while the other two nitrogen compounds are, almost, negligible. In Petrarella spring waters, the nitrogen compounds are detectable in slight mean weighed concentrations but the ammoniac rate shows higher percentages (8.98 %) than the other nitrogen forms analyzed. So, the annual weighed average concentrations increase with the raising of the subtended basin surface (Fig. 5a), appearing, however, lower than those of atmospheric depositions (0.376 mg N/L). The nitrogen monthly mean concentrations show, in all the stations, a temporal trend close to the discharge rates so that it could be predictable that the outflow workings could affect, also, the nitrogen release processes. Really, the nitrogen concentrations in deposition processes are affected by rainfall regime and so by discharge rates, Therefore, higher values of hydrological quantities correspond to lower values of nitrogen concentrations for watering effects (Fig. 5b). Regarding the discharge coefficients related to Station C, the leaks, caused by de-nitrification processes from living organisms, are valuable in 77 % as regards to those of atmospheric depositions. Likewise, to discharge flows, Petrarella spring shows nitrogen concentrations with a summer peak and a winter minimum. This behavior leads to assume that the nitrogen loading, stored in winter, could be discharged during summer months, as highlights the cyclic pattern of concentrations diagram related to discharge flows (Fig. 6). Instead, in A and B stations, the nitrogen concentrations show an opposite hydrological trend with winter peaks and summer minima. Finally, the closing station (St. C) is characterized by a mean pattern between those of spring and discharge flows. Indeed, in summer months, these concentrations, despite their falls, do not achieve the levels of the other two sections. Probably, the spring supply, feeding watercourse, is noticeable compared with runoff processes, as highlighted, also, by the temporal trend of mean concentrations. The P-PO<sub>4</sub> annual mean weighed concentrations, in atmospheric depositions, are scanty with values of 0.009 mg P-PO<sub>4</sub>/L close to those detected in watercourse stations (Fig. 7a). Indeed, from the analysis of discharge coefficients, it is pointed out that about 57 % of phosphorous is retained inside the basin from increasing biomasses for growing and infiltration processes as highlighted by biological and chemical loops (Duvigneaud and Denaeyer De-Smet 1973). The mean weighed concentration of phosphorous (0.085 mg P-PO<sub>4</sub>/L) at Petrarella spring station (S.P.) is at a higher degree than those of depositions, confirming its deep nature. From the comparison between the monthly trend of concentration in

**Fig. 5 a** Annual mean weighed concentrations of nitrogen related to the surface area of subtended basin and its contribution in depositions; **b** monthly mean weighed concentrations of nitrogen measured in A, B, C and Petrarella spring (S.P.) stations



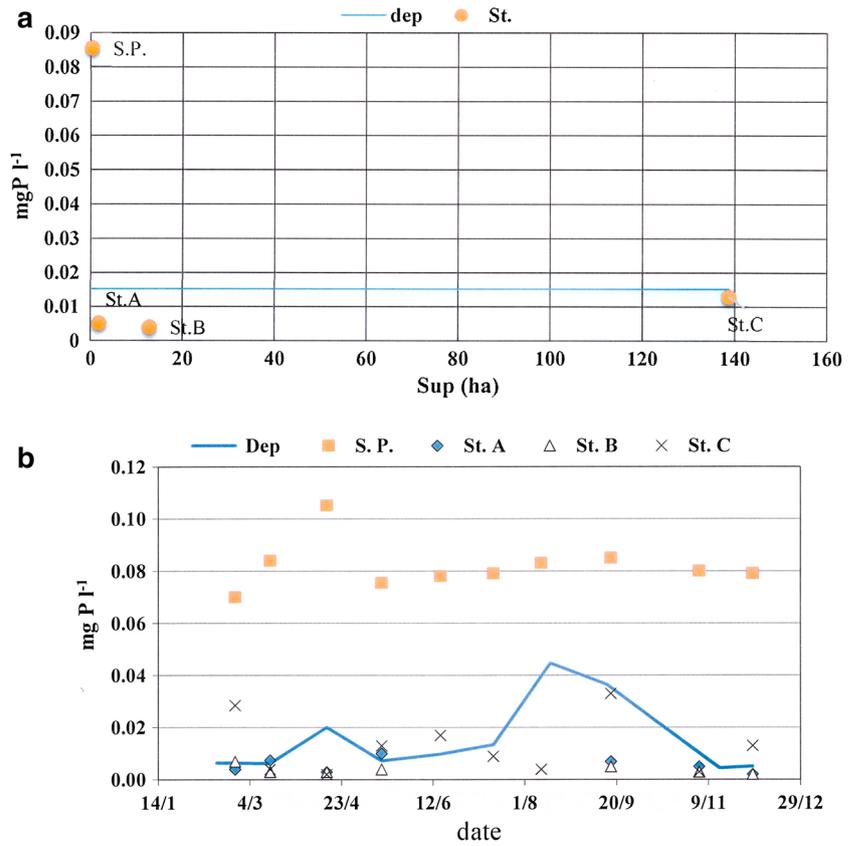
**Fig. 6** Annual mean weighed concentrations of nitrogen related to discharge flows in Petrarella spring (S.P.) and in C stations



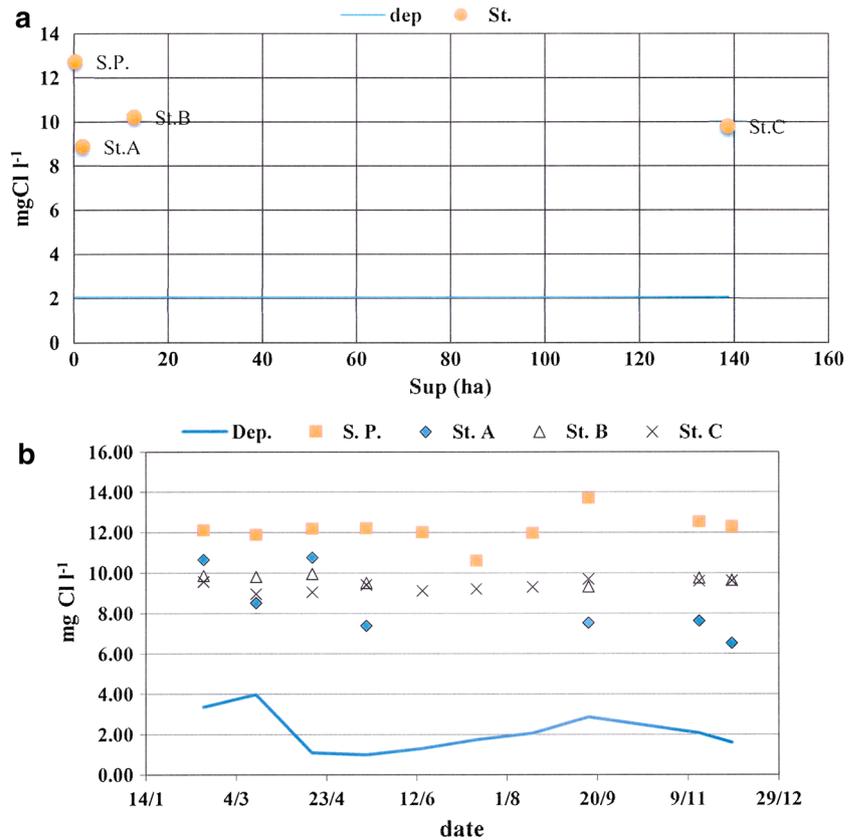
depositions at Petrarella spring station and those at Station C (Fig. 7b), it is pointed out, particularly in the maximum values checked, that the remarkable inflow, coming from depositions, is balanced, with some delay, to a similar one in the outflows. The time lag is, meanly, of 40 days in spring and 60 days in summer, confirming the fast loop of phosphorous. Especially, in Petrarella spring, the phosphorous concentrations are less affected by the trend of atmospheric depositions because spring waters tend to buffer the peak effects coming from external inputs. Likewise, nitrogen, also the phosphorous depositions are

lower than those pointed out in the catchment of Crati river (26–64 %), probably for the scanty presence of powders, fertilizers, and atmospheric emissions (Tamm 1951; Callegari and Infusino 1997; Callegari et al. 2005, 2006). The annual mean weighed concentrations of chlorides (Fig. 8a) in the watercourse are little changeable, including 8.88–10.21 mg Cl/L values (Fig. 8b), except Station P with a greater one of 12.73 mg Cl/L. So, the chlorides and the phosphates concentrations are much higher than those of atmospheric depositions, of about 2 mg/L, attesting a process of enrichment of spring waters

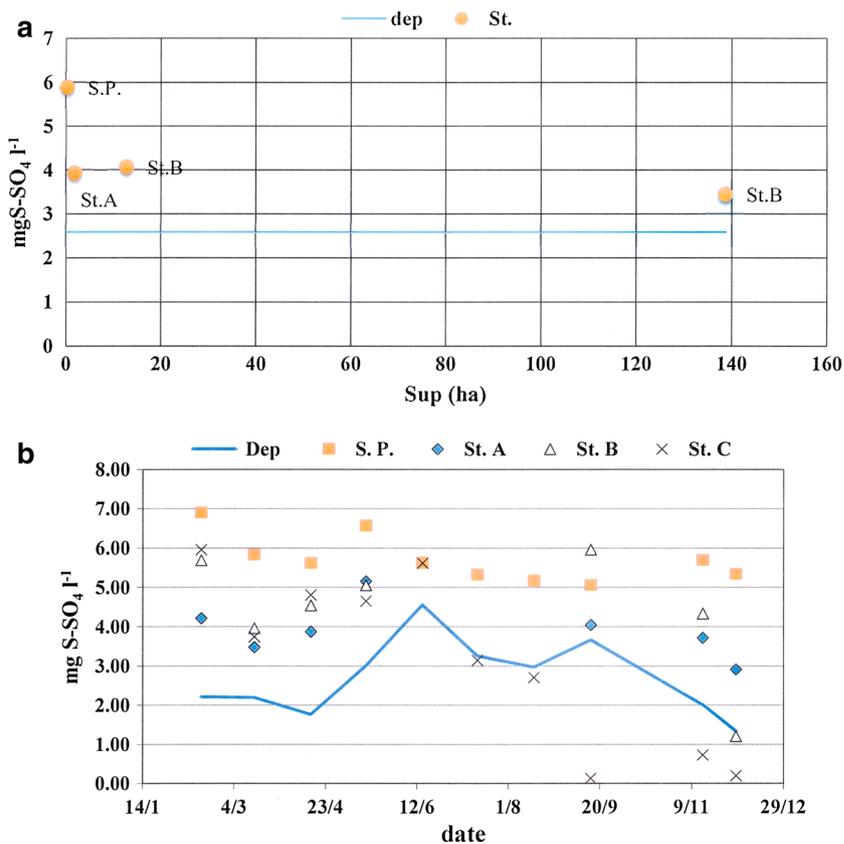
**Fig. 7 a** Annual mean weighed concentrations of phosphorous related to the surface area of subtended basin and their contribution in depositions; **b** monthly mean weighed concentrations of phosphorous



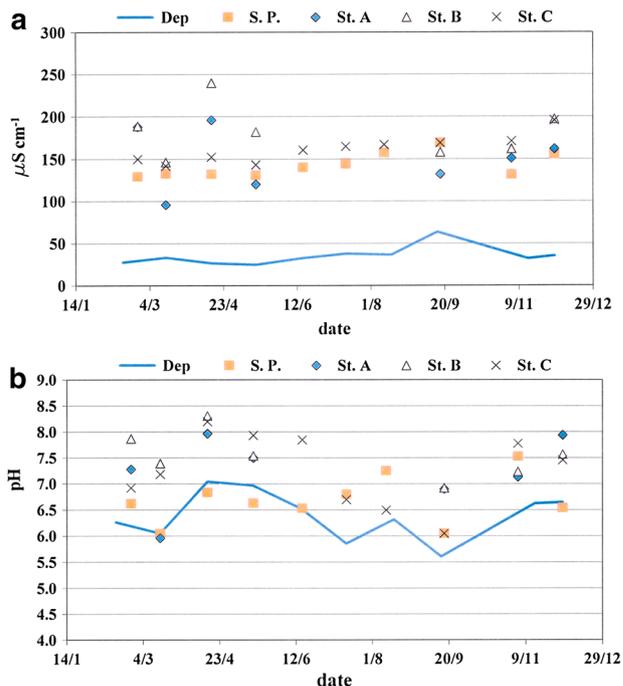
**Fig. 8 a** Annual mean weighed concentrations of chlorides related to the surface area of subtended basin and their contribution in depositions; **b** monthly mean weighed concentrations of chlorides



**Fig. 9 a** Annual mean weighed concentrations of sulphates related to the surface area of subtended basin and their contribution in depositions; **b** monthly mean weighed concentrations of sulphates



caused by their time contact with rocky substrata and contiguous soils. The annual weighed concentrations of sulfates (Fig. 9a) are quite steady along the watercourse (St. A = 3.933 mg S-SO<sub>4</sub>/L, St. B = 4.069 mg S-SO<sub>4</sub>/L and St. C = 3.449 mg S-SO<sub>4</sub>/L) and a little higher than those of atmospheric depositions (2.584 mg S-SO<sub>4</sub>/L). The spring water of Station P shows higher concentrations (5.89 mg S-SO<sub>4</sub>/L) than those of watercourse with a steady trend in time (Fig. 9b). The values of conductivity (St. A = 149.3 μS/cm, St. B = 182.1 μS/cm and St. C = 152.7 μS/cm) highlight that waters, draining in the catchment, are characterized by low salty content, while the relative values are, basically, unchangeable during the year showing an increasing trend in the dry period, on outflow decreasing, at the closing section (St. C) (Fig. 10a). The pH of watercourse feels the effects of depositional trend because the soils, crossed by waters, show a low buffering power. In fact, the pH values, checked in atmospheric depositions, are just lower than those of acid rain in the summer period (pH 5.65). These occurrences agree with the minimum values of watercourse, while pH values in the spring waters (S.P.) are, usually, little variable (Fig. 10b).



**Fig. 10 a** Monthly mean weighed conductivity; **b** monthly mean weighed pH

## 4 Conclusions

The tested catchment is a typical pattern of the effects of a widespread pollution while the punctual ones are absent. The reported study highlights that biogenic cycles result from the hydrological loop of watercourse, from deposition extents and from biotic environment.

The periods of minimum flow, in depositional absence, affect the concentrations of analyzed elements in surface waters, while spring waters perform a rolling action not only on flow discharges but also on ionic concentrations. These last ones, indeed, are quite regular but they are affected, in a greater way, by the lithological composition of the effective feeding basin. The concentrations of analyzed substances are all below the national thresholds for supporting the aquatic life of salmons. In these mountain areas whose waters are in a good-quality level, according to the ranking fixed by 152/2006 decree, the presence of a bottom pollution decreases according to the altitude and to the distance from pollution sources. In conclusion, it is necessary to study and protect these mountain catchments, that, nowadays, are barely monitored while, instead, could supply useful data about the global changes of atmospheric chemistry.

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