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Soil affects throughfall and stemflow under Turkey oak (*Quercus cerris* L.)

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## 24 **Abstract**

25 To investigate how soil properties affect throughfall and stemflow, we conducted a study in a forest  
26 of central Italy over a full hydrologic year to compare the chemical composition and the water  
27 fluxes of the throughfall and stemflow generated by Turkey oaks (*Quercus cerris* L.). The study  
28 was achieved on two adjacent areas that showed the same topography, supported Turkey oaks of the  
29 same height (about 20 m) and age (about 60 years), and received uniform precipitation (835 mm  
30 year<sup>-1</sup>). However, the two areas differed for soil reaction, one being acidic (area A, mean profile-  
31 weighted  $\text{pH}_{\text{H}_2\text{O}} = 5.84$ ) and the other sub-alkaline (area B, mean profile-weighted  $\text{pH}_{\text{H}_2\text{O}} = 7.55$ ).  
32 The branching angle and canopy volume of the oaks differed statistically (Wilcoxon signed-rank  
33 test at  $\alpha = 0.05$ ) between areas, with the slender trees of area A having more upward thrust  
34 branches. As a consequence, the oaks of area A produced more stemflow per unit canopy surface  
35 than those of area B, as indicated by the amount of stemflow per unit soil surface (15-cm radius)  
36 around the trunk base and by the stemflow funneling ratio per basal area ( $F_{P,B}$ ). The annual fluxes  
37 determined for 17 solutes were higher in throughfall than in rainfall, except for F and  $\text{HCO}_3^-$ ,  
38 reflecting the enrichment and acidification of the precipitation water as it flows through the canopy.  
39 For the full hydrological year, the enrichment ratios ( $E_{P,B}$  and  $E_{P,T}$ ) indicated that the stemflow of  
40 area A was more enriched than that of area B for the following solutes: total N, TOC, total acidity,  
41 carboxylic acidity, phenolic acidity, and  $\text{NH}_4^+$ . Several significant differences in throughfall  
42 (electrical conductivity, Ca, Mg, K,  $\text{NO}_3^-$ , total N, total organic C, organic anions) and in stemflow  
43 (pH, electrical conductivity, Ca, Mg, Na, Cl,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ) chemistry were observed between areas  
44 over the course of three time-series of rainfall events (throughfall series T1, from September to  
45 November 2004; throughfall series T2, from December 2004 to February 2005; stemflow series S1,  
46 from March to September 2004). The study further demonstrated the existence of strong links  
47 between the significant differences in soil properties (pH, exchangeable Ca and K, effective cation  
48 exchange capacity, total and organic C content, mineralogy) and the significant differences in  
49 throughfall and stemflow chemistry (pH,  $\text{HCO}_3^-$ , Ca, K, electrical conductivity) recorded between

50 the two areas. The main processes involved in the short-scale spatial differentiation of throughfall  
51 and stemflow at the site appeared to be either soil-dominated like pedogenesis, mineral weathering  
52 and organic matter transformation, or tree-mediated such as elemental biocycling.

53

54 **Keywords:** atmospheric precipitation; water fluxes; elemental fluxes; biocycling; pedogenesis.

55

## 56 **1. Introduction**

57 Before reaching the soil surface, the chemical composition of incident atmospheric precipitation can  
58 be strongly modified by the vegetation. In the case of individual trees or of a full vegetation canopy,  
59 two major downward water fluxes were defined: the water percolating and dripping through the  
60 canopy, termed throughfall, and the rainfall that flows downward along branches and trunks, termed  
61 stemflow. Both throughfall and stemflow fluxes can release substances by solubilizing and washing  
62 off a wide range of compounds derived from atmospheric deposition or released by plant tissues  
63 such as organic compounds, gases, and dissolved ions (Cronan and Reiners, 1983; Levia and Frost,  
64 2003; Levia and Herwitz, 2005; Zimmermann et al., 2007; Levia et al., 2011). In contrast, some of  
65 the dissolved substances included in the throughfall and stemflow solutions can be absorbed by  
66 plant and, under some conditions, adsorbed onto plant surfaces (Alcock and Morton, 1985;  
67 Chuyong et al., 2004; Song et al., 2016). Furthermore, the reaction of rainfall with gases such as  
68 CO<sub>2</sub>, NO<sub>x</sub>, and SO<sub>x</sub> present in the atmosphere and/or trapped within the canopy produces acids  
69 (H<sub>2</sub>CO<sub>3</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>), which increase the total acidity of the solutions moving through the  
70 canopy (van Breemen et al., 1982; Fenn and Bytnerowicz, 1997; Held et al., 2017). To partly  
71 counterbalance these acidifying reactions, the dissolution of the fine carbonate and silicate particles  
72 present in the atmospheric dust was reported to neutralize some of the acidity of throughfall and  
73 stemflow solutions (Celle-jeanton et al., 2009; Brecciaroli et al., 2012; Shen et al., 2013). Other  
74 factors known to affect properties and composition of throughfall and stemflow are the type of plant  
75 association (Freedman and Prager, 1986; Crockford and Richardson, 2000; Levia and Frost, 2003),  
76 the presence of adventitious roots (Herwitz, 1991), and the chemical and physical properties of  
77 rainfall (Lovett et al., 1985; Matschonat and Falkengren-Grerup, 2000; Nanko et al., 2011).

78 The impact of throughfall and stemflow on soil properties and processes has been assessed under  
79 deciduous and coniferous trees, bushes and in various agricultural settings (Zinke, 1962; Brecciaroli  
80 et al., 2012; Gaitán et al., 2016; Zhang et al., 2016). Throughfall inputs were shown to contribute to  
81 the soil elemental supply by transferring nutrients accumulated on leaves as dissolved substances or

82 particulate matter in dripping throughfall solutions (Sheppard et al., 1989; Macinnis-Ng et al., 2012;  
83 Návar, 2013). Throughfall also influenced the structure of microbial communities and their spatial  
84 variability in soil (Rosier et al., 2015). Stemflow chemistry was reported to increase soil acidity and  
85 organic C content (Kaneko and Kofuji, 2000; Levia and Germer, 2015; da Costa et al., 2017), while  
86 stemflow chemical composition and fluxes were recognized able to trigger the podzolization  
87 process by inducing the formation of E material around the trunk and the largest roots of Corsican  
88 pines (*Pinus nigra* Arn. ssp. *laricio*) on sandstone derived soils (Certini et al., 1998).

89 Paradoxically, to the best of our knowledge, studies on the exclusive effects of distinct soil types –  
90 with all other environmental factors (climatic conditions, chemistry of the atmosphere, exposition,  
91 elevation, slope, stand age, etc.) being constant – on the fluxes and chemical composition of the  
92 throughfall and stemflow produced by trees have not been reported. This situation is probably due  
93 to the scarcity of environmental settings adequate for performing such a study, since soils with  
94 significantly different properties produce contrasted biogeochemical environments and generally  
95 host different plant species and vegetation types. The lack of studies like this could also be due to  
96 the challenge of controlling confounding factors posed by a field study of this type.

97 A field site that satisfied the requirements of a study able to disclose the effects of soil properties on  
98 throughfall and stemflow chemistry under a single tree species was identified in a forest of central  
99 Italy. The site covers an area of 8 ha and hosts a forest dominated by Turkey oak (*Quercus cerris*  
100 L.) and, to a lesser extent, Downy oak (*Quercus pubescens* Willd.). Interestingly, the soil of the  
101 forest has a sub-alkaline reaction over much of its surface, but also contains an area of about 5400  
102 m<sup>2</sup> where soil is acidic. The peculiarity of this site was discovered because of the presence of an  
103 acidophilic bush (*Erica arborea* L.) in a landscape dominated by basophilic plants, and was used to  
104 conduct works dealing with soil evolution and ecology (Corti et al., 2005; Cocco et al., 2013).

105 In this context, the aim of this work was to test the hypothesis that soil properties affect, directly or  
106 via plant-mediated processes, the chemistry of throughfall and stemflow solutions. Therefore, we  
107 conducted a field study in the two adjacent areas with acidic and sub-alkaline soils, respectively,

108 which were dominated by the same even-aged tree species, Turkey oak, and had different  
109 physicochemical properties. Our specific objectives were: 1) to compare the chemical composition  
110 and the water fluxes of the throughfall and stemflow solutions generated by Turkey oaks growing  
111 on the two soil types, and 2) to identify the links existing between the differences in the throughfall  
112 and stemflow chemistry on the one hand, and in the soil properties and processes on the other hand.

113

## 114 **2. Materials and methods**

### 115 *2.1. Study areas*

116 The study site is located in the Gallignano forest (43°33'42'' N, 13°25'47'' E), Ancona province,  
117 Italy. The mean annual air temperature is 13.6 °C, and the mean annual precipitation is 780 mm.

118 The site is at about 5.5 km from the shoreline of the Adriatic sea, ranges from 125 to 195 m above  
119 sea level, has a 10-15 % slope with a NNW exposure, and receives the dominant and strong winds  
120 from N and NW (Brecciaroli et al., 2012). Within a radius of 2 km from the site there are four small  
121 villages for a total of about 600 inhabitants, several dozens of country homes for a total of not more  
122 than 400 inhabitants, and a dozen of small craft activities. At about 10 km to NNW, there is a small  
123 to medium sized oil refinery; previous investigations have shown that the refinery has no socio-  
124 environmental impacts farther than 4-5 km from the plant (Corti et al., 2009; ARPAM, 2012).

125 The site is covered by a mixed forest dominated by Turkey oak (*Quercus cerris* L.) with Downy  
126 oak (*Quercus pubescens* Willd.) as the main accompanying tree species, and has been managed as  
127 coppice for centuries (Table 1). The mean age of trees was about 60 years at sampling in 2004. This  
128 even-aging is typical of the coppice systems, where plants are all cut at the same moment, except  
129 for few dozens of saplings per hectare.

130 The soil developed from sequential beds of Plio-pleistocene marine sediments (Cocco et al., 2013).

131 For the present study, we selected two areas located 50-m apart supporting only Turkey oaks in all  
132 the upper canopy strata but with different soil types: area A (0.54 ha) has an acid soil, whereas area  
133 B (7.5 ha) surrounds area A and has a sub-alkaline soil. The genesis of the acid soil within an

134 alkaline environment was due to the presence of geological layers (lenses) with a low content of  
135 carbonates that were progressively acidified by organic acids or ligands carried down by the soil  
136 solution. This, combined with erosion processes, generated a soil with sub-acid reaction at the  
137 surface (Corti et al., 2005). A further acidification of the soil, which brought the  $\text{pH}_{\text{KCl}}$  around  
138 values of 4, was attributed to the presence and activity of *Erica* plants (Cocco et al., 2013).

139

## 140 2.2. Soil morphology and sampling

141 At an altitude of about 180 m, three different soil profiles were dug in area A and area B in 2004  
142 with a distance of 10 m between the profiles. Each profile was opened at about 1 m from a Turkey  
143 oak trunk. The soils were described according to Shoeneberger et al. (2002), and their mean  
144 morphological descriptions are reported in Table 1. In area A, the topsoil of flat surfaces was  
145 formed by thin Oi, Oe, and A horizons resting on a sequence of two bleached horizons (E and EB),  
146 while in the sloping surfaces a thin Oi horizon covered the sequence of bleached horizons. In both  
147 cases a series of Bw horizons followed, reaching the top of a BCk horizon at about 80 cm depth.  
148 This soil was classified as fine, mixed, acidic, mesic, Typic Dystrudept (Soil Survey Staff, 2014). In  
149 area B, rather continuous Oi and Oe horizons covered a dark layer about 20-cm thick made of an A  
150 and an AB horizon; underneath, a sequence of Bw horizons reached the depth of 60-70 cm, where  
151 the upper limit of a BC horizons was found. This soil was classified as fine, mixed, calcareous,  
152 mesic, Typic Eutrudept (Soil Survey Staff, 2014).

153 In each of the six profiles, a sample of at least 1 kg was collected from every horizon, air-dried in  
154 the laboratory, and sieved at 2 mm.

155

## 156 2.3. Soil analyses

157 The pH was determined potentiometrically in water and in a 1M KCl solution at a solid: liquid ratio  
158 of 1:2.5. The exchangeable cations were determined on 2-g specimens that were placed into  
159 centrifuge tubes, submerged with a 0.2 M BaCl<sub>2</sub> solution (solid: liquid ratio of 1:10) and shaken for



160 20 min at room temperature (Hendershot et al., 2007). The mixture was left to rest for 10 minutes,  
161 gently shaken for few seconds to re-suspend the sediments, and then centrifuged at 1400 g for 5  
162 minutes. The extracted solutions were filtered through Whatman 42 filter paper. The filtered  
163 solutions were analyzed for exchangeable Ca, Mg, K and Na with a Shimadzu AA-6300 atomic  
164 absorption spectrophotometer (Tokyo, Japan), and for Al with a Varian SpectrAA 220Z atomic  
165 absorption spectrophotometer (Mulgrave, Australia) equipped with a pyrolytically coated graphite  
166 furnace. Exchangeable H was calculated from the pH difference between the 0.2 M BaCl<sub>2</sub> solution  
167 before and after contact with the soil samples (Corti et al., 1997). Effective cation exchange  
168 capacity (ECEC) was obtained as the summation of exchangeable cations. Base saturation was  
169 obtained by dividing the sum of exchangeable Ca, Mg, K, and Na by the ECEC value. Total C and  
170 N contents were measured using a Carlo Erba EA-1110 dry combustion analyzer (Carlo Erba  
171 Instruments, Milan, Italy), while the organic C content was estimated by the Walkley–Black method  
172 without application of heat (Allison 1965). Available P was determined according to Olsen et al.  
173 (1954).

174 Particle-size distribution was determined after the removal of organic matter with Na-hypochlorite  
175 (NaOCl) solution at 6 % of active chlorine adjusted to pH 9 with HCl (Lavkulich and Wiens, 1970).  
176 The coarse (2.00–0.50 mm), medium (0.50–0.25 mm) and fine (0.25–0.05 mm) sands were obtained  
177 by wet sieving, while silt (50–2 µm) was separated from clay (< 2 µm) by sedimentation.

178 The mineralogical composition was determined on manually compressed powdered specimens  
179 (Whitting and Allardice, 1986). The x-ray diffractograms were acquired by a Philips PW 1830  
180 diffractometer (Philips, Eindhoven, Netherlands), using the Fe-filtered Co-K $\alpha$ 1 radiation and  
181 operating at 35 kV and 25 mA. The step size was 0.02°2 $\theta$  and the scanning speed was 1 second per  
182 step. Semi-quantitative estimation was obtained by identifying the minerals on the basis of their  
183 characteristic peaks (Brindley and Brown, 1980; Dixon and Schulze, 2002). Clay minerals were  
184 differentiated using the standard treatments: saturation with Mg and K at 25°C, solvation of the Mg-  
185 saturated specimens with glycerol, and heating of the K-saturated specimens at 550°C. The

186 abundance of each mineral was estimated from the surface area of the respective primary peak by  
187 multiplying the peak height by the width at the peak half-height.

188 Each soil analysis was run in duplicate. Duplicate values were averaged and these averages were  
189 used to calculate the horizon mean and the standard deviation ( $n = 3$ , the number of profiles per  
190 area) for any given soil horizon of area A and area B.

191

#### 192 *2.4. Tree metrics*

193 In 2004, 10 Turkey oak trees were selected in both areas A and B to measure tree properties. To  
194 avoid intraspecific variability of the oaks, we excluded the saplings left during the last cut, and only  
195 selected plants with similar bark and leaves morphology. For these 20 trees, the metrics measured  
196 were: the age determined by ring counting on samples taken with a Pressler auger, the trunk  
197 diameter at breast height (DBH) measured using a calibrated caliper, the vertical height obtained  
198 with a Haga gun altimeter, the projection of the canopy to the soil surface determined by direct  
199 delineation of the canopy periphery, the volume of the canopy estimated by multiplying the canopy  
200 thickness (Haga altimeter) by its projection to the soil, and the insertion angle of the two main  
201 branches measured with a scale protractor.

202

#### 203 *2.5. Sampling and analysis of leaves*

204 To sample leaves, one cluster of three Turkey oaks trees was defined in each area using the above  
205 10 trees. The trees were selected in order to obtain clusters with similar age and height in the two  
206 areas, and with no other tree species under the canopy. The two clusters were also used to sample  
207 throughfall and stemflow solutions (see below). Ten leaves were collected in July 2004 from each  
208 tree using a sling-shot because the lower branches were at a height exceeding 15 meters. For a given  
209 tree, a composite sample was prepared with the 10 leaves and air-dried to constant mass. The leaves  
210 were pulverized and digested using the hot acid method (Cloutier-Hurteau et al., 2014). Briefly, 200  
211 mg of specimen were treated overnight with 2 mL of concentrated nitric acid (trace metal grade,

212 HNO<sub>3</sub>) in 16×125 mm Pyrex ignition tubes. The mixtures were then heated at a mean temperature  
213 of 120°C for five hours in a block digester. The solution volume was adjusted to 50 mL with  
214 deionized water and the suspensions were decanted and filtered through a nylon membrane (Magna  
215 – 0.45 µm). The concentration of total Ca, Mg, K, Na, P, S, Cu and Zn was obtained by optical  
216 emission spectrometry (Perkin-Elmer ICP-OES, Optima 8300).

217

## 218 *2.6. Sampling of rainfall, throughfall, and stemflow*

219 Rainfall, throughfall, and stemflow solutions were collected in the two areas during a full annual  
220 hydrological cycle, from March 10, 2004 to February 28, 2005. Throughfall was sampled using six  
221 bulk collectors positioned under the Turkey oak clusters described above. They were made of a 26-  
222 cm Ø (528.3 cm<sup>2</sup> surface area) plastic, permanently open funnel standing at 1.5 m from the forest  
223 floor, covered with a plastic (polypropylene) net (18 mesh) and connected to a buried 25-L high-  
224 density polyethylene (HDPE) container via a coiled tube to limit evaporation. Stemflow was  
225 collected from the three trees forming the cluster by a 3-cm Ø plastic half-tube attached and closely  
226 sealed to the trunk surface. It circled around the trunk from a height of 1.7 to 0.5 m and was  
227 attached to a buried 60-L HDPE container. Rainfall was sampled in the open in two throughfall-  
228 type collectors set 30-m apart, one close to each of the two areas. All the containers were acid  
229 washed (10 % HCl) and rinsed with deionized-ultrapure water between rainfalls.

230 Rainfall, throughfall, and stemflow were all collected the same day, after each precipitation event  
231 (or series of events) of more than 20 mm in order to obtain a sufficient solution volume for  
232 analyses. The collecting equipment used and the burying of the containers insured that solute  
233 concentration due to evaporation was negligible. Because of this approach and the use of  
234 permanently open funnels, we collected the waters periodically, but we obtained a continuous water  
235 sampling over the hydrological year. According to Nihlgård (1992) and Zimmermann et al. (2010),  
236 this is the most correct method to highlight differences in throughfall and stemflow fluxes and  
237 chemistry, because discontinuous sampling based on a single event collection leads to biased results

238 since periods with low rainfall but with highest concentrations are not included. Over the course of  
239 this study, rainfall, throughfall, and stemflow were collected for a total of 20 different sampling  
240 periods: six during spring, from March 23 to June 8, 2004; two during summer, from June 22 to  
241 September 20, 2004; seven during autumn, from September 29 to December 7, 2004; and five  
242 during winter, from December 23, 2004 to February 28, 2005 (plus the March 10, 2004 event). In  
243 each case, water fluxes were determined in the field. Once collected, the solutions were stored in a  
244 portable refrigerator and brought to the laboratory where they were immediately processed for  
245 chemical analysis.

246 The rainfall depth was expressed in mm, and the same was done for throughfall after its collected  
247 amount (L) was divided by the surface of the canopy projection to the soil (m<sup>2</sup>). Because stemflow  
248 does not infiltrates on a defined soil surface, we divided the collected stemflow amount (L) by a soil  
249 surface (m<sup>2</sup>) surrounding the trunk base with 15-cm of radius. Following Herwitz (1986) and Levia  
250 and Germer (2015), we also calculated the stemflow funneling ratio per basal area ( $F_{P,B}$ ). This  
251 parameter does not refer to the infiltration area at the soil surface but has the advantage of being  
252 related to easily measurable data. This ratio is expressed by equation (1)

$$253 \quad F_{P,B} = S_y / P \cdot B \quad (1)$$

254 where,

255  $S_y$ , stemflow yield, is the stemflow volume per tree, in L;

256  $P$  is the precipitation depth, in mm;

257  $B$  is the basal area of the trunk at breast height, in m<sup>2</sup>.

258 This ratio describes the efficiency of each tree to capture rainfall and to generate stemflow, and  
259 allows comparing stemflow amounts for plants with different DBH (Siegert and Levia, 2014; Levia  
260 and Germer, 2015).

261

## 262 2.7. Solution analysis

263 The pH was determined by a combined glass-calomel electrode while electrical conductivity (EC)

264 was measured by a WTW multi 340i conductivity meter (Weilheim, Germany). Total N and total  
265 organic C (TOC) were measured with a Carlo Erba EA1110 combustion analyzer after the  
266 specimens were acidified and freeze-dried. Total organic acidity was determined according to  
267 Schnitzer and Khan (1972) and Perdue (1985) by back titration of a BaOH treated solution with a  
268 0.1 M HCl solution. Carboxylic acidity was determined by treating the samples with dissolved  
269 calcium acetate (CH<sub>3</sub>COOCa) and by a potentiometric titration of the produced CH<sub>3</sub>COOH with a  
270 0.1 M NaOH solution. The phenolic-OH groups were calculated by subtracting the carboxylic  
271 acidity from the total organic acidity.

272 After filtration through a 0.45- $\mu$ m polycarbonate membrane (Millipore), the Ca, Mg, K and Na  
273 concentrations were measured by a Shimadzu AA-6300 atomic absorption spectrophotometer. The  
274 NH<sub>4</sub> and inorganic anions (F, Cl, Br, NO<sub>3</sub>, HPO<sub>4</sub>, and SO<sub>4</sub>) concentrations were measured with a  
275 Dionex Ions System Chromatograph 4500i model (Houston, Texas). The HCO<sub>3</sub> ions were  
276 determined by potentiometric titration after bringing the solutions to pH 3.8 with a 0.1 M HCl  
277 solution (Fishman and Friedman 1989). Organic anions were estimated, on an equivalent basis, by  
278 calculating the difference between the sum of total dissolved cations and anions.

279 The rainfall, throughfall and stemflow solutions were analyzed in triplicate. These analytical  
280 replicates were averaged for each collector. The mean and standard deviation of each event were  
281 then calculated for area A and area B using the analytical mean obtained from all collectors of a  
282 given type (rainfall = 1; throughfall = 6; stemflow = 3).

283 To examine the extent of solute enrichment as rainfall is transformed into stemflow, we calculated  
284 two stemflow enrichment ratios per basal area. The first one relates stemflow enrichment to rainfall  
285 flux,  $E_{P,B}$  (Levia and Herwitz, 2000), and the second relates stemflow enrichment to throughfall  
286 flux,  $E_{T,B}$  (Levia and Germer, 2015). These parameters are expressed as equations (2) and (3),  
287 respectively:

$$288 \quad E_{P,B} = S_y \cdot C_s / P \cdot B \cdot C_p \quad (2)$$

289 where,

290  $C_S$  is the solute concentration in stemflow ( $\text{mmol L}^{-1}$  or  $\mu\text{eq L}^{-1}$ );  
291  $C_P$  is the solute concentration in the precipitation ( $\text{mmol L}^{-1}$  or  $\mu\text{eq L}^{-1}$ );  
292 with  $S_y$ ,  $P$ , and  $B$  as in equation (1);  
293 and

$$294 \quad E_{T,B} = S_y \cdot C_S / T \cdot B \cdot C_T \quad (3)$$

295 where,  
296  $T$  is the amount of throughfall, in mm;  
297  $C_T$  is the solute concentration in throughfall ( $\text{mmol L}^{-1}$  or  $\mu\text{eq L}^{-1}$ );  
298 with  $S_y$ ,  $C_S$ , and  $B$  as in equations (1) and (2).

299

### 300 *2.8. Data treatment and statistical analysis*

301 To complement the above analysis of stemflow enrichment with the  $E_{P,B}$  and  $E_{T,B}$  parameters, we  
302 ran a preliminary analysis on the variability of the chemical composition of throughfall and  
303 stemflow. The datasets clearly showed that the temporal variability of solution chemistry was high  
304 across the 20 events for both areas A and B. The magnitude of differences in the chemistry of  
305 throughfall and stemflow between the two areas also appeared to vary substantially among events.  
306 To address variability, we used principal component analysis (PCA), a data reduction technique, to  
307 explore for the presence of temporal trends (grouping of events on the PCA ordination plot) or of  
308 spatial patterns (grouping of solution collectors on the PCA ordination plot) in throughfall and  
309 stemflow chemistry. We first conducted four separate PCA, two for area A (throughfall, stemflow)  
310 and two for area B (throughfall, stemflow) on the full datasets including the 20 sampling periods.  
311 To explore in more detail the existence of temporal trends in the differences between areas A and B,  
312 we subsequently performed 40 different PCAs [one for each sampling period for throughfall ( $n=20$ )  
313 and for stemflow ( $n=20$ )], which considered the overall chemistry (18 chemical variables in each  
314 PCA) of the solutions. This yielded PCA plots showed, for a single event, the collectors of the two  
315 areas positioned as a function of their overall chemistry. The PCA plots first led to the observation

316 that collectors from areas A and B were either closely grouped together (no chemical difference  
317 between areas for that event) or dispersed (apparent chemical difference between areas for that  
318 event). Secondly, the events showing apparent differences in throughfall and/or stemflow chemistry  
319 between areas A and B were consecutive. These temporal sequences were organized as three time-  
320 series of events that did not strictly matched seasons (Fig. 1). One series was composed of  
321 throughfall data (series T1) and covered the period September 20 to November 4, 2004 for a total of  
322 five events. Another series also contained throughfall data (series T2) and included the four events  
323 from December 23, 2004 to February 28, 2005. A third series was composed of stemflow data  
324 (series S1) and extended over nine consecutive events from March 10 to September 20, 2004.  
325 Statistical analyses were run for individual chemical variables on these three time-series.

326 The normality of distributions was tested for all variables with the Shapiro-Wilk test in SPSS  
327 version 20 (Razali and Wah, 2011). Because distributions were still not normal after data  
328 transformations (log and square root), the non-parametric Wilcoxon signed-rank test at  $\alpha=0.05$  was  
329 used to establish the significance of differences between the two areas in the concentration of  
330 individual chemical variables for rainfall, throughfall, and stemflow. This test is particularly suited  
331 when comparing two dependent datasets, like it is the case in this study of two adjacent sites sharing  
332 similar environmental settings. The Wilcoxon test was first performed on each of the rainfall,  
333 throughfall and stemflow full datasets (20 sampling periods for each solution type) for chemical  
334 variable individually. It was then conducted to compare the rainfall, throughfall and stemflow  
335 differences in individual chemical parameters between areas for each of the three time-series. The  
336 Wilcoxon test was also used to compare the chemistry of soils and leaves, the metrics of trees and  
337 water fluxes in rainfall, throughfall and stemflow between area A and area B.

338 Of note is the fact that the mean values reported in some tables are weighted to take into account the  
339 contrasts in horizon thickness for means of soil properties or the differences in water depth between  
340 events for rainfall, throughfall or stemflow means across time-series.

341

### 342 **3. Results**

#### 343 *3.1. Properties of the soils*

344 The weighted mean profile  $\text{pH}_{\text{KCl}}$  of area A was significantly more acidic than that of area B (Table  
345 2). The difference in pH between the two areas was marked until the 2Bw2 horizon, down to a 40-  
346 60 cm depth, and could be traced deeper, in the lower Bw horizons (Data in brief, Table S1). In the  
347 bottom tier, below a depth of about 75 cm, the soil pH similarly rose to sub-alkaline values in the  
348 two areas. The exchangeable Ca and K levels together with effective cation exchange capacity  
349 (ECEC) significantly differed between areas with values being higher in area B, in agreement with  
350 pH data. Total C was also higher in area B, signaling the higher abundance of carbonates at this site  
351 compared to the soil of the more acidic area A. Organic C content was much higher in area B than  
352 in area A, mostly because of differences between the superficial horizons. The significantly finer  
353 texture of the soil of area A, with less sand and more silt, reflected, at least in part, the higher  
354 intensity of weathering reactions occurred at this site because of its acidity (Tables 1 and 2).

355 In both areas, the mineralogy of soils was mostly inherited from the parent material, and resulted  
356 dominated by quartz, plagioclases, and the HIV/HIS mixture (hydroxy-interlayered vermiculite and  
357 hydroxy-interlayered smectite) with micas and kaolinite as accessory minerals, despite a decrease of  
358 the former in area A (Data in brief, Table S2). Hydroxy-interlayered vermiculite (HIV) was only  
359 detected in the soil of area B, while calcite abounded in area B and was present solely at depth in  
360 area A.

361

#### 362 *3.2. Metrics for Turkey oak trees*

363 The Turkey oak trees were of similar age and height in the two areas ( $n = 10$  trees per area), but  
364 significantly differed with respect to their diameter at breast height and to the angle of insertion of  
365 the two main branches in the trunk (Table 3). The narrower branching angle of the Turkey oaks in  
366 area A than in area B ( $39.5^\circ$  versus  $61.2^\circ$ ) was associated to significantly smaller canopy projection



367 and volume. When only the three trees of the two clusters were considered for the comparisons,  
368 none of the six metrics varied between the areas.

369

### 370 *3.3. Chemistry of Turkey oak leaves*

371 The total elemental contents of the Turkey oak leaves at site A were systematically higher in the  
372 leaves of the trees from area A (Fig. 2), when the eight elements were considered simultaneous in  
373 the statistical analysis (composite sample of 10 leaves per tree; three trees per area). For Mg, K, Na  
374 and P, the differences between areas ranged from 27 to 29 % and were more pronounced than for  
375 Ca, S and Cu (11 to 20 %). At 7 %, the micronutrient Zn showed the lowest concentration increase  
376 in the leaves of area A.

377

### 378 *3.4. Water fluxes in rainfall, throughfall and stemflow*

379 The total annual amount of rainfall and throughfall was similar in areas A and B (Table 4). In  
380 contrast, stemflow (calculated both on a trunk-surrounding surface basis and as  $F_{P,B}$ ) differed  
381 significantly between the two areas and was higher in area A where trees had a narrower branching  
382 angle, smaller canopy volume, and lower projection to the ground. With 835 mm, the rainfall during  
383 the 2004-2005 hydrological year was slightly higher than the historic mean of 780 mm. It was  
384 mostly recorded during spring (29%) and autumn (37%), when two-thirds of the total rain fell (Data  
385 in brief, Table S3). Throughfall water fluxes represented close to 80% of total rainfall, whereas 0.39  
386 to 0.67% of annual rain was transformed into stemflow (Table 4). Interception loss and subsequent  
387 evaporation was estimated at about 20% of rainfall on a yearly basis.

388 The amount of rain that fell over areas A and B during the time-series T1, T2, and S1 represented  
389 24.2, 20.6 and 41.9 %, respectively, of annual rainfall (Table 5). They generated about 24.0 % (T1)  
390 and 23.3 % (T2) of the yearly throughfall and 39-41% (S1) of the annual stemflow at both areas  
391 (Table 6). The T1 series occurred during the growing season whereas T2 was a dormant season  
392 series; S1 was intermediate and covered the two seasons (Fig. 1).

393

### 394 3.5. Chemical composition of rainfall solutions

395 The overall results indicated that the chemistry of rainfall was spatially uniform at the scale of the  
396 experimental site during the whole study period (Data in brief, Table S3). Thus, when the 20  
397 hydrologic events were considered simultaneously, total N was the only rainfall solute that differed  
398 significantly between area A and area B (Appendix A1).

399 Except for the higher pH and  $\text{HCO}_3$ , the mean concentrations in rainfall were always lower than in  
400 the throughfall and stemflow solutions during the whole period (Appendixes A1, A2, and A3) and  
401 in the three-time series (Tables 5 and 6). It reflected the acidification and the solute enrichment the  
402 rain undergoes when the incoming water percolates through the oak canopy. The mean  
403 concentrations in rainfall did not differ between areas during the two throughfall time-series, but  
404 some differences were noted for S1 with total N, TOC, and Na concentrations, which were  
405 significantly higher in area B (Table 5).

406

### 407 3.6. Chemical composition of throughfall and stemflow solutions

408 When the 20 hydrologic events were considered simultaneously in the statistical analysis, only  
409  $\text{HCO}_3$  differed significantly between the areas in throughfall solutions (Appendix A2). For  
410 stemflow solutions, differences between areas included pH, Ca, Mg, Na, Cl, and  $\text{HCO}_3$  (Appendix  
411 A3). Based on  $E_{P,B}$  and  $E_{P,T}$ , the stemflow of area A was more enriched than that of area B for  
412 several solutes, with total N, TOC, total acidity, carboxylic acidity, phenolic acidity, and  $\text{NH}_4$  being  
413 common to both parameters (Fig. 4). However, these contrasts were not due to permanent  
414 differences between areas along the year as the magnitude of differences in the throughfall and  
415 stemflow chemistry between the two areas varied substantially among events.

416 Out of a total of 19 variables used for the comparison of throughfall and stemflow between areas,  
417 the time-series T1, T2, and S1 had respectively 6, 11 and 10 variables that showed significant  
418 differences between area A and area B (Table 6). Note that Br and  $\text{HPO}_4$  data are presented only in

419 Data in brief (Tables S3, S4, and S5) and were not used for statistical analyses because the  
420 concentration of most samples was below the detection limit of the method. Among the 19  
421 variables, EC, Ca, and NO<sub>3</sub> were the only three that differed significantly between areas for all  
422 time-series (T1, T2, and S1). For these three variables, solutions were always more concentrated in  
423 area B. A group of five other variables (pH, Mg, K, HCO<sub>3</sub>, and organic anions) had significantly  
424 different levels during two of the three series. These latter differences were equally distributed  
425 among the throughfall and stemflow time-series. Similar to EC, Ca, and NO<sub>3</sub> values, the Mg, K, and  
426 organic anions concentrations were higher in the solutions of area B; the differences in pH and  
427 HCO<sub>3</sub> were however not similarly partitioned between the areas (Table 6). Eight other variables  
428 significantly differed between areas but for only one of the three series, either T2 (total N, TOC,  
429 total acidity, and phenolic acidity) or S1 (amount, Na, Cl, and SO<sub>4</sub>).

430

### 431 *3.7. Chemical fluxes in throughfall*

432 Annual fluxes of matter per unit surface area were calculated for rainfall and throughfall to estimate  
433 net fluxes and to determine elemental behavior during water percolation through the oak canopy  
434 (data not shown). Among the 17 variables (water and EC were excluded), the total net fluxes  
435 (throughfall minus rainfall fluxes, in meq m<sup>-2</sup> for major ions and mmol m<sup>-2</sup> for organic compounds)  
436 were almost always positive for both areas A and B, indicating that throughfall was enriched  
437 following contact with leaves, twigs and branches. The main elemental behavior in the incoming  
438 rainwater was therefore characterized by the removal of particulate, dissolved, and gaseous matter  
439 from the canopy due to the release of organic and inorganic substances from oak tissues and/or to  
440 the dissolution of compounds that had accumulated on plant surfaces between rain events. The three  
441 variables that showed the largest increase in net throughfall flux were TOC (increased by a factor of  
442 20, +20x), organic anions (+18x), and K (+5x). The total N, carboxylic group, Mg, Na, Cl, and SO<sub>4</sub>  
443 fluxes also increased with factors ranging from 1.1 to 3.9. The only two variables that showed

444 negative net throughfall fluxes, or a net retention in the oak canopy, were F and HCO<sub>3</sub>, the latter  
445 reflecting the overall decrease in pH from rainfall to throughfall.

446

#### 447 **4. Discussion**

##### 448 *4.1. Contribution of rainfall to throughfall and stemflow*

449 The very high similarity of both volume and chemical composition of the rain falling over areas A  
450 and B essentially ruled out a major role for incident precipitation in determining the significant  
451 differences existing between the two areas in the chemical composition of throughfall and stemflow  
452 during the three time-series, and over the whole study period (Tables 4 and 5). The only exception  
453 was the higher total N in the rainfall of area B during the study period. As such, the throughfall  
454 differences during T2 (total N, NO<sub>3</sub>) and S1 (NO<sub>3</sub>) can be viewed as direct effects of rainfall  
455 chemistry, notably because the soil total N content is identical in the two areas (Tables 2, 5, and 6).  
456 These observations, however, do not negate the indisputable and well documented role exerted by  
457 the chemical composition of incoming rainfall on the nature, concentration or proportion of the  
458 chemical mixture found, at any location, in throughfall and, to a lesser extent, in stemflow solutions  
459 (Macinnis-Ng et al., 2012).

460

##### 461 *4.2. Spatial differences in the properties of Turkey oak trees*

462 The morphological properties of oak trees differed substantially between the two areas (Table 3).  
463 Yet, because the areas were immediately adjacent, there were no significant differences in climatic  
464 conditions and in topography (Table 1). Similarly, local records report no differences in forest  
465 management between areas. In this context, we associated some of the differences in tree  
466 morphology to soil spatial differences arising from the local variability in parent material. Soil was  
467 not only significantly more acidic and poorer in organic C at site A than at site B, but it also had  
468 lower exchangeable Ca and K, and ECEC (Table 2). In brief, the soil of area A was less fertile and  
469 we submit that soil variability could have had an effect on oak morphology over a 60-year period of

470 growth, in conjunction with other determinants of tree morphology such as competition for space  
471 and light. Low soil N and P levels were indeed reported to lead to more vertical crown and lateral  
472 root branching angles in maize and *Arabidopsis* (Kozlowski, 1997; Aphalo and Rikala, 2003;  
473 Roychoudhry and Kepinski, 2015). It follows that any potential effect that tree morphology could  
474 have on the production and chemical composition of throughfall and stemflow should be considered  
475 as a soil-mediated effect, not as unidirectional impact of vegetation on throughfall and stemflow.

476 Morphological data also revealed the existence of clear links between the connection angle of the  
477 main oak branches, canopy volume and the canopy projection to the ground surface. The trees with  
478 the narrower branching angle were structured along a more vertical axis than trees with a wider  
479 angle and, therefore, had a smaller canopy volume and canopy projection surface (Table 3).  
480 Consequently, these slender trees with upward thrust branches were more efficient in funneling  
481 incoming rainwater and in directing water flow towards the trunk (Levia and Germer, 2015). All  
482 other factors being constant, these trees produced a higher amount of stemflow per unit canopy  
483 interception surface. This type of interactions in oak morphology could explain the significantly  
484 higher amount of stemflow produced in area A than in area B (Table 4). No effect was noted on  
485 throughfall production probably because differences in stemflow amounts were low compared to  
486 throughfall water fluxes. The fact that several solutes gave the highest  $E_{P,B}$  and  $E_{P,T}$  values in area A  
487 was ascribed to the narrower branching angle of the oaks of this area, which were able to increase  
488 substantially the stemflow fluxes. The different oak morphology of the two areas, with more slender  
489 trees and lower DBH in area A than in area B, further supports the hypothesis the lower soil fertility  
490 has affected the morphology of oak canopy.

491 Oaks not only differed in morphology but also with respect to leaf chemistry (Fig. 2). The  
492 systematic difference found between areas, with oak leaves being always more nutrient-rich in area  
493 A than in area B, was rather unexpected and could not be fully explained. In fact, in sclerophyll  
494 species like Turkey oak, leaves show a decrease in the concentration of inorganic constituents when  
495 plants increase structural carbon compounds like cellulose, lignin, cutin and waxes to overcome soil

496 stress conditions (Bussotti et al., 2000; Orgeas et al., 2002; Asner et al., 2014). Following this  
497 rationale, the trees in area A should have produced leaves poorer in nutrient cations than in area B  
498 because the soil of the latter area was more fertile and had a higher level of plant available solutes.  
499 Yet, and similar to our observations, Orgeas et al. (2002) also found opposite trends between the  
500 chemical composition of soil and leaves, but only for K and P. However, we also ascribed our  
501 results to the smaller canopy volume of the trees from area A with respect to those of area B. It is  
502 possible that, notwithstanding the tendency of Turkey oaks of area A to reduce inorganic  
503 constituents in the leaves because of poor soil fertility, there could have been a concentration of  
504 nutrients since they were distributed in a smaller canopy.

505

#### 506 *4.3. Relationships between soil processes and throughfall or stemflow properties*

507 Our results suggested a dominant role of soil properties and processes in explaining the differences  
508 in throughfall and stemflow chemistry between areas. This role apparently exceeded that of  
509 precipitation and vegetation with soil pH, total and organic C content, ECEC, exchangeable Ca and  
510 K, texture and mineralogy being the main soil properties that were statistically linked to the  
511 observed differences (Table 2). In some cases, almost direct links could be determined between soil,  
512 throughfall and stemflow properties.

513 The soils of the two areas formed from similar parent materials and their genesis involved processes  
514 like soil acidification, mineral weathering and transformation, solute leaching and the lessivage of  
515 fine particles (Cocco et al., 2013). The progression of pedogenesis over the last millennia not only  
516 resulted in the vertical segregation of the parent material into distinct soil horizons (Table 1), but  
517 also established differences in texture, mineralogy, pH, exchangeable Ca and K, ECEC, and total C  
518 that can presently be observed between the soils of areas A and B (Table 2, and Tables S1 and S2 of  
519 Data in brief). At the Gallignano Forest, the presence and polarity (ranking of the value of a  
520 variable in area A versus area B) of some of these differential soil changes was echoed in the  
521 throughfall and stemflow solutions. For example, differences in soil total C and in exchangeable Ca

522 and K were linked to significant differences in Ca concentrations (Fig. 3) and EC during the three  
523 time-series, and in K concentrations during T1 and T2 (Table 6). Other processes, namely soil  
524 acidification and the concomitant dissolution of calcite at site A (Data in brief, Table S2), were also  
525 mirrored by the higher pH and HCO<sub>3</sub> values of the stemflow of area B during S1.

526 The input of organic matter to soil is mainly due to litterfall, root exudation, root decomposition and  
527 throughfall processes. The subsequent decomposition of organic substances is controlled by  
528 microbial activity that, in turn, is a function of soil properties like pH, aeration, and nutrient  
529 availability (Coleman et al., 2004). The soil of area B was sub-alkaline and contained more  
530 nutrients and clay particles than the soil of area A (Table 2), a set of properties favoring biomass  
531 production and, consequently, the accumulation of organic matter as organo-mineral complexes.  
532 This is reflected by its higher organic C, hence organic matter, content (Data in brief, Table S1).  
533 Because soil organic matter controls ECEC (Sposito, 1989), the organic C difference between areas  
534 contributed directly to the difference in exchangeable Ca and K, and to the higher throughfall (Ca  
535 and K) and stemflow (Ca) concentrations of area B discussed above. The organic anions (T1 and  
536 T2) and TOC (T2) concentrations in throughfall could also be a reflection of soil organic C  
537 differences, but these signals were too weak to be conclusive.

538 Soil genesis and organic matter changes are affected by biological activity but elemental biocycling  
539 clearly appears as a plant-mediated process. Biocycling is the uplift of elements by plants, notably  
540 trees, from deep horizons towards the top of the soil profile (Jobbagy and Jackson, 2004; Agnelli et  
541 al., 2016). The cycled elements concentrate at the surface after a sequence of dissolution,  
542 absorption, transport, and litterfall reactions. Nutrient cations are strongly affected by biocycling  
543 and, thus, tend to concentrate in the topsoil where most fine roots are located. Biocycling, together  
544 with organic matter accumulation, explains why the highest soil exchangeable Ca and K  
545 concentrations are found in the A or AB horizons of area B (Data in brief, Table S1) and, thus,  
546 jointly contributed to increase the dissolved Ca (T1, T2, and S1) and K (T1 and T2) in throughfall  
547 and stemflow solutions.

548

#### 549 *4.4 Input of airborne sea salts*

550 Sodium and Cl concentrations were significantly higher in the stemflow solutions of area B during  
551 time-series S1 (Table 6). No such trend was noted for Na and Cl during the two throughfall time-  
552 series. Moreover, only Na was higher in the rainfall of area B during S1. These differential  
553 stemflow Na and Cl fluxes could be linked to wind-blown salt particles or sea sprays from the  
554 Adriatic Sea located about 5.5 km from the study site. The larger and wider oak canopy of area B  
555 (Table 3) conferred superior interception efficiency to the trees, allowing each tree to capture more  
556 Na- and Cl-containing particles or water droplets. The absence of sea salt effect in throughfall  
557 solutions further suggests that the Na- and Cl-bearing particles and sprays were mainly present on  
558 branch and trunk surfaces, possibly because most Na and Cl were impacted during the leafless  
559 period. Since the trees of area B also produced less stemflow than those of area A (Table 4), Na and  
560 Cl should therefore be expected to be higher in the stemflow of area B. The sea salt input process  
561 could also explain the increase in SO<sub>4</sub> concentrations during S1 in area B (Table 6).

562

### 563 **5. Conclusions**

564 This study is one of the very first to reveal the direct effect of soil properties, together with plant-  
565 mediated effects, on the chemical composition of throughfall and stemflow solutions. The study ran  
566 over a full hydrologic year and was conducted under Turkey oak in a unique forest ecosystem  
567 where confounding environmental factors like climate, topography, stand age, and forest  
568 management were the same in the two studied areas. The results showed the existence of strong  
569 links between the nature of the significant differences in soil properties (pH, exchangeable Ca and  
570 K, ECEC, total and organic C content, mineralogy) across the areas and the nature of the significant  
571 differences in throughfall and stemflow chemistry (pH, EC, Ca, K, HCO<sub>3</sub>), over the course of three  
572 series of rainfall events (T1, T2, and S1). The main processes invoked to explain these short-scale  
573 spatial differences in throughfall and stemflow were either soil-dominated like differential



574 pedogenesis, mineral weathering, and organic matter transformation, or tree-mediated such as  
575 elemental biocycling. Furthermore, the different branching angle and canopy volume between the  
576 two areas supports the influence of soil fertility on oak morphology and, consequently, on fluxes.  
577 Indeed, the slender trees of area A having more upward thrust branches produced higher stemflow  
578 amounts per unit canopy surface. In summary, the wealth of data gathered during the course of this  
579 study not only establishes strong links between spatial patterns in pedogenesis and  
580 throughfall/stemflow chemistry, but also constitutes a first step in reviewing our understanding on  
581 the overall role of soils on elemental fluxes under forest canopies.

582

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589

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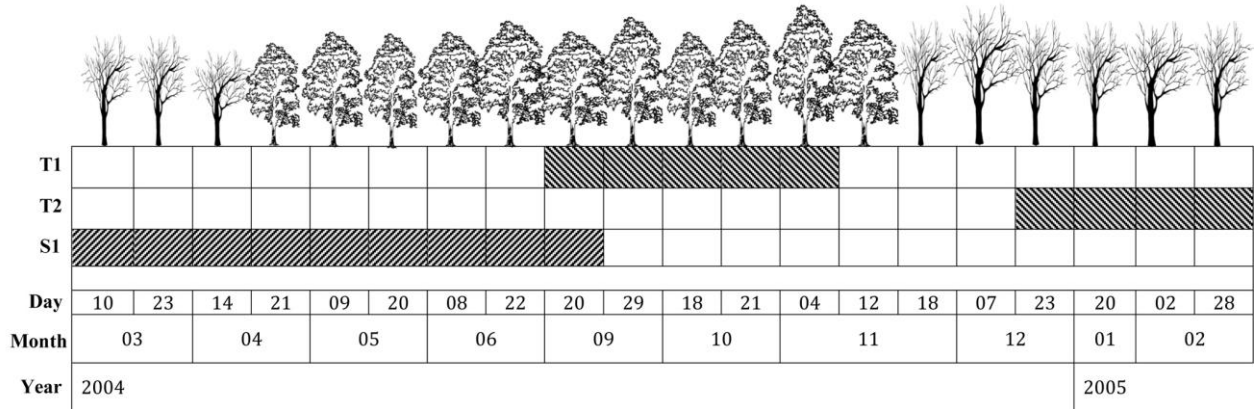
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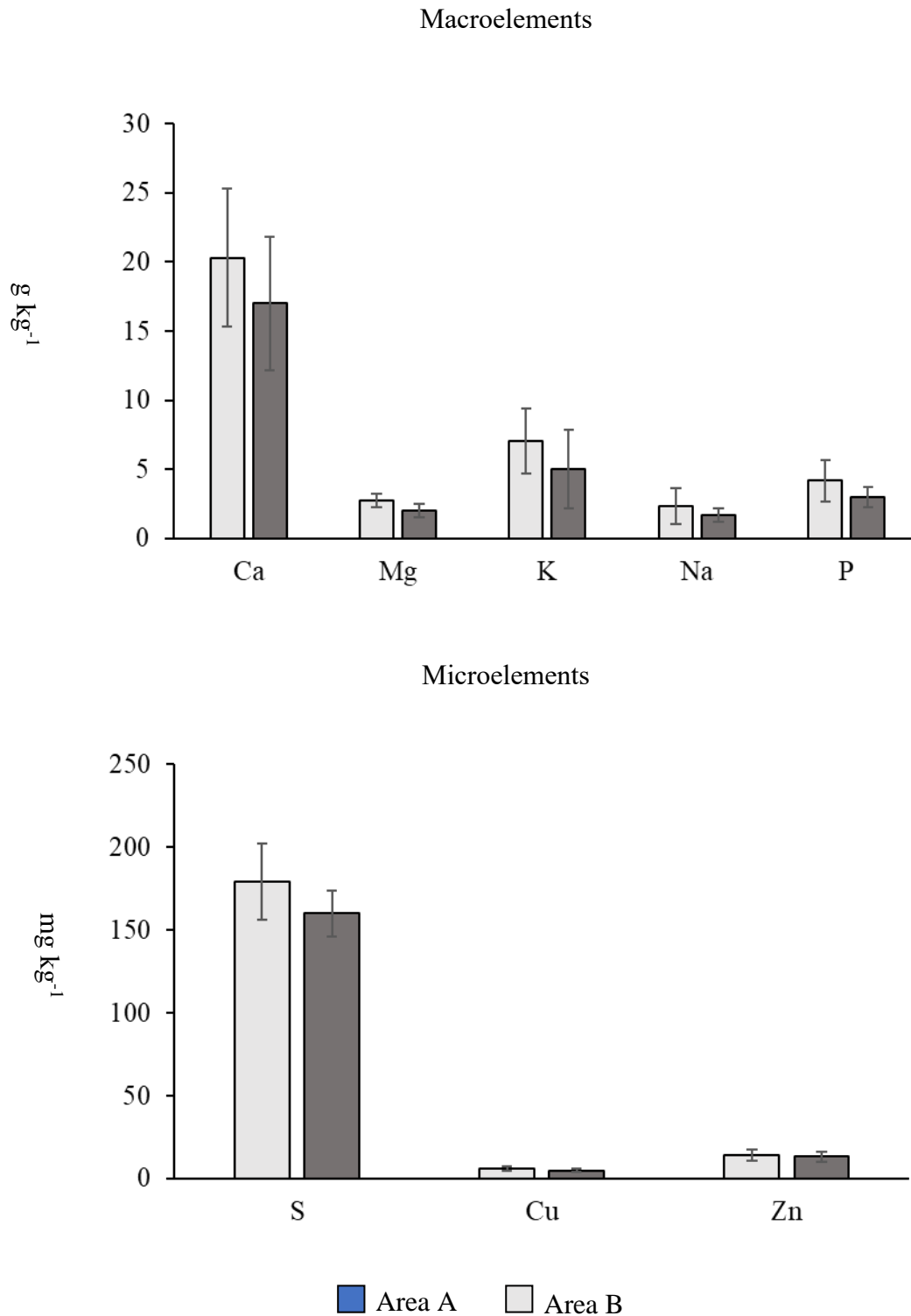
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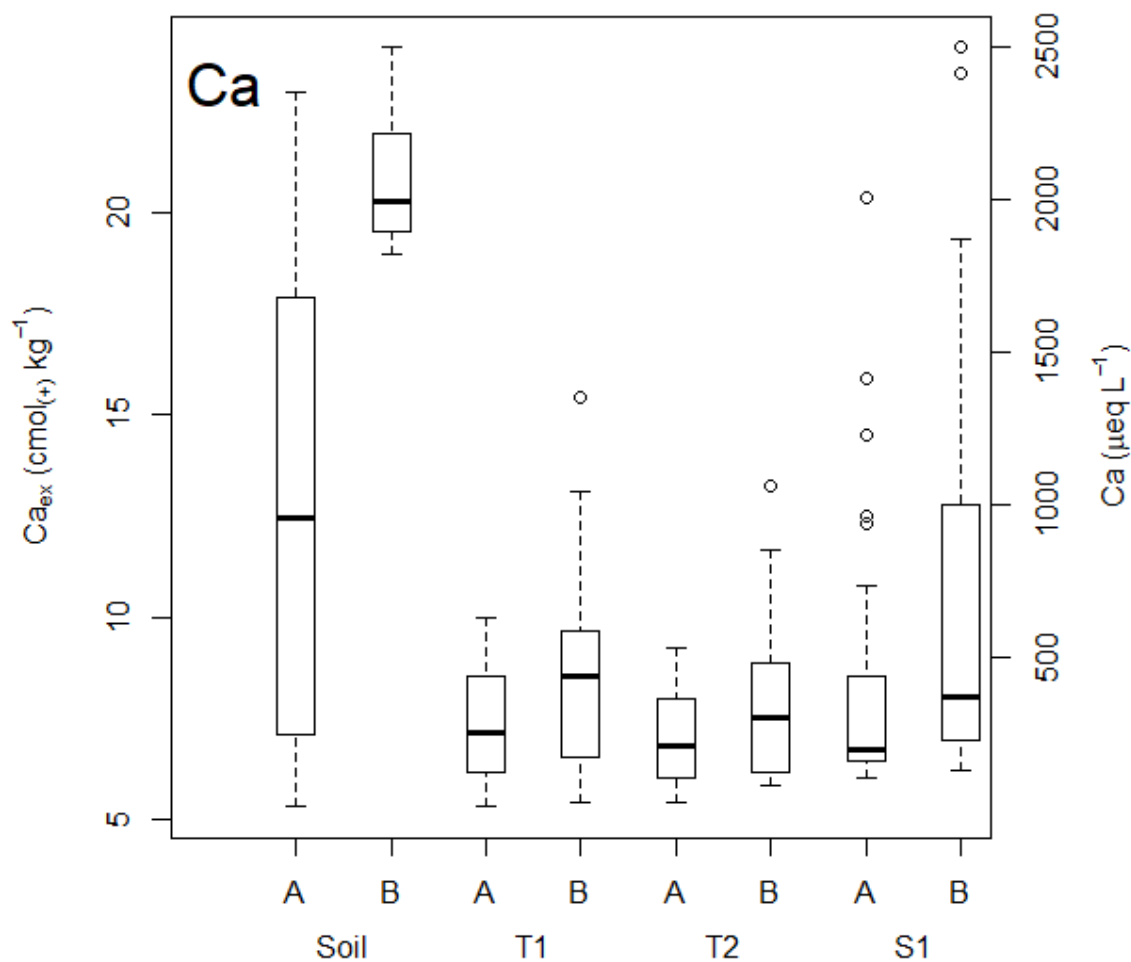


**Figure 1.** Duration (dark rectangles) of the three time-series used to compare the chemical composition of throughfall and stemflow solutions between area A and area B at Gallignano Forest, Ancona (central Italy), as a function of the 20 sampling periods collected during the 2004-2005 hydrological year. The total number of consecutive sampling periods per time-series was five for T1, four for T2 and nine for S1. The dormant season is indicated by leafless trees whereas the growth season is illustrated by trees with leaves. The months 07 (July) and 08 (August) are not represented because no precipitation was recorded in those months.

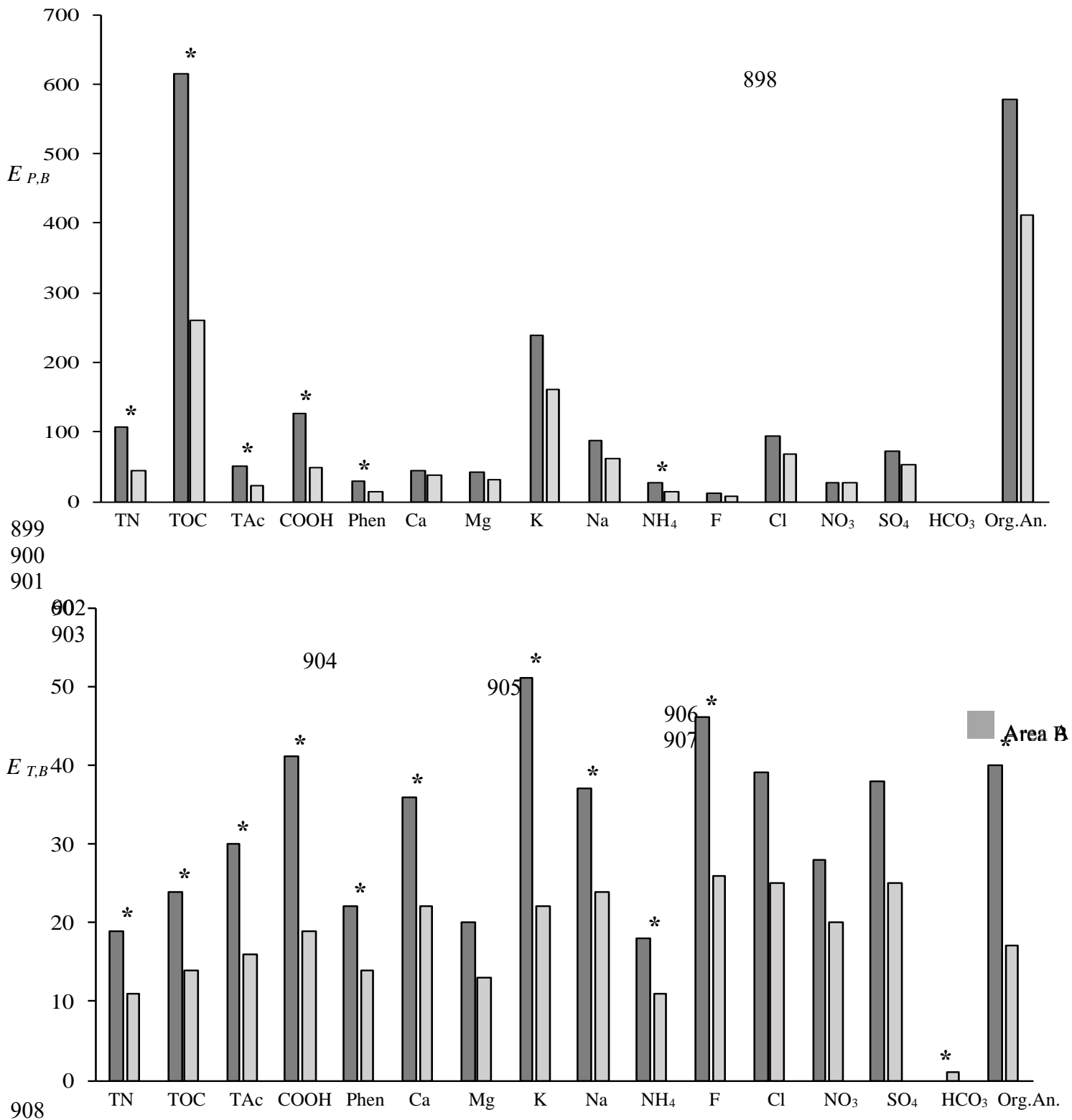
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**Figure 2.** Mean concentrations of macroelements and microelements of Turkey oak (*Quercus cerris* L.) leaves (on a dry mass basis) collected from clusters of three trees (composite sample of 10 leaves per tree) in area A and area B. Gallignano Forest, Ancona (central Italy). Based on the non-parametric Wilcoxon signed-rank test ( $\alpha = 0.05$ ), the datasets of area A and area B are significantly different. Error bars show standard deviations ( $n = 3$ ).



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 890 **Figure 3.** Boxplots of the distribution of soil exchangeable Ca, in  $\text{cmol}_{(+) } \text{kg}^{-1}$  on the primary Y-  
 891 axis, and of dissolved Ca in the solutions of throughfall time series 1 (T1), throughfall time-series 2  
 892 (T2), and stemflow time-series 1 (S1), in  $\mu\text{eq L}^{-1}$  on the secondary Y-axis, from area A and area B.  
 893 Gallignano Forest, Ancona (central Italy). A total of eight soil horizons were collected and analyzed  
 894 in area A and area B. The total number of consecutive sampling periods per series was five for T1,  
 895 four for T2 and nine for S1 with number of collectors being six for throughfall and three for  
 896 stemflow. See Tables 2 and 6 for statistical significance of differences between area A and area B.  
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909 **Figure 4.** Enrichment ratio per unit of tree trunk basal area compared to precipitation flux ( $E_{P,B}$ ) and  
 910 throughfall flux ( $E_{T,B}$ ) for the stemflow chemical properties of area A and area B. Gallignano Forest,  
 911 Ancona (central Italy). For a given variable, asterisk (\*) indicates that datasets are significantly different  
 912 between area A and area B, based on the non-parametric Wilcoxon signed-rank test ( $\alpha = 0.05$ ).  
 913 TN=Total N; TOC=Total organic C; TAc=Total acidity; Phen=Phenolic acidity; Org.An.=Organic  
 914 anions.

**Table 1.** Morphological description of the soil profiles from area A and area B at the Gallignano Forest, Ancona province (central Italy).

Landform: steep slope (10-15%); creeping phenomena have formed diffuse soil cracks (maximum depth is around 60 cm) and few small humps along the slope  
 – Exposure: NNW – Altitude: 180 m – Mean annual air temperature: 13.6°C – Warmest month: July (23.1°C) – Coldest month: January (4.9°C) – Mean annual precipitation: 780 mm – Drainage class: moderately well drained – Parent material: Plio-pleistocene fine-textured marine sediments.

**Soil of area A**

**Vegetation:** Upper stratum: *Quercus cerris* L. – Lower stratum: *Fraxinus ornus* L., *Sorbus torminalis* (L.) Crantz, *Ostrya carpinifolia* Scop., *Acer campestre* L.  
 – Understory: *Erica arborea* L., *Juniperus communis* L., *Lonicera xylosteum* L., *Lonicera caprifolium* L., *Ruscus aculeatus* L., *Smilax aspera* L., *Rubia peregrina* L., *Cyclamen repandum* S.S., *Festuca heterophylla* Lam., seedlings. **Forest management:** abandoned coppice. **Soil:** fine, mixed, acidic, mesic, Typic Dystrudept (Soil Survey Staff, 2014).

	Depth <sup>a</sup> cm	Mean thickness cm	Colour <sup>b</sup>	Texture <sup>c</sup>	Structure <sup>d</sup>	Consistency <sup>e</sup>	Plasticity <sup>f</sup>	Roots <sup>g</sup>	Mycelia <sup>h</sup>	Boundary <sup>i</sup>	Other observations
Oi	3/2-0	2.3	-	-	-	-	-	0	0	cb	undecomposed leaves of <i>Q. cerris</i> , <i>E. arborea</i> , <i>F. ornus</i> , and <i>O. carpinifolia</i>
Oe	2/1-0	1.3	10YR 3/2	-	-	-	-	v <sub>1</sub> mi,vf,f	+	cb	
A	0-5/9	6.6	10YR 3/2	sil	3m cr	mfr, wss	wps	2mi,vf,f,m	0	cb	
E	0-3/5	4.0	10YR 4/2 10YR 5/2	sil	2f,m cr 2f,m abk	cr=mfi, wss abk=mfr, wss	wps	2mi,vf,f,m; 3co 2mi,vf,f,m,co	0	cw	roots abound into the cracks
EB	3/5-8/9	4.3	10YR 6/4 2.5Y 5/6	sil	2m,c abk-sbk 3m abk-sbk	mfi-fr, wss	wps	2mi,vf,f,m; 3co 2mi,vf,f,m,co	0 +	cw	cracks fulfilled of A and E material colonized by few mycelia
Bw	8/9-23/29	17.6	10YR 4/4 10YR 5/6	sil	2m,c abk-sbk 3m,co abk	mfi-fr, wss mfi, wss	wps	2mi,vf,f,m,co 2mi,vf,f; 1m,co	0 +	cw	cracks fulfilled of A and E material colonized by abundant mycelia and roots. Few Mn nodules.

2Bw1	23/29-42/43	16.3	10YR 5/4 2.5Y 5/6	sic	2f,m abk 3m abk	mfi, wss	wps ws	2mi,vf,f,m,co 2mi,vf,f; 1m,co	++ +++	cs	few Mn nodules
2Bw2	42/43-61/62	19.0	10YR 5/2 10YR 5/6	sic	2m,c abk 3m abk	mfi, wss mfi, ws	wps ws	2mi,vf,f,m,co 2mi,vf,f; 1m,co	++ +++	cw	few Mn nodules
2Bw3	61/62-70/73	10.3	10YR 4/4 10YR 5/4	sic	2m,c abk 2m abk	mfi, wss	wps	2mi,vf,f,m,co 2mi,vf,f; 1m;	+	cs	few Mn nodules
3Bw	70/73-79/83	9.0	2.5Y 5/2 2.5Y 5/4	sicl	2f,m sbk 2m abk	mfi, wss	wps	1mi,vf,f; 2m,co 1mi,vf,f,m; v <sub>1</sub> co	0	as	few concretions of CaCO <sub>3</sub>
4BCk	79/83-94/98	15.0	2.5Y 7/2 2.5Y 7/4	sil	3m sbk→1th pl	mfr, wss	wps	2mi,vf; 3f,m,co 1mi,vf,f,m,co	0	-	plentiful concretions of CaCO <sub>3</sub>

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### Soil of area B

**Vegetation:** Upper stratum: *Quercus cerris* L. – Intermediate stratum: *Quercus pubescens* Willd. – Lower stratum: *Fraxinus ornus* L., *Sorbus torminalis* (L.) Crantz, *Ostrya carpinifolia* Scop., *Carpinus betulus* L., *Acer campestre* L., *Fraxinus oxycarpa* Bieb. – Understory: *Juniperus communis* L., *Ruscus aculeatus* L., *Lonicera xylosteum* L., *Lonicera caprifolium* L., *Rubia peregrina* L., *Cyclamen repandum* S.S., *Smilax aspera* L., *Festuca heterophylla* Lam., seedlings.

**Forest management:** abandoned coppice. **Soil:** fine, mixed, calcareous, mesic, Typic Eutrudept (Soil Survey Staff, 2014).

	Depth <sup>a</sup> cm	Mean thickness cm	Colour <sup>b</sup>	Texture <sup>c</sup>	Structure <sup>d</sup>	Consistency <sup>e</sup>	Plasticity <sup>f</sup>	Roots <sup>g</sup>	Mycelia <sup>h</sup>	Boundary <sup>i</sup>	Other observations
Oi	6/4-2/1	3.3	-	-	-	-	-	0	0	cw	undecomposed leaves of <i>Q. cerris</i> , <i>F. ornus</i> , <i>S. aspera</i> , and <i>O. carpinifolia</i>
Oe	2/1-0	1.7	5YR 2/1	-	-	-	-	0	+++	cw	
A	0-7/10	8.3	10YR 3/1 10YR 5/2	sl	3m,sbk 3m, cr	mfi, wss mfr, wss	wps	3mi,vf; 2f,m; 1co 3mi,vf,f,m; 1co 2mi,vf; 3f,m;	+++	cw	cracks fulfilled of A material colonized by abundant mycelia
AB	7/10-16/22	10.3	10YR 4/3 10YR 4/4	sicl	3m, sbk 3f,m, cr	mfi, wss mfr, wss	wps	1co 3mi,vf,f,m; 1 co	0 +	cw	cracks fulfilled of A material colonized by few mycelia

Bw1	16/22- 27/34	13.3	10YR 5/2 10YR 5/4	sicl	3m sbk 3m, cr	mfi, wss mfr, wss	wps	2mi,vf; 3f,m; 1co	0 +	cw	cracks fulfilled of A material colonized by few mycelia
Bw2	27/34- 47/55	19.7	10YR 4/4 10YR 4/2	sicl	3f,m sbk 2m sbk	mfi, wss	wps	3mi,vf,f,m; 1co 3mi,vf,f; 2m; 1co	+ ++	cw	cracks fulfilled of A material colonized by abundant mycelia
Bw3	47/55- 60/71	16.0	10YR 5/6 10YR 6/4	sicl	3f sbk 2m sbk	mfi, wss mfi, ws	wps wp	1mi,vf; 2f; 3m,co	0	as	
2BCk	60/71- 70/81	10.3	2.5YR 6/2	scl	2f,m,c abk- sbk	mfi, wss	wps wp	2mi,vf 2mi,vf,f; 1m,co	0	as	common concretions of CaCO <sub>3</sub>
3BC	70/81- 81/93	11.0	2.5Y 6/4 2.5Y 7/4	scl	3f,m abk-sbk 2m sbk	mfr, wss mfi, ws	wps wp	1mi,vf; 3f,m,co 2mi,vf,f,m; 1co	0	as	between 2BCk and 3BC, fine, medium and coarse roots show horizontal trend
4BCk	81/93- 100/106	16.3	2.5Y 7/2 2.5Y 7/3	scl	2m abk	mfi, wss	wps wp	1mi,vf,f; 2m,co 1mi,vf,f,m;	0	-	plentiful concretions of CaCO <sub>3</sub>

<sup>a</sup> Numbers separated by slash (/) indicate the range of depths observed in the three profiles, while the hyphen (-) means “from (what is before the sign) to (what is after the sign)”.

<sup>b</sup> moist and crushed, according to the Munsell Soil Color Charts.

<sup>c</sup> sl=sandy loam, sil=silt loam, sic=silty clay, sicl=silty clay loam, scl=sandy clay loam.

<sup>d</sup> 1=weak, 2=moderate, 3=strong; th=thin, f=fine, m=medium, c=coarse; cr=crumb, abk=angular blocky, sbk=subangular blocky, pl=platy; → breaking into.

<sup>e</sup> m=moist, fr=friable, fi=firm; w=wet, ss=slightly sticky, s=sticky.

<sup>f</sup> w=wet, ps=slightly plastic, p=plastic.

<sup>g</sup> 0=absent, v<sub>1</sub>=very few, 1=few, 2=plentiful, 3=abundant; mi=micro, vf=very fine, f=fine, m=medium, co=coarse.

<sup>h</sup> we referred to the mycelia visible at naked eyes. 0=absent, +=few, ++=plentiful, +++=abundant.

<sup>l</sup> a=abrupt, c=clear; b=broken, w=wavy, s=smooth.



**Table 2.** Weighted mean profile properties of the soils of area A and area B weighted as a function of horizon thickness. Gallignano Forest, Ancona (central Italy).

Variable (unit)	Area <sup>a</sup>		
	A	B	
pH in H <sub>2</sub> O	5.84	7.55	
pH in KCl	3.96	6.53	*
Exchangeable Ca (cmol <sub>(+)</sub> kg <sup>-1</sup> )	13.6	20.6	*
Exchangeable Mg (cmol <sub>(+)</sub> kg <sup>-1</sup> )	3.26	3.08	
Exchangeable K (cmol <sub>(+)</sub> kg <sup>-1</sup> )	0.27	0.40	*
Exchangeable Na (cmol <sub>(+)</sub> kg <sup>-1</sup> )	0.12	0.12	
Exchangeable Al (cmol <sub>(+)</sub> kg <sup>-1</sup> )	2.12	0.14	
Exchangeable H (cmol <sub>(+)</sub> kg <sup>-1</sup> )	0.81	0.05	
Effective cation exchange capacity (cmol <sub>(+)</sub> kg <sup>-1</sup> )	20.1	24.3	*
Base saturation (%)	84	99	
Total C (g kg <sup>-1</sup> )	14.8	57.0	*
Organic C (g kg <sup>-1</sup> )	4.65	16.10	*
Total N (g kg <sup>-1</sup> )	1.62	1.63	
Available P (mg kg <sup>-1</sup> )	0.95	3.32	
Organic C/Total N ratio	2.8	7.5	*
Sand (g kg <sup>-1</sup> )	152	375	*
Silt (g kg <sup>-1</sup> )	533	200	*
Clay (g kg <sup>-1</sup> )	315	425	

<sup>a</sup> For a given soil variable, weighted means followed by an asterisk (\*) indicate that datasets are significantly different between area A and area B, based on the non-parametric Wilcoxon signed-rank test ( $\alpha = 0.05$ ).

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**Table 3.** Age, diameter of the trunks at breast height (DBH), vertical height, canopy volume, canopy projection to the soil surface, and insertion angle of the main two branches of ten Turkey oak (*Quercus cerris* L.) trees from area A and area B. Gallignano Forest, Ancona (central Italy).

	Age years	DBH m	Vertical height m	Canopy volume m <sup>3</sup>	Canopy projection m <sup>2</sup>	Insertion angle (°)
Area A						
<b>1*</b> <sup>a</sup>	62	0.27	21.7	412	45.8	34.0
<b>2*</b>	56	0.29	19.0	397	24.8	29.0
<b>3*</b>	54	0.30	19.7	970	69.3	59.5
<b>4</b>	61	0.28	21.0	353	24.7	42.0
<b>5</b>	57	0.25	20.5	326	36.3	50.0
<b>6</b>	54	0.26	18.5	246	32.1	26.0
<b>7</b>	56	0.27	16.4	377	64.0	23.5
<b>8</b>	60	0.31	18.8	440	49.2	45.5
<b>9</b>	62	0.23	19.2	147	18.0	42.5
<b>10</b>	53	0.23	19.8	521	36.1	43.0
<b>Mean</b> <sup>b</sup>	57.5 (3.5)a	0.27 (0.03)a	19.5 (1.5)a	419 (220)a	40.0 (17.0)a	39.5(11.3a)
Area B						
<b>1*</b>	62	0.36	25.0	862	43.1	54.5
<b>2*</b>	54	0.31	25.7	1428	75.2	64.5
<b>3*</b>	63	0.37	26.0	1042	74.4	78.0
<b>4</b>	60	0.29	19.4	592	70.4	91.0
<b>5</b>	58	0.32	20.0	630	62.0	46.0
<b>6</b>	61	0.32	20.3	604	68.8	74.5
<b>7</b>	58	0.28	19.6	644	66.7	51.0
<b>8</b>	56	0.28	21.4	337	56.5	69.5
<b>9</b>	61	0.24	21.3	253	34.0	35.0
<b>10</b>	62	0.28	18.1	629	37.2	48.0
<b>Mean</b>	59.5 (2.9)a	0.31 (0.04)b	21.7 (2.9)a	702 (340)b	58.8 (15.5)b	61.2(17.2)b

<sup>a</sup> Trees marked with asterisk (\*) are part of the three-tree clusters used to collect throughfall and stemflow solutions.

<sup>b</sup> For a given variable, mean values (in parentheses the standard deviation) followed by different letters indicate that datasets are significantly different between area A and area B, based on the non-parametric Wilcoxon signed-rank test ( $\alpha = 0.05$ ).

**Table 4.** Amounts of total annual rainfall in the open (expressed in mm), of throughfall (expressed in mm and as percentage of the total rainfall), and of stemflow [expressed in mm and as percentage of the total rainfall, and as stemflow funnelling ratio ( $F_{P,B}$ )] collected under a cluster of three Turkey oak (*Quercus cerris* L.) trees at area A and area B. Gallignano Forest, Ancona (central Italy). Total number of sampling periods is 20, subdivided into 6 for spring, 2 for summer, 7 for autumn and 5 for winter. Number of collectors per area = 1 for rainfall, 6 for throughfall, and 3 for stemflow.

	Rainfall	Throughfall		Stemflow		
	mm	mm	%	mm	%	$F_{P,B}$
<b>Area A</b>						
Total annual <sup>a</sup>	835a	665a	79.6	5.58a	0.67	14a
<b>Area B</b>						
Total annual	833a	656a	78.8	3.27b	0.39	8b

<sup>a</sup> Values followed by distinct letters indicate that datasets (n = 20 sampling periods) are significantly different between area A and area B, based on the non-parametric Wilcoxon signed-rank test ( $\alpha = 0.05$ ).

**Table 5.** Mean volume-weighted concentrations of the chemical properties for the rainfall solutions collected in the open during time series T1, T2 and S1 at area A and area B. Gallignano Forest, Ancona (central Italy).

Variable (unit) <sup>a</sup>	Rainfall - T1 <sup>b</sup>		Rainfall - T2 <sup>c</sup>		Rainfall - S1 <sup>d</sup>		
	A	B	A	B	A	B	
Amount (mm)	202	201	172	172	351	350	
pH	6.98	6.93	5.43	5.00	6.76	6.78	
Electrical conductivity (dS m <sup>-1</sup> )	62.0	72.1	181	189	32.6	34.1	
Total N (mM)	0.10	0.14	0.05	0.08	0.16	0.19	*
Total organic C (mM)	0.09	0.12	0.51	0.78	0.09	0.12	*
Total acidity (mM)	0.10	0.16	0.56	0.64	0.29	0.31	
Carboxylic acidity (mM)	0.07	0.11	0.03	0.07	0.09	0.11	
Phenolic acidity (mM)	0.04	0.05	0.53	0.57	0.20	0.21	
Ca (µeq L <sup>-1</sup> )	316	322	188	191	206	211	
Mg (µeq L <sup>-1</sup> )	36.4	40.1	93.0	93.6	80.4	82.6	
K (µeq L <sup>-1</sup> )	15.7	17.2	47.9	50.0	30.8	32.1	
Na (µeq L <sup>-1</sup> )	64.5	69.3	751	771	96.2	103.0	*
NH <sub>4</sub> (µeq L <sup>-1</sup> )	13.3	15.5	5.39	6.43	15.5	16.5	
F (µeq L <sup>-1</sup> )	7.57	8.63	6.85	7.98	6.83	7.21	
Cl (µeq L <sup>-1</sup> )	75.5	80.7	846	864	112	118	
NO <sub>3</sub> (µeq L <sup>-1</sup> )	14.6	15.7	42.3	44.3	35.2	37.0	
SO <sub>4</sub> (µeq L <sup>-1</sup> )	7.18	8.63	103	106	16.2	17.2	
HCO <sub>3</sub> (µeq L <sup>-1</sup> )	298	304	77.8	81.0	222	228	
Organic acid (µeq L <sup>-1</sup> )	44.9	46.7	12.6	13.2	30.4	31.5	

<sup>a</sup> For a given variable, means followed by an asterisk (\*) indicate that datasets are significantly different between area A and area B, based on the non-parametric Wilcoxon signed-rank test ( $\alpha = 0.05$ ).

<sup>b</sup> Throughfall series T1 includes five consecutive rainfall events (September 20, 2004 to November 4, 2004), for a total of n=10 rainfall measurements (5 events x 2 collectors) used for statistical analysis.

<sup>c</sup> Throughfall series T2 includes four consecutive rainfall events (December 23, 2004 to February 28, 2005), for a total of n=8 rainfall measurements (4 events x 2 collectors) used for statistical analysis.

<sup>d</sup> Stemflow series S1 includes nine consecutive rainfall events (March 10, 2004 to September 20, 2004), for a total of n=18 rainfall measurements (9 events x 2 collectors) used for statistical analysis.

**Table 6.** Mean volume-weighted concentrations for the chemical properties of throughfall solutions collected during time series T1 and T2, and of stemflow solutions collected during time series S1 at area A and area B. Gallignano Forest, Ancona (central Italy).

Variable (unit) <sup>a</sup>	Throughfall - T1 <sup>b</sup>		Throughfall - T2 <sup>c</sup>		Stemflow - S1 <sup>d</sup>				
	A	B	A	B	A	B			
Amount (mm)	160	158	153	154	2.29	1.27	*		
pH	6.37	6.41	5.01	4.81	*	5.20	5.45	*	
Electrical conductivity (dS m <sup>-1</sup> )	103	130	*	266	357	*	136	164	*
Total N (mmol L <sup>-1</sup> )	0.21	0.22		0.14	0.17	*	1.68	1.72	
Total organic C (mmol L <sup>-1</sup> )	6.88	7.27		7.01	7.62	*	9.60	10.32	
Total acidity (mmol L <sup>-1</sup> )	0.79	0.89		0.63	0.56	*	1.19	1.10	
Carboxylic acidity (mmol L <sup>-1</sup> )	0.38	0.43		0.07	0.09		0.92	0.79	
Phenolic acidity (mmol L <sup>-1</sup> )	0.41	0.45		0.56	0.47	*	0.27	0.31	
Ca (µeq L <sup>-1</sup> )	225	427	*	241	333	*	391	696	*
Mg (µeq L <sup>-1</sup> )	79	101	*	387	424		152	242	*
K (µeq L <sup>-1</sup> )	144	192	*	203	309	*	827	913	
Na (µeq L <sup>-1</sup> )	569	703		1 828	1 928		384	710	*
NH <sub>4</sub> (µeq L <sup>-1</sup> )	22.6	18.9		20.3	19.0		28.4	25.3	
F (µeq L <sup>-1</sup> )	2.61	3.91		1.70	1.74		9.80	13.50	
Cl (µeq L <sup>-1</sup> )	639	772		2 112	2 262		441	820	*
NO <sub>3</sub> (µeq L <sup>-1</sup> )	55.6	87.4	*	38.4	64.1	*	98.1	204	*
SO <sub>4</sub> (µeq L <sup>-1</sup> )	104	118		202	212		208	292	*
HCO <sub>3</sub> (µeq L <sup>-1</sup> )	152	207		11.9	0.03	*	0.10	20.0	*
Organic anions (µeq L <sup>-1</sup> )	88	252	*	317	481	*	923	1063	

<sup>a</sup> For a given variable, means followed by an asterisk (\*) indicate that datasets are significantly different between area A and area B, based on the non-parametric Wilcoxon signed-rank test ( $\alpha = 0.05$ ).

<sup>b</sup> Throughfall series T1 includes five consecutive rainfall events (September 20, 2004 to November 4, 2004) for a total of n=30 throughfall measurements (5 events x 6 collectors) per area used for statistical analyses.

<sup>c</sup> Throughfall series T2 includes four consecutive rainfall events (December 23, 2004 to February 28, 2005) for a total of n=24 throughfall measurements (4 events x 6 collectors) per area used for statistical analyses.

<sup>d</sup> Stemflow series S1 includes nine consecutive rainfall events (March 10, 2004 to September 20, 2004) for a total of n=27 stemflow measurements (9 events x 3 collectors) per area used for statistical analyses.