

1 **Soil solution fluxes and composition trends reveal risks of nitrate leaching from forest soils of Italy.**

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7  
8 **Abstract**

9 Although acidification is a natural soil formation process, atmospheric emissions of nitrogen and  
10 sulphur have exposed forest ecosystems to accelerated anthropogenic acidification for many decades. In Italy  
11 nitrogen deposition loads are high, and among the highest in Europe. Data from the Italian ICP-Forests  
12 monitoring network have shown that nitrogen deposition increases tree growth, and consequently the  
13 organic carbon sequestration. However, the accumulation of nitrogen in the ecosystem could cause nutrient  
14 imbalances and contribute to soil acidification. Within this context, we investigated the temporal changes of  
15 atmospheric deposition and soil solution concentration in the Italian ICP-Forests using the non-parametric  
16 Seasonal Mann Kendall (SMK) test. Further, we applied input-output models, to evaluate the capabilities of  
17 the soil-forest system to retain deposited nitrogen and thus protect underground waters.

18 Increase of soil solution pH was observed in most of the sites, likely due to sulphate deposition  
19 decrease with a concomitant high and stable natural exchangeable base deposition. For the sites around the  
20 Po plain, however, high levels of nitrogen deposition impede pH increase. The site with the maximum mineral  
21 N deposition showed signs of active acidification. The analysis of the fluxes of nitrogen compounds  
22 demonstrates a complete retention of the ammonium forms, which further contribute to acidification  
23 through nitrification. Furthermore, the Italian monitoring network showed that the retention of nitrogen in  
24 the soil-forest system was effective since the observed N fluxes in mineral soil were strongly reduced  
25 compared to mineral N input in most of the plots. In spite of this, significant  $NO_3^-$  fluxes from the subsoil  
26 were observed in sites with high deposition, and also in the southernmost site which is exposed to relatively

27 low mineral N loads. Drivers other than pollution should also be considered since N can follow different  
28 pathways at different time scales, influencing N leaching independently from the amount of deposition.

29

## 30 1. Introduction

31 Since the late 1970s, post-industrial human activities caused a distortion of major biogeochemical  
32 cycles, arising from high emissions of sulphur (S) and nitrogen (N) from fossil fuel combustion and agriculture,  
33 and resulting in increased levels of acid deposition in many ecosystems (Phoenix et al., 2006; Galloway et al.,  
34 2008). Recently, several “planetary boundaries” (PB) have been proposed to define a safe operating space  
35 for humanity on a stable Earth system (Rockstrom et al., 2009). According to this concept, certain boundaries  
36 concerning biogeochemical fluxes have already been exceeded, especially those related to nitrogen cycles  
37 (Steffen et al., 2015).

38 High nitrate ( $NO_3^-$ ) and sulphate ( $SO_4^{2-}$ ) concentrations in atmospheric deposition can be related to  
39 water and soil acidification (Ronse et al., 1988; Norton et al., 2004; De Schrijver et al., 2006; Sherman et al.,  
40 2006; Stevens et al., 2009; Oulehle et al., 2010). Long-term excesses of N and S compound deposition cause  
41 unfavourable conditions in forest soils (Verstraeten et al., 2012). Despite the positive function of N deposition  
42 as a nutrient on forest growth rates, a potential negative effect at sites with high N deposition has been  
43 recognized at continental scale in Europe (Etzold et al., 2020). Further, high nitrate concentrations in surface  
44 and ground waters can lead to eutrophication of waters (Aber et al., 1998; Fenn et al., 1998; Rabalais, 2002)  
45 and potential health problems (Briand et al., 2017). Critical limits for N concentrations in soil solution were  
46 frequently exceeded between the early 1990s and 2006 in Europe (Iost et al., 2012). With respect to the  
47 acidifying effects of nitrogen deposition on soils, the potential contribution of ammonium ( $NH_4$ ) deposition  
48 also needs to be considered, in addition to the effect of nitric acids, as microbial nitrification and assimilation  
49 in soil involve the within-soil production of large amounts of protons (Rodhe et al., 2002).

50 In recent decades, emission abatement strategies, drawn within the Convention on Long-Range  
51 Transboundary Air Pollution (CLRTAP; UNECE, 1979) in Europe, have resulted in large decreases in S

52 emissions, while nitrogen emissions also decreased, but not to the same extent (EEA, 2018). In Europe,  $SO_4^{-2}$   
53 and  $NO_3^-$  depositions decreased by 73% and 33%, respectively, between 1990 and 2012 (Colette et al., 2016).  
54 In Italy, emissions decreased by 93%, 63% and 19%, respectively for  $SO_2$ ,  $NO_x$  and  $NH_3$  from 1990 to 2016  
55 (Taurino et al., 2018). As an effect of decreasing emissions, a substantial reduction in acid deposition has  
56 occurred in Italy (De Marco et al., 2019), as in most of Europe (Waldner et al., 2014; Karlsson et al., 2011).

57 A comprehensive study on the response of soil solution chemistry to decreasing acid deposition  
58 across Europe found that a reduction of acidifying atmospheric deposition has not produced clear signs of  
59 soil recovery (Johnson et al., 2018). The concomitant decrease of BCE at European scale may partly explain  
60 the observed low soil recovery (Johnson et al., 2018). Some authors have demonstrated how BCE deposition  
61 can also be due to industrial activities, such as mining (Davidson et al., 2020; Watmough et al., 2014) or  
62 quarrying (Oulehle et al., 2006) and that the general decrease of “heavy” industrial activities in the developed  
63 world is a likely cause of BCE deposition decrease.

64 Italy, due to its geographical position, receives large amounts of deposition from marine aerosol and  
65 Saharan dust (Lequy et al., 2012; Costantini et al., 2018; Cecchini et al., 2019) and is subjected to a component  
66 of atmospheric deposition which is lesser or absent in northern European countries. The most represented  
67 chemical species in this Mediterranean pattern of deposition are base cations and chloride, for which a  
68 significant gradient of decrease from south to north is observed (Ehrmann et al., 2017; Cecchini et al., 2019).  
69 Episodic inputs like those associated with Saharan dust events were registered in the Alps (Rogora et al.,  
70 2004) and can also have a significant impact on ecosystems in remote areas (Psenner, 1999). In the  
71 meantime, anthropogenic nitrogen and sulphur depositions play a major role in Northern Italy. Some of the  
72 highest N deposition loads are concentrated in the Po plain, one of the most urbanised and industrialised  
73 areas of Europe. Studying the long-term trends of alkaline and acid compounds in both atmospheric  
74 deposition and soil solutions is of interest for the Italian territory where sites cover different geographical  
75 patterns. The soil solution composition provides an indication of nutrient availability (Sherman et al., 2006),  
76 potential acid stress to vegetation (Oulehle et al., 2010; Binkley and Fisher, 2013), as well as on potential  
77 exceedances of deposition critical loads. However, in contrast to studies on surface waters, the few regional

78 Mediterranean studies on the response of soil solution chemistry to deposition (Avila et al., 1995, Rodà et  
79 al., 1990) focused on short time periods without capturing temporal trends. Long term assessments of  
80 changes in soil solution in relation to deposition are lacking for Mediterranean forest ecosystems,  
81 notwithstanding the peculiarities of the atmospheric deposition in this region.

82         Within this context, we aim to explore the specific impacts of peculiar atmospheric deposition,  
83 hypothesising a strong influence of aeolian dusts and aerosol on forest soil ecosystem in Italy, as  
84 representative of the Mediterranean region. Our main objectives are a) to evaluate the long-term trends in  
85 soil solution concentrations in relation to deposition trends; b) to investigate the soil response to pollution  
86 changes, defining trends in soil solution pH; and c) to identify sites where the transfer of reactive N from  
87 atmospheric pollution to groundwater is a potential concern. We tested the hypothesis that the processes of  
88 Italian forest soil acidification, as indicated by soil solution composition, showed different trends compared  
89 with those of other European countries. We expect a positive impact on soil solution pH due to a decrease  
90 of atmospheric sulphate deposition whereas BCE deposition is constant. At the same time, we hypothesize  
91 that the constant high levels of nitrogen deposition around the Po valley, a “hot N point” in the North of Italy,  
92 could neutralize the positive impact of declining atmospheric sulphate deposition.

## 93         2. Materials and methods

94

### 95             2.1 Study sites

96         We used data of deposition and elemental concentrations in soil solutions recorded at six forest plots  
97 of the ICP Forests Level II intensive monitoring network in Italy (Table 1 and Fig 1). The main site and soil  
98 characteristics of LAZ1, EMI1, VEN1 and PIE1 were previously described by Cecchini et al. (2019). The other  
99 two sites are both represented by beech forest (*Fagus sylvatica*). The ABR1 site is located at an altitude of  
100 1500 m a.s.l. in the upper slopes of the calcareous Serra Lunga ridge, in the Apennines. “Terra Rossa” soils  
101 develop on a hard, stratified, Cretaceous-age limestone and the soil parent-material is likely made up of a  
102 mixture of limestone residue and aeolian dusts (Cecchini et al., 2002). A relevant contribution from air-fall

103 volcanic ashes is known for this area (Ferrari and Malesani 1973). The CAL1 area is located at an altitude of  
104 1100 m a.s.l., on the edge of the Aspromonte National Park (RC). It is rainy site, with an average annual  
105 precipitation of 1300 mm, and this balances for the relatively southern location of this beech forest.

## 106 2.2 Sample collection and analysis

107 For the 6 studied sites (Table 1), almost continuous data series covering the period 1998-2017 are  
108 available. Deposition was sampled using “bulk” samplers, i.e. funnels continuously exposed. Three bulk  
109 samplers were located in the open field, in a clearance close to the monitoring plot, while 16 samplers were  
110 located under forest canopy, to collect the “throughfall” deposition. Deposition sample collection and  
111 analysis were subject to quality assurance and quality control checks including the use of control charts for  
112 internal reference, charge balance and participation in laboratory ring tests (König et al., 2013).

113 The soil solution sampling started in 1997 with a single site (ABR1), was extended in 1999 to LAZ1  
114 site and then progressively, to the other sites, as detailed in Table 1. Soil solutions were collected at several  
115 depths. The gravity lysimeters (filtering plates) were inserted just below the forest floor (FF), except at the  
116 steeply sloping sites (PIE1). The tension lysimeters (suction cups) were inserted at three different depths  
117 (15/20 cm, 40 cm and 60/70 cm), according to ICP-Forests (2011). The sampling took place bi-weekly, with  
118 significant interruptions in winter, due to a permanent snow cover and freezing for the northern sites (PIE1  
119 and VEN1). Sample treatment, preservation, analysis and quality control follow ICP-Forests (2011) and  
120 preceding versions (Nieminen et al., 2016).

## 121 2.3 Data handling and statistical analysis

122 For sulphur and nitrogen deposition, the monitoring results were compared with the results of the  
123 model developed by the EMEP Meteorological Synthesizing Centre – West (MSC-W), hosted by the  
124 Norwegian Meteorological Institute, for the modelling of transboundary fluxes of acidifying and eutrophying  
125 air pollutants (EMEP 2012). This model mainly consists in a source-receptor matrix estimating the  
126 contribution of the emissions to the depositions of main pollutants.

127 In this study, we analysed data from the forest floor (0 cm), representing the basic conditions and  
128 trend of soil input, and from the subsoil (60 or 70 cm), which should be seen as a measure of the potential  
129 risk of nitrate transfer to the watershed. Forest floor gravity lysimeters were characterized by high inter-  
130 annual variability and were not installed at all sites, thus data from the shallowest tension lysimeters (topsoil,  
131 at 15 to 20 cm depth) were also systematically analysed. The soil mineral layer refers to the sum of topsoil  
132 and subsoil. For each site at each depth, data from different collectors were averaged for all sampling periods.

133 Temporal changes were tested using the non-parametric Seasonal Mann Kendall (SMK) test for  
134 monthly atmospheric deposition and for monthly concentrations of soil solutions in R statistical environment  
135 (R version 3.5.0 (2018-04-23)) using rkt package (Marchetto, 2015). For the atmospheric deposition, the  
136 mean relative change per year ( $y^{-1}$ ) was estimated:

$$137 \quad rslope = \frac{b}{mean(y)} (1)$$

138 where  $b$  is the absolute long-term slope, and  $mean(y)$  is the mean value of the time series (Waldner et al.,  
139 2014). Results of the time series are then reported in  $\% y^{-1}$ . Ammonium in soil solution was close to or below  
140 the detection limit for most plots in the lysimeters installed in the mineral soil and only data from the organic  
141 layer were analysed for trends.

142 Spearman's rank correlation coefficient was applied as a nonparametric measure of rank correlation between  
143 nitrogen deposition and precipitation.

#### 144 2.3.1 Soil mineral N fluxes

145 The chloride tracer approach was adopted to estimate water flux through the soil as described by  
146 Cecchini et al. (2019). Briefly, the water fluxes for each soil layer  $l$  were calculated as follows:

$$147 \quad Jwl = \frac{TFCl}{rCl} (2)$$

148 where  $Jwl$  is the water flux, in  $mm y^{-1}$ , at layer  $l$ ;  $TFCl$  is  $Cl^-$  TF deposition, in  $mg m^{-2} y^{-1}$  and  $rCl$  is the median  
149  $Cl^-$  soil solution concentration at  $l$ , in  $mg l^{-1}$ .

150 The flux of  $NO_3^-$  and  $NH_4^+$ ,  $J_{il}$ , was estimated by multiplying the relevant  $J_{wl}$  value for the median soil solution  
151 concentration,  $ril$ , for the same layer and period. The overall budget for  $NO_3^-$  and  $NH_4^+$  ( $Bi$ ) was then  
152 calculated as follows:

$$153 \quad Bi = TDi - J_{is} \quad (3)$$

154 where  $s$  is the layer of the deepest samplers.

155

### 156 3. Results

#### 157 3.1 Long-term trends in deposition chemistry

158 Data on bulk and throughfall deposition are presented in Table 2 and in Fig. S1. All the time series  
159 were long enough to guarantee the robustness of the results. No significant temporal changes were detected  
160 for open field precipitation (BDH) and throughfall precipitation among all the studied sites. A seasonal Kendall  
161 test (SKT) performed on monthly  $SO_4^{2-}$  deposition values showed significant decreasing trend for all sites  
162 (Table 3), with a marked year variability due to the high marine contribution to sulphate from the  
163 Mediterranean Sea. In deposition nitrogen was found in the form of the two major compounds: ammonium  
164 ( $NH_4^+$ ) and nitrate ( $NO_3^-$ ). Year-to-year variability was less marked than in the case of sulphate deposition  
165 (Fig. S1), but a slight decreasing trend was shown by nitrate deposition (Table 3). For  $NH_4^+$ , significant  
166 decreasing trends were found only in sites in Central Italy. BCE deposition was high (Table 2), stable, and no  
167 significant changes were observed at all sites except for EMI1, where a decreasing trend was observed (Table  
168 3).

169

#### 170 3.2 Soil solution chemistry and temporal trends

171 The sulphate concentration in soil solution (Fig. 2) showed change with depth for most of the sites,  
172 except for CAL1 and ABR1. For EMI1 and LAZ1 a significant increase of sulphate from the shallow to the  
173 deepest soil was observed. Nitrates were present in the organic layers at all sites, while differences in  $NO_3^-$

174 concentration were found in the mineral soil layers, and for CAL1, EMI1 and VEN1 the values were higher  
175 than 1 mg N l<sup>-1</sup>, a proposed threshold for critical N leaching and saturation (Gundersen et al., 2006). A  
176 common feature to all sites is the almost complete absence of  $NH_4^+$  in the mineral soils at both depths,  
177 topsoil and subsoil. The base cation concentration was the lowest in the northern sites, and a latitudinal  
178 trend was observed in the organic layers. Soil solution of the organic layers was moderately to slightly acidic  
179 at most of the plots. The lowest levels of pH were found at the topsoil for EMI1, PIE1 and LAZ1 sites (Fig 2).  
180 This pH increase with depth is in accordance with observations on soil solution chemistry at European scale  
181 (Johnson et al., 2018). The observation of the time series of the forest floor (Fig. S2) clearly evidenced year-  
182 to-year variation. The  $SO_4^{-2}$  in the FF samplers showed a strong interannual fluctuation with different  
183 behaviours between the monitoring sites (Fig. S2). No trend was found at the forest floor except for LAZ1  
184 site, where  $SO_4^{-2}$  significantly decreased. At both analysed mineral layers, significant decreasing  $SO_4^{-2}$  trends  
185 were dominant among the sites (Fig. 3). However, at the subsoil, for LAZ1 and for sites with historically high  
186  $SO_4^{-2}$  deposition, as EMI1 and VEN1, no temporal changes were observed. Interestingly, these latter sites  
187 were those that exhibited the largest decrease at the topsoil.

188 Nitrate concentration showed different trends between sites and depths.  $NO_3^-$  concentrations were  
189 unchanged at all the depths at VEN1, while significantly increased at the deepest samplers for PIE1 and CAL1,  
190 and at the topsoil for EMI1 (Fig. 3). In the forest floor,  $NO_3^-$  increased at EMI1 and LAZ1, and decreased at  
191 ABR1 and CAL1. Trends for LAZ1 and ABR1 were detected only for the forest floor due to a sporadic presence  
192 of  $NO_3^-$  within the mineral soil that precluded any statistical processing. No significant changes in  $NH_4^+$   
193 concentration in soils solution at the forest floor were found for most of the sites. However, a decreasing  
194 trend was observed at LAZ1 (slope: - 0.03 mg l<sup>-1</sup> y<sup>-1</sup>,  $p < 0.001$ ) and CAL1 (slope: -0.02 mg l<sup>-1</sup> y<sup>-1</sup>,  $p < 0.01$ ) sites.  
195 Increasing trends of the soil solution BCE concentration clearly dominated at most of the sites, except for  
196 ABR1 and LAZ1, which had a decreasing trend in the forest floor and in the mineral layers, respectively. The  
197 soil solution pH from the FF lysimeters showed no prevalent trends, except for VEN1 that showed a positive  
198 trend (Fig 3).



199 3.3 Seasonal patterns of N deposition

200 BD and TF deposition of  $NO_3^-$  and  $NH_4^+$  show little dependence on precipitation, as evidenced by the relatively  
201 low coefficients of correlation in the scatter plots at most sites (Fig. 4), except for EMI1 and PIE1. Monthly  
202 BD and TF deposition of  $NO_3^-$  and  $NH_4^+$  indicated an overall month to month variability, with different  
203 seasonal patterns between sites (Fig. S3). For the alpine sites (PIE1 and VEN1), a peak in spring and summer  
204 was observed for TF and BD deposition of both nitrogen compounds, while the other sites showed a spring  
205 maximum followed by a slow decrease of deposition in summer. At EMI1 a fall peak was observed for all  
206 kinds of deposition.

207 At most sites,  $NO_3^-$  and  $NH_4^+$  throughfall deposition were higher than bulk deposition (Fig. S3), with  
208 significant differences in the summer, from June to September. This is particularly evident for  $NO_3^-$   
209 deposition, while for  $NH_4^+$  this pattern was less marked at all sites, with very low differences between bulk  
210 and throughfall deposition throughout the year at PIE1 and for the sites with low N loads as ABR1 and LAZ1.

211 3.4 Nitrogen fluxes from the forest floor and subsoil

212 The outflow of N from the forest floor was higher than deposition at all the sites (Table 4), with a  
213 generally high contribution of  $NO_3^-$ . EMI1 also showed a high amount of  $NH_4^+$ . The principal seasonal pattern  
214 was the increase of the forest floor N outflow in spring (Fig. 5). The forest floor outflow decreased in summer  
215 due to scarcity of water flow, then raised to the maxima in fall, when the N accumulated in summer was  
216 leached (Fig. 5). At EMI1 high level of N outflow were observed also in summer. Differently from the other  
217 sites, VEN1 and ABR1 showed the maximum forest floor outflow of nitrogen in summer, when deposition  
218 was high and then regularly decreased to the end of the sampling period, despite increasing water flows.

219 N leaching from subsoil layers was completely inactive at LAZ1 and ABR1, limited at VEN1 and PIE1,  
220 and substantial at EMI1 and CAL1 (Table 4 and Fig. 6). The overall presence of  $NH_4^+$  was sporadic in the  
221 lysimeters at the mineral soil layers, thus mineral N leaching was normally made up of  $NO_3^-$ . At all sites, the  
222 amount of N leached out was much smaller than either forest floor outflow or throughfall deposition.  
223 Unfortunately, for the sites on the Alps, VEN1 and PIE1, our data on soil solution chemistry were available

224 only for the period between May and November/December (Fig. 5 and 6); low temperatures did not allow to  
225 sample in winter. Thus, the incomplete time series provides only partial results on N leaching, and we can  
226 suppose that N leached is underestimated for PIE1 and VEN1.

227

## 228 4. Discussion

### 229 4.1 Impact of deposition on concentration and long-term trends of soil solution chemistry

230 The year-to-year high variability observed for soil solution concentration at the forest floor suggests  
231 a linkage with the climatic characteristics of the years that modulate processes at the forest floor- through  
232 the indirect influence on forest stand and soil biological activity of microorganisms and pedofauna. These  
233 processes likely masked changes due to atmospheric deposition. Thus, the discussion will be mainly focus on  
234 the time series extracted from the mineral soil samplers, which show a much less complex behaviour with  
235 smoother long-term changes and limited seasonal effects. The deposition trends for  $SO_4^{-2}$ ,  $NO_3^-$  and  $NH_4^+$   
236 were within the range of relative slope observed for earlier studies on European deposition trends comparing  
237 rslope values (Waldner et al., 2014). The most evident and generalized trend for all the sites was the  
238 concomitant decrease of  $SO_4^{-2}$  from atmospheric deposition and soil solution, thus confirming the  
239 effectiveness of the abatement emission polices regarding S compounds. This result agrees with observations  
240 at the European scale (Johnson et al., 2018) and from individual forest plots (i.e. Karlsson et al., 2011;  
241 Vanguelova et al., 2010; Verstraeten et al., 2012; Waldner et al., 2014). At EMI1 and LAZ1 sites, however, a  
242 high  $SO_4^{-2}$  concentration and no long-term decrease were observed in soil solution at 60-80 cm. At the subsoil  
243 lysimeters,  $Na^+$  concentration was also high compared to the other sites (Cecchini et al., 2019). Past marine  
244 intrusion might explain the high levels of  $Na^+$  and  $SO_4^{-2}$ , compounds typical of marine environments.  
245 Furthermore, for EMI1, despite a reduction of sulphur deposition in recent decades, the presence of sulphur-  
246 contaminated soils is plausible. Before the start of the monitoring, high acid loads may have caused sulphate  
247 accumulation in soils around the Po plain (EMI1 and VEN1). For these sites, the absence of significant changes  
248 in soil solution of  $SO_4^{-2}$  at the subsoil implied a delay of response to observed decreasing sulphate deposition,

249 which may be ascribed to desorption of previously deposited  $SO_4^{-2}$  from soils (Fakhraei et al., 2016). This  
250 result is in agreement with higher release of  $SO_4^{-2}$  from soils found in sites with historically high deposition  
251 (Oulehle et al., 2006). For the most southerly sites,  $SO_4^{-2}$  peaks are likely linked to dry deposition of sulphate-  
252 laden dusts or aerosols of marine and/or African origin, as was already found for ABR1 (Cecchini et al., 2002).  
253 Furthermore, the strong decrease of  $SO_4^{-2}$  at 20 cm (topsoil) might suggest that the desorption process is  
254 proceeding as a front from topsoil to subsoil, which is still saturated and is receiving large  
255  $SO_4^{-2}$  concentrations from the topsoil, thus explaining high  $SO_4^{-2}$  concentration at the subsoil.

256 Inorganic N in soil solutions show no significant trends in response to decreasing nitrogen deposition  
257 in most of the sites. The decreasing trends of  $NO_3^-$  deposition seem too slight to act on mineral N in soil  
258 solution (Table 3). Furthermore, a continuous contribution to N input due to  $NH_4^+$  deposition has to be  
259 considered for all sites. The low percentage of plots with significant trends for  $NH_4^+$  deposition, in the Italian  
260 forests, is comparable with findings for the rest of Europe (Waldner et al., 2014). Agriculture is the main  
261 source of  $NH_3$  emissions (94% of the total; Taurino et al., 2018) and, although abatement technologies have  
262 been introduced following the implementation of the EU IPPC Directive,  $NH_3$  emissions are still too high in  
263 Italy.

264 For EMI1, PIE1 and CAL1, an increasing trend in  $NO_3^-$  concentration has been recorded at the shallow  
265 and subsoil samplers, respectively. EMI1 and PIE1 sites were loaded by nitrogen ( $NO_3^- + NH_4^+$ ) throughfall  
266 deposition higher than  $10 \text{ Kg N ha}^{-1} \text{ y}^{-1}$ , a threshold that corresponds to imbalance in input-output models  
267 (Dise and Wright 1995; Gundersen et al., 1998).

268 Aeolian dust contribution from Saharan sources that preferentially impact sites located in south  
269 (CAL1; Fig.1) and central Italy (LAZ1; Fig. S1; Rogora et al., 2004; Cecchini et al., 2019) likely also explain the  
270 highest level of BCE for these sites where large peaks were noticeable, since Sahara outbreaks were found to  
271 be conspicuous in atmospheric deposition particulate matter also at a site 1500 km away from the source  
272 (Lequy et al., 2018). The importance of the episodic deposition of Saharan dust was underscored by the large  
273 peaks in base cation deposition at the southernmost monitoring sites (CAL1; Fig. S1) and in Central Italy (LAZ1;

274 Fig. S1). This likely explains the observed unchanged trends for BCE at all sites. On the other hand, the  
275 significant negative trend observed at EMI, a site located in the Po Plain, can be explained by a concomitant  
276 decrease of the pollution component to BCE (Watmough et al., 2014).

277 At most of the sites, a positive pH trend was found for soil solution from mineral soil samplers. This  
278 was likely related to a combining effect of a general decrease of sulphate and the increase of BCE in soil  
279 solution. These results could be interpreted as the most evident response to the decrease in  $SO_4^{-2}$  deposition  
280 as was also suggested in previous studies (de Vries et al., 2003, Verstraeten et al., 2012; Fuss et al., 2015). On  
281 the other hand, a negative topsoil pH trend was observed at EM11, which is known to be a site with significant  
282 exceedance of critical load for N deposition (Ferretti et al., 2014). This suggests that the effect of decreasing  
283 S deposition can be neutralised by high N depositions. Furthermore, N at this site included a large amount of  
284  $NH_4^+$ : the production of 2 moles of  $H^+$  through nitrification of 1 mole of  $NH_4^+$  increases the strength of  
285 acidification.

#### 286 4.2 Nitrogen fluxes from the atmosphere to the subsoil.

287 The overall N throughfall deposition higher than bulk deposition suggests an important contribution  
288 of dry deposition, which was previously recognised as the main form of atmospheric N input in  
289 Mediterranean ecosystems (Sanz et al., 2002; Avila and Rodà 2012). The importance of dry deposition was  
290 also recently supported by isotopic analysis conducted in Mediterranean holm oak forests (Guerrieri et al.,  
291 2019). In summer, total depositions generally decreased, but increased dry deposition causes TF depositions  
292 to increase their contribution and, often, to reach the highest levels. The observed input pulses of nitrogen  
293 into the forest soil after dry periods presumably originated from the washing of dry deposition accumulated  
294 in the canopy (García-Gomez et al., 2016). The observed seasonal pattern in N TF deposition may also be  
295 explained by a seasonal partitioning between atmospherically and biologically derived N- $NO_3$ ; especially in  
296 summer, after a drought period, a high proportion of  $NO_3^-$  has been suggested to derive from nitrification at  
297 the canopy (Guerrieri et al., 2019). At EM1 and LAZ1 sites, high spring N TF deposition, may also originate  
298 from flowers and insects falling in the collectors and trapped on the filters.

299 From October to December, the most common pattern was for a general decrease; in the  
300 southernmost site, CAL1, the decrease was marked with respect to precipitations. For most sites, deposition  
301 appeared to be controlled either by changes in source emissions or, more likely, by changes in atmospheric  
302 circulation that either strengthen or weaken the connection with the source. The exceptions are EMI1 and  
303 PIE1 sites, where deposition of both nitrogen forms was highest and strongly correlated with precipitation,  
304 which was not observed for the other sites. It appears that sources of pollution are close, and emissions are  
305 constant, so that transport is independent from atmospheric circulation. EMI1 and PIE1 are close to the “hot  
306 N point” of the Po Plain, one of the most urbanized and cultivated area of Italy, and both NO<sub>x</sub> emission from  
307 mobile sources and the largest source of NH<sub>3</sub> emissions due to livestock waste (Taurino et al., 2018) play a  
308 key role, being a source of pollution also for forest sites.

309 At all sites, N released by the forest floor was higher than N deposition. This suggests that these soil-  
310 forest systems were well loaded with N, which was then intensely cycled. A general increase of flux in spring,  
311 together with typical summer maxima at EMI1 and VEN1, were likely induced by increasing deposition at  
312 most sites (Fig. S3) and by the influence of high temperature on mineralization rates within the forest floor.  
313 On the other hand, at the more southern sites (CAL1 and LAZ1), the low water availability in summer strongly  
314 reduced the N outflow, while an increase was observed in fall. This was likely due to a release of nitrates  
315 previously produced and accumulated in summer. Nitrification process was observed to begin at the canopy  
316 level, on the leaf surface, by ammonia-oxidizing archea (Guerrieri et al., 2015) and in throughfall deposition  
317 (Watanabe et al., 2016). Oxidizing microbes reach the soil via throughfall deposition and fallen leaves, further  
318 explaining the maximum release of nitrate from the forest floor in fall for all sites (Fig. 5). The low flux of  
319  $NH_4^+$  out from the forest floor compared with the  $NH_4^+$  throughfall input, and the high flux of nitrates leached  
320 out of the FF (Table 4), likely suggest that ammonium was at least partly nitrified within the forest floor. The  
321 H<sup>+</sup> cation produced during nitrification possibly caused soil acidification. These observations confirm that the  
322 high level of  $NH_4^+$  in atmospheric deposition represents a potential soil acidification factor in the northern  
323 sites (EMI1, VEN1 and PIE1) where  $NH_4^+$  deposition were relatively high (Table 2). Furthermore, most soil N  
324 stores in dead organic matter and can be converted from insoluble organic nitrogen to dissolved organic N

325 (DON) by microorganisms in natural forest ecosystems, and then converted in  $NH_4^+$  into the soil. Part of  
326  $NH_4^+$  is assimilated by plants, immobilized by microbes, or absorbed by clay minerals.

327 A notable feature in mineral soil was the absence of  $NH_4^+$ , which represents a high proportion of  
328 deposition and which is only partially retained in the forest floor (Table 4). At all sites, N was essentially  
329 retained within the mineral soil. The organic layers of most of the Italian forests is normally too thin to  
330 function as a storage (Andreetta et al., 2011), although it seems to be very active, being more a nitrogen  
331 source than a sink. The absence of  $NH_4^+$  in soil solution at the deepest samplers is in line with what was  
332 observed for other European countries (eg., MacDonald et al., 2002). This is attributed to the nitrification  
333 process, converting  $NH_4^+$  into  $NO_3^-$  (Gilliam et al., 2001) after possible temporary adsorption on soil negative  
334 charges, thus impeding fast leaching.

335 Although the seasonal distribution showed different patterns among sites (Fig. 6), N leaching  
336 mostly took place in fall and spring. The peaks observed during the vegetative season followed either high  
337 deposition (Fig S3) or FF outflow (Fig. 5). The winter peak at CAL1 appears to be associated with low  
338 biological uptake and high water flow. The different characteristics of the soils are likely to play a role. Soils  
339 at EMI1 and VEN1 are fine-textured, with long residence times for water; this maximizes uptake  
340 opportunities when biological activity is high, thus explaining low level of N leached in spring despite high  
341 water flow. On the contrary, soils in CAL1 and PIE1 have high permeability and short water residence times,  
342 so that peak N inputs at forest floor/mineral soil interface are transferred downwards.

343 Fluxes of nitrogen through the studied forest-soil ecosystems thus appear to be rather complex. N  
344 deposition indirectly induced a state of N saturation that caused a high flux of N from the forest floor. In turn,  
345 N flux was heavily controlled by the effects of the mineralization rate and the water flow, thus following time  
346 patterns independent from deposition. High N forest floor outflow is very efficiently retained within the  
347 mineral soil. Leaching of N at subsoil level is absent or small in most sites (Table 4) and is important at the  
348 very-high-deposition EMI1 site but also at CAL1, despite its relatively low N deposition loads (Table 4). At EMI  
349 relevant deposition caused a continuous nitrate loss from the soil, but the observed annual outflux is lower

350 than at CAL1 (Table 4). This might be explained by lower precipitation and higher soil clay content at EMI1,  
351 with likely higher accumulation of N in mineral soils (Fuss et al., 2019). Moreover, microbial N uptake could  
352 lead to a significant long-term sink for N in forests if that N is subsequently transferred to stable soil organic  
353 matter (Curtis et al., 2011). Differences in SOM mineral association may influence soil biogeochemical cycling  
354 at different timescales, leading to different response to atmospheric deposition.

355 Furthermore, the forest at CAL1 is reaching mature age and trees are showing signs of distress in the  
356 last few years; consequently, it would be expected to have declining N accumulation in biomass. This is in  
357 agreement with conceptual models of nutrient retention in ecosystems for which mature forests should  
358 experience increased nitrate ( $NO_3^-$ ) losses in response to decreased plant demand (Aber et al., 2002;  
359 Pourmokhtarian et al., 2012). On the other hand, the EMI1 forest is undergoing succession (Bertini et al.,  
360 2011), thus vegetation is growing rapidly and nitrogen (N) leaching to groundwater should be lower than  
361 expected.

362 These results on N leaching in Italian forest soils demonstrate that data on atmospheric deposition  
363 alone does not allow us to always predict the nitrogen fate in the soil. The complex nature of plant-soil  
364 feedbacks involved in the nitrogen cycle has to be considered, since the interchange of N between vegetation  
365 and soil can decouple N export and biomass dynamics, and cause forest ecosystems to retain N longer than  
366 expected (Lovett et al., 2018). Further, N dynamics depend on N-mineral association (Fuss et al., 2019) and  
367 on the nature of soil organic matter that emergent views describe as a continuum of progressively  
368 decomposing organic compounds (Lehmann and Kleber 2015). Thus, N can follow different pathways at  
369 different time scales influencing N leaching independently from the amount of deposition.

370

## 371 5 Conclusions

372 The evaluation of the time series for atmospheric deposition and soil solution chemistry provides  
373 evidence of reductions in  $SO_4^{2-}$  deposition and soil water  $SO_4^{2-}$  concentrations at all Level II intensive  
374 monitoring sites across Italy, confirming the successful implementation of the emission reduction policies.

375 However, concerns over the local effects of excess nitrogen deposition pollution remain. Despite slightly  
376 decreasing  $NO_3^-$  deposition, high  $NH_4^+$  deposition to northern Italian forests still appears to continue at a  
377 constant rate. For the site (EMI1) located in the Po plain, a “hot spot” concerning N deposition, soil solution  
378 pH is decreasing at the topsoil. For all the other sites, a positive response of soil solution pH to decreases in  
379 acid deposition is evident. Although acidification does not seem to be a real concern for most of the forest  
380 soils in Italy, the analysis of nitrogen fluxes from the atmosphere to the subsoil points to a potential risk of  
381 nitrate leaching. For inorganic N, the decreasing trends seem too slight to avoid exceedance of critical loads  
382 in the north, where further reduction of N emissions is needed to prevent air pollution effects on forests.  
383 Furthermore, factors other than pollution have to be considered, as evidenced by CAL1, a site in the south of  
384 Italy where, despite the relative low N atmospheric deposition, nitrate leached out from the subsoil is  
385 significant. The large variability of the Italian territory in terms of climate, geology and soil type requires  
386 careful monitoring of the forest ecosystems in order to follow up chemistry trends and fluxes in soil solutions  
387 with particular attention to nitrogen leaching concerns.

388

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398

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## 610 **Figure captions**

611 Fig. 1 Location of the 6 studied sites.

612 Fig. 2 Concentration of S-  $\text{SO}_4^{2-}$ , N- $\text{NO}_3^-$ , base cations and pH for the forest-floor (0 cm), topsoil (20  
613 cm) and subsoil (60 cm) samples at each site.

614 Fig. 3 Results of the trend analysis by Seasonal Kendall Test (SKT) applied to monthly data of sulphate, nitrate,  
615 ammonia and base cation concentrations at the forest floor (0 cm), topsoil (20 cm) and subsoil (60 cm) for  
616 each site. Significance of Sen's slope: \* $p \leq 0.05$ ; \*\* $p \leq 0.01$ ; \*\*\* $p \leq 0.001$ ; n.s.: not significant.

617 Fig. 4 Scatterplot of precipitation (mm) and deposition of N- $\text{NO}_3^-$  (red) and N- $\text{NH}_4^+$  (black). Numbers at  
618 the top-left indicate the Spearman's coefficient of correlation.

619 Fig. 5 Representation of the monthly fluxes of water (Jw -bars) and nitrates (JNO3-lines) out of the forest  
620 floor for each site. Dashed lines represent the minimum and the maximum recorded nitrate flux within each  
621 time series.

622 Fig. 6 Representation of the monthly fluxes of water (Jw -bars) and nitrates (JNO3 -lines) out of the deepest  
623 layer for each site. At ABR1 and LAZ1 sites, no presence of nitrates was observed in the deepest samplers.

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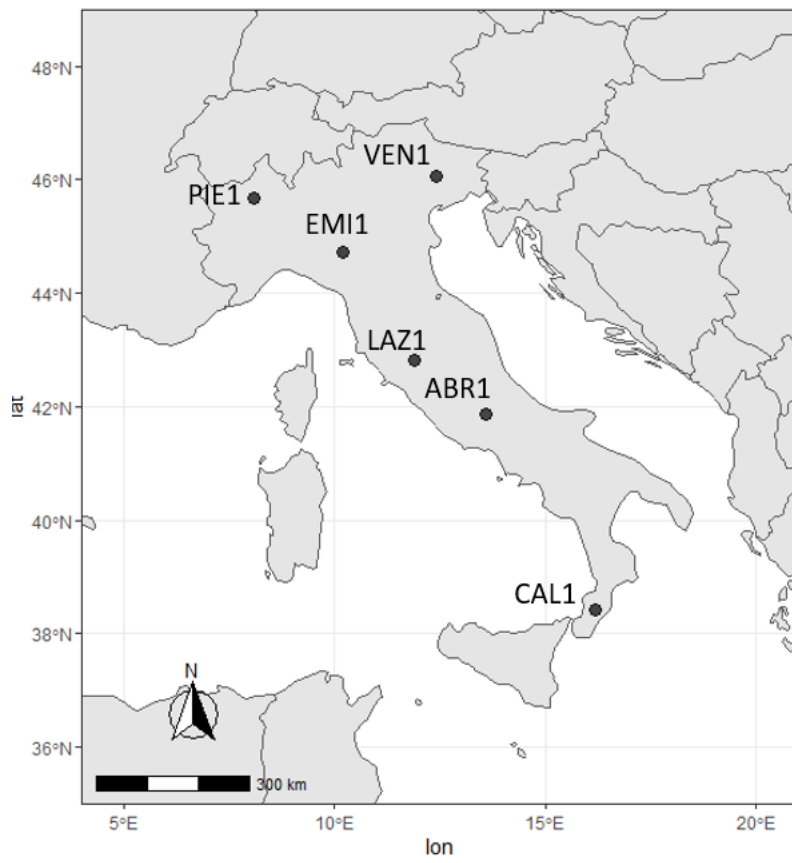
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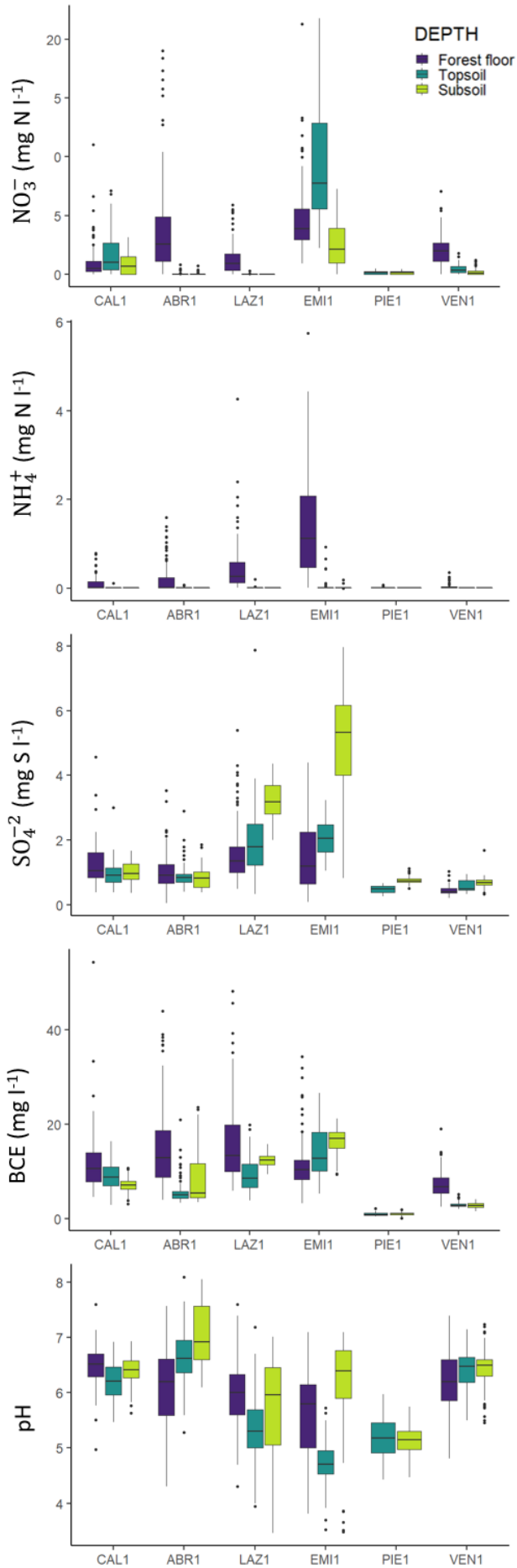
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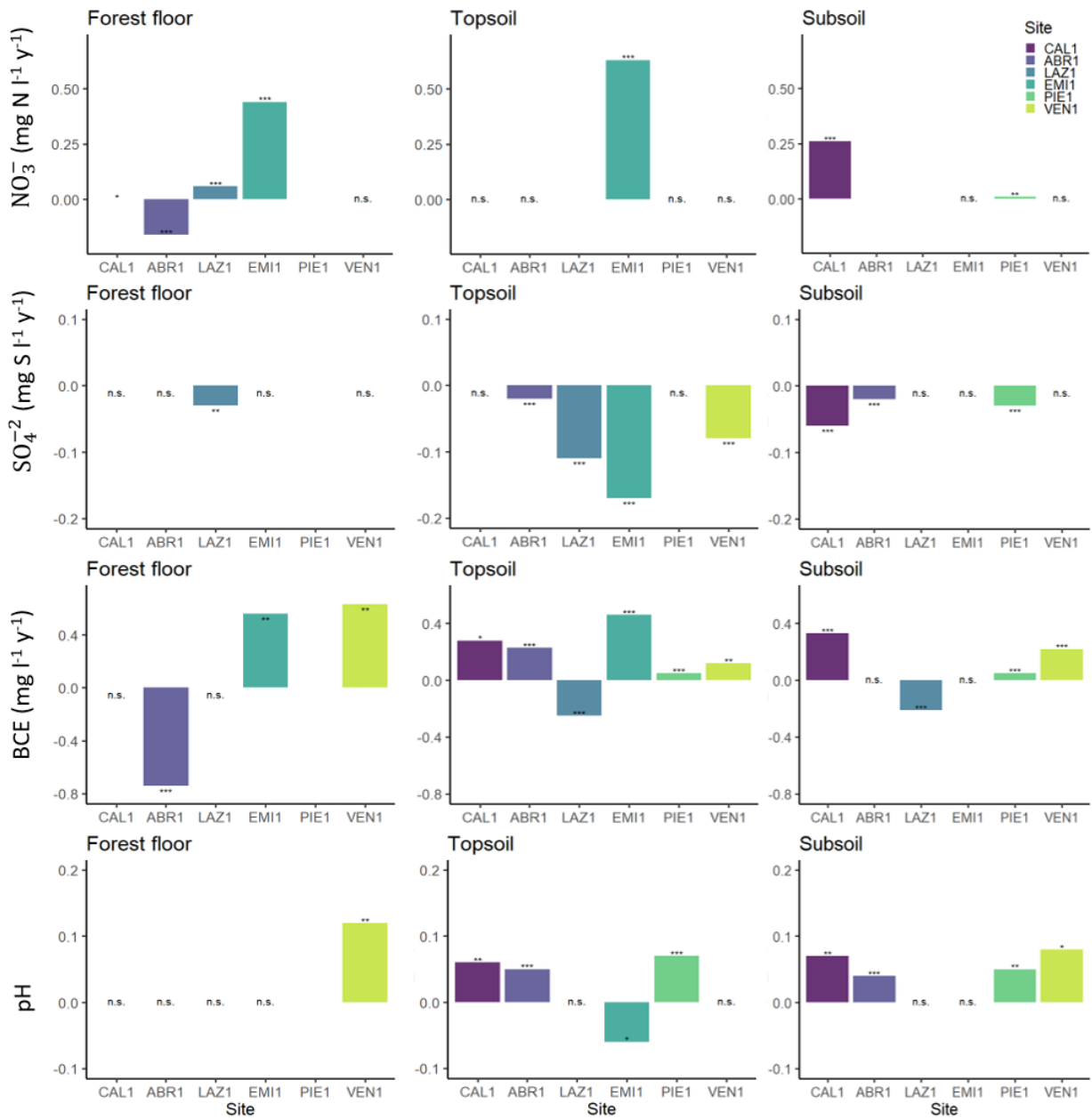


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636 Fig. 1



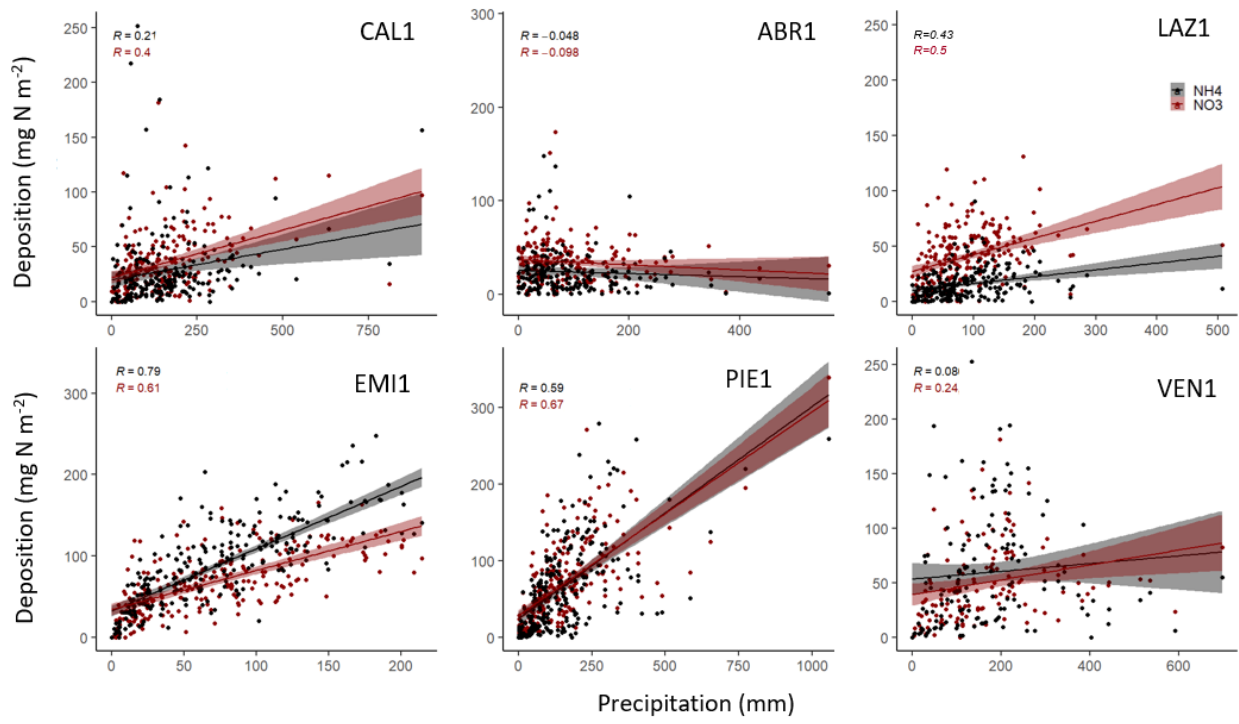




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639 Fig. 3

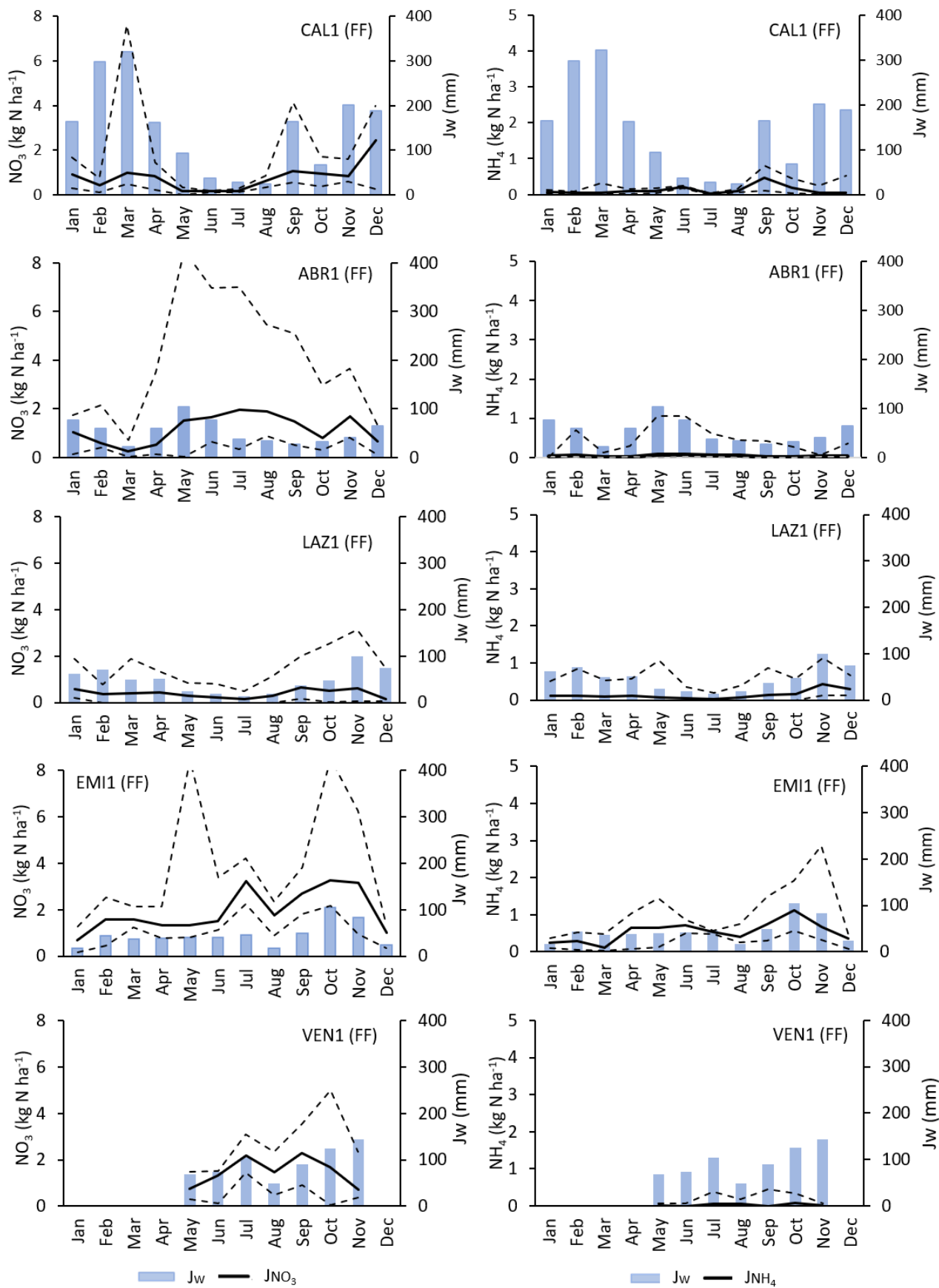
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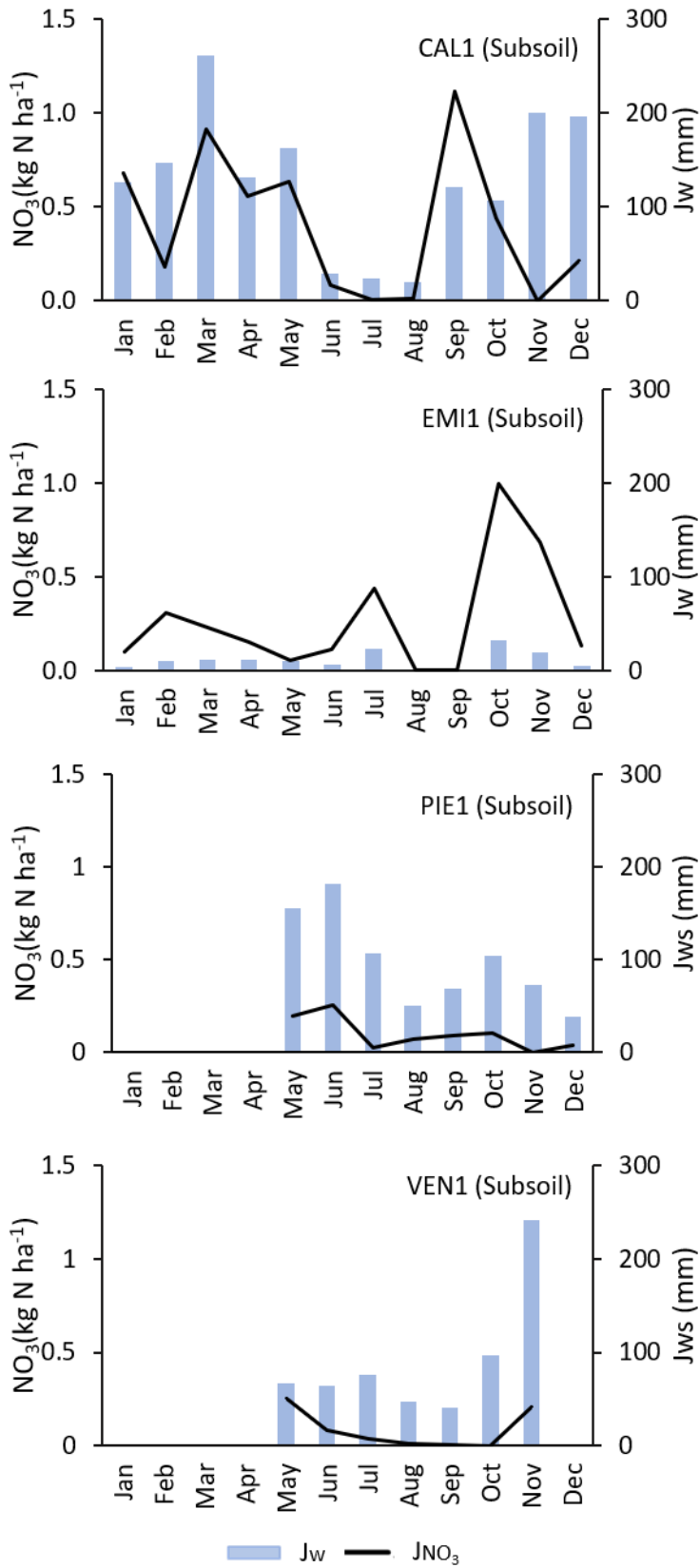
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645 Fig. 5

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648 Fig. 6

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651 Table 1  
652 Main characteristics of the sampling sites and soils.

Code	Position	Altitude (m a.s.l.)	Precipitation (mm)	Vegetation	Soil	BS* (%)	Period for trend analysis**
CAL1	38°25'N, 16°10'E	975	1880	<i>Fagus sylvatica</i>	Haplic Umbrisol	13	2009-2017
ABR1	41°51'N, 13°34'E	1500	950	<i>Fagus sylvatica</i>	Humic Alisol	75	1997-2017
LAZ1	42°49'N, 11°54'E	675	1019	<i>Quercus cerris</i>	Cutanic Alisol	48	1999-2017
EMI1	44°43'N, 10°12'E	225	859	<i>Quercus petraea</i> , <i>Q. cerris</i>	Endostagnic Luvisol	51	2010-2017
PIE1	45°41'N, 8°04'E	1150	1811	<i>Fagus sylvatica</i>	Haplic Cambisol	16	2006-2017
VEN1	46°03'N, 12°01'E	1125	1900	<i>Fagus sylvatica</i>	Haplic Luvisol	100	2010-2017

653 \*Soil base saturation (B horizon)

654 \*\* Soil solution

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656

657 Table 2  
658 Average annual deposition for the time series (1998 to 2017) among sites

Site	Bulk deposition (kg N ha <sup>-1</sup> y <sup>-1</sup> )				Throughfall deposition (kg N ha <sup>-1</sup> y <sup>-1</sup> )			
	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	S-SO <sub>4</sub> <sup>2-</sup>	BCE	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	S-SO <sub>4</sub> <sup>2-</sup>	BCE
CAL1	3.47	2.85	34.96	67.28	4.01	3.23	53.09	133.18
ABR1	3.31	2.68	12.99	29.90	3.48	2.10	12.45	47.10
LAZ1	3.32	2.42	14.70	27.20	4.56	2.07	18.10	54.17
EMI1	4.84	6.68	12.87	12.31	8.15	10.34	18.76	37.50
PIE1	7.34	7.97	20.18	13.46	7.99	7.68	19.16	23.92
VEN1	5.01	12.73	20.16	22.37	5.81	6.80	18.91	42.96

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661 Table 3  
662 Results of the trend analysis by Seasonal Kendall Test (SKT) applied to monthly data of atmospheric  
663 deposition, expressed as relative change for the period 1998-2017.

Site	Throughfall deposition (% y <sup>-1</sup> )			
	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	BCE	S-SO <sub>4</sub> <sup>2-</sup>
CAL1	n.s.	n.s.	n.s.	-4.03 *
ABR1	-7.32 *	-4.97 *	n.s.	-4.37 *
LAZ1	-3.2 *	-1.38 *	n.s.	-7.27 ***
EMI1	-2.41 *	n.s.	-2.1 *	-10.13 ***
PIE1	-4.08 ***	n.s.	n.s.	-5.96 ***
VEN1	-3.78 **	n.s.	n.s.	-5.29 **

664 Level of significance: \*\*\*p < 0.001; \*\*p < 0.01; \*p < 0.05

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666 Components of the  $N_{\min}$  soil budget (TF-based estimate, in  $\text{kg ha}^{-1} \text{y}^{-1}$ ):  $J_{\text{ff}}$ : flux out of the forest floor;  $B_{\text{ff}}$ : budget of the forest floor;  $J_{\text{s}}$ : flux out of the deepest  
 667 layer;  $B_{\text{TFD}}$ : budget with TFD as input (from starting soil solution sampling year to 2015).

	CAL1			ABR1			LAZ1			EMI1			PIE1 <sup>§</sup>			VEN1 <sup>§</sup>		
	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	N <sub>tot</sub>	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	N <sub>tot</sub>	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	N <sub>tot</sub>	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	N <sub>tot</sub>	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	N <sub>tot</sub>	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	N <sub>tot</sub>
	(kg N ha <sup>-1</sup> y <sup>-1</sup> )			(kg N ha <sup>-1</sup> y <sup>-1</sup> )			(kg N ha <sup>-1</sup> y <sup>-1</sup> )			(kg N ha <sup>-1</sup> y <sup>-1</sup> )			(kg N ha <sup>-1</sup> y <sup>-1</sup> )			(kg N ha <sup>-1</sup> y <sup>-1</sup> )		
BD	2.8	3.2	6	3.5	3.1	6.6	3.6	2.6	6.2	4.9	6.3	11.2	2.9	3.5	6.4	2.4	8.5	10.9
TFD	4.5	4.6	9.1	4.4	2.7	7.1	6.4	1.9	8.3	7.7	10.4	18.1	3.6	3.7	7.3	3.7	4.5	8.2
$J_{\text{ff}}$	8.4	0.8	9.2	5	0.2	5.2	8.4	2.3	10.7	20.9	5.2	26.1	-	-	-	15.8	0.3	16.1
$B_{\text{ff}}$	-3.9	3.8	-0.1	-0.6	2.5	1.9	-2	-0.4	-2.4	-13.2	5.2	-8	-	-	-	-12.1	4.2	-7.9
$J_{\text{s}}$	3.3	0	3.3	0	0	0	0	0	0	2.6	0	2.6	0.8	0	0.8	0.9	0	0.9
$B_{\text{TFD}}$	1.2	4.6	5.8	4.4	2.7	7.1	6.4	1.9	8.3	5.2	10.4	15.6	2.8	3.7	6.5	2.8	4.5	7.3

668 <sup>§</sup>For PIE1 and VEN1 sites, since soil solution sampling cover only the period from May to November, also the data reported for bulk and throughfall deposition are related to  
 669 this period. The values of N deposition for the full year are reported in Table 2.

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