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1 **Twenty-five year record of chemicals in open field precipitation and throughfall from a**  
2 **medium-altitude forest catchment (Strengbach - NE France): an obvious response to**  
3 **atmospheric pollution trends.**

4

5 Marie-Claire Pierret<sup>a,\*</sup>, Daniel Viville<sup>a</sup>, Etienne Dambrine<sup>b</sup>, Solenn Cotel<sup>a</sup>, Anne Probst<sup>c</sup>

6

7 <sup>a</sup> Laboratoire d'Hydrologie et Géochimie de Strasbourg LHyGeS-Ecole et Observatoire  
8 des Sciences de la Terre EOST-Université de Strasbourg, CNRS -1 rue Blessig, 67084 Strasbourg  
9 Cedex, France. marie-claire.pierret@unistra.fr; dviville@unistra.fr; cotel@unistra.fr

10 <sup>b</sup> INRA-Université de Savoie - Centre Interdisciplinaire Scientifique de la Montagne, Belledonne  
11 226, 73376 Le Bourget-du-Lac Cedex, France. etienne.dambrine@univ-savoie.fr

12 <sup>c</sup> EcoLab, Université de Toulouse, CNRS, Toulouse, France; anne.probst@ensat.fr

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14 *\*Corresponding author.*

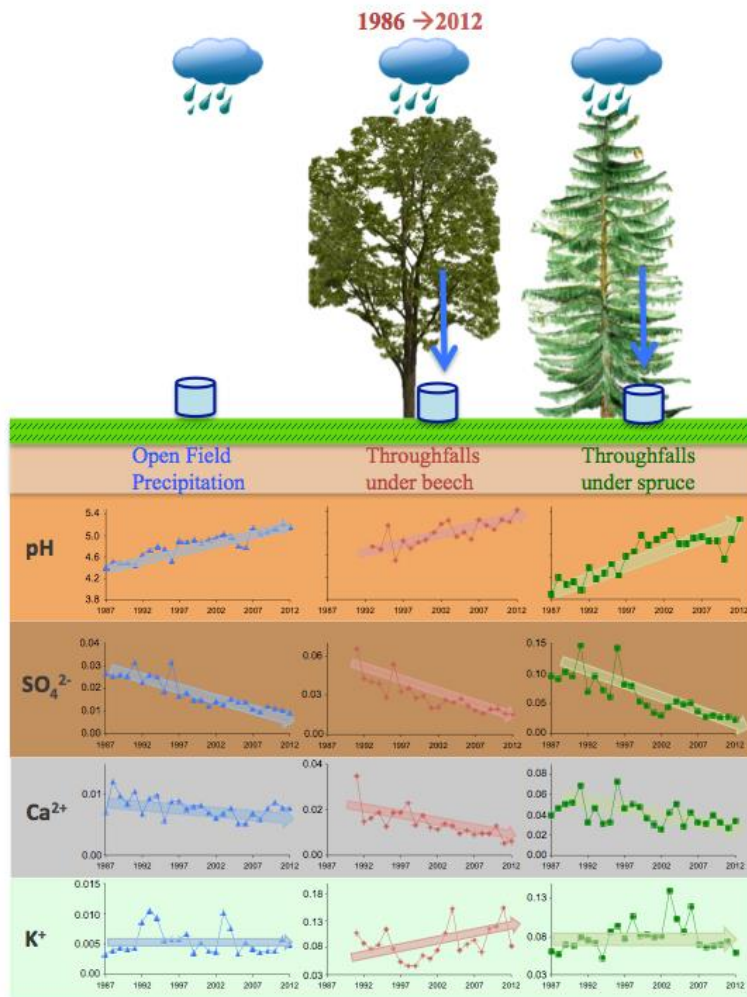
15 *Marie-Claire Pierret marie-claire.pierret@unistra.fr*

16 *Anne Probst anne.probst@ensat.fr*

17

18 **Graphical Abstract**

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20

21

22 **Abstract**

23 This study concerned a 25 yr continuous record of bulk precipitation and throughfall composition in  
24 a medium-altitude forested environment. The 1986-2012 survey from the more intense acid rain  
25 period in the mid-eighties until the present allowed the quantification of the interaction between  
26 atmospheric deposition and vegetation and the long-term evolution following pollutant emission  
27 trends.

28 The long-term monitoring evidenced some significant temporal trends (pH, conductivity,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  
29  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ ). Significant decreases in the concentrations and fluxes of several ions  
30 were observed ( $\text{H}^+$  and  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{Ca}^{2+}$ ) in open field precipitation and throughfalls. The regular  
31 and strong decrease in protons and sulfate followed the decreases in anthropogenic  $\text{SO}_2$  and  $\text{NO}_x$   
32 (proton precursors) since the 1980s. The decrease in  $\text{Cl}^-$  concentrations was weaker and could have  
33 been related to the regional reduction in HCl emissions and/or to changes in the precipitation

34 regime. The annual calcium fluxes were reduced from approximately 15 to 9 and 6 to 2 kg.ha<sup>-1</sup>  
35 under spruces and beeches, respectively, as a consequence of reductions in anthropogenic industrial  
36 dust. In such calcium-limited resource soils, the atmospheric Ca flux exceeded the Ca flux from  
37 mineral weathering and was highly bioavailable for vegetation growth. This decrease in nutrient  
38 input had strong consequences for soil nutrients and may thus have participated in forest decline.  
39 The two tree plantations had contrasting effects on the physico-chemical parameters of the  
40 incoming precipitation with higher water interception and chemical concentrations under spruces  
41 than under beeches, which underlined the role of tree species in atmospheric inputs to soils. The  
42 structure and persistence of spruce needles enhanced the capture of particles and water,  
43 accentuating the acidity of the deposition and leading to the intensification of acidification  
44 processes, nutrient leaching in soils and forest decline. In contrast, beech leaves were able to  
45 neutralize a portion of the atmospheric protons, which minimized and reduced the negative effects  
46 of acid rain. In addition, the throughfalls represented an important part of the biological cycle of  
47 trees for some elements such as K or N, as indicated by the contrasting patterns at year and long-  
48 term scales regarding the vegetation type. However, our study indicated that the influence of tree  
49 species might change over time with changes in atmospheric pollution, in precipitation regime, or in  
50 stand structure.  
51 This study outlined the importance of the long-term record of open field precipitation and  
52 throughfalls under various tree types to better evaluate the real inputs of elements to forest  
53 ecosystems and among them, essential mineral nutrients.

54  
55

56 **Keywords:** atmospheric deposits; acid rain; throughfall; spruce; beech; nutrient; long-term data

57

58 **Highlights:**

- 59 - 1986-2012: a 2.5-decade survey of atmospheric deposition in the Vosges Mountains
- 60 - The sulfate decrease in precipitation and throughfall matched that of SO<sub>2</sub> emissions.
- 61 - The strong Ca decrease was related to changes in anthropogenic and natural sources.
- 62 - Beeches and spruces modified the atmospheric inputs to soil differently with time.
- 63 - N depositions decrease in OFP and under beech but increase under spruce.

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66  
67

68 **1. Introduction**

69 Atmospheric deposition supplies nutrients (N, base cations) as well as contaminants (sulfur and  
70 nitrogen ions, trace metals, organic compounds) and acidity to ecosystems. Understanding how the  
71 environment reacts to anthropogenic or natural disturbances at short- and long-term time scales is  
72 one of the major societal and scientific challenges in the field of natural resource management and  
73 conservation.

74 Among the anthropogenic perturbations, acid rain and more generally atmospheric acid deposition  
75 have impacted, sometimes deeply, the biogeochemical cycles of several elements (C, N, S, P, Al, H  
76 and other nutrients such as Ca and Mg; Paces, 1985; Cosby et al., 1985; Martin and Harr 1988;  
77 Landman and Bonneau (eds) 1995; Norton et al., 2000; De Vries et al., 2003; Hruska and Kram,  
78 2003; Oulehe et al., 2006; Vanguelova et al., 2010; Norton et al., 2014; McHale et al., 2017;  
79 Oulehle et al., 2017; Probst and Ambroise, 2018). The acidification of surface waters and soils  
80 degraded the quality of stream and spring waters, lakes and soils, notably by increasing the release  
81 of base cations and metals, leading to nutrient imbalances and causing forest decline, fish death,  
82 eutrophication of lakes and corrosion of monuments and water pipes (Likens and Bormann, 1974;  
83 Charlson and Rodhe, 1982; Schulze, 1989; Probst et al., 1990a,b, 1995a; Likens et al., 1996;  
84 Dambrine et al., 1998a; Evans et al., 2001; Jenkins et al., 2003; Watmough and Dillon, 2003;  
85 Moldan et al., 2004; Zhang et al., 2007).

86 Forest decline related to acid precipitation had been evidenced during the eighties in several places  
87 from northern Europe to northeastern America (Ulrich, 1981; Paces, 1985; Probst et al., 1992b;  
88 Landman and Bonneau, 1995; Dambrine et al. 2000; Thimonier et al., 2000; Watmough and Dillon,  
89 2003; Watmough et al., 2005; Heijden et al., 2011; Linken, 2013; de Vries et al., 2014; Norton et  
90 al., 2014) and more recently in Asia (King et al., 2006; Zhang et al., 2007; Zhang et al., 2012; Shen  
91 et al., 2013).

92 Sulfur dioxide (SO<sub>2</sub>) and nitrogen oxide (NO<sub>x</sub>) are the major sources of acid compounds in the  
93 atmosphere contributing to acid precipitation. Anthropogenic SO<sub>2</sub> originates mainly from coal and  
94 petroleum as energy sources (Smith et al., 2001; Sudalma et al., 2015). At the global scale, SO<sub>2</sub>  
95 emissions have strongly increased from 1850 (approximately 5 000 Gg/yr to the 1980s  
96 (approximately 150 000 Gg/yr) and then progressively decreased with a slight increase from 2000  
97 (approximately 105 000 Gg/yr) to 2005/2007 (approximately 112 000 Gg/yr; Kopacek and Vesely,  
98 2005, Stern, 2006; Smith et al., 2011; Klimont et al., 2013).

99 Due to implemented policies (Hettelingh et al., 2008) and economic factors, SO<sub>2</sub> emissions to the  
100 atmosphere have been reduced since the 1980s by 50-85% in North America and Europe (Reinds et

101 al., 2008; Norton et al., 2014; Kopacek et al., 2016; Fioletov et al., 2016) and by 90% in France  
102 since the 1990s (CITEPA: <https://www.citepa.org/fr>).

103 Anthropogenic NO<sub>x</sub> emissions reflect the dominant energy sector, and the major sources are high-  
104 temperature combustion processes (motor vehicles, electric power plants) and fuel combustion.  
105 Like SO<sub>2</sub>, NO<sub>x</sub> emissions decreased in the early nineties but less significantly and were followed  
106 more swiftly by an increase of up to 6% in the newly industrialized countries. Since 1970, NO<sub>x</sub>  
107 emissions have almost doubled (70 Gt/yr in 1970 to 120 Gt/yr in 2005; EDGAR - July 2010).

108 NH<sub>3</sub> emission, mainly due to agricultural activities, globally still increased until now at a world  
109 scale. In France, the annual NH<sub>3</sub> emissions are almost stable since 1980 (CITEPA:  
110 <https://www.citepa.org>). By its acidifying and eutrophication role, the both forms of nitrogen has an  
111 impact on ecosystem safety and particularly on biodiversity, which remains a key problem to be  
112 solved (de Vries et al. 2003, Bobbink et al., 2010; Gaudio et al., 2015; Probst et al., 2015; Rizzetto  
113 et al., 2016).

114 Despite the decrease in the emissions of some precursors of acid rain such as SO<sub>2</sub> in some places  
115 around the world over the past three decades, the question of air pollution and ecosystem  
116 acidification remains a societal and scientific challenge. This situation occurs particularly because  
117 the emissions of such contaminants and their deposition remain significant, especially regarding  
118 nitrogen (Rogora et al., 2006; Nanus et al., 2017).

119 Therefore, it is important to have an accurate evaluation of “true” atmospheric deposition (Pascaud,  
120 2013; Coddeville et al., 2016) and to monitor these inputs over long time periods in “supposed  
121 pristine” ecosystems taken as observatories and “sentinels” of these disturbances (i.e., Pace 1985;  
122 Moldan and Schnoor, 1992; Matzner and Meiwes, 1994; Probst et al., 1995a; Kram et al., 1997;  
123 Laudon et al., 1999; Linkens and Baileys, 2014; Pierret et al., 2018).

124 More generally, in such ecosystems, wet and dry atmospheric deposits are the only external sources  
125 of chemical elements including nutrients and pollutants for ecosystems that could affect soil quality  
126 and aquatic resources. Their quantification is thus a key factor to better understand (i) how natural  
127 and anthropogenic stresses affect, for example, forest ecosystems in the long term (e.g., de Vries et  
128 al., 2003) particularly resource-limited ones (Ulrich, 1984; Probst et al., 1995a) and (ii) the  
129 biogeochemical cycle of nutrients. In Ca- and Mg-poor environments, the biological recycling and  
130 the atmospheric input of some elements, such as Ca and Mg, can be predominant for forest health  
131 (Dambrine et al., Probst et al., 1995b, de Vries et al., 2003, 2014; Navratil et al., 2007).

132 Because the measure of dry and occult deposition is very complicated (Lindberg and Garten, 1988a;  
133 Lindberg et al., 1988b, 1992; Balestrini et al., 2007), the sampling and analysis of throughfall have  
134 been developed to estimate the entire atmospheric deposition of contaminants to forest ecosystems

135 and thus indirectly determine the dry deposition. However, the main difficulty is that throughfall  
136 integrates various types of deposition and sorption processes when precipitation interacts with the  
137 trees: 1) wet deposition by rain or snow, 2) sedimentation of particles caught by the leaves during  
138 dry episodes and dissolution by the next rainfall, 3) impact of dry aerosols from fog and cloud  
139 droplets, 4) absorption of gases inside stomata and 5) recretion/absorption of elements by leaf cells  
140 following exchange processes with rainwater (Ulrich, 1983; Parker, 1983; De Vries et al., 2003;  
141 Probst et al., 1990a; Dambrine et al., 1998b; Thimonier et al., 2008, Berger et al., 2008; Kopacek et  
142 al., 2009; Adriaenssens et al., 2012; Skeffington and Hill 2012; Kato et al., 2013; Shen et al., 2013;  
143 Klos et al., 2014). Although throughfall result from a mixture of several processes, it currently  
144 remains an efficient way to estimate accurately the in-situ input flux of most of the element  
145 deposition to forest ecosystems (e.g., Zimmermann and Zimmermann, 2014; Skeffington et al.,  
146 2012), except for a proportion of the nitrogen deposited which can be taken up by leaves and needle  
147 (Harrison et al., 2000).

148 Numerous publications have concerned acid precipitation and acidification processes. Nevertheless,  
149 few studies have examined in detail the long-term (several decades) evolution of atmospheric  
150 element inputs to ecosystems with different tree types, particularly in the context of the changes in  
151 pollutant emissions during the past decades. This study benefits from a 25-year record of chemical  
152 and water fluxes for open field precipitation and throughfall in a mountainous granitic forested  
153 environment. Two contrasting types of trees (coniferous and deciduous) allowed study of the impact  
154 of tree species on contaminant and nutrient element inputs to soils.

155 The main objectives of the investigations performed in this paper are to contribute to answering the  
156 following questions:

- 157     ▪ How did the global and local changes in NO<sub>x</sub> and SO<sub>2</sub> emissions since the 1980s influence  
158         the sulfate and nitrate concentrations and fluxes in precipitation in a mountainous forest  
159         ecosystem?
- 160     ▪ What are the respective long-term trends of the main cation and anion inputs in open field  
161         precipitation and in throughfall?
- 162     ▪ How may tree species affect the atmospheric inputs by interception and canopy exchanges?

163

## 164 **2. Site description**

165

166 The symptoms of forest decline appeared in the mid-80s in the Vosges massif (France) at the same  
167 time as in other parts of northern Europe. Investigations in the Strengbach catchment have been  
168 developed in order to better understand the relationships between acid atmospheric deposition and

169 forest decline (Probst et al., 1990a; 1992a, b, Dambrine et al., 1991). The Vosges Mountains in  
170 northeastern France are one of the areas in the country most sensitive to acid precipitation (Probst et  
171 al., 1990b, 1992a, 1995a, Pascaud et al., 2016).

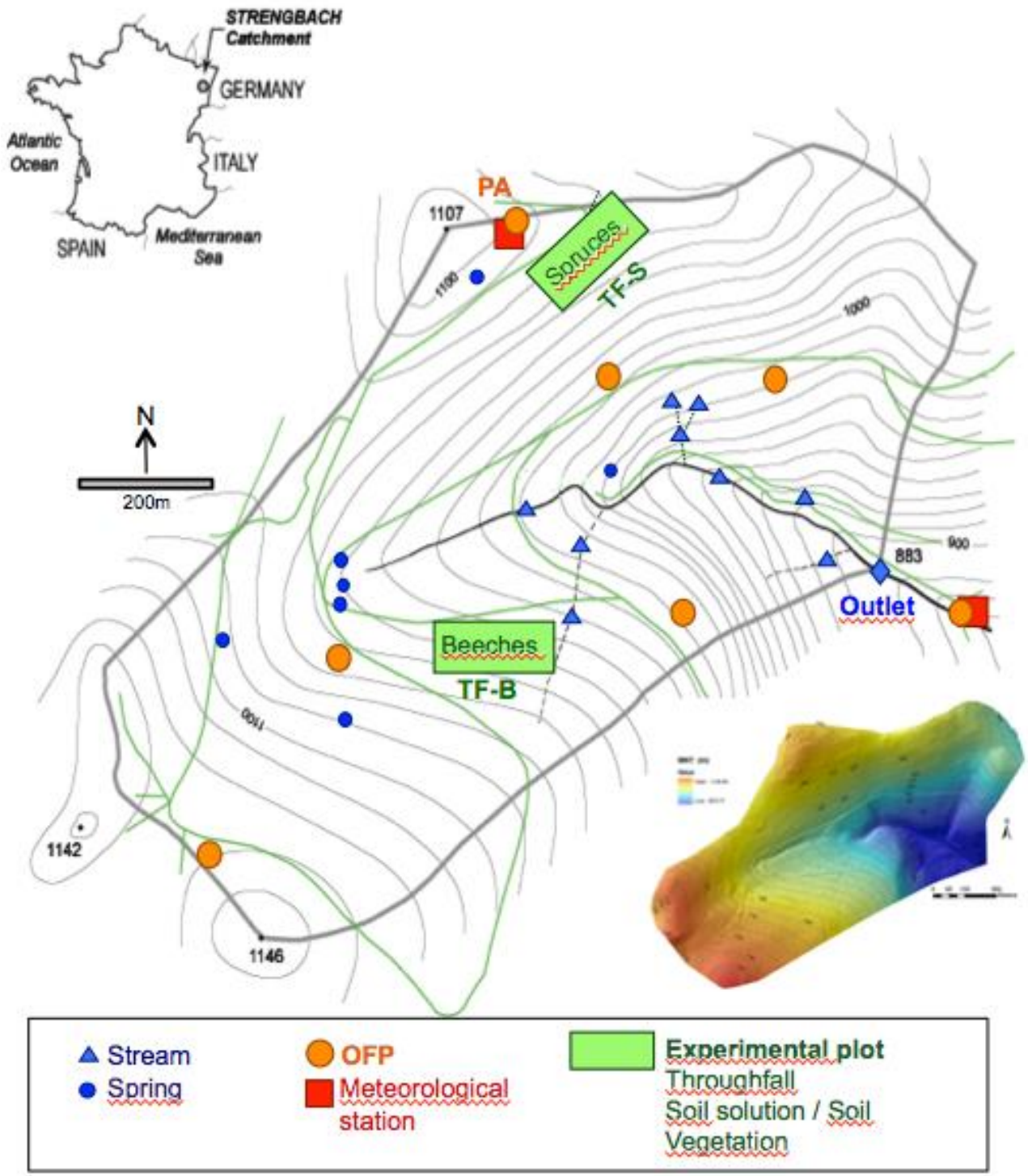
172 The Strengbach catchment is a small granitic watershed (80 ha) where hydrological and  
173 geochemical data have been recorded since 1986 (Observatoire Hydro-Géochimique de  
174 l'Environnement; <http://ohge.u-strasbg.fr>, Pierret et al., 2018). It is situated in northeastern France in  
175 the Vosges Mountains with an elevation between 880 and 1150 m a.m.s.l. and with highly incised  
176 side slopes (mean 15°, Fig. 1). The bedrock is mainly composed of Hercynian Ca-poor granite (315  
177 ± 7 Ma Bonhomme, 1967). The soils belong to the brown acidic to ochreous podzolic series and are  
178 generally approximately 1 meter thick. The forest covers 90% of the area and consists of  
179 approximately 80% spruce plantations (mainly *Picea abies* L.) and 20% beech stands (*Fagus*  
180 *sylvatica*).

181 The whole catchment is a commercially managed forest, and the plantation ages range between 50  
182 and 120 years.

183

184





185  
 186 *Fig. 1. Map of the Strengbach watershed with the locations of the outlet, rain gauges (OFP: open*  
 187 *field precipitation), meteorological stations, and spruce and beech stands where throughfalls (TF-S*  
 188 *and TF-B, respectively) are sampled for analyses. PA corresponds to the OFP site where the rain*  
 189 *has been sampled and analyzed since 1986.*

190

191

192 The climate is temperate oceanic mountainous (mean annual temperature of 6°C and mean monthly  
193 temperature ranges from -2 to 14°C; Probst et al., 1990a, 1992a; Viville et al., 2012, OHGE data)  
194 with an average rainfall of 1370 mm/yr (the snowfall lasts 2-4 month/yr), ranging from 896 to 1713  
195 mm/yr over the period 1986-2012 (Table 1, Supplementary materials).

196 The mean annual runoff for the corresponding period is 760 mm (24.5 ls<sup>-1</sup>km<sup>-2</sup>) ranging from 494 to  
197 1132 mm/yr (Table 1, Supplementary materials). The precipitation is characterized by low intra-  
198 monthly variability due to the dominant westerly wind regime.

199 These data underline the large interannual/pluriannual variations in annual drainage and rainfall,  
200 with very strong heterogeneities illustrated by the factor of two between the low and high values of  
201 precipitation and discharge (Table 1, Supplementary materials). The outlet discharge varies between  
202 a few l/s to 300 l/s during high-flow discharge corresponding particularly to the snow-melting  
203 period (Idir 1999; OHGE data).

204 Two experimental plots representing specific environmental characteristics of the catchment have  
205 been equipped for studying atmosphere/soil/plant interactions: one under a spruce stand on a north-  
206 facing slope and the other under a beech stand on a south-facing slope (Fig. 1). In each plot, soil,  
207 soil solution, litter, plant and throughfalls have all been investigated over the past decades.

208

### 209 **3. Methods**

210

#### 211 **3.1. Sampling of open field precipitation and throughfall measurements**

212 Bulk precipitation so-called here after open field precipitation (OFP) was sampled weekly from  
213 1986 to 2005 and fortnightly later in a clearing (PA site; Fig. 1) using a funnel supported by a  
214 bucket. An accurate measurement of OFP in mountains, and especially in forested areas, is difficult,  
215 particularly due to the heterogeneity of the environmental conditions such as the altitude, the  
216 exposure, the wind direction and the vegetation cover (Fig. 1).

217 The above heterogeneity was evaluated by considering data from different rain gauges spatially  
218 distributed throughout the catchment. For this study, the amount of precipitation was estimated at  
219 the whole catchment scale and at the spruce and beech stations in order to evaluate accurately the  
220 interception by the canopy at the plot scale. Significant relationships between the data of the 7 open  
221 field precipitation stations (for 0.8 km<sup>2</sup>, Fig. 1), together with the intercalibration of ten rain gauges  
222 spatially dispersed across the catchment, were used to estimate the precipitation amount at the  
223 catchment scale (P-catchment). This mean value was finally expressed by a multiplicative factor as  
224 a function of precipitation at site PA (P-PA, Eq. 1; Fig. 1) (Viville et al., 1993; Biron, 1994; this  
225 study). The same method was applied for precipitation at the beech stand (P-beech, Eq. 2). The

226 precipitation amount of the spruce station (P-spruce) was assimilated with the data measured at site  
227 PA because of the site proximity (Fig. 1).

228

$$229 \quad P\text{-catchment} = P\text{-PA} \times 1.07 \quad (\text{Eq. 1})$$

$$230 \quad P\text{-beech} = P\text{-PA} \times 1.12 \quad (\text{Eq. 2})$$

$$231 \quad P\text{-spruce} = P\text{-PA} \quad (\text{Eq. 3})$$

232 where P is the precipitation amount.

233

234 The annual interception (in %) was calculated as the ratio between 1) the difference between annual  
235 open field precipitation (OFP) and annual throughfall (TF) water flux and 2) the annual open field  
236 precipitation (Table 1, Supplementary materials).

237 Throughfall has been sampled using 2 gutters (2.0 x 0.2 m) since October 1986 and 5 bucket  
238 collectors since 1990 for the spruce and the beech stands, respectively (Fig. 1), with a frequency of  
239 two weeks.

240 In addition to the analysis of major elements, several physico-chemical parameters have been  
241 determined (among them, pH and conductivity; see 3.2). The database used for this study includes a  
242 large number of measurements over the 25 years under consideration with approximately 1650  
243 samples i.e., more than 16000 data points.

244 All the water samples (open field precipitation and throughfalls) were collected in clean  
245 polyethylene (HDPE) bottles (250 ml for major element analysis) and filtered the same day through  
246 a 0.45  $\mu\text{m}$  pore diameter membrane (Millipore ester cellulose, 47 mm diameter). The protocols of  
247 sampling, filtration and bottle washing remain the same throughout the duration of the study. The  
248 type and the location of collectors for precipitation and throughfall did't change since 1986.

249

### 250 **3.2. Physico-chemical analysis**

251 Since 1986, all the physico-chemical parameters were always measured in the same laboratory  
252 (water analysis service from our research center in Strasbourg).

253 The pH and conductivity were measured, immediately after filtration, with a constant precision of  $\pm$   
254 0.02 units.

255 The cations Ca, Mg, Na and K were measured by atomic absorption spectrometry until 2004 and  
256 then by ionic chromatography.  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were measured by automatic colorimetry  
257 until 1990 and then by ionic chromatography (Probst et al., 1990a, 1992a, 1995a, 2000; Pierret et al.,  
258 2014). Due to the changes in the analytical devices, the continuity of data and time series were  
259 controlled by ionic balance calculation for each sample, statistical and graphical tests, regular

260 analysis of the SLRS-4 riverine and Big Moose Lake standards, and by regular participation in the  
261 intercomparison program of the Norwegian Institute for Water Research (NIVA). The analytical  
262 uncertainty for anions and cations remained  $\pm 2\%$ .

263

### 264 **3.3. Calculations**

265 The data cover the period from 1 October 1986 to 30 September 2012, representing 25 years of  
266 record. The annual average concentrations and annual fluxes were calculated on the basis of a  
267 hydrological year from 1 October to 30 September (according to Probst et al., 1992a).

268 The fluxes of elements were calculated as the product of the sample concentration and the  
269 corresponding amount of water, and these fluxes were added to estimate the total annual flux,  
270 expressed in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$  (Table 2, Supplementary materials). The annual chemical fluxes were  
271 generally expressed as element flux (for instance, S for sulfate). The total N flux corresponded to  
272 the sum of  $\text{N-NO}_3^-$  and  $\text{N-NH}_4^+$  fluxes (Table 2, Supplementary materials).

273 The Seasonal Kendall test (SK test) is an extension of the Mann-Kendall (MK) test and is a non  
274 parametric test that analyzes data for monotonic trends in seasonal data (Mann, 1945 ; Kendall,  
275 1975 ; Hirsch, Slack and Smith 1982), allowing elimination of variation associated with seasonality.  
276 This method is often used for analyzing long-term trends in series with seasonal periodicity and one  
277 of the advantages of this test is that it is rank based, making it suitable for nonnormally distributed  
278 data, data containing outliers, and nonlinear trends (Murdoch et al., 2006; Rogorra et al., 2006;  
279 Vuorenmaa et al., 2014; Fuss et al., 2015). The test was performed for the entire data set, considering  
280 12 seasons (months) on raw data concentrations and on volume-weighted concentrations, to assess  
281 the overall changes in the concentration of each solute.

282 A positive value of tau indicated an increasing trend and vice versa. The trend was significant if the  
283 p-value was lower than the standard normal variation, here 0.01.

284 The magnitude of the trend was evaluated with the Theil Sen estimator. The slope was determined  
285 as the median of all slopes calculated for each data pair by the method of Theil (1950) and Sen  
286 (1968).

287

$$m = \text{Median} \left( \frac{x_j - x_l}{j - l} \right), \quad \forall l < j$$

288

289 where  $x_j$  and  $x_l$  were the  $j^{\text{th}}$  and  $l^{\text{th}}$  observations, respectively. Unlike a simple linear regression, this  
290 method allowed reducing the effect of outliers and is not sensitive to assumptions of normality and  
291 equal variance as is the case with regression and other parametric methods.

292 The figures showing the time-series data included annual average concentrations or fluxes in order  
293 to clarify their interpretation because the massive number of samples was difficult to display  
294 (approximately 1650 samples and then more than 16 000 data points) and the chemical composition  
295 was very highly variable over the year for both OFP and TF. Indeed, this variability was due to air  
296 mass origin, atmospheric circulation, interaction with vegetation, rainfall amount, season, climate,  
297 etc.

298 Annual average values were especially suitable and appropriate since the aim of this paper was to  
299 study and interpret long-term evolution (25 years) rather than seasonality or specific phenomena.

300

## 301 **4. Results**

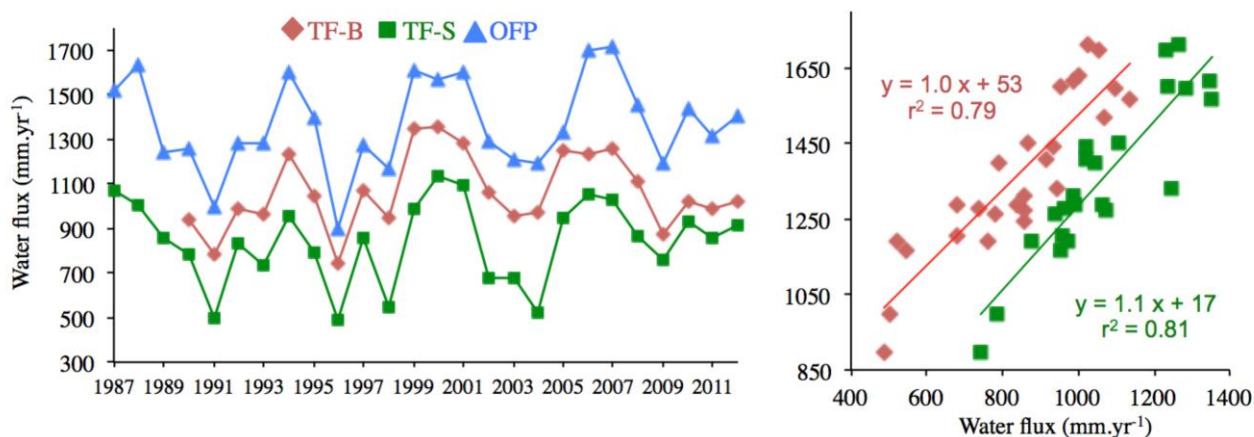
### 302 **4.1. Water fluxes**

303 The average P-catchment for the period 1986-2012 was 1368 mm/yr with a wide range of data  
304 between the driest year (896 mm in 1996) and the wettest year (1712 mm in 2007; Table 1  
305 Supplementary materials). Similarly, a factor of approximately two between low and high values  
306 applied to annual throughfall under both spruce and beech plantations. These data highlighted the  
307 important inter-annual variability, which can be estimated by the standard deviation for the annual  
308 open field precipitation at the catchment scale of 200 mm for a period of 25 years (Fig. 2; Table 1,  
309 Supplementary materials). The interception was systematically higher under the spruce stand than  
310 under the beech stand (Table 1, Supplementary materials). The average annual interceptions for the  
311 1986-2012 period were 35% and 25% under spruce and beech stands, respectively (Table 1,  
312 Supplementary materials). These data were comparable with those published by Viville et al. (1993)  
313 and Dambrine et al. (1998b) for the same spruce plot during a summer period (34 to 35%) and for  
314 the same beech plot (Biron, 1994; 25%) or with other similar spruce and beech plantations (Delfs,  
315 1965; Nihlgard, 1970; Boultot et al., 1972; Johnson, 1990; Staenlens et al., 2006; Berger et al.,  
316 2008).

317 Precipitation and throughfall amounts were significantly positively correlated (Fig. 2b) ( $r^2=0.80$  for  
318 TF-S and 0.81 for TF-B) for the studied period. The slopes of the linear regressions were not very  
319 different (1.0 and 1.1 for TF-B and TF-S, respectively), but the intercepts were not the same (529  
320 and 169 for TF-B and TF-S, respectively; Fig. 2). However, the inter-annual variabilities in  
321 throughfalls (17 and 23% for TF-B and TF-S, respectively) were higher than in open field  
322 precipitation (15%; Table 1, Supplementary materials).

323

324



325

326 *Fig. 2: a) Annual water fluxes in open field precipitation (OFP) and throughfalls under spruces*  
 327 *(TF-S) and under beeches (TF-B) for the period 1987-2012; b) Open field precipitation (X axis) vs.*  
 328 *throughfall (Y axis) under spruces (TF-S) or under beeches (TF-B) in the Strengbach catchment for*  
 329 *the period 1986-2012.*

330

## 331 4.2. Chemical composition of precipitation

### 332 4.2.1 Chemical background

333 The annual average, the global mean, the standard deviation, minimum and maximum values of  
 334 concentrations and fluxes were described in Table 2 (Supplementary materials) for the 1986-2012  
 335 period. They summarized the 16 000 data points, which are detailed and available at the OHGE  
 336 website (<http://ohge.unistra.fr>).

337 The mean annual electrical conductivity ranged from 10 to 28, 31 to 98 and 20 to 53  $\mu\text{S}/\text{cm}$  and the  
 338 mean pH ranged from 4.41 to 5.24, 3.98 to 5.26 and 4.38 to 5.42 for OFP, TF-S and TF-B,  
 339 respectively, illustrating the wide range of chemical characteristics of the samples. Similarly, the TF  
 340 concentrations were 2 to 9 times greater than OP concentrations for the mean annual concentrations  
 341 of major elements ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ). The standard deviation calculated for  
 342 the whole set of data and not only with the annual average illustrated the extremely large variability  
 343 of the data set.

344

### 345 4.2.2 Sea-salt contribution

346 The chemical elements in atmospheric precipitation originated from various sources such as  
 347 continental terrigenous dust, volcanic or anthropogenic emissions and sea salts, with regional and  
 348 long-range transport (McDowell et al., 1990; Laouli et al., 2012; Akpo et al., 2015; Mimura et al.,

349 2016; Keene et al., 1986). To identify the natural sea-salt contribution, the enrichment factor (EF)  
350 of an element X may be calculated as follows (Keene et al., 1986; Akpo et al., 2015):

$$351 \text{ (EF)X} = (\text{X/Na})_{\text{precip}} / (\text{X/Na})_{\text{seawater}}$$

352 *where*  $\text{X/Na}_{\text{precip}}$  is the ratio between the element X and the concentration of Na in the  
353 corresponding sample of precipitation and  $\text{X/Na}_{\text{seawater}}$  is the ratio between the element X and the  
354 concentration of Na in seawater.

355 The non-sea-salt concentration of  $\text{X}_{\text{nss}}$  can be calculated as

$$356 \text{ X}_{\text{nss}} = (\text{X})_{\text{precip}} - (\text{X/Na})_{\text{seawater}} * (\text{Na})_{\text{precip}}$$

357 *where*  $\text{X}_{\text{precip}}$  is the concentration of the element X in precipitation,  $\text{X/Na}_{\text{seawater}}$  is the ratio between  
358 element X and the concentration of Na in seawater and  $\text{X/Na}_{\text{precip}}$  is the ratio between element X  
359 and the concentration of Na in the corresponding sample of precipitation.

360 These calculations supposed that sodium originated from sea spray and had a conservative behavior.  
361 An  $\text{EF} > 1$  indicated a contribution of non-sea sources, which was generally the case in the  
362 literature for most of elements, except for Cl with EF ranging from 0.6 to 0.9 in precipitation from  
363 various environments such as Sahelian savannas, tropical Brazil, Benin or Puerto Rico (Singh et al.,  
364 2007; Laouli et al., 2012; Mimura et al., 2016; Akpo et al., 2015).

365 The average EF and nss concentration values for  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  (with the  
366  $(\text{X/Na})_{\text{seawater}}$  ratios from Singh et al., 2007; Mimura et al., 2016) were calculated for open field  
367 precipitation and throughfalls from the Strengbach catchment and summarized in Table 1. Open  
368 field precipitation and throughfalls exhibited higher EFs for Cl, ranging from 1.05 to 1.14 and with  
369 a very large dispersion (0.1 to 8), and even much higher for K, Ca and  $\text{SO}_4$ , compared with the  
370 studies noted above.

371 The concentration corrected from sea-salt contribution ( $\text{X}_{\text{nss}}$ ) was frequently negative for Cl and  
372 Mg, especially in throughfall samples, indicating that the correction was overestimated and  
373 inappropriate.

374 Different factors could be invoked. Indeed, due to the distance from the sea (600 km), the influence  
375 of sea salt in precipitation was lowered. The mean annual Na concentration in OFP was  $12.3$   
376  $\text{mmol.l}^{-1}$ , notably lower than those measured in coastal areas ( $70\text{-}150$   $\text{mmol.l}^{-1}$ , Mimura et al.,  
377 2016). Indeed, part of the Na in precipitation might be terrigenous with (partial) dissolution of soil  
378 dust components (Galy Lacaux et al., 2009). Finally, the sea spray generated several elements with  
379 different physico-chemical properties, implying potential fractionation among them. This  
380 observation was particularly true if we considered the throughfalls. The chemical elements from wet  
381 and dry atmospheric deposits interacted physical, chemically and biologically with the leaf surface  
382 of the trees, which might imply fractionation and non-conservative behavior.

383 Indeed, for the anthropogenic-influenced elements, the sea-salt contribution was weak. For instance,  
 384 for sulfate, the sea-salt fractions were on average 4, 5 and 9% in OFP, TF-S and TF-B, respectively.  
 385 This result was confirmed by Pascaud (2013) and Pascaud et al. (2016) for a set of northeastern  
 386 French stations. In the same way, the differences between the initial and nss concentrations for K  
 387 and Ca were weak, which were confirmed by the high EF (Table 1)  
 388 For all these reasons, the data and discussion in the following concern the bulk data, without any  
 389 sea-salt corrections.

390

	K	Mg	Ca	Cl	SO <sub>4</sub>	K	Mg	Ca	Cl	SO <sub>4</sub>
	concentration (μmol.l <sup>-1</sup> )					EF				
<i>OFP- nc</i>	5.5	2.8	8.0	15.2	18.3					
<b>OFP-nss</b>	<b>5.2</b>	<b>1.4</b>	<b>7.7</b>	<b>0.7</b>	<b>17.6</b>	<b>21.3</b>	<b>2.1</b>	<b>30.0</b>	<b>1.05</b>	<b>24.4</b>
<i>TF-S nc</i>	80.1	14.3	40.7	71.9	59.5					
<b>TF-S nss</b>	<b>78.9</b>	<b>8.2</b>	<b>39.5</b>	<b>7.3</b>	<b>55.8</b>	<b>72.4</b>	<b>2.4</b>	<b>35.3</b>	<b>1.14</b>	<b>20.5</b>
<i>TF-B nc</i>	89.1	7.0	13.6	36.5	27.7					
<b>TF-B-nss</b>	<b>88.5</b>	<b>3.6</b>	<b>13.5</b>	<b>2.6</b>	<b>24.7</b>	<b>157.1</b>	<b>2.2</b>	<b>22.7</b>	<b>1.11</b>	<b>17.4</b>

391 *Table 1: Initial (non-corrected - nc) and non-sea-salt (nss) concentrations and enrichment factors*  
 392 *(EF) in open field precipitation (OFP) and throughfalls under spruces (TF-S) and under beeches*  
 393 *(TF-B) for K, Mg, Ca, Cl and SO<sub>4</sub>. The data corresponded to the average values during the 1986-*  
 394 *2012 period considering the entire sample data set (n=623 for OFP; n=591 for TF-S, and n=510*  
 395 *for TF-B).*

396

### 397 **4.3. Trends in chemical composition and fluxes**

398 The time series of annual average values for both concentrations and fluxes were presented in Fig.  
 399 3. A large variation in the physico-chemical signature of precipitation inputs (open field and under  
 400 forest) was observed during the 25 years of the study period (1986-2012).

401 The general temporal trends were evaluated by the Seasonal Kendall Test (SKT; see 3.3), as  
 402 presented in Table 2.

403 The most obvious decreases in the concentrations and fluxes over time were for; protons, SO<sub>4</sub><sup>2-</sup>, and  
 404 Ca<sup>2+</sup> for the three types of precipitation (OFP, TF-B, and TF-S). The decreases in the acidity and  
 405 sulfate concentration and fluxes were the highest, reaching 75% for sulfate concentration in TF-S  
 406 (Table 2; Fig. 3; Table 2, Supplementary materials).

407



Seasonal Kendall Test		NH <sub>4</sub>	Na	K	Mg	Ca	Cl	NO <sub>3</sub>	SO <sub>4</sub>	pH	H+
<b>OFP</b>	tau	-0.03	<b>-0.12</b>	<b>-0.10</b>	0.06	-0.05	<b>-0.17</b>	<b>-0.11</b>	<b>-0.42</b>	<b>0.35</b>	<b>-0.37</b>
	p	0.44	<b>&lt;0.01</b>	<b>&lt;0.01</b>	0.12	0.19	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>
<b>TF-S</b>	tau	0.04	0.06	0.04	0.03	<b>-0.13</b>	-0.04	0.02	<b>-0.47</b>	<b>0.49</b>	<b>-0.51</b>
	p	0.3	0.13	0.29	0.48	<b>&lt;0.01</b>	0.32	0.65	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>
<b>TF-B</b>	tau	-0.09	-0.04	0.07	<b>-0.15</b>	<b>-0.32</b>	<b>-0.1</b>	<b>-0.14</b>	<b>-0.42</b>	<b>0.30</b>	<b>-0.30</b>
	p	0.03	0.35	0.12	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>

Theil Sen slope (mmol/year)											
<b>OFP</b>		0	-1.04E-04	0	0	0	-1.83E-04	-2.45E-04	-5.39E-04	3.37E-02	-7.1E-07
<b>TF-S</b>		2.01E-04	1.83E-04	1.67E-04	0	-4.14E-04	-2.92E-04	2.27E-04	-2.18E-03	4.44E-02	-1.8E-06
<b>TF-B</b>		-3.24E-04	-8.08E-05	1.66E-04	-9.97E-05	-4.56E-04	-3.03E-04	-8.18E-04	-1.10E-03	3.46E-02	-1.1E-07

409

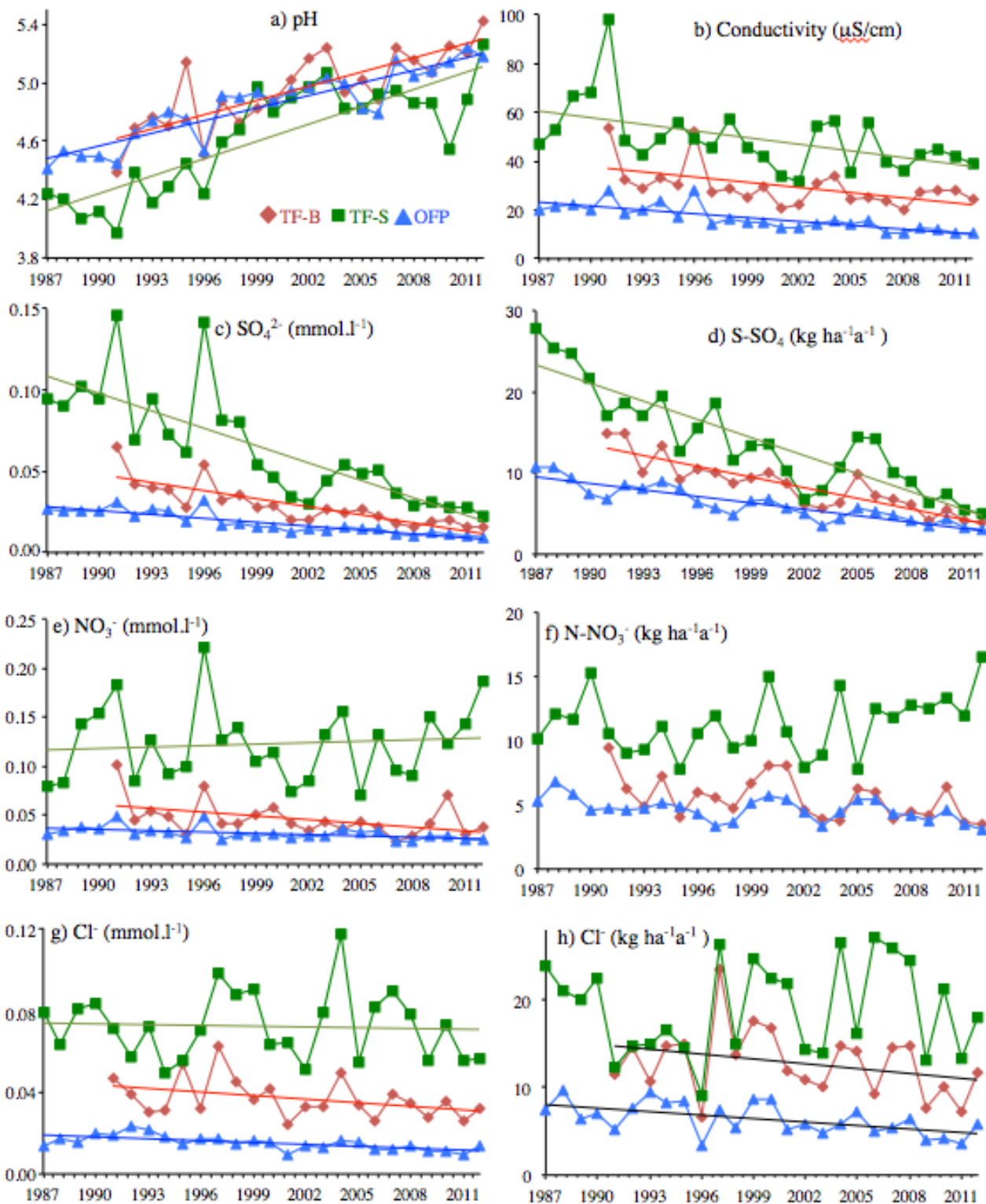
410 *Table 2: Results of the Seasonal Kendal Test (SKT) and the Teil Sen slope obtained for different*  
411 *chemical elements with the 25 years data set of open field precipitation (OFP), spruce-throughfall*  
412 *(TF-S) and beech-throughfall (TF-B).*

413

414 The mean annual pH in open field precipitation increased from 4.41 in 1986 to 5.18 in 2012 (Table  
415 2, Supplementary materials) and from 4.24 to 5.26 and 4.38 to 5.42 in throughfalls below spruce and  
416 beech stands, respectively (Fig. 3, Table 2, Supplementary materials). The Theil-Sen tests calculated  
417 positive slope for the three sets of data (Table 2), and the average trend was approximately 0.3 to  
418 0.4 pH unit per 10 years.

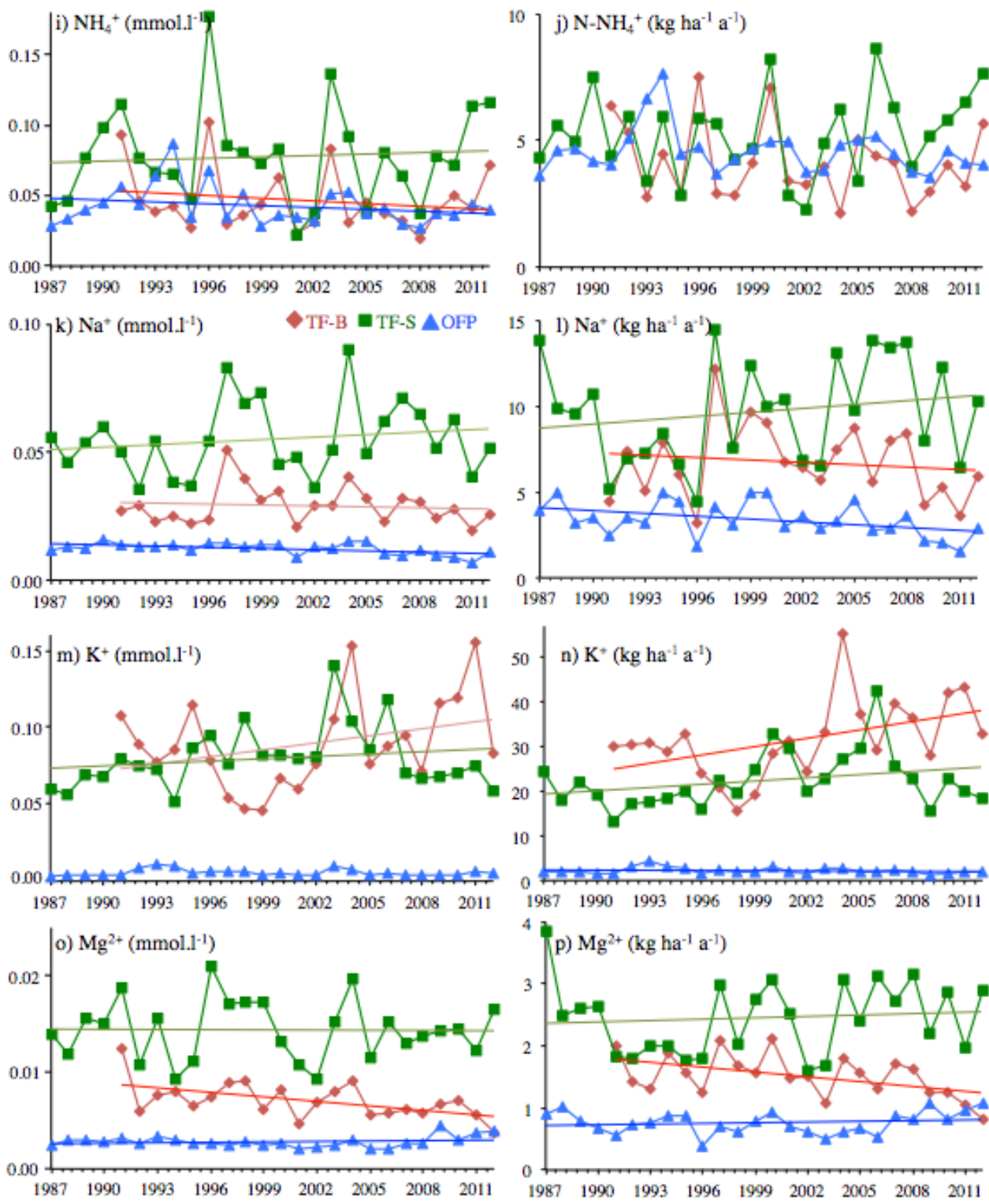
419 The mean annual SO<sub>4</sub><sup>2-</sup> concentrations decreased from 27 to 9, 65 to 15 and 94 to 23 μmol l<sup>-1</sup> in  
420 open field precipitation and throughfalls under beech and spruce, respectively, during the period  
421 (Fig. 3; Table 2, Supplementary materials). The Theil-Sen mean slopes suggested reductions of 0.5,  
422 1.1 and 2.2 10<sup>-3</sup> mmol l<sup>-1</sup>yr<sup>-1</sup> for OFP, TF-B and TF-S, respectively (Table 2). Similarly, the mean  
423 annual S fluxes decreased from approximately 11 to 3, 15 to 4 and 28 to 5 kg ha<sup>-1</sup>a<sup>-1</sup> in OFP, TF-B  
424 and TF-S, respectively (Fig. 3; Table 2, Supplementary materials). Considering that forest cover  
425 represents 90% of the catchment area (80 ha) with 80% spruce cover and 20% beech, the total  
426 sulfur atmospheric deposition can be calculated. At the Strengbach catchment scale, the annual  
427 sulfur deposition has decreased from 2 t of S in 1986 to 360 kg in 2012.

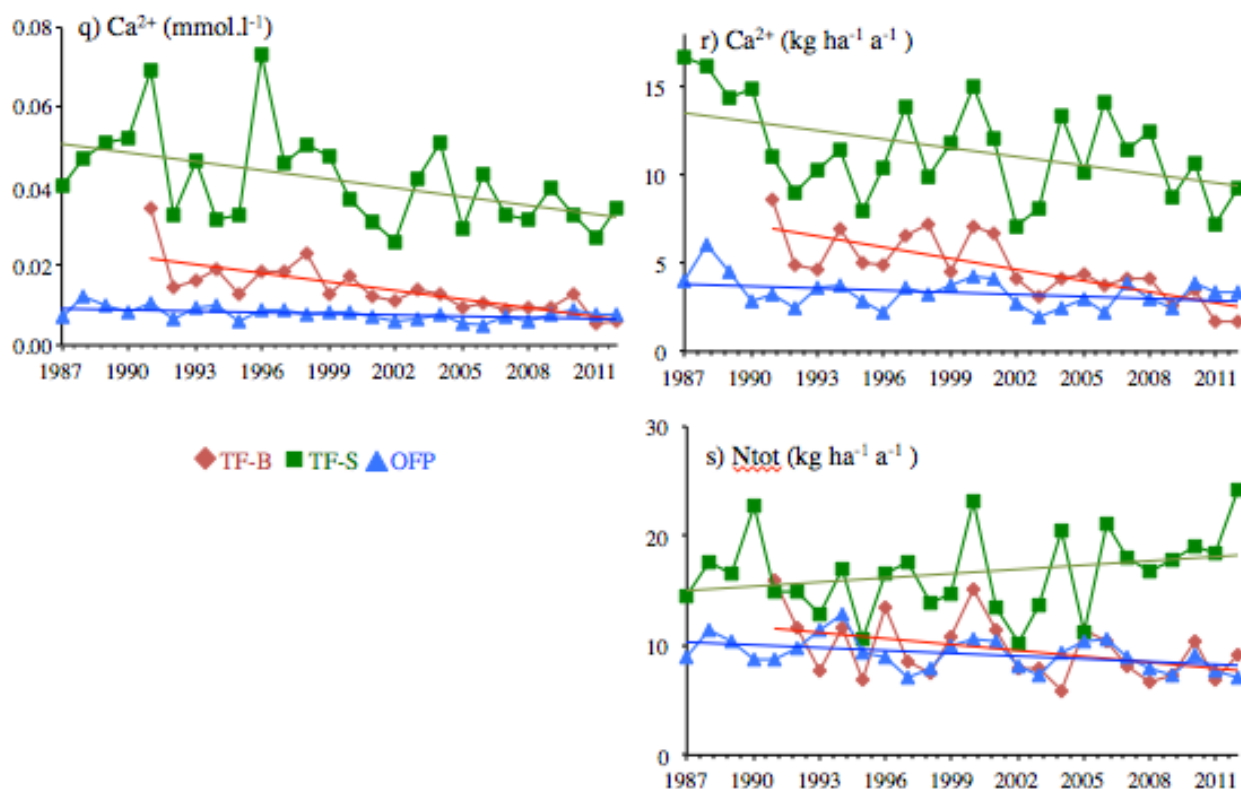
428



429

430





432  
 433 Fig. 3: Evolution of the mean annual a) pH, b) conductivity ( $\mu\text{S cm}^{-1}$ ), c) concentration of  $\text{SO}_4^{2-}$  in  
 434  $\text{mmoles.l}^{-1}$ , d) fluxes ( $\text{kg ha}^{-1} \text{a}^{-1}$ ) of  $\text{S-SO}_4$ , e) concentration of  $\text{NO}_3^-$  in  $\text{mmoles.l}^{-1}$ , f) fluxes ( $\text{kg ha}^{-1}$   
 435  $\text{a}^{-1}$ ) of  $\text{N-NO}_3$ , g) concentration of  $\text{Cl}^-$  in  $\text{mmoles.l}^{-1}$ , h) fluxes ( $\text{kg ha}^{-1} \text{a}^{-1}$ ) of  $\text{Cl}$ , i) concentration of  
 436  $\text{NH}_4^+$  in  $\text{mmoles.l}^{-1}$ , j) fluxes ( $\text{kg ha}^{-1} \text{a}^{-1}$ ) of  $\text{N-NH}_4$ , k) concentration of  $\text{Na}^+$  in  $\text{mmoles.l}^{-1}$ , l) fluxes  
 437 ( $\text{kg ha}^{-1} \text{a}^{-1}$ ) of  $\text{Na}$ , m) concentration of  $\text{K}^+$  in  $\text{mmoles.l}^{-1}$ , n) fluxes ( $\text{kg ha}^{-1} \text{a}^{-1}$ ) of  $\text{K}$ , o)  
 438 concentration of  $\text{Mg}^{2+}$  in  $\text{mmoles.l}^{-1}$ , p) fluxes ( $\text{kg ha}^{-1} \text{a}^{-1}$ ) of  $\text{Mg}$ , q) concentration of  $\text{Ca}^{2+}$  in  
 439  $\text{mmoles.l}^{-1}$ , r) fluxes ( $\text{kg ha}^{-1} \text{a}^{-1}$ ) of  $\text{Ca}$ , and s) fluxes ( $\text{kg ha}^{-1} \text{a}^{-1}$ ) of  $\text{N}_{\text{tot}}$  in open field precipitation  
 440 (OFP), throughfall under spruce (TF-S) and under beech (TF-B) for the 1987-2012 period.

441  
 442 For the other elements, the trends were not always significant for the three types of precipitation.  
 443 The mean annual concentrations of nitrate ranged from 49-23, 100-23 and 221-71  $\mu\text{mol l}^{-1}$  in OFP,  
 444 TF-B and TF-S, respectively (Fig. 3; Table 2, Supplementary materials), and the concentrations  
 445 decreased at an average of -0.4 and -1.3  $\text{mmol l}^{-1}\text{yr}^{-1}$  in OFP and TF-B, respectively (as confirmed  
 446 by the SKT test, Table 2). No significant trend in nitrate was observed under spruces (TF-S).  
 447 Similarly,  $\text{NH}_4^+$  concentrations decreased in open field precipitation and throughfall under the  
 448 beech stand and increased in throughfall under the spruce stand but with higher interannual  
 449 variability and weaker SKT-tau for OFP and TF-S (Fig. 3; Table 2).

450 The mean annual N<sub>tot</sub> fluxes ranged from 5.9 kg.ha<sup>-1</sup>a<sup>-1</sup> (TF-B in 2004) to 24.2 kg.ha<sup>-1</sup>a<sup>-1</sup> (TF-S in  
451 2012) with the highest values systematically for TF-S (Table 2, Supplementary materials).  
452 Concerning base cations other than Ca<sup>2+</sup>, concentrations decreased significantly for Na<sup>+</sup> and K<sup>+</sup>  
453 only in OFP and for Mg<sup>2+</sup> in TF-B, with SKT p<0.01 (Table 2).  
454 The highest cation fluxes in OFP were for Na<sup>+</sup> and Ca<sup>2+</sup> (3.4 and 3.3 kg.ha<sup>-1</sup>a<sup>-1</sup>, respectively, on  
455 average for the 1986-2012 period), whereas the highest cation fluxes were for K<sup>+</sup> in throughfall  
456 (22.4 and 31.6 kg.ha<sup>-1</sup>a<sup>-1</sup>, respectively, in TF-S and TF-B for the 1986-2012 period).  
457 The precipitation composition was strongly modified after passing through the tree canopy. The  
458 element concentration in throughfall was systematically higher than in open field precipitation, with  
459 an increase of 1.25 for NH<sub>4</sub><sup>+</sup> and to 20-fold for K<sup>+</sup> (Table 2, Supplementary materials). These ratios  
460 were consistent with previous estimates in this area (Probst et al., 1990a; 1992a; 1995b) and were  
461 closely comparable to data published by Balestrini and Tagliaferri (2001) and Shen et al. (2013).  
462 The mean annual concentration was always higher in TF-S than in TF-B, except for K<sup>+</sup> (Table 2,  
463 Supplementary materials). Even if the long-term trends of pH in throughfall and precipitation  
464 increased in similar ways (Fig. 3a, Table 2), the modification of acidity by the canopy differed  
465 between the two types of plantation. The pH in throughfall under spruces was lower than that in  
466 open field precipitation, whereas the acidity decreased when rain passed through beeches (Fig. 3a,  
467 Table 2, Supplementary materials). The annual elemental fluxes followed the same trends as the  
468 elemental concentrations and were systematically the highest in TF-S, except for K<sup>+</sup> (Fig. 3).

469

#### 470 4.4. Correlations between chemical composition and fluxes

471

##### 471 4.4.1. Relationship between elements

472

	<b>NH<sub>4</sub></b>	<b>Na</b>	<b>K</b>	<b>Mg</b>	<b>Ca</b>	<b>H</b>	<b>Cl</b>	<b>NO<sub>3</sub></b>	<b>SO<sub>4</sub></b>
	<i>vs SO<sub>4</sub></i>	<i>vs SO<sub>4</sub></i>	<i>vs SO<sub>4</sub></i>	<i>vs SO<sub>4</sub></i>	<i>vs SO<sub>4</sub></i>	<i>vs SO<sub>4</sub></i>	<i>vs SO<sub>4</sub></i>	<i>vs SO<sub>4</sub></i>	<i>vs SO<sub>4</sub></i>
<b>OFP</b>	<b>0.65</b>	0.28	0.26	0.39	0.48	<b>0.62</b>	0.31	<b>0.82</b>	<b>1</b>
<b>TF-S</b>	<b>0.59</b>	0.49	0.43	<b>0.70</b>	<b>0.77</b>	<b>0.60</b>	0.47	<b>0.58</b>	<b>1</b>
<b>TF-B</b>	<b>0.59</b>	0.38	0.16	<b>0.63</b>	<b>0.63</b>	<b>0.63</b>	0.33	<b>0.68</b>	<b>1</b>
	<i>vs Cl</i>	<i>vs Cl</i>	<i>vs Cl</i>	<i>vs Cl</i>	<i>vs Cl</i>	<i>vs Cl</i>	<i>vs Cl</i>	<i>vs Cl</i>	<i>vs Cl</i>
<b>OFP</b>	0.18	<b>0.92</b>	0.16	0.49	0.16	0.24	<b>1</b>	0.27	0.31
<b>TF-S</b>	0.34	<b>0.95</b>	0.45	<b>0.76</b>	<b>0.61</b>	0.11	<b>1</b>	0.40	0.47
<b>TF-B</b>	0.14	<b>0.90</b>	0.23	0.49	0.31	0.20	<b>1</b>	0.18	0.33
	<i>vs Ca</i>	<i>vs Ca</i>	<i>vs Ca</i>	<i>vs Ca</i>	<i>vs Ca</i>	<i>vs Ca</i>	<i>vs Ca</i>	<i>vs Ca</i>	<i>vs Ca</i>
<b>OFP</b>	0.42	0.13	0.33	<b>0.55</b>	<b>1</b>	-0.04	0.16	0.49	0.48
<b>TF-S</b>	<b>0.68</b>	<b>0.61</b>	<b>0.65</b>	<b>0.91</b>	<b>1</b>	0.37	<b>0.61</b>	<b>0.81</b>	<b>0.77</b>
<b>TF-B</b>	0.46	0.35	0.10	<b>0.81</b>	<b>1</b>	0.17	0.31	<b>0.67</b>	<b>0.63</b>
	<i>vs H</i>	<i>vs H</i>	<i>vs H</i>	<i>vs H</i>	<i>vs H</i>	<i>vs H</i>	<i>vs H</i>	<i>vs H</i>	<i>vs H</i>
<b>OFP</b>	0.07	0.25	-0.20	0.02	-0.04	<b>1</b>	0.24	<b>0.54</b>	<b>0.62</b>
<b>TF-S</b>	0.09	0.15	0.02	0.24	0.37	<b>1</b>	0.11	0.18	<b>0.60</b>

<b>TF-B</b>	0.21	0.26	-0.20	0.21	0.17	<b>1</b>	0.20	0.42	<b>0.63</b>
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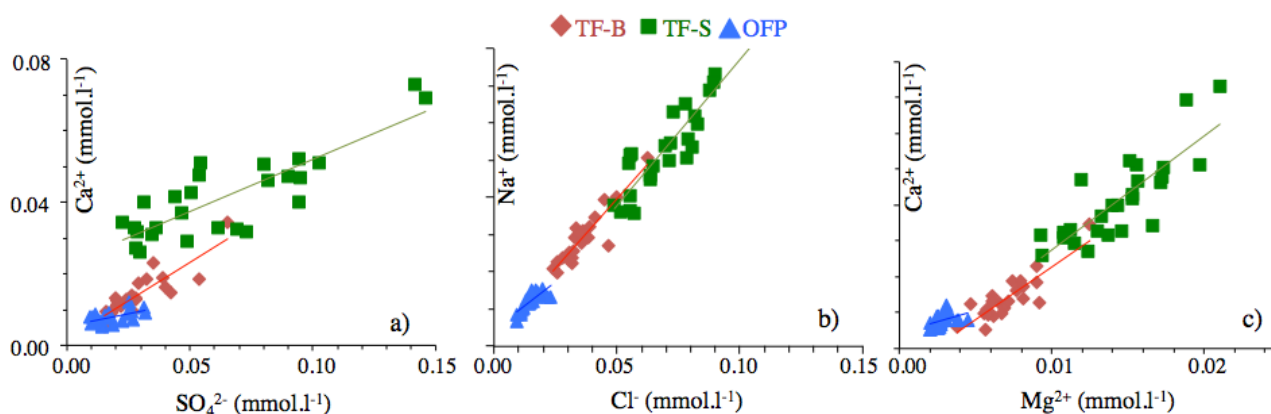
473 Table 3: Pearson correlation coefficients  $r$  between concentrations of some chemical elements in  
474 open field precipitation (OFP) and throughfalls under spruces (TF-S) and under beeches (TF-B)  
475 during the 1986-2012 period considering the entire sample dataset ( $n=623$  for OFP,  $n=591$  for TF-  
476 S and  $n=510$  for TF-B). In bold:  $r>0.5$ .

477

478 To discuss the comparison between TF-S and TF-B, we calculated the Pearson correlation  
479 coefficient between the elements and 1) sulfate, representing mainly the anthropogenic influence; 2)  
480 chloride, representing mainly the oceanic origin; 3) calcium from continental (natural and  
481 anthropogenic) sources; and 4) protons, representing global acid deposition (Table 3).

482 The highest correlation coefficient was for the correlation between Na and Cl. Significant  
483 correlations were observed for OFP, TF-S and TF-B between  $\text{SO}_4/\text{H}$ ,  $\text{SO}_4/\text{NO}_3$ , Mg/Ca and Na/Cl  
484 and for the two throughfalls (TF-S and TF-B) between Ca/ $\text{SO}_4$ , Mg/ $\text{SO}_4$ , Ca/ $\text{NO}_3$  and Mg/ $\text{SO}_4$   
485 (Table 3; Fig. 4). The correlations between Mg/Cl, Ca/Cl,  $\text{NH}_4/\text{Ca}$ , Na/Ca and K/Ca were  
486 significant only for TF-S (Table 3).

487



488

489 Fig. 4: Relationships between concentrations (mmol/l) of (a) Ca vs.  $\text{SO}_4$ , (b) Na vs. Cl and (c) Mg  
490 vs. Ca for the open field precipitation (OFP) and throughfalls under beech (TF-B) and under  
491 spruce (TF-S) for the 1986-2012 period in the Strengbach catchment.

492

493

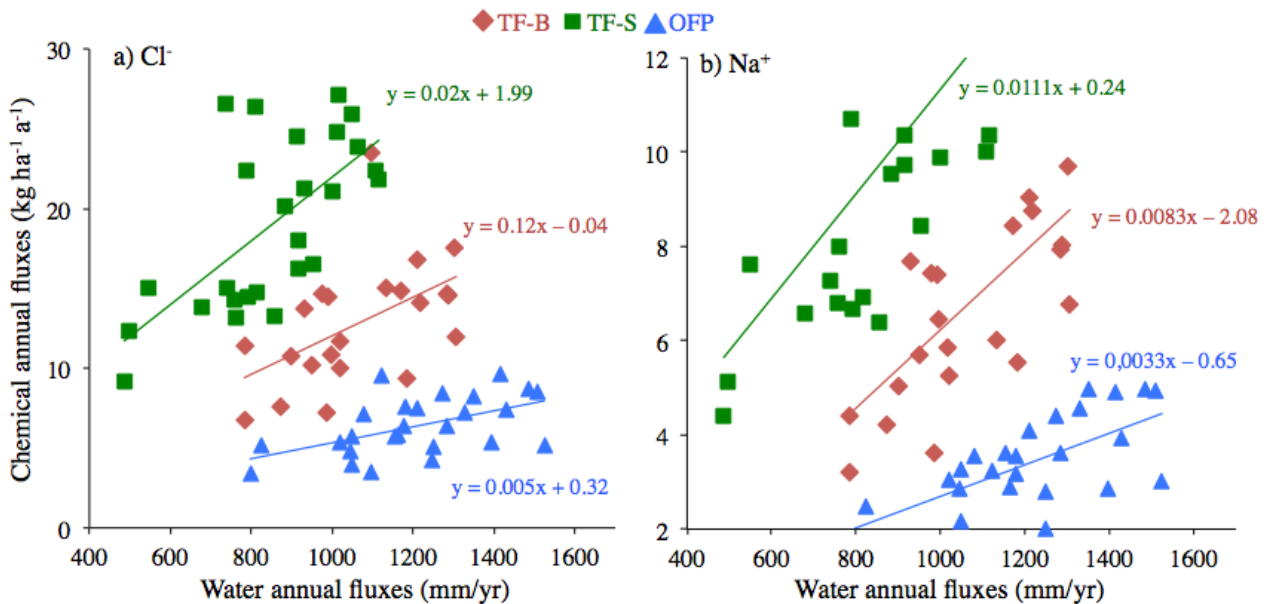
#### 494 4.4.2. Relationships between fluxes of elements and water

495 The relationships between annual chemical fluxes and the corresponding water fluxes were very  
496 significant for Na or Cl both in open field precipitation and throughfalls. Nevertheless, Na and Cl  
497 linear relationships had different slopes (0.003, 0.011 and 0.008 for Na and 0.005, 0.02 and 0.012  
498 for OFP, TF-S and TF-B, respectively; Fig. 5), underlining that these two elements did not have the  
499 same behavior, despite the fact that they were correlated (Fig. 4).

500 A significant correlation was also observed for  $K^+$  and  $Mg^{2+}$  in TF-S and for  $NO_3^-$  and  $Ca^{2+}$  in OFP.  
 501 Except these two relations, no other flux of an element correlated significantly with the  
 502 precipitation amount for TF-B (Table 6).

	$NH_4^+$	$Na^+$	$K^+$	$Mg^{2+}$	$Ca^{2+}$	$Cl^-$	$NO_3^-$	$SO_4^{2-}$
OFP	0.21	<b>0.64</b>	0.15	<b>0.48</b>	<b>0.59</b>	<b>0.53</b>	<b>0.55</b>	0.29
TF-S	0.21	<b>0.64</b>	<b>0.60</b>	<b>0.62</b>	0.45	<b>0.66</b>	0.26	0.11
TF-B	-0.12	<b>0.63</b>	0.03	0.28	0.10	<b>0.52</b>	0.17	0.02

504  
 505 Table 4: Pearson correlation coefficients  $r$  between the annual chemical fluxes and the  
 506 corresponding water fluxes for the main cations and anions in open field precipitation (OFP) and  
 507 throughfalls under spruce (TF-S) and under beech (TF-B).  $n=25$ . In bold:  $r>0.5$ .



509  
 510 Fig. 5: Relationships between the annual chemical flux and the water flux (mm/yr) for contrasting  
 511 and representative elements a)  $Cl^-$  and b)  $Na^+$  for open field precipitation (OFP) and throughfalls  
 512 under spruce (TF-S) and under beech (TF-B).

513  
 514 **5. Discussion**  
 515 **5.1. Link between atmospheric deposition and emission trends**  
 516 **5.1.1. Anthropogenic compounds**  
 517 **Sulfate**

518 The long-term decrease in sulfate concentrations in open field precipitation and throughfalls by  
519 factors of approximately 3 to 5 underlined a strong reduction in atmospheric sulfate input at the  
520 Strengbach catchment scale since 1986.

521 As a comparison, the measured annual throughfall depositions of S in 1994 in spruce forests were  
522 approximately 20 kg ha<sup>-1</sup> and 30 kg ha<sup>-1</sup> in the Strengbach catchment and at Načetín in the Ore Mts,  
523 Czech Republic, respectively (Table 2, Supplementary materials; Dambrine et al., 2000; Oulehle et  
524 al., 2006). The differences between these two sites resulted from the intensities of SO<sub>2</sub> emissions,  
525 which were greater in Central Europe (Dambrine et al., 2000; Vet et al.; 2014). On the basis of 37  
526 sites located throughout France, Pascaud et al. (2016) identified a decline of 30 to 40% in SO<sub>4</sub><sup>2-</sup>  
527 concentrations in wet open field precipitation from 1995 to 2007, close to that observed at the  
528 Strengbach catchment (30 to 45% in OFP, TF-S and TF-B). Similarly sulfate in rain and throughfall  
529 decreased significantly since 1990 in Europe or US (Balestrini et al., 2000; Pannatier et al., 2001;  
530 Thimonier et al., 2005; Rogora et al., 2006; Lehmann et al., 2007; Watmough et al., 2007; Oulehle  
531 et al., 2017; Vuorenmaa et al., 2018; 2018). By the 1980s, the rate of anthropogenic SO<sub>2</sub> emissions  
532 have decreased significantly (e.g., Klimont et al., 2013; Kopacek et al., 2005; 2016; Fioletov et al.,  
533 2016). The European annual amounts of emitted SO<sub>2</sub> peaked in 1975 (60 000 t; Mylona et al., 1996;  
534 Torseth et al., 2012; Hunova et al., 2014; Crippa et al., 2016). In France, the SO<sub>2</sub> emissions  
535 decreased from 3613 kT in 1973 to 232 kT in 2012 (-94%; Fig. 6; CITEPA: <http://www.citepa.org>).  
536 At a more local scale, the record of SO<sub>2</sub> emissions in the Alsace Region (ASPA: <http://www.atmo-alsace.net>;  
537 Fig. 7a) showed a similarly important decrease, explaining the global trend observed for  
538 the Strengbach catchment (Fig. 6).

539 However, starting in 2001, the global SO<sub>2</sub> emissions presented annual increases mainly caused by  
540 the economically emerging countries and regions such as China, India, the Middle East and Brazil  
541 (Smith et al., 2011; Klimont et al., 2013; Vet et al., 2014; McLinden et al., 2016; Li et al., 2017;  
542 EDGARV4.2 <http://edgar.jrc.ec.europa.eu/background.php>; Fig. 6). Fioletov et al. (2016) made an  
543 inventory of global SO<sub>2</sub> emissions for the period 2005-2014 and observed a maximum in 2007  
544 mainly related with China emissions, which was consistent with our observations. Similarly,  
545 according to Yang et al., (2016) for the period 1995-2014, the China SO<sub>2</sub> emissions were maximum  
546 in 2006. Finally, the SO<sub>2</sub> emissions in several other countries increased, or stop to decrease, during  
547 the 2001/2008 period as Ukraine, Russia, Turkey and even United State  
548 (<http://webdab1.umweltbundesamt.at>).

549 According to different studies or models, the world SO<sub>2</sub> emissions have decreased again since 2008,  
550 (Klimont et al., 2013; Yang et al., 2016).



551 Until 2002, the sulfate concentration declined in open field precipitation and throughfalls in the  
552 Strengbach catchment, following the decrease in Alsace, French and worldwide SO<sub>2</sub> emissions as a  
553 whole (Fig. 6). However, the increase in sulfate deposition by 2001 (Fig. 3) cannot be related to  
554 regional influence of gaseous SO<sub>2</sub> emissions since no increase was observed in local and national  
555 emissions (Fig. 6). Intercontinental transports of anthropogenic sulfur dioxide have been observed  
556 and traced (Tu et al., 2004; Clarisse et al., 2011).

557 In addition, SO<sub>2</sub>, as well as NO<sub>x</sub> can be oxidized in the atmosphere as H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>  
558 respectively, which can move into the stratosphere and being transported over long-range scale  
559 (Read et al., 1993; Wilson et al., 1992). Anthropogenic sulfate have been recored for exemple in ice  
560 cores in Greenland, in Svalbard or in alps glaciers and are attributed to long-range transport  
561 (Mayewski et al., 1986; Moore et al., 2006; Preunkert et al., 2001). Balestrini et al. (2007) estimated  
562 the dry distribution for sulfate from 43 to 47% in the canopy.

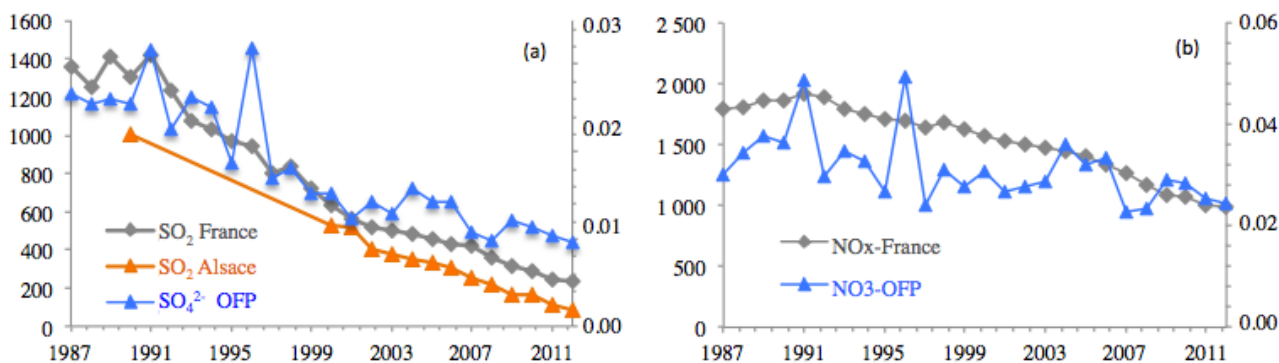
563 The increase in SO<sub>4</sub><sup>2-</sup> concentrations observed in OFP and throughfalls during the period 2001-2008  
564 (Fig. 3; 6) could be related to the SO<sub>2</sub> emitted in middle or long distance regions and transport as  
565 SO<sub>2</sub> gaz or as degradation products and aerosols.

566 Two peaks in the mean annual concentrations of sulfate were recorded in 1991 and 1996, as well as  
567 in nitrate, ammonium, magnesium and calcium (Fig. 3). They can be related to very high  
568 concentrations during the spring season and more precisely from 01/03 to 15/05 (database OHGE).  
569 At the opposite, periods from 01/03 to 15/05 represented 15% and 4% of the annual water flux of  
570 for 1991 and 1996, respectively. Thus, contrary to the annual concentrations, the annual fluxes were  
571 not very much influenced by these high values (Fig. 3). No peaks were recorded for Cl, Na or K.  
572 Because SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were influenced by human activities, the high concentrations during  
573 spring for OFP, TF-S and TF-B could have been of anthropogenic origin from continental air  
574 masses (which would explain the absence of peaks for Na, Cl or K). Vieno et al. (2014) proposed  
575 that the primary cause of episodes of elevated nitrate and sulfate in atmospheric particulate matter  
576 was the meteorological conditions, i.e., persistent high-pressure system keeping air pollution.

577

578 In summary, the long-term sulfate concentrations in the precipitation trends could be explained by  
579 1) mainly the global SO<sub>2</sub> gaseous emissions trend, 2) the long-distance transport of sulfur  
580 compounds, in agreement with the concept of long-range transport of atmospheric pollutants  
581 (Matejko et al., 2009; Posch et al., 2008, Hettelingh et al., 2008). and 3) local/regional conditions  
582 (climatic conditions, atmospheric gaseous and particulate concentrations) inducing specific seasonal  
583 variations within the global trend.

584



585  
586  
587

588 *Fig. 6: a) SO<sub>2</sub> and b) NO<sub>x</sub> emissions from 1987 to 2012 in France (in kT, CITEPA ordinate scale)*  
 589 *and in Alsace (multiplied by a factor 50 in order to use the same scale, source: ASPA-*  
 590 *http://www.atmo-grandest.eu (ordinate scale at the left), compared with the evolution of the mean*  
 591 *annual a) sulfate and b) nitrate concentrations (mmol/l; ordinate scale at the right) in open field*  
 592 *precipitation in the Strengbach catchment.*

593

#### 594 **Protons**

595 The increase in pH in atmospheric deposition (Fig. 4) was generally related to the decrease in  
 596 anthropogenic emissions of the precursor gases of acid rain such as SO<sub>2</sub> and NO<sub>x</sub>, as mandated by  
 597 legislation (e.g., Likens et al., 1996; Norton et al., 2014; Pascaud et al., 2016). Nevertheless, the  
 598 decrease in protons was mainly related to the decrease in SO<sub>4</sub> anions, both in open field  
 599 precipitation and throughfalls. The linear relationships were as follows:

600  $(\text{SO}_4^{2-})_{\text{OFP}} = 633 (\text{H}^+)_{\text{OFP}} + 0,075 \quad r = 0,62 \quad n = 623$

601  $(\text{SO}_4^{2-})_{\text{TF-B}} = 1343 (\text{H}^+)_{\text{TF-B}} + 0,011 \quad r = 0,63 \quad n = 509$

602  $(\text{SO}_4^{2-})_{\text{TF-S}} = 835 (\text{H}^+)_{\text{TF-S}} + 0,034 \quad r = 0,60 \quad n = 591$

603 where (SO<sub>4</sub><sup>2-</sup>) and (H<sup>+</sup>) are the sulfate and proton concentrations (mmole.l<sup>-1</sup>), respectively, r is the  
 604 Pearson correlation coefficient and n is the number of samples in OFP, TF-B and TF-S.

605 At the global scale, Vet et al. (2014) observed that patterns of pH in wet deposition generally  
 606 matched the emissions patterns of SO<sub>2</sub>.

607 The slopes of the pH trends for the period 1995-2007 (0.4, 0.5 and 0.5 obtained for OFP, TF-S and  
 608 TF-B, respectively) were consistent with those observed for open field precipitation at 37 sampling  
 609 sites throughout France (average pH increased 0.3 ± 0.1 over the period; Pascaud et al., 2016a).  
 610 Similarly, between 1992 and 2005, in the bulk precipitation in Nacetin (forested site in the Czech  
 611 Republic), pH evolved from 4.29 to 4.45 with a slope of + 0.36 (Oulehle et al., 2006).

612 The pH values of open field precipitation and throughfalls were still increasing, and the mean  
613 annual pH of rain in 2012 (5.18; Table 2, Supplementary material) was still lower than the  
614 preindustrial pH value (estimated as 5.7 to 6; Pallares, 1993; Kopacek et al., 2016), which indicated  
615 that a steady-state, and recovery, had not yet been reached. Even if world SO<sub>2</sub> emissions had  
616 strongly decreased during the past decades, the NO<sub>x</sub> emissions were still higher than in 1960. These  
617 observations revealed that the pH of precipitation was still impacted by anthropogenic activities.  
618 Considering the trend observed in the precipitation data over the period from 1986 to 2012 and the  
619 annual concentrations ( $\text{pH} = 0.029 \times \text{year} - 52.41$ ;  $r = 0,82$ ;  $n=25$ ), the preindustrial pH of 5.7 could  
620 be reached in 2032 in the Strengbach catchment, if the emissions trends remain constant as at  
621 present and without any changes in environmental parameters.

622

### 623 **Nitrogen (nitrate and ammonia)**

624 The NO<sub>x</sub> emissions have decreased since the 1990s in France and Europe (Fig. 6b), but they were  
625 still increasing at the global scale (Galloway et al., 2004; Vet et al., 2014). The decrease in french  
626 NO<sub>x</sub> emissions could be estimated at 47% over the period 1985-2012 (CITEPA data; Fig. 6), but  
627 declines were less than those observed for sulfate because of the development of road transportation  
628 or international shipping (Vestreng et al., 2009; Eyring et al., 2010).

629 The decrease in nitrate observed in open field precipitation and beech throughfall in the Strengbach  
630 catchment could thus be related to the decrease in NO<sub>x</sub> anthropogenic gaseous emissions (Fig. 7b)  
631 in France or in Europe. However, surprisingly, the nitrate concentration in TF-S did not manifest a  
632 significant time-dependent evolution, with a large variability (Fig. 4a) of annual fluxes ranging  
633 from 19 in 2002 to 88 kg ha<sup>-1</sup> a<sup>-1</sup> in 1990 (Fig. 4). Similarly, NO<sub>3</sub> concentrations in throughfall  
634 under spruce (Nacetin site, Czech Republic; Oulehele et al., 2006) or under pine (Whithehead et al.,  
635 2002; Skeffington et al., 2012) had not changed significantly since the eighties or nineties. In  
636 contrast to sulfate, nitrate concentrations in throughfall were not only the result of atmospheric  
637 deposits because of foliar uptake and biological excretions occurring at the water/leaf interfaces  
638 (Ulrich 1983; Lovett and Lindberg, 1984; Skeffington et al., 2012).

639 Pascaud et al. (2016) highlighted the lack of a systematic relationship between the reduction in NO<sub>x</sub>  
640 emissions and the changes in NO<sub>3</sub> concentrations in open field precipitation from 37 French rural  
641 sites with both significant increasing and decreasing trends depending on the sites.

642 Ammonium concentrations, similarly to those of nitrate, decreased in OFP and TF-B but  
643 interestingly increased in TF-S. However, the trend was only statistically significant for the  
644 throughfall under beech ( $-0,6 \text{ mmol l}^{-1}\text{yr}^{-1}$ ), according to the SK Test (Table 2). The NH<sub>3</sub> emissions  
645 (NH<sub>4</sub> precursor) have been approximately stable since 1980 in France (704 Gg in 1985 and 694 Gg

646 in 2012; CITEPA data). Nevertheless, Pascaud et al. (2016) observed a decrease in  $\text{NH}_4^+$   
647 concentration in precipitation from nine sampling sites (among the 37 French rural sites studied).  
648 Ammonium concentration could have been influenced by trends in atmospheric emissions of  $\text{SO}_2$   
649 (Ferm and Hellsten, 2012) and then displayed a decrease. Consistently with nitrate, the increase in  
650  $\text{NH}_4$  concentrations observed in throughfall under spruce could have been the result of vegetation  
651 interactions.  $\text{NH}_4^+$  is not an acid compound but may generate acidity (during plant uptake or  
652 nitrification in soil, Van Bremen et al., 1983, Cui et al., 2015; Messenburg et al., 2016).  
653 Because of its strong influence on biogeochemical cycle in soils and forests, the decrease in  $\text{NH}_4$   
654 deposition and its long-term evolution should be addressed in the future.

655

### 656 **5.1.2. Compounds with marine and continental origins**

#### 657 **Chloride**

658 Compared to sulfate or protons, the chloride concentrations did not vary strongly with time, neither  
659 in bulk precipitation nor in the two throughfalls (Fig. 2). However, a weak decrease for  
660 concentrations and fluxes was observable over the studied period in open field precipitation and  
661 beech throughfall, whereas no trend was observed for TF-S (Fig. 2 and see section 5.2), as  
662 confirmed by the SK Test (Table 2).

663 The main source of chloride in the atmosphere was related to sea spray. The anthropogenic  
664 emissions were marginal in comparison to  $\text{SO}_2$  or  $\text{NO}_x$  and might have resulted primarily from the  
665 combustion of coal and from accidental release during the incineration of chlorinated organic  
666 wastes but also in some places from road deicing salt (during winter).

667 Two hypotheses could be advanced to explain the slight reduction observed in  $\text{Cl}^-$  in open field  
668 precipitation (Fig. 3).

669 1) A modification of the rainfall regime, with an increase of the continental *vs.* oceanic contribution  
670 could have explained the long-term evolution. This hypothesis was supported by the simultaneous  
671 Na decrease in OFP (Table 2), which could have been associated with the marine origin of the two  
672 species. The Na/Cl ratio of OFP ranged from 0.64 to 1.04 during the period 1986-2012, which  
673 might have indicated a change in the wind mass origin with, for example, various contributions of  
674 Na from sea salt and Na from continental dust (Na/Cl ranging from 0.95 for west-origin air masses  
675 to 0.34 for the continental ratio, Dambrine et al., 1998b). However, the Theil-Sen slope was higher  
676 for Cl than for Na, suggesting additional processes or sources.

677 2) A decrease in the anthropogenic fraction of chloride, which has been regulated for several years.  
678 Indeed, the measures to reduce S emissions and the changes in energy supply have led to a 95%  
679 reduction in HCl emissions in the United Kingdom within 20 years (Evans et al., 2011).  
680 Thus, we propose to relate the small decrease in Cl concentrations observed in the open field  
681 precipitation (Fig. 3) at least in part to the decrease in the anthropogenic part of chloride (regulated  
682 for several years). However, a variation in air mass origin can be envisaged.

683

## 684 **Calcium**

685 Calcium in atmospheric deposits was rarely discussed as an element affected by anthropogenic  
686 activities because it originates mainly from sea salts and natural dusts from loess areas and deserts  
687 (mainly Saharan dust in our case; Lindberg et al., 1986; 1988b; Love-Pilot and Morelli, 1988;  
688 Sequeira, 1993; Torseth et al., 2012; Heijden et al., 2014; Vet et al., 2014; Pascaud et al., 2016). In  
689 contrast to sulfur, nitrogen or even ozone, POPs (persistent organic pollutant) and trace metals (Pb  
690 and Cd), the long-term records of Ca, Mg, Na or K in atmospheric deposition has received little  
691 attention.

692 Long-term declines in annual Ca concentration in precipitation have also been documented in two  
693 German forests from 1969 to 1990 (Matzner and Meiwes, 1994) and in the Hubbard Brook  
694 catchment between 1960 and 2010 (Linkens and Baileys, 2014). In Europe, the average decrease for  
695 Ca concentration in precipitation for the period 1980-2009 was -47% (Vuorenmaa, 2004; Torseth et  
696 al., 2012).

697 Indeed, in contrast to arid regions, where dust from deserts was a dominant source of airborne base  
698 cations, industrial dust significantly modified the precipitation chemistry in humid industrial  
699 regions similar to Central Europe (Torseth et al., 2012; Kopacek et al., 2016).

700 In the Strengbach catchment, we propose that the significant decreasing calcium trends of -0.1, -0.7  
701 and -0.7 mmol l<sup>-1</sup>yr<sup>-1</sup> for OFP, TF-B and TF-S, respectively (Fig. 3q, r), were the result of the  
702 decrease in emissions of particles containing calcium from industrial processes (implementation  
703 of processes for the reduction of industrial dust and/or closing of lignite-fired power stations;  
704 Kopacek et al., 2016; Torsten et al., 2012).

705 The annual Ca flux produced in soils by mineral weathering at the Strengbach catchment was  
706 estimated as < 2 kg.ha<sup>-1</sup>a<sup>-1</sup> (Dambrine et al., 1998a; Fichter et al., 1998), and the annual Ca flux in  
707 soil solution at 10 cm depth for the period 1993-2012 ranged from approximately 5 to 2.5 and from  
708 5 to 1.5 kg.ha<sup>-1</sup>a<sup>-1</sup> under spruce and beech plots, respectively (Prunier et al., 2015). Similarly, in the  
709 1990s, at the spruce stand scale, the soil solution flux (10.2 kg.ha<sup>-1</sup>a<sup>-1</sup>) was almost equivalent to the

710 input by precipitation ( $11.6 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$ ) (Probst et al., 1990a). Thus, the input of Ca by atmospheric  
711 deposition was a significant source of this nutrient in such a Ca-limited ecosystem (Probst et al.,  
712 2000), particularly because half of the deposition was used for the growth of biomass. During the  
713 period 1986-2012, the annual flux of atmospheric Ca has been reduced by 40 and 70%, from  
714 approximately 15 to 9 and approximately 6 to 2  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$ , respectively, under spruce and beech  
715 stands (Fig. 4i, j), which corresponded to a loss of 900 and 400  $\text{kg}\cdot\text{km}^{-2}$  per year. The long-term  
716 decreases observed in Ca soil solution concentrations at the two plots (Dambrine et al., 1998a;  
717 Prunier et al., 2015) could probably be associated, at least partly, with the decrease in inputs by  
718 throughfalls.

719 Since the Ca reduction in atmospheric input was related to the modification of human industrial  
720 activities and seemed to continue to the present, the decrease in Ca atmospheric deposition became  
721 a very important factor to be considered for monitoring and modeling the future of soil fertility.  
722 Ecosystems already depleted in nutrients such as Ca and Mg were particularly concerning, since the  
723 atmospheric Ca represented a high fraction of the Ca in soil solution and was highly bioavailable for  
724 vegetation.

725

## 726 **5.2. Influence of type of vegetation cover and rainfall amount on atmospheric deposition**

727 The chemical concentrations in throughfalls were higher than in open field precipitation (Table 2,  
728 Supplementary material, Fig. 7), as had already been observed in many places (Ulrich 1983; Probst et  
729 al., 1990a,b; Draaijers et al., 1995; Dambrine et al., 1998b; Balestrini et al., 2001; 2007; Vogt et al.,  
730 2006; Schrumpf et al., 2007; Berger et al., 2008; Staelens et al., 2008; Kopacek et al., 2009;  
731 Skeffington et al., 2012; Eaisalou et al., 2013).

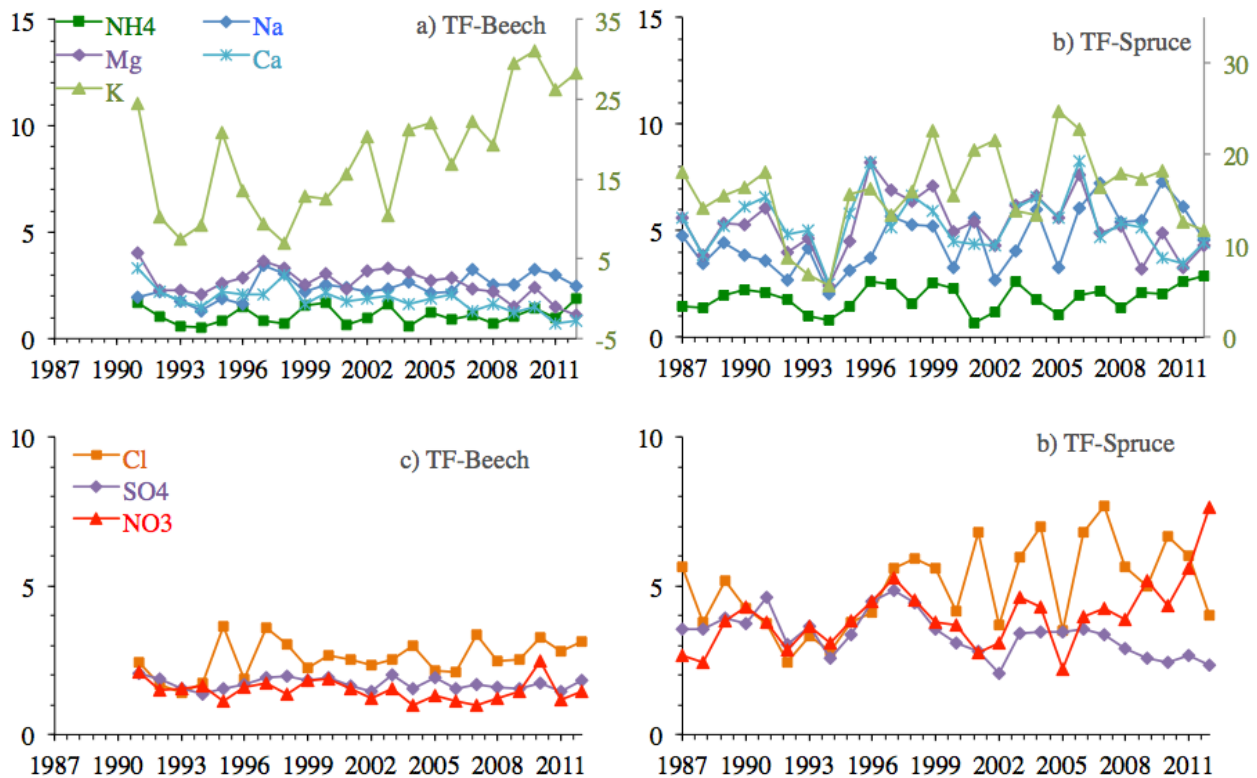
732 The processes of interaction between the rainwater and the canopy varied with the characteristics of  
733 the forest stand (density, age, geometry, altitude, structure, height, density, LAI; e.g., Bréda, 1999;  
734 2003; Erisman and Draaijers, 2003; Adriaenssens et al., 2012; Eaisalou et al., 2013; He et al., 2014).  
735 Indeed, few publications have compared these interactions for different tree species and for all the  
736 major chemical elements (especially cations and anions together) in the same study.

737 The rainfall interceptions in TF-S were higher than in TF-B (Fig.2). The global explanation was that  
738 the small, needle-like structures of spruce are more efficient (acting as a comb) in collecting  
739 particles and cloud droplets compared with the larger leaf-like structures of deciduous trees as  
740 beech (Berger et al., 2008; Adriaenssens et al., 2012). The leaf area index (LAI), which expressed  
741 the foliar surface per surface unit, was often considered as an indicator (or proxy) of rainfall  
742 interception (Breda, 1999; 2003). The LAIs determined in the Strengbach catchment were 3.23 and  
743 3.58 for the old spruce stand (110 yr with 557 trees/ha) and the beech stand (140 yr with 429

744 trees/ha), respectively (Asael, 1990), which was in agreement with the lower LAI measured for  
 745 spruces (7.1-37% interception) than for beeches (7.9-25% interception) at the Kreisbach site (Lower  
 746 Austria, Berger et al., 2008). However, LAI was probably not the best indicator to explain the  
 747 differences in interception. The plant area index (PAI), referring to all the light-blocking elements  
 748 (leaves, stems, twigs; He et al. 2014), seemed more appropriate to explain the variation in  
 749 interception. The higher interception observed under spruces in the Strengbach catchment could  
 750 thus be explained by the global geometry.

751 In addition, spruce needles persisted during the whole year, compared with the limited leaf period  
 752 for deciduous species. Indeed, during 6 months in the winter (November to early May in the  
 753 Strengbach catchment), there were no leaves to intercept precipitation in the beech stand.

754



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 757

758 *Fig. 7: Ratio of mean annual concentration in throughfall to open precipitation for NH<sub>4</sub>, Na, K, Ca*  
 759 *and Mg in a) beech and b) spruce stand and Cl, SO<sub>4</sub> and NO<sub>3</sub> in c) beech and d) spruce stands from*  
 760 *the Strengbach catchment (period 1986-2012). Scale on the right corresponds to K concentrations.*

761 Similar to interception, the conductivity and most of the elemental concentrations (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>,  
 762 Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were higher in TF-S than in TF-B, and both were enriched  
 763 compared with open field precipitation (Fig. 3, 4, 8). However, the chemical behavior and the  
 764 interaction with the canopy depended on the nature and origin of the elements; some elements such  
 765

766 as  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  were not biologically reemitted or absorbed by the foliage, but they were  
767 mainly physically deposited as wet and dry atmospheric aerosols on the foliage area (Ulrich, 1983;  
768 Probst et al., 1992b; Dambrine et al. 1998b; Thimonier et al., 2008; Kopacek et al., 2009). In  
769 contrast,  $\text{K}^+$  was strongly excreted by leaves, whereas Ca and Mg were weakly influenced by  
770 biological canopy exchange (e.g., Lovett and Lingberg, 1984; Kopacek et al., 2009; Adriaenssens et  
771 al., 2012). The concentration ratio between throughfall and OFP was used to compare the  
772 atmospheric input under the two types of canopy (Fig. 7).

773

#### 774 **$\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Cl}^-$ and $\text{SO}_4^{2-}$ .**

775 For the 1991-2012 period, the S atmospheric depositions under spruces (36 on average, ranging  
776 from 15 to 60  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$ ) are almost one third higher than under beeches (25 during the same period,  
777 ranging from 11 to 42  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$ ). Since no other source of sulfur occurred in the soils, the  
778 atmospheric inputs were the main origin of S in soil solution (Dahire, 1988, Probst et al., 1990a).  
779 As an illustration, the annual fluxes of S in soil solutions at 10 cm depth under spruces for the  
780 period between 1992 (beginning of the study of soil solution) and 2012 decreased from 18 to 4  
781  $\text{kg}/\text{ha}/\text{yr}$  (Dambrine et al., 1998a; Prunier et al., 2015), confirming the atmospheric-derived source  
782 of sulfur. This observation highlighted 1) the strong impact of the nature and type of the canopy on  
783 the S cycle in such an ecosystem and 2) the strong link with anthropogenic activities since a large  
784 proportion of S in the atmosphere was due to human activities, although at least in the Northern and  
785 Western Hemispheres, this contribution had tended to decrease since the 1980s.

786  $\text{Na}^+$  and  $\text{Cl}^-$  were well correlated in open field precipitation and in throughfalls (Table 3; Fig. 5),  
787 underling their primary oceanic origin. Nevertheless, the decrease of  $\text{Cl}^-$  observed and discussed  
788 above (see 5.1.1) both in OFP and TF-B might have reflected the decrease of an anthropogenic  
789 fraction and/or changes in climatic influence. The significant and similarly increasing Cl and Na  
790 ratios over OFP (Fig. 7) observed in throughfall under spruce for the past years while these values  
791 remained constant in TF-B was questionable and lacked any consistent explanation. Na was  
792 generally considered inert with respect to the canopy (neither uptake nor excretion occurred; De  
793 Schrijver et al., 2007). Because of the good correlation of Cl with Na, chloride could also be  
794 considered inert. Moreover, the equilibrated Cl budget at the catchment scale confirmed the inert  
795 character of chloride in the Strengbach catchment (Probst et al., 1992a). The annual Cl and Na  
796 ratios over OFP were related to the annual  $\text{H}_2\text{O}$  flux, especially for the past decade with high values  
797 for the years 2001, 2007 and 2010. A modification of the rainfall regime and the wind mass origin,  
798 as discussed in 5.1.2, could have impacted the chemistry of the TF-S more deeply because of  
799 needles geometry and persistence, explaining why the variation was not significant for TF-B.



800 In addition, the lack of a global trend and the strong interannual variations in the Cl and Na  
801 concentrations and annual fluxes in TF-S could have been related to the interannual variation in  
802 water fluxes (Table 1, Supplementary materials), which was illustrated by the significant correlation  
803 between annual Cl or Na flux and annual water flux ( $r=0.66$  and  $0.64$ , respectively, for TF-S; Table  
804 4, Fig. 6).

805  $Mg^{2+}$  and  $Ca^{2+}$  were well correlated, which indicated similar behavior in both throughfalls (Fig. 4c,  
806 Table 3). It was difficult to distinguish between anthropogenic and natural atmospheric deposits.  
807 Correlations between  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$  and  $SO_4^{2-}$  were better in throughfall under spruces than in that  
808 under beeches. This difference could be related to the increased capture of these elements, which  
809 mainly originated from atmospheric particles and accumulated on surface needles, particularly  
810 during the periods of elevated dry deposits.

811 In addition, the higher annual  $Ca^{2+}$  concentrations and fluxes in TF-S than in TF-B (Fig. 3r)  
812 explained the differences observed in soil solutions between the two plots (see 5.1.2). The nature of  
813 the plantation was thus an essential and critical parameter in the Ca biogeochemical cycle at the  
814 soil/stand scale, and consequently for forest health, especially in the Ca-poor Strengbach soils.

815 The comparison of  $K^+$  concentrations in the two types of throughfalls was contrasting, with higher  
816 concentrations in TF-S at some periods (1996-2003, for example) and lower concentrations during  
817 other periods (1991-1995 or since 2007), illustrating complex behavior. Potassium was not  
818 correlated with  $SO_4^{2-}$  or  $Cl^-$ , which confirmed that the major influence was not dry deposits (Table  
819 3), as proposed by Lovett and Lindberg (1984). Laboratory experiments had shown that the  
820 leaching of base cations increased when the acidity of eluent increased (Balestrini and Tagliaferri,  
821 2001). However, this hypothesis was excluded here since no correlation was observed between  
822 potassium and protons. A significant correlation was found between the annual K flux and the  
823 annual water flux ( $r= 0.60$  for TF-S, Table 4), converging with Likens et al. (1994) who proposed  
824 that the precipitation amount influenced the canopy leaching of K. Finally, no significant long-term  
825 trends were detected for  $K^+$  concentrations in TF-S.

826 In contrast, the long-term evolution of  $K^+$  in TF-B differed strongly from those of other cations,  
827 with higher variations and a significant increase since 2003 (Fig. 7). Potassium was a very mobile  
828 element in trees and was the most enriched cation in xylem sap (Dambrine et al., 1992).  
829 Adriaenssens et al. (2012) observed that the ratio between  $K^+$  concentrations in throughfall and bulk  
830 precipitation decreased with increasing canopy height and that this effect is more important in beech  
831 stands than in spruce stands. The  $K^+$  concentrations in throughfalls thus seemed more influenced by  
832 the canopy structure under beeches than that under spruces. Indeed, with the beech stand aging, the  
833 canopy structure changed over time.

834 This latter point was difficult to demonstrate, but the increasing K ratio observed for beech (Fig. 7)  
835 could be an indicator that the plantation was still growing/changing. The plant area index (see  
836 above) may be still increasing with denser lower branches, which might increase the contribution of  
837 biological foliar excretion with time.

838

### 839 **Protons**

840 As suggested above, the geometry and persistence of spruce needles explained the higher  
841 concentration of acidic atmospheric-derived elements in the corresponding throughfall compared  
842 with OFP and TF-B (Fig. 3a). On the other hand, the throughfall under beeches was less acidic than  
843 in open field precipitation (Fig. 3a). Such a pattern had already been observed for coniferous and  
844 deciduous trees (Rothe et al., 2002; Berger et al., 2008; Erismann and Draaijers, 2003; Adriaenssens  
845 et al., 2012; Eaisalou et al., 2013). Indeed, some deciduous trees were able to partly neutralize the  
846 incoming atmospheric acidity by the uptake of H<sup>+</sup> through the canopy and the exchange with base  
847 cations or ammonium on the inner leaf surfaces (Zeng et al., 2005).

848 The more acidic litter in the upper soils under coniferous, especially spruce, than under deciduous  
849 forest (Dambrine et al., 1998a,b; Aubert et al., 2002), also observed by Turk et al. (2008), supported  
850 the higher acidity of needles in the coniferous stand.

851 The strong pH difference between throughfalls under spruces and beeches (0.5 unit on average; Fig.  
852 3a) highlighted the strong influence of the tree species on the geochemical cycle. In particular, it  
853 determined the number of protons entering the system and thus the acidification and leaching  
854 processes in soils and in stream waters. Conifers contributed to an increase in the acidification of  
855 forest ecosystems, whereas beeches were able to neutralize a portion of the proton inputs.

856

### 857 **Nitrate and ammonium**

858 Depending on the year, the nitrate concentrations in spruce throughfall were 2 to 5 times higher  
859 than in beech throughfall (Fig. 3e, 7c-d, Table 2, Supplementary materials). In addition to the effect  
860 of the canopy geometry, the processes of biological N incorporation and excretion, especially the  
861 canopy uptake, differed with tree species (Erismann and Draaijers, 2003; Adriaenssens et al., 2012;  
862 Shen et al., 2013) and might explain the difference observed between the two stands. Meesenburg et  
863 al. (2016) also observed higher nitrate concentrations in throughfalls under a spruce plot than under  
864 a beech plot, with higher fluctuations in N input under spruce than under beech.

865 The annual fluxes of nitrogen derived from NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were similar in OFP with averages of  
866 4.49 and 4.52 kg ha<sup>-1</sup> a<sup>-1</sup>, respectively, for the 1986-2012 period. The results were also comparable  
867 for throughfall under beech with 5.51 and 4.13 kg ha<sup>-1</sup> a<sup>-1</sup>, respectively, for the same period, even

868 though nitrogen from nitrate was slightly higher than that from ammonia. The throughfall under  
869 spruce showed various amounts, with 11.33 and 5.29 kg ha<sup>-1</sup> a<sup>-1</sup> of N-NO<sub>3</sub> and N-NH<sub>4</sub>, respectively,  
870 on average for the 1986-2012 period (Table 2, Supplementary material). Thus, at first approximation,  
871 half of the atmospheric nitrogen inputs were derived from nitrate except under spruce where this  
872 proportion was approximately 70%.

873 Meesenburg et al. (2016) found that approximately 57% of N deposition was in the form of NH<sub>4</sub><sup>+</sup> in  
874 beech and spruce plots from a forested plateau in Central Germany. In four Mediterranean forests  
875 with mainly oak trees, the nitrate dominated the total nitrogen atmospheric flux but with different  
876 percentage in agricultural, rural or urban site (58 to 80%; Avila et al., 2017), underlining the role  
877 played by the tree species, but also the site location (distance from urban or agricultural zone).

878 The nitrate concentration in throughfall was influenced by foliar activity (uptake *vs* excretion) but  
879 also by stress factors such as insects, fungi or water stress (Fischer et al., 2007). In addition, the age  
880 of the tree and its structure played roles in the atmospheric nitrate absorption. Wilson and Tiley  
881 (1998) showed that the branches of young spruces were more effective than needles for absorbing  
882 nitrate. One possible explanation might be that with aging and stand decline (which was the case for  
883 the considered spruce forest), the nitrogen nutrient requirements and thus the uptake by the spruce  
884 needles decreased, explaining the increase of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in TF-S. However, in general NH<sub>4</sub><sup>+</sup>  
885 was more efficiently retained in canopy than NO<sub>3</sub><sup>-</sup> (Avila et al., 2017), which could explain why the  
886 increase in nitrate is higher than that in ammonia in TF-S (Fig. 7b, 7d).

887 Whereas the nitrate and ammonia atmospheric inputs to soil remained nearly constant under  
888 beeches and even decreased consistently with the slight decrease in OFP (constant ratio, Fig. 7a, c),  
889 they were higher and increased with time under spruces (increasing ratios, Fig. 7b, d). This  
890 observation highlighted the strong impact of tree species and tree health on the inputs of a major  
891 nutrient such as N and their evolution with time.

892

## 893 **6. Conclusion**

894 The long-term monitoring (several decades) of open field precipitation and throughfalls in the  
895 Strengbach catchment allowed the identification of some significant temporal trends (pH,  
896 conductivity, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup>). The decrease in acidity and sulfate  
897 concentration is likely related to the decrease in anthropogenic SO<sub>2</sub> and NO<sub>x</sub> (proton precursors)  
898 emissions since the 80s in the Northern Hemisphere, whereas the worldwide emissions might have  
899 explained the increase during the late period, namely, in particulate form, and underlined the  
900 influence of the long-range transport of gaseous pollutants. Similarly, the open field precipitation

901 displayed a decreasing trend in nitrate and ammonium concentrations. Considering the long-term  
902 trend slope, the preindustrial pH of 5.7 could be reached in 2032 in the Strengbach catchment.

903 The chloride concentrations showed a weak but obvious decrease, which could also have been  
904 related to the reduction in anthropogenic HCl emissions and/or to changes in precipitation and  
905 meteorological regime, since the sodium pattern followed a similar trend.

906 The slight long-term  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  decreases were probably due to global atmospheric source  
907 reductions (decreases in emissions of particles from industrial processes).

908 The canopy cover had significant and various impacts on the water and elemental fluxes because  
909 atmospheric particle deposition and biological interactions (via leaching or uptake processes on leaf  
910 surfaces) depended on the type of tree, the geometry of the canopy (LAI, age, density, etc.) or the  
911 persistence during the whole year.

912 As an illustration, the interception of water was two times more important under spruces than under  
913 beeches. Similarly, the concentrations of elements coming mainly or partly from atmospheric dry  
914 deposits ( $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$ ) were notably higher in TF-S than in TF-B.  
915 For example, the annual Ca fluxes were on average half as important under beeches as under  
916 spruces, and during the period 1986-2012, they were reduced by 40 and 70%, from approximately  
917 15 to 9 and approximately 6 to 2  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$  under spruce and beech stands, respectively. These  
918 decreases could have been substantial in such an environment with Ca- and Mg-poor bedrock and  
919 participated in nutrient depletion in soils, which endangered soil fertility and might have contributed  
920 to forest decline.

921 Spruce needles accentuated the acidity and induced the intensification of acidification processes and  
922 consequently nutrient leaching in soils, which led to forest decline. In contrast, beech leaves were  
923 able to neutralize a portion of the atmospheric protons, which minimized the negative effects of acid  
924 rain. Thus, the type of tree had a significant influence on the transfer of elements (nutrients and  
925 pollutants) in ecosystems.

926 In contrast to throughfall under beech, the throughfall under spruce recorded a weak increase in  
927 nitrate, which might have been linked to a decrease in foliar nitrate uptake due to spruce decline and  
928 aging.

929 Finally, a large proportion of  $\text{K}^+$  in throughfall came from biological excretion with more than a  
930 factor of 15 between rain and throughfall fluxes. K was the chemical element the most influenced  
931 by the canopy. The increase in  $\text{K}^+$  concentrations in beech throughfall could have been related to  
932 the increased amount of biomass.

933 Thus, the nature of the cover (clearing, spruce or beech plantations) but also the age and health of  
934 the plantation could strongly impact the nature of throughfalls, the chemical inputs in soils, and  
935 therefore the biogeochemical cycle of nutrients.

936 This study outlined and attested to the importance of long-term records of throughfalls and open  
937 field precipitation in order to obtain a real and accurate estimate of the inputs in term of water,  
938 nutrients and pollutants. Due to long-range atmospheric pollution, the economic development in  
939 emerging countries might influence the atmospheric chemistry at the global scale and thus even the  
940 biogeochemical cycles at the local scale. The long-term observations and records in forested sites  
941 such as the Strengbach catchment then become of public utility to address the potential impacts of  
942 long-range atmospheric pollutants even in rural areas in remote regions.

943 Forest management and silvicultural practices, by promoting coniferous or deciduous plantations,  
944 could sometimes strongly influence the fertility of soils (throughfall inputs more or less acidic or  
945 concentrated in nutrients). Such actions are particularly challenging in mountainous environments  
946 where forests represent a substantial economic resource.

947

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949

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960

961

#### 962 **References:**

963

964 Adrianssens S., Hansen K., Staelens J., Wuyts K., De Schrijver A., Baeten L., Boeckx P., Samson R. and  
965 Verheyens K., 2012. Throughfall deposition and canopy exchange processes along a vertical gradient  
966 within the canopy of beeches (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* (L.) Karst). *Science of*  
967 *the Total Environment* 420, 168-182.

968 Akpo, A. B., Galy-Lacaux, C., Laouali, D., Delon, C., Liousse, C., Adon, M., Gardrat E., Mariscal A. and  
969 Darakpa, C., 2015. Precipitation chemistry and wet deposition in a remote wet savanna site in West  
970 Africa: Djougou (Benin). *Atmospheric Environment*, 115, 110-123.

971 Asael S., 1990. Analyse structurale de quelques peuplements forestiers du bassin versant du Strengbach à  
972 Aubure (Haut-Rhin). DEA de biologie végétale et forestière. Université de nancy I. 91p.

- 973 Aubert, D., Stille, P., Probst, A., Gauthier-Lafaye, F., & Pourcelot, L., 2002. Characterization and migration  
974 of atmospheric REE in soils and surface waters. *Geochimica et Cosmochimica Acta*, 66(19), 3339-3350.
- 975 Avila, A., Aguilhaume, L., Izquieta-Rojano, S., García-Gómez, H., Elustondo, D., Santamaría, J. M., and  
976 Alonso, R., 2017. Quantitative study on nitrogen deposition and canopy retention in Mediterranean  
977 evergreen forests. *Environmental Science and Pollution Research*, 24(34), 26213-26226.
- 978 Balestrini, R., Galli, L., and Tartari, G., 2000. Wet and dry atmospheric deposition at prealpine and alpine  
979 sites in northern Italy. *Atmospheric Environment*, 34(9), 1455-1470.
- 980 Balestrini, R. and Tagliaferri, A., 2001. Atmospheric deposition and canopy exchange processes in alpine  
981 forest ecosystems (northern Italy). *Atmospheric Environment*, 35(36), 6421-6433.
- 982 Balestrini, R., Arisci, S., Brizzio, M. C., Mosello, R., Rogora, M., and Tagliaferri, A., 2007. Dry deposition  
983 of particles and canopy exchange: Comparison of wet, bulk and throughfall deposition at five forest sites  
984 in Italy. *Atmospheric Environment*, 41(4), 745-756.
- 985 Biron, P., 1994. *Le cycle de l'eau en forêt de moyenne montagne: flux de sève et bilans hydriques*  
986 *stationnels: bassin versant du Strengbach à Aubure, Hautes Vosges* (Doctoral dissertation, Université  
987 Louis Pasteur (Strasbourg)).
- 988 Bonhomme M., 1967. Âge, par la méthode au strontium, des micas du granite des Crêtes (Vosges). 92e  
989 congrès des Sociétés savantes.
- 990 Berger T.W., Untersteiner H., Schume H. and Jost G., 2008. Throughfall fluxes in a secondary spruce (*Picea*  
991 *abies*), a beech (*Fagus sylvatica*) and a mixed spruce-beech stand. *Forest Ecology and Management*. 255,  
992 605-618.
- 993 Bréda N.J.J., 1999. L'indice foliaire des couverts forestiers: mesure, variabilité et rôle fonctionnel. *Rev. For.*  
994 *Fr* 2, 1999- p.135-150
- 995 Bréda N.J.J., 2003. Ground-based measurements of leaf area index: a review of methods, instruments and  
996 current controversies. *Journal of experimental Botany*. 54, 2403-2417.
- 997 Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., ... and Emmett, B. 2010.  
998 Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecological*  
999 *applications*, 20, 30-59.
- 1000 Bultot, F., Dupriez, G. L., and Bodeux, A., 1972. Interception de la pluie par la végétation forestière  
1001 estimation de l'interception journalière à l'aide d'un modèle mathématique. *Journal of Hydrology*, 17(3),  
1002 193-223.
- 1003 Charlson, R. J., and Rodhe, H., 1982. Factors controlling the acidity of natural rainwater. *Nature*, 295, 683-  
1004 685.
- 1005 Clarisse, L., Fromm, M., Ngadi, Y., Emmons, L., Clerbaux, C., Hurtmans, D. and Coheur, P. F., 2011.  
1006 Intercontinental transport of anthropogenic sulfur dioxide and other pollutants: An infrared remote  
1007 sensing case study. *Geophysical research letters*, 38(19).
- 1008 Coddeville, P., Pascaud, A., Sauvage, S., Nicolas, M., Mathias, E. and Probst, A., 2016. Évolution des  
1009 émissions, de la qualité de l'air et des dépôts atmosphériques dans les espaces ruraux, notamment  
1010 forestiers. Changes in atmospheric emissions, air quality and deposition in rural areas, especially in  
1011 forests. *Pollution Atmosphérique*, (229-230).
- 1012 Cosby, B. J., Hornberger, G. M., Galloway, J. N., Wright, R. F., 1985. Modelling the effects of acid  
1013 deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Water*  
1014 *Resour. Res.* 21, 51-63.
- 1015 Crippa, M., Janssens-Maenhout, G., Dentener, F., Guizzardi, D., Sindelarova, K., Muntean, M., ... and  
1016 Granier, C., 2016. Forty years of improvements in European air quality: regional policy-industry  
1017 interactions with global impacts. *Atmospheric Chemistry and Physics*, 16(6), 3825-3841.
- 1018 Cui, J., Zhou, J., Peng, Y., Chan, A., and Mao, J., 2015. Effects of atmospheric deposition nitrogen flux and  
1019 its composition on soil solution chemistry from a red soil farmland, southeast China. *Environmental*  
1020 *Science: Processes & Impacts*, 17(12), 2082-2091.
- 1021 Dahire M., 1988. Granites et leucogranites péralumineux du Brézouard et du Bilstein (Vosges moyennes) :  
1022 caractères pétrographiques, géochimiques et minéralogiques. Thèse de Doctorat. Université de Nancy,  
1023 155p
- 1024 Dambrine E., Le Goaster S., Ranger J., 1991. Croissance et nutrition minérale d'un peuplement d'épicéa sur  
1025 sol pauvre. II Prélèvement racinaire et transferts internes d'éléments minéraux au cours de la croissance.  
1026 *Acta Oecologica*, 12, 791-808.

- 1027 Dambrine E., Carisey N., Pollier B., Granier A., Girard S., Lu P., Biron P. 1992. Dynamique des éléments  
1028 minéraux dans la sève xylémique d'épicéas de 30 ans. *Ann. Sci. For.* 49, 489-510.
- 1029 Dambrine E., Pollier, Poszwa A., Ranger J., Probst A., Viville D., Biron P. and Granier A., 1998a. Evidence  
1030 of current soil acidification in spruce (Strengbach catchment, Vosges mountains, North-Eastern France).  
1031 *Water, Air and Soil Poll.* 105, 43-52.
- 1032 Dambrine E., Pollier B., Bonneau M. and Ignatova N., 1998b. Use of artificial trees to assess dry deposition  
1033 in spruce stands. *Atmospheric Environment* 32, 1817-1824.
- 1034 Dambrine E., Probst A., Viville D., Biron P., Belgrand M.C., Paces T., Novak M., Buzey J., Cerny J. and  
1035 Groscheova H., 2000. Spatial variability and long term trends in mass balance of N and S in central  
1036 european forested catchments. In : *Ecological Studies*, E.-D. Schulze (ed.) Carbon and Nitrogen cycling  
1037 in European Forested Ecosystems. Springer Verlag, Berlin, Heidelberg, vol. 142, Chap. 19, pp. 405-418.
- 1038 Delfs J., 1965. Interception and stemflow in stands of Norway spruce and beech in West Germany. In : W.E.  
1039 Sopper and H.W. Lull (Editors), *Forest Hydrology, Proceedings of a National Science Advanced*  
1040 *Seminar, 29 August-10 September 1965, University Park PA.* Pergamon Press, pp 179-185
- 1041 De Schrijver, A., Geudens, G., Augusto, L., Staelens, J., Mertens, J., Wuyts, K., Gielis L. and Verheyen, K.,  
1042 2007. The effect of forest type on throughfall deposition and seepage flux: a review. *Oecologia*, 153(3), 663-  
1043 674.
- 1044 De Vries, W., Dobbertin, M. H., Solberg, S., Van Dobben, H. F., and Schaub, M., 2014. Impacts of acid  
1045 deposition, ozone exposure and weather conditions on forest ecosystems in Europe: an overview. *Plant*  
1046 *and soil*, 380, 1-45.
- 1047 De Vries, W., Reinds, G.J., Vel, E., 2003. Intensive monitoring of forest ecosystems in Europe 2.  
1048 Atmospheric deposition and its impacts on soil solution chemistry. *Forest Ecology and Management* 174,  
1049 97-115.
- 1050 Draaijers, G. P. J., and Erisman, J. W., 1995. A canopy budget model to assess atmospheric deposition from  
1051 throughfall measurements. *Water, Air, & Soil Pollution*, 85(4), 2253-2258.
- 1052 Eaisalou H.K., Sengönül K., Gökbülak F., Serengil Y. and Uygur B., 2013. Effects of forest canopy cover and  
1053 floor on chemical quality of water in Broad leaves and coniferous forests of Istanbul, Turkey. *Forest*  
1054 *Ecology and Management*. 289, 371-377.
- 1055 Erisman JW, Draaijers G., 2003. Deposition to forests in Europe: most important factors influencing dry  
1056 deposition and models used for generalisation. *Environ Pollut.*124:379-88. [SEP]
- 1057 Evans C.D., Cullen J.M., Alewell C., Kopacek J., Marchetto A., Moldan F., Prechtel A., Rogora M. Vesely  
1058 J. and Wright R.F., 2001. Recovery from acidification in European surface waters. *Hydrol. Earth Syst.*  
1059 *Sci.* 5, 282-297.
- 1060 Evans C.D., Monteith D.T., Fowler D., Cape J.N. and Brayshaw S., 2011. Hydrochloric acid: an overlooked  
1061 driver of environmental change. *Environ. Sci. Technol.*, 45, 1887-1894. doi: 10.1021/es103574u.
- 1062 Eyring, V., Isaksen, I.S.A., Berntsen, T., Collins, W.J., Corbett, J.J., Endresen, O., Grainger, R.G.,  
1063 Moldanova, J., Schlager, H., Stevenson, D.S., 2010. Transport impacts on atmosphere and climate:  
1064 Shipping. *Atmos. Environ.* 44 (37)
- 1065 Ferm, M., Hellsten, S., 2012. Trends in atmospheric ammonia and particulate ammonium concentrations in  
1066 Sweden and its causes. *Atmos. Environ.* 61 (0), 30-39.
- 1067 Fioletov, V. E., McLinden, C. A., Krotkov, N., Li, C., Joiner, J., Theys, N. and Moran, M. D., 2016. A  
1068 global catalogue of large SO2 sources and emissions derived from the Ozone Monitoring Instrument.  
1069 *Atmospheric Chemistry & Physics*, 16(18).
- 1070 Fisher R., Mues V., Ulrich E., Becher G. and Lorenz M., 2007. Monitoring of atmospheric deposition in  
1071 European forests and an overview on its implication on forest condition. *Applied Geochemistry* 2, 1129-  
1072 1139.
- 1073 Fichter, J., Dambrine, E., Turpault, M. P., & Ranger, J., 1998. Base cation supply in spruce and beech  
1074 ecosystems of the Strengbach catchment (Vosges mountains, NE France). *Water, Air, and Soil Pollution*,  
1075 104(1-2), 125-148.

- 1076 Fuss, C. B., Driscoll, C. T., & Campbell, J. L., 2015. Recovery from chronic and snowmelt acidification:  
1077 Long-term trends in stream and soil water chemistry at the Hubbard Brook Experimental Forest, New  
1078 Hampshire, USA. *Journal of Geophysical Research: Biogeosciences*, 120(11), 2360-2374
- 1079 Galy-Lacaux, C., Laouali, D., Descroix, L., Gobron, N., and Lioussé, C., 2009. Long term precipitation  
1080 chemistry and wet deposition in a remote dry savanna site in Africa (Niger). *Atmospheric Chemistry and*  
1081 *Physics*, 9(5), 1579-1595.
- 1082 Gaudio N., Belyazid S., Gendre X., Mansat A., Rizzetto S., Nicolas M., Sverupt H. and Probst A., 2015.  
1083 Combined effect of atmospheric nitrogen deposition and climate change on temperate forest soil  
1084 biogeochemistry: a modelling approach. *Ecological Modelling*, 306, 24-34.
- 1085 Harrison, A.F., Schulze, E.D., Gebauer, G. and Bruckner, G., 2000. Canopy uptake and utilization  
1086 of atmospheric pollutant nitrogen. In *Carbon and nitrogen cycling in European forest ecosystems*  
1087 (pp. 171-188). Springer, Berlin, Heidelberg
- 1088 He, Z. B., Yang, J. J., Du, J., Zhao, W. Z., Liu, H., and Chang, X. X., 2014. Spatial variability of canopy  
1089 interception in a spruce forest of the semiarid mountain regions of China. *Agricultural and forest*  
1090 *meteorology*, 188, 58-63.
- 1091 Heijden G. Legoud A. Pollier B., Ranger P. and Dambrine E., 2014. The dynamics of calcium and  
1092 magnesium inputs by throughfall in a forest ecosystem on base poor soil are very slow and conservative:  
1093 evidence from an isotopic tracing experiment ( $^{26}\text{Mg}$  and  $^{44}\text{Ca}$ ). *Biogeochemistry* 118, 413-442.
- 1094 Heijden G., Legoud A., Nicolas M., Ulrich E., Johnson D.W. and Dambrine E., 2011. Long-term  
1095 sustainability of forest ecosystems on sandstone in the Vosges Mountains (France) facing atmospheric  
1096 deposition and silvicultural change. *Forest Ecology and Management*. 261, 730-740.
- 1097 Hettelingh, J. P., Posch, P., and Slootweg, J. 2008. Critical Load, Dynamic Modelling and Impact  
1098 Assessment in Europe, CCE Status Report 2008, Report 500090003. *Coordination Center for Effects,*  
1099 *Netherlands Environmental Assessment Agency, The Netherlands.*
- 1100 Hirsch, R. M., J. R. Slack, and R. A. Smith, 1982. Techniques of trend analysis for monthly water quality  
1101 data, *Water Resour. Res.*, 18, 107-121.
- 1102 Hruska J. and Kram P. 2003. Modelling long-term changes in stream water and soil chemistry in catchments  
1103 with contrasting vulnerability to acidification (Lysina and Pluhuv Bor, Czech republic). *Hydrology and*  
1104 *earth Syst. Sci.* 7, 525-539
- 1105 Hunova, I., Maznova, J., Kurfürst, P., 2014. Trends in atmospheric deposition fluxes of sulphur and nitrogen  
1106 in Czech forests. *Environ. Pollut.* 184, 668-675.
- 1107 Idir S., Probst A., Viville D. and Probst J.L., 1999. Contribution des surfaces saturées et des versants aux  
1108 flux d'eau et d'éléments exportés en période de crue : tracage à l'aide du carbone organique dissous et de  
1109 la silice. Cas du petit bassin versant du Strengbach (Vosges, France). *C.R. Acad Sci Paris*. 328, 89-96.
- 1110 Jenkins, A., Camarero, L., Cosby, B. J., Ferrier, R. C., Forsius, M., Helliwell, R. C., Kopáček, J., Majer, V.,  
1111 Moldan, F., Posch, M., Rogora, M., Schöpp, W., Wright, R. F., 2003. A modelling assessment of  
1112 acidification and recovery of European surface waters. *Hydrol. Earth Syst. Sci.* 2003, 7, 447-455.
- 1113 Johnson R.C., 1990, The interception, throughfall and stemflow in a forest in highland Scotland and the  
1114 comparison with other upland forests in the U.K. *Journal of Hydrology* 118, 281-287.
- 1115 Kato, H., Onda, Y., Nanko, K., Gomi, T., Yamanaka, T., and Kawaguchi, S., 2013. Effect of canopy  
1116 interception on spatial variability and isotopic composition of throughfall in Japanese cypress plantations.  
1117 *Journal of hydrology*, 504, 1-11.
- 1118 Keene, W. C., Pszenny, A. A., Galloway, J. N., and Hawley, M. E., 1986. Sea-salt corrections and  
1119 interpretation of constituent ratios in marine precipitation. *Journal of Geophysical Research:*  
1120 *Atmospheres*, 91(D6), 6647-6658.
- 1121 Kendall M.G., 1975. Rank correlation methods, fourth ed. Charles Griffin, London.
- 1122 King H.B., Wang M.K., Zhuang S.Y., Hwong J.L., Liu C.P. and Kang M.J., 2006. Sorption of sulphate and  
1123 retention of cations in forest soils of Lien-Hua-Chi watershed in central Taiwan. *Geoderma* 131, 143-153.
- 1124 Klimont Z., Smith S.J., Cofala J., 2013. The last decade of global anthropogenic sulphur dioxide 2000-2011  
1125 emissions. *Environ. Res. Lett.* 8, 6pp.



- 1126 Klos, P. Z., Chain-Guadarrama, A., Link, T. E., Finegan, B., Vierling, L. A., and Chazdon, R., 2014.  
 1127 Throughfall heterogeneity in tropical forested landscapes as a focal mechanism for deep percolation.  
 1128 *Journal of hydrology*, 519, 2180-2188.
- 1129 Kopacek, J., Vesely, J., 2005. Sulfur and nitrogen emissions in the Czech Republic and Slovakia from 1850  
 1130 till 2000. *Atmos. Environ.* 39, 2179–2188.<sup>[1]</sup><sub>[SEP]</sub>
- 1131 Kopacek J., Turek J., Hejzlar J. and Santruckova H., 2009. Canopy leaching of nutrients and metals in a  
 1132 mountain spruce forest. *Atmospheric Environment* 43, 5443-5453.
- 1133 Kopacek J., Hejzlar J., Kram P., Oulhele F and Posch M., 2016. Effect of industrial dust on precipitation  
 1134 chemistry in the Czech Republic (Central Europe) from 1850 to 2013. *Water Research* 103, 30-37.
- 1135 Kram P., Hruska J., Wenner B.S., Driscoll C.T. and Johnson C.E., 1997. The biogeochemistry of basic  
 1136 cations in two forest catchments with contrasting lithology in the Czech Republic. *Biogeochemistry* 37,  
 1137 173-202
- 1138 Landmann, G. and Bonneau M. 1995). *Forest decline and atmospheric deposition effects in the French*  
 1139 *mountains*. Technical Editor: Michele Kaennel. Springer, Berlin, Heidelberg. 453p.
- 1140 Laouali, D., Galy-Lacaux, C., Diop, B., Delon, C., Orange, D., Lacaux, J. P., Akpo A., Lavenu F., Gardrat E.  
 1141 and Castera, P., 2012. Long term monitoring of the chemical composition of precipitation and wet  
 1142 deposition fluxes over three Sahelian savannas. *Atmospheric environment*, 50, 314-327.
- 1143 Laudon, H., Köhler, S., and Bishop, K. H., 1999. Natural acidity or anthropogenic acidification in the spring  
 1144 flood of northern Sweden? *Science of the Total Environment*, 234, 63-73.
- 1145 Lehmann, C. M., Bowersox, V. C., Larson, R. S., & Larson, S. M., 2007. Monitoring long-term trends in  
 1146 sulfate and ammonium in US precipitation: Results from the National Atmospheric Deposition  
 1147 Program/National Trends Network. In *Acid Rain-Deposition to Recovery* (pp. 59-66). Springer,  
 1148 Dordrecht.
- 1149 Li, C., McLinden, C., Fioletov, V., Krotkov, N., Carn, S., Joiner, J., ... Dickerson, R. R. (2017). India Is  
 1150 Overtaking China as the World's Largest Emitter of Anthropogenic Sulfur Dioxide. *Scientific Reports*,  
 1151 7(1). <https://doi.org/10.1038/s41598-017-14639-8>
- 1152 Lindberg, S. E., Lovett, G. M., Richter, D. D., & Johnson, D. W., 1986. Atmospheric deposition and canopy  
 1153 interactions of major ions in a forest. *Science*, 231, 141-146.
- 1154 Lindberg, S.E., Garten, C.T., 1988a. Sources of sulphur in forest canopy throughfall. *Nature* 336, 148–  
 1155 151.<sup>[1]</sup><sub>[SEP]</sub>
- 1156 Lindberg S.E., Lovett G.M., Schaefer D.A. and Bredemeier M., 1988b. Dry deposition velocities and  
 1157 surface-to-canopy scaling factors for aerosol calcium from forest canopy throughfall. *Journal of Aerosol*  
 1158 *Science, Volume 19, Issue 7, 1988, Pages 1187-1190*
- 1159 Likens G E and Bormann F H 1974 Acid rain: a serious regional environmental problem *Science* 184 1176–9
- 1160 Likens, G. E., Driscoll, C. T., Buso, D. C., Siccama, T. G., Johnson, C. E., Lovett, G. M., ... & Reiners, W.  
 1161 A., 1994. The biogeochemistry of potassium at Hubbard Brook. *Biogeochemistry*, 25, 61-125.
- 1162 Likens, G. E., Driscoll, C. T., & Buso, D. C., 1996. Long-term effects of acid rain: response and recovery of  
 1163 a forest ecosystem. *Science*, 272, 244.
- 1164 Lovett G. M., and Lindberg, S. E., 1984. Dry deposition and canopy exchange in a mixed oak forest as  
 1165 determined by analysis of throughfall. *Journal of Applied Ecology*, 1013-1027.
- 1166 Lovett G. M., 1992. Dry deposition of sulfure to the Hubbard Brook Experimental Forest: a preliminary  
 1167 comparison of methods. *Precipitation Scavenging and Atmosphere-Surface Exchange*, 1391-1401.
- 1168 Loyer-Pilot, M. D. and J. Morelli, 1988. Fluctuations of ionic composition of precipitations collected in  
 1169 Corsica related to changes in the origins of incoming aerosols. *Journal of Aerosol Science* 19(5): 577-585
- 1170 Mann H. B., 1945. On a test for randomness based on signs of differences. *The Annals of Mathematical*  
 1171 *Statistics*, 16, 193-199.
- 1172 Matejko, M., Dore, A. J., Hall, J., Dore, C. J., Błaś, M., Kryza, M., ... and Fowler, D. (2009). The influence  
 1173 of long term trends in pollutant emissions on deposition of sulphur and nitrogen and exceedance of  
 1174 critical loads in the United Kingdom. *Environmental Science & Policy*, 12(7), 882-896.
- 1175 Matzner E. and Meiwes K.J., 1994. Long-Term Development of Element Fluxes with Bulk Precipitation and  
 1176 Throughfall in Two German Forests/ *Journal of Environmental Quality*, 23, 162-166.
- 1177 Martin C.W. and Harr R.D., 1988. Precipitation and streamwater chemistry from undistributed watersheds in

1178 the Cascade Mountains of Oregon, USA. *Water Air and Soil Pollution* 42, 203-220.

1179 Mayewski, P. A., Lyons, W. B., Spencer, M. J., Twickler, M., Dansgaard, W., Koci, B. and Honrath, R. E.,  
1180 1986. Sulfate and nitrate concentrations from a south Greenland ice core. *Science*, 232(4753), 975-977.

1181 McHale, M.R., Burns, D.A., Siemion, Jason, and Antidormi, M.R., 2017, The response of soil and stream  
1182 chemistry to decreases in acid deposition in the Catskill Mountains, New York, USA: *Environmental*  
1183 *Pollution*, v. 229, p. 607-620

1184 McLinden, C. A., Fioletov, V., Shephard, M. W., Krotkov, N., Li, C., Martin, R. V. and Joiner, J., 2016.  
1185 Space-based detection of missing sulfur dioxide sources of global air pollution. *Nature Geoscience*, 9(7),  
1186 496–500. <https://doi.org/10.1038/ngeo2724>

1187 McDowell, W. H., Sánchez, C. G., Asbury, C. E. and Pérez, C. R. R., 1990. Influence of sea salt aerosols and  
1188 long range transport on precipitation chemistry at El Verde, Puerto Rico. *Atmospheric Environment. Part*  
1189 *A. General Topics*, 24(11), 2813-2821.

1190 Meesenburg, H., Ahrends, B., Fleck, S., Wagner, M., Fortmann, H., Scheler, B., and Meiwes, K. J. 2016.  
1191 Long-term changes of ecosystem services at Solling, Germany: Recovery from acidification, but  
1192 increasing nitrogen saturation?. *Ecological Indicators*, 65, 103-112.

1193 Mimura, A. M. S., Almeida, J. M., Vaz, F. A. S., de Oliveira, M. A. L., Ferreira, C. C. M., and Silva, J. C. J.,  
1194 2016. Chemical composition monitoring of tropical rainwater during an atypical dry year. *Atmospheric*  
1195 *Research*, 169, 391-399.

1196 Moldan B., Schnoor, J., 1992. Czechoslovakia: examining a critically ill environment. *Environmental*  
1197 *Science and Technology* 26, 14–21.

1198 Moldan, F.; Kronnäs, V.; Wilander, A.; Karlun, E.; Cosby, B. J. 2004. Modelling acidification and recovery  
1199 of Swedish lakes. *Water, Air, Soil Pollut.: Focus* 4, 139–160.

1200 Moore, J., Kekonen, T., Grinsted, A., & Isaksson, E., 2006. Sulfate source inventories from a Svalbard ice  
1201 core record spanning the Industrial Revolution. *Journal of Geophysical Research: Atmospheres*, 111-D15,  
1202 1-13

1203 Nanus, L., McMurray, J. A., Clow, D. W., Saros, J. E., Blett, T., and Gurdak, J. J., (2017). Spatial variation of  
1204 atmospheric nitrogen deposition and critical loads for aquatic ecosystems in the Greater Yellowstone  
1205 Area. *Environmental Pollution*, 223, 644-656.

1206 Navratil T., Kurz D., Kram P., Hofmister J. and Hruska J., 2007. Acidification and recovery of soil at a  
1207 heavily impacted forest catchment (Lysina, Czech Republic)- SAFE modelling and field results.  
1208 *Ecological modelling* 205, 464–474.

1209 Nihlgård, B., 1970. Precipitation, its chemical composition and effect on soil water in a beech and a spruce  
1210 forest in south Sweden. *Oikos*, 208-217.

1211 Norton S.A., Wagai R., Navratil T., Kaste J.M. and Rissberger F.A., 2000. Response of a first-order stream  
1212 in Maine to short-term in-stream acidification. *Hydrology and Earth System Sciences* 4, 383-391.

1213 Norton S.A., Kopáček J. and Fernandez I.J., 2014. Acid Rain – Acidification and Recovery. In: Holland H.D.  
1214 and Turekian K.K. (eds.) *Treatise on Geochemistry*, Second Edition, vol. 11, pp. 379-414. Oxford:  
1215 Elsevier.

1216 Oulehle F., Hofmeister J., Cudlin P. and Hruska J., 2006. The effect of reduced atmospheric deposition on  
1217 soil and soil solution chemistry at a site subjected to long-term acidification, Nacetin, Czech Republic.  
1218 *Science of the Total Environment* 370, 532-544.

1219 Oulehle F., Chuman T., Hruska J., Kram P., McDowell W.H., Myska O., Navratil T. and Tesar M., 2017.  
1220 Recovery from acidification alters concentrations and fluxes of solutes from Czech catchments.  
1221 *Biogeochemistry* 132, 251-272

1222 Paces T., 1985. Source of acidification in central Europe estimated from elemental budgets in small basins.  
1223 *Nature* 315, 31-36

1224 Pallares C., 1993. Etude cinétique Etude cinétique de l'oxydation du dioxyde de soufre par des oxydants forts  
1225 dans l'eau troposphérique. Thèse de doctorat, Université Louis Pasteur. Strasbourg

- 1226 Pannatier, E. G., Thimonier, A., Schmitt, M., Walthert, L., & Waldner, P. (2011). A decade of monitoring at  
1227 Swiss Long-Term Forest Ecosystem Research (LWF) sites: can we observe trends in atmospheric acid  
1228 deposition and in soil solution acidity?. *Environmental monitoring and assessment*, 174(1-4), 3-30.
- 1229 Parker GG., 1983. Throughfall and stemflow in the forest nutrient cycle. *Adv Ecol Res* 1983;13: 57-133.<sup>[1]</sup>
- 1230 Pascaud C., Sauvage S., Coddeville P., Nicolas M., Croisé L., Mezhdour A. and Probst A., 2016. Contrasted  
1231 spatial and long-term trends in precipitation chemistry and deposition fluxes at rural stations in France.  
1232 *Atmospheric Environment* 146, 28-43.
- 1233 Pascaud A., 2013. Déterminants des évolutions spatio-temporelles des retombées atmosphériques  
1234 acidifiantes et eutrophisantes en France et élaboration d'un modèle de projection. Thèse, École des Mines  
1235 de Douai, université des Sciences et Technologies de Lille.
- 1236 Pierret, M. C., Stille, P., Prunier, J., Viville, D., and Chabaux, F., 2014. Chemical and U–Sr isotopic  
1237 variations in stream and source waters of the Strengbach watershed (Vosges mountains, France), *Hydrol.*  
1238 *Earth Syst. Sci.*, 18, 3969-3985, doi:10.5194/hess-18-3969-2014
- 1239 Pierret, M.C., Cotel S., Ackerer P., Beaulieu E., Benarioumlil S., Boucher M., Boutin R., Chabaux F., Delay  
1240 F., Fournet C., Friedmann P., Fritz B., Gangloff S., Girard J.F., Legtchenko A., Viville D., Weill S. and  
1241 Probst A., 2018. The Strengbach Catchment: a multidisciplinary environmental sentry for 30 years.  
1242 *Vadose Zone Journal*. doi: 10.2136/vzj2018.04.0090
- 1243 Posch, M., Seppälä, J., Hettelingh, J. P., Johansson, M., Margni, M., & Jolliet, O., 2008. The role of  
1244 atmospheric dispersion models and ecosystem sensitivity in the determination of characterisation factors  
1245 for acidifying and eutrophying emissions in LCIA. *The International Journal of Life Cycle Assessment*,  
1246 13(6), 477.
- 1247 Preunkert, S., Legrand, M., and Wagenbach, D., 2001. Sulfate trends in a Col du Dome (French Alps) ice  
1248 core: A record of anthropogenic sulfate levels in the European midtroposphere over the twentieth century.  
1249 *Journal of Geophysical Research: Atmospheres*, 106(D23), 31991-32004.
- 1250 Probst A., Dambrine E., Viville D., Fritz B. 1990a. Influence of acid atmospheric inputs on surface water  
1251 chemistry and mineral fluxes in a declining spruce stand within a small granitic catchment (vosges  
1252 massif- France). *J. of Hydrology* 116, 101-124.
- 1253 Probst A., Massabuau J.C., Probst J.L. and Fritz B., 1990b. Acidification des eaux de surface sous  
1254 l'influence des précipitations acides : role de la vegetation et du substratum, consequences pour les  
1255 populations de truites. Le cas des ruisseaux des Vosges. *C.R. Acad. Sci. Paris* 311, 405-411
- 1256 Probst A., Viville D., Fritz B., Ambroise B., Dambrine E. 1992a. Hydrochemical budgets of a small forested  
1257 catchment exposed to acid deposition : the Strengbach catchment case study (Vosges massif, France).  
1258 *Water, Air, Soil, Pollut.* 62, 337-347.
- 1259 Probst A., Fritz B., Stille P. 1992b. Consequence of acid deposition on natural weathering processes: field  
1260 studies and modelling. In: *Water Rock Interaction* (Eds.Kharaka Y.K.and Maest A.S.)  
1261 Balkema/Rotterdam/ Brookfield, 581-584.
- 1262 Probst A., Fritz B., Viville D., 1995a. Mid-term trends in acid precipitation, streamwater chemistry and  
1263 element budgets in the Strengbach catchment (Vosges mountains, France). *Water, Air and Soil Pollution*  
1264 79:39-59.
- 1265 Probst A., Dambrine E., Viville D., Ezzahar B., Fritz B., Ambroise B. 1995b. Fonctionnement et bilan  
1266 hydrobiogéochimique du petit bassin versant forestier du Strengbach à Aubure (hautes Vosges, France).  
1267 *Ann. Géo.*, 581-582 176-182.
- 1268 Probst A., El Gh'Mari A., Aubert D., Fritz B., McNutt R. 2000. Strontium as a tracer of weathering  
1269 processes in a silicate catchment polluted by acid atmospheric inputs, Strengbach, France. *Chem. Geol.*,  
1270 170, 1-4, 203-219.
- 1271 Probst A., Obeidy C. Gaudio N., Belyazid S., Gégout J.C., Alard D., Corket E., Party J.P., Gauquelin T.,  
1272 Mansat A., Nihlgard B., Leguédois S., Sverdrup H.U., 2015. *Evaluation of plant-responses to*  
1273 *atmospheric nitrogen deposition in France using integrated soil-vegetation models*. In *W. de Vries, J-P*  
1274 *Hettelingh and M. Posch (eds):Critical loads and Dynamic Risk Assessments: Nitrogen, Acidity and*  
1275 *Metals in Terrestrial and Aquatic ecosystems, Springer, Dordrecht, Netherlands: 359-379.*
- 1276 Probst A. and Ambroise B., 2018. Disturbance and resilience of a granitic critical zone submitted to acid

1277 atmospheric influence (the Ringelbach catchment, Vosges Mountains, France): Lessons from a  
1278 hydrogeochemical survey in the nineties. *Journal of Hydrology*. DOI :10.1016/j.jhydrol.2018.11.01  
1279 Prunier, J., Chabaux, F., Stille, P., Gangloff, S., Pierret, M. C., Viville, D., and Aubert, A., 2015.  
1280 Geochemical and isotopic (Sr, U) monitoring of soil solutions from the Strengbach catchment (Vosges  
1281 mountains, France): Evidence for recent weathering evolution. *Chemical Geology*, 417, 289-305.  
1282 Read, W. G., L. Froidevaux and J. W. Waters, Microwave limb sounder measurements of stratospheric SO<sub>2</sub>  
1283 from the Mt. Pinatubo volcano (1993), *Geophys. Res. Lett.*, 20, 1299-1302.  
1284 Reinds, G. J., Posch, M., De Vries, W., Slootweg, J., and Hettelingh, J. P., 2008. Critical loads of sulphur  
1285 and nitrogen for terrestrial ecosystems in Europe and Northern Asia using different soil chemical criteria.  
1286 *Water, air, and soil pollution*, 193, 269.  
1287 Rizzetto S., Belyazid S., Gegout J.C., Nicolas M., Alard D., Corcket E., Gaudio N., Sverdrup H., Probst A.,  
1288 2016. Modelling the impact of climate change and atmospheric N deposition on French forests  
1289 biodiversity. *Env. Poll.*, 213, 1016-1027.  
1290 Rogora, M., R. Mosello, S. Arisci, M. Brizzio, A. Barbieri, R. Balestrini, P. Waldner, M. Schmitt, M. Stähli,  
1291 A. Thimonier, M. Kalina, H. Puxbaum, U. Nickus, E. Ulrich and A. Probst, 2006. An overview of  
1292 atmospheric deposition chemistry over the Alps: present status and long-term trends. *Hydrobiologia* 562,  
1293 17-40.  
1294 Rothe, A., Huber, C., Kreuzer, K., & Weis, W., 2002. Deposition and soil leaching in stands of Norway  
1295 spruce and European beech: results from the Höglwald research in comparison with other European case  
1296 studies. *Plant and soil*, 240(1), 33-45.  
1297 Schrupf M., Axmacher J.C., Zech W., Lehmann J. and Lyaruu H.V.C., 2007. Long-term effect of  
1298 rainforest disturbance on the nutrient composition of throughfall, organic layer percolate and soil solution  
1299 At Mt Kilimanjaro., *Science of the Total Environment* 376, 241-254.  
1300 Schulze E.-D., 1989. Air pollution and forest decline in a spruce stand (*Picea abies*) forest. *Science* 244, 776-  
1301 783.  
1302 Sequeira, R., 1993. On the large-scale impact of arid dust on precipitation chemistry of the continental  
1303 northern hemisphere. *Atmospheric Environment. Part A. General Topics*, 27(10), 1553-1565.  
1304 Sen, P. K., 1968. Estimates of the regression coefficient based on Kendall's tau. *Journal of the American*  
1305 *statistical association*, 63(324), 1379-1389.  
1306 Shen W., Ren H., Jenerette G.D., Hui D. and Ren H., 2013. Atmospheric deposition and canopy exchange of  
1307 anions and cations in two plantation forests under acid rain influence. *Atmospheric Environment* 64, 242-  
1308 250.  
Singh, K. P., Singh, V. K., Malik, A., Sharma, N., Murthy, R. C. and Kumar, R., 2007. Hydrochemistry of  
wet atmospheric precipitation over an urban area in Northern Indo-Gangetic Plains. *Environmental*  
*monitoring and assessment*, 131(1-3), 237.  
1309 Skeffington R.A. and Hill T.J., 2012. The effects of a changing pollution climate on throughfall deposition  
1310 and cycling in a forested area in southern England. *Science of the Total Environment*. 434, 28-38.  
1311 Smith S.J., Pitcher H. and Wigley T.M., 2001. Global and regional anthropogenic sulfure dioxides emissions.  
1312 *Global planet Change* 29, 99-119.  
1313 Smith S J, van Aardenne J, Klimont Z, Andres R, Volke A C and Delgado Arias S 2011. Anthropogenic  
1314 sulfur dioxide emissions: 1850–2005 *Atmos. Chem. Phys.* 11 1101–16  
1315 Staelens, J., De Schrijver, A., Verheyen, K., & Verhoest, N. E. (2008). Rainfall partitioning into throughfall,  
1316 stemflow, and interception within a single beech (*Fagus sylvatica* L.) canopy: influence of foliation, rain  
1317 event characteristics, and meteorology. *Hydrological Processes*, 22(1), 33-45.  
1318 SternD.I., 2006. Reversal ofb the trend in global anthropogenic sulphur emissions. *Global Environmental*  
1319 *Change*, 16, 207-220.  
1320 Sudalma, S., Purwanto, P., and Santoso, L. W., 2015. The effect of SO<sub>2</sub> and NO<sub>2</sub> from transportation and  
1321 stationary emissions sources to SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in rain water in Semarang. *Procedia Environmental*  
1322 *Sciences*, 23, 247-252.  
1323 Theil, H., 1950. A rank-invariant method of linear and polynomial regression analysis, I, II, and III, *Nederl.*  
1324 *Akad. Wetensch. Proc.*, 53, 386-92, 521-5 and 1397-41

- 1325 Thimonier, A., Dupouey, J. L., and Le Tacon, F., 2000. Recent losses of base cations from soils of *Fagus*  
1326 *sylvatica* L. stands in northeastern France. *AMBIO: A Journal of the Human Environment*, 29, 314-321.
- 1327 Thimonier, A., Schmitt, M., Waldner, P., and Rihm, B., 2005. Atmospheric deposition on Swiss long-term  
1328 forest ecosystem research (LWF) plots. *Environmental monitoring and assessment*, 104(1-3), 81-118.
- 1329 Thimonier A. Schmitt M., Waldner P. and Schleppei P., 2008. Seasonality of the Na/Cl ratio in precipitation  
1330 and implications of canopy leaching in validating chemical analyses of throughfall samples. *Atmospheric*  
1331 *Environment*, 42, 9106-9117.
- 1332 Torseth, K., Aas, W., Breivik, K., Fjæraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre, C., Solberg,  
1333 S., and Yttri, K. E., 2012. Introduction to the European Monitoring and Evaluation Programme (EMEP)  
1334 and observed atmospheric composition change during 1972–2009. *Atmospheric Chemistry and Physics*,  
1335 12, 5447-5481.
- 1336 Tu, F. H., Thornton, D. C., Bandy, A. R., Carmichael, G. R., Tang, Y., Thornhill, K. L., and Blake, D.  
1337 R., 2004. Long-range transport of sulfur dioxide in the central Pacific. *Journal of Geophysical Research:*  
1338 *Atmospheres*, 109(D15).
- 1339 Turk, T.D., Schmidt, M.G., Roberts, N.J., 2008. The influence of bigleaf maple on forest floor and mineral  
1340 properties in a coniferous forest in coastal British Columbia. *Forest Ecol. Manage.* 255, 1874–1882.
- 1341 Ulrich B., 1981. 5. Soil processes B. ULRICH, P. BENECKE, WF HARRIS. PK KHANNA & R. MAYER.  
1342 *Dynamic properties of forest ecosystems*, 23, 265.
- 1343 Ulrich B., 1983. Interaction of forest canopies with atmospheric constituents: SO<sub>2</sub>, alkali and earth alkali  
1344 cations and chloride. In: Ulrich, B., Pankrath, J. (Eds.), *Effects of Accumulation of Air Pollutants in*  
1345 *Forest Ecosystems*. Reidel, Dordrecht, pp. 33–45.
- 1346 Ulrich B., 1984. Effects of air pollution on forest ecosystems and waters: the principles demonstrated at a  
1347 case study in central Europe. *Atmosph Environ* 18, 621-628.
- 1348 Van Breemen N, Mulder J. Driscoll CT, 1983. Acidification and alkalization of soil. *Plant and Soil*  
1349 75:283-308
- 1350 Vanguelova E.I., Benham S., Pitman R., Moffat A.J., Broadmeadow M., Nisbet N., Durrant D., Barsoum N.,  
1351 Wilkinson M., Bocheureau F., Hutchings T., Broadmeadow S., Crow P., Taylor P., Durrant Houston T.,  
1352 2010. Chemical fluxes in time through forest ecosystems in the UK – Soil response to pollution recovery.  
1353 *Environmental Pollution*, 158, 1857-1869
- 1354 Vet, R., Artz, R.S., Carou, S., Shaw, M., Ro, C.-U., Aas, W., Baker, A., Bowersox, V.C., Dentener, F., Galy-  
1355 Lacaux, C., Hou, A., Pienaar, J.J., Gillett, R., Forti, M.C., Gromov, S., Hara, H., Khodzher, T., Mahowald,  
1356 N.M., Nickovic, S., Rao, P.S.P., Reid, N.W., 2014. A global assessment of precipitation chemistry and  
1357 deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus.  
1358 *Atmospheric Environment* 93: 3-100
- 1359 Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I.S.A., Tarrason, L., 2009. Evolution of NOX  
1360 emissions in Europe with focus on road transport control measures. *Atmos. Chem. Phys.* 9 (4), 1506.
- 1361 Vieno, M., Heal, M. R., Hallsworth, S., Famulari, D., Doherty, R. M., Dore, A. J., ... & Reis, S. (2014). The  
1362 role of long-range transport and domestic emissions in determining atmospheric secondary inorganic  
1363 particle concentrations across the UK. *Atmospheric Chemistry and Physics*, 14(16), 8435-8447.
- 1364 Vogt, R. D., Seip, H. M., Larssen, T., Zhao, D., Xiang, R., Xiao, J., ... & Zhao, Y. (2006). Potential  
1365 acidifying capacity of deposition: Experiences from regions with high NH<sub>4</sub><sup>+</sup> and dry deposition in China.  
1366 *Science of the Total Environment*, 367(1), 394-404.
- 1367 Viville D., Biron P., Granier A., Dambrine E. and Probst A., 1993. Interception in a mountainous declining  
1368 spruce stand in the Strengbach catchment (Vosges, France). *Journal of Hydrology.* 144, 273-282.
- 1369 Viville D., Chabaux F., Stille P., Pierret M.C., Gangloff S., 2012. Erosion and weathering fluxes in granitic  
1370 basins: The example of the Strengbach catchment (Vosges massif, eastern France). *Die Bodenkultur*  
1371 *Journal for Land Management, Food and Environment.* 64, 121-126.
- 1372 Vuorenmaa, J., Augustaitis, A., Beudert, B., Bochebeck W., Clarke, N., de Wit, H. A., Dirnböck, T., Frey J.,  
1373 Hakola H., Kleemola S., Kobler, J., Kram P., Lindroos A-J., Lundin L., Löfgren S., Marchetto A., Pecka  
1374 T., Schulte-Bisping H., Skotak K., Srybny A., Szpikowski J., Ukonmaanaho L., Ukonmaanaho L., Vana  
1375 M., Akerblom S and Forsius M., 2018. Long-term changes (1990-2015) in the atmospheric deposition and

1376 runoff water chemistry of sulphate, inorganic nitrogen and acidity for forested catchments in Europe in  
1377 relation to changes in emissions and hydrometeorological conditions. *Science of the Total Environment*  
1378 625, 1129-1145.

1379 Vuorenmaa, J., Augustaitis, A., Beudert, B., Clarke, N., de Wit, H. A., Dirnböck, T., Kobler, J., Kram P.,  
1380 Lindroos A-J., Lundin L., Löfgren S., Marchetto A., Pecka T., Schulte-Bisping H., Skotak K., Srybny A.,  
1381 Szpikowski J., Ukonmaanaho L., Vana M., Akerblom S and Forsius M., 2017. Long-term sulphate and  
1382 inorganic nitrogen mass balance budgets in European ICP Integrated Monitoring catchments (1990–  
1383 2012). *Ecological Indicators*, 76, 15-29.

1384 Vuorenmaa, J., Salonen, K., Arvola, L., Mannio, J., Rask, M., and Horppila, P., 2014. Water quality of a  
1385 small headwater lake reflects long-term variations in deposition, climate and in-lake processes.

1386 Vuorenmaa, J., 2004. Long-term changes of acidifying deposition in Finland (1973–2000). *Environmental*  
1387 *Pollution*, 128(3), 351-362.

1388 Watmough S.A. and Dillon P.J., 2003. Base cation and nitrogen budgets for seven forested catchments in  
1389 central Ontario, 1983-1999. *Forest Ecology and Management* 177, 155-177.

1390 Watmough, S. A., Aherne, J., Alewell, C., Arp, P., Bailey, S., Clair, T., and Foster, N., 2005. Sulphate,  
1391 nitrogen and base cation budgets at 21 forested catchments in Canada, the United States and Europe.  
1392 *Environmental Monitoring and Assessment*, 109(1-3), 1-36.

1393 Wilson, J. C., M. R. Stolzenburg, W. E. Clark, M. Loewenstein, G. V. Ferry, K. R. Chan and K. K. Kelly,  
1394 Stratospheric sulfate aerosol in and near the northern-hemisphere polar vortex -the morphology of the  
1395 sulfate layer, multimodal size distributions, and the effect of denitrification (1992) ,*J. Geophys. Res.*, 97  
1396 (D8), 7997-8013.

1397 Wilson E and Tiley C., 1998. Foliar uptake of wet-deposited nitrogen by Norway spruce – an experiment  
1398 using N-15. *Atmospheric Environment* 32, 513-518.

1399 Whitehead P.G., Lapworth D.J., Skeffington R.A. and Wade A., 2002. Excess nitrogen leaching and C/N  
1400 decline in the Tillingbourne catchment, southern England: INCA process modeling for current and  
1401 historic time series. *Hydrology and Earth System Sciences* 6, 455-466.

1402 Yang, X., Wang, S., Zhang, W., Li, J., and Zou, Y., 2016. Impacts of energy consumption, energy structure,  
1403 and treatment technology on SO<sub>2</sub> emissions: A multi-scale LMDI decomposition analysis in China.  
1404 *Applied energy*, 184, 714-726.

1405 Zeng G.M., Zhang G., Huang G.H., Jiang Y.M., Liu H.L., 2005. Exchange of Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> and  
1406 uptake of H<sup>+</sup> and NH<sub>4</sub><sup>+</sup> for the subtropical forest canopies influenced by acid rain in Shaoshan forest  
1407 located in Central South China. *Plant Science* 168, 259-266.

1408 Zimmermann A., and Zimmermann B., 2014. Requirements for throughfall monitoring: the roles of temporal  
1409 scale and canopy complexity. *Agricultural and forest meteorology*, 189, 125-139.

1410 Zhang, M., Wang, S., Wu, F., Yuan, X., & Zhang, Y., 2007. Chemical compositions of wet precipitation and  
1411 anthropogenic influences at a developing urban site in southeastern China. *Atmospheric Research*, 84,  
1412 311-322.

1413 Zhang X., Jiang H., Jin J., Xu X. and Zhang Q., 2012. Analysis of acid rain patterns in northeastern China  
1414 using a decision tree method. *Atmospheric Environment* 46, 590-596.

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**Supplementary materials:**

		P-catchment	P-Spruces PS	P-Beeches PB	TF-S	TF-B	S Inter	B Inter
		mm	mm	mm	mm	mm	%	%
86-87	1987	1520	1425	1592	1070	nd	25	-
87-88	1988	1631	1530	1708	1001	nd	35	-
88-89	1989	1242	1164	1300	855	nd	27	-
89-90	1990	1262	1184	1322	781	940	34	29
90-91	1991	996	934	1043	500	783	46	25
91-92	1992	1287	1207	1348	837	991	31	26
92-93	1993	1279	1200	1339	738	961	38	28
93-94	1994	1600	1501	1676	953	1234	37	26
94-95	1995	1397	1310	1463	791	1043	40	29
95-96	1996	896	841	939	487	742	42	21
96-97	1997	1271	1192	1331	855	1073	28	19
97-98	1998	1167	1094	1222	547	951	50	22
98-99	1999	1614	1514	1690	989	1344	35	20
99-00	2000	1568	1471	1642	1136	1353	23	18
00-01	2001	1598	1499	1674	1096	1283	27	23
01-02	2002	1288	1208	1349	680	1062	44	21
02-03	2003	1205	1131	1262	680	956	40	24
03-04	2004	1191	1118	1248	521	971	53	22
04-05	2005	1331	1248	1394	945	1248	24	10
05-06	2006	1700	1594	1780	1052	1232	34	31
06-07	2007	1713	1607	1794	1027	1262	36	30
07-08	2008	1452	1362	1521	865	1108	37	27
08-09	2009	1192	1118	1248	761	874	32	30
09-10	2010	1441	1352	1510	932	1020	31	32
10-11	2011	1313	1232	1375	857	985	30	28
11-12	2012	1407	1320	1474	915	1018	31	31
<b>Average</b>		<b>1368</b>	<b>1284</b>	<b>1433</b>	<b>837</b>	<b>1068</b>	<b>35</b>	<b>25</b>
STD		209	204	228	194	177	8	5
variation %		15	16	16	23	17	23	21

1423 *Table 1: Total amount of annual open field precipitation at the catchment scale (P-catchment), at*  
1424 *the spruce plot (P-Spruces) and at the beech plot (P-Beeches), and throughfall amounts under*  
1425 *spruces (TF-S) and under beeches (TF-B) in mm.yr<sup>-1</sup>, for the Strengbach catchment between 1986*  
1426 *and 2012. (-) means no data. S- and B-Inter correspond to the interception amounts under spruce*  
1427 *(PS – TF-S) / PS x 100 and beech (PB - TF-B) / PB x 100 stands, respectively. The average and*  
1428 *standard deviation of the annual value are given, as well as the variation in % (STD/average x*  
1429 *100). The hydrological year (1<sup>st</sup> October to 30<sup>th</sup> September) was considered.*

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	pH	Cond	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	N-NH <sub>4</sub>	Na	K	Mg	Ca	Cl	N-NO <sub>3</sub>	N Tot	S-SO <sub>4</sub>	
<b>OFP</b>		mS/cm	μmol/l	μmol/l	μmol/l	μmol/l	μmol/l	μmol/l	μmol/l	μmol/l	kg ha-1a-1									
1987	4.41	20.3	28.8	11.7	3.3	2.5	7.2	14.0	30.1	26.7	3.6	3.9	1.8	0.9	4.0	7.4	23.6	9.0	10.6	
1988	4.53	21.1	33.9	13.3	4.0	3.1	12.2	16.8	34.5	25.5	4.6	4.9	1.9	1.0	6.0	9.6	29.9	11.4	10.8	
1989	4.50	22.5	39.3	12.0	4.4	2.9	9.8	15.6	37.6	26.1	4.7	3.2	1.9	0.8	4.5	6.3	25.7	10.5	9.4	
1990	4.50	20.1	44.4	15.6	4.2	2.9	8.5	19.8	36.3	25.4	4.2	3.6	1.7	0.7	2.9	7.1	20.1	8.7	7.5	
1991	4.45	27.8	55.7	13.8	4.4	3.1	10.5	19.1	48.8	31.6	4.0	2.5	1.3	0.6	3.2	5.2	21.1	8.8	6.8	
1992	4.65	18.4	43.7	13.2	8.7	2.7	6.8	23.2	29.9	22.6	5.1	3.6	3.0	0.7	2.5	7.6	20.5	9.7	8.6	
1993	4.74	20.0	64.3	13.2	10.5	3.4	9.4	21.7	34.9	26.1	6.7	3.2	4.5	0.8	3.6	9.5	20.8	11.4	8.1	
1994	4.84	23.1	78.6	19.0	9.3	3.8	12.6	17.5	29.8	28.3	7.7	5.0	3.0	0.9	3.8	8.2	23.0	12.9	9.0	
1995	4.75	17.2	34.6	11.8	5.6	2.6	5.8	14.8	26.8	18.8	4.5	4.4	2.9	0.9	2.8	8.4	21.7	9.4	8.1	
1996	4.53	28.3	67.9	14.4	5.8	2.6	8.9	17.0	49.4	31.8	4.7	1.9	1.5	0.4	2.2	3.4	19.0	9.0	6.3	
1997	4.91	13.9	34.8	14.7	5.8	2.5	9.0	17.5	24.2	16.9	3.7	4.1	2.5	0.7	3.6	7.5	15.0	7.0	5.7	
1998	4.89	16.4	50.6	13.0	6.6	2.7	7.6	14.9	31.0	18.1	4.3	3.0	2.1	0.6	3.2	5.3	15.9	7.9	4.8	
1999	4.93	14.9	28.7	14.0	3.6	2.4	8.0	16.1	27.8	15.3	4.7	4.9	2.0	0.8	3.8	8.6	23.1	9.9	6.5	
2000	4.87	14.6	36.6	13.7	5.3	2.7	8.3	15.3	30.8	15.2	5.0	5.0	3.0	0.9	4.3	8.7	25.2	10.7	6.8	
2001	4.94	13.0	34.4	8.6	3.9	2.0	7.0	9.5	26.9	12.3	4.9	3.0	1.9	0.7	4.1	5.1	24.2	10.4	5.6	
2002	4.97	12.9	31.7	13.3	3.7	2.2	6.1	13.9	27.8	14.3	3.8	3.6	1.5	0.6	2.7	5.8	19.5	8.2	5.1	
2003	5.04	14.1	51.5	12.5	10.2	2.5	6.9	13.2	28.7	13.0	3.9	2.8	2.6	0.5	2.0	4.8	14.9	7.2	3.4	
2004	4.99	15.9	52.2	15.0	7.7	3.0	7.8	16.7	36.2	15.8	4.8	3.3	2.7	0.6	2.4	5.7	19.8	9.3	4.3	
2005	4.82	14.2	36.8	15.0	3.5	2.0	5.2	15.5	32.0	14.2	5.0	4.6	1.8	0.7	2.9	7.3	23.9	10.4	5.8	
2006	4.79	15.3	40.7	10.2	5.2	2.0	5.2	12.0	33.4	14.2	5.2	2.8	2.1	0.5	2.3	5.1	24.0	10.6	5.2	
2007	5.15	10.4	29.8	9.8	4.3	2.6	6.9	11.6	22.8	10.8	4.5	2.9	2.3	0.9	3.8	5.4	19.3	8.9	4.8	
2008	5.04	10.7	26.9	12.0	3.7	2.6	6.0	13.8	23.4	9.9	3.7	3.6	1.8	0.8	3.0	6.4	18.8	8.0	4.1	
2009	5.08	12.4	37.2	9.4	3.9	4.5	7.7	11.1	29.2	12.2	3.6	2.2	1.3	1.1	2.4	4.0	16.4	7.3	3.4	
2010	5.14	12.0	35.7	8.6	3.8	3.0	8.8	10.9	28.4	11.4	4.6	2.0	1.6	0.8	3.9	4.2	20.3	9.2	4.3	
2011	5.24	10.5	43.1	6.6	5.9	3.8	7.9	9.3	25.5	10.4	4.1	1.5	2.1	1.0	3.3	3.5	15.7	7.6	3.2	
2012	5.18	10.8	39.9	11.3	5.0	3.9	7.8	13.9	24.5	9.6	4.1	2.9	2.1	1.1	3.4	5.9	13.7	7.1	3.0	
<b>Average</b>	<b>4.78</b>	<b>16.4</b>	<b>42.0</b>	<b>12.3</b>	<b>5.3</b>	<b>2.8</b>	<b>7.9</b>	<b>15.0</b>	<b>31.2</b>	<b>18.0</b>	<b>5.9</b>	<b>3.4</b>	<b>2.2</b>	<b>0.8</b>	<b>3.3</b>	<b>6.4</b>	<b>20.6</b>	<b>9.2</b>	<b>6.2</b>	
STD	0.69	12.09	48.06	10.3	7.5	2.0	8.4	12.3	24.8	15.4	1.2	1.0	0.7	0.2	0.9	1.8	3.9	1.5	2.3	
variation (%)	14	74	114	84	141	72	107	82	79	86	19.8	29.2	32.0	23.1	26.5	28.2	18.9	16.2	36.3	
Max	5.24	86.0	519.0	75.0	85.0	25.0	63.0	95.0	192.0	121.0	9.9	5.0	4.5	1.1	6.0	9.6	29.9	12.9	10.8	
Min	4.41	2.5	0.1	0.1	0.1	0.1	0.1	1.0	0.1	1.0	4.6	1.5	1.3	0.4	2.0	3.4	13.7	7.0	3.0	
<b>TF-S</b>	<b>pH</b>	<b>Cond</b>	<b>NH4</b>	<b>Na</b>	<b>K</b>	<b>Mg</b>	<b>Ca</b>	<b>Cl</b>	<b>NO3</b>	<b>SO4</b>	<b>NH4</b>	<b>Na</b>	<b>K</b>	<b>Mg</b>	<b>Ca</b>	<b>Cl</b>	<b>NO3</b>	<b>N Tot</b>	<b>S</b>	
1987	4.24	47.2	42.0	55.7	60.3	13.9	40.0	79.0	79.8	94.1	5.5	13.8	24.3	3.9	16.7	23.9	45.0	14.5	27.9	



1988	4.20	53.2	46.0	45.8	56.4	11.9	47.2	63.3	83.5	90.0	7.2	9.9	18.0	2.5	16.2	21.1	53.3	17.6	25.3
1989	4.07	66.3	76.8	53.5	68.8	15.6	51.1	80.3	143.4	102.5	6.4	9.5	22.1	2.6	14.4	20.1	51.5	16.6	24.7
1990	4.12	67.8	98.3	59.9	68.5	15.1	52.3	83.5	155.0	94.1	9.7	10.7	19.2	2.6	14.9	22.4	67.5	22.8	21.7
1991	3.98	97.9	115.3	49.8	79.2	18.8	69.3	71.1	184.0	145.8	5.6	5.1	13.3	1.8	11.1	12.3	46.6	14.9	17.0
1992	4.38	48.6	76.6	35.8	75.0	10.8	32.6	56.7	85.4	69.0	7.7	6.9	17.4	1.8	9.0	14.8	39.8	15.0	18.6
1993	4.18	42.5	66.2	54.7	72.2	15.7	46.8	71.8	126.5	94.7	4.4	7.3	17.6	2.0	10.3	15.0	41.3	12.8	17.1
1994	4.29	49.3	65.3	38.0	52.2	9.3	31.8	49.0	91.8	72.9	7.7	8.4	18.3	2.0	11.4	16.5	49.1	17.1	19.6
1995	4.45	55.4	47.4	36.6	86.2	11.2	33.0	55.3	100.2	61.4	3.7	6.7	20.2	1.8	8.0	14.5	34.2	10.6	12.7
1996	4.24	49.5	176.6	54.0	94.6	21.0	73.1	69.8	221.5	141.7	7.6	4.4	15.9	1.8	10.4	9.2	46.9	16.5	15.7
1997	4.59	45.3	85.9	82.8	76.7	17.2	46.2	98.1	127.5	81.6	7.3	14.5	22.3	3.0	13.9	26.4	53.0	17.6	18.7
1998	4.68	57.2	80.5	68.7	106.1	17.3	50.7	87.7	139.7	80.3	5.5	7.6	19.5	2.0	10.0	15.0	42.1	13.8	11.5
1999	4.97	45.7	72.9	73.2	81.5	17.2	47.8	90.1	105.0	53.8	6.1	12.4	24.8	2.8	11.8	24.8	44.4	14.7	13.3
2000	4.79	42.0	83.0	45.0	82.5	13.2	37.0	63.5	113.6	46.7	10.6	10.0	32.8	3.1	15.0	22.4	66.3	23.2	13.6
2001	4.90	33.6	22.6	48.4	79.2	10.8	30.8	64.4	74.1	34.4	3.6	10.4	29.5	2.5	12.1	21.8	47.2	13.5	10.3
2002	4.97	31.5	37.1	36.2	80.4	9.3	26.2	51.4	85.2	29.5	2.9	6.8	20.1	1.6	7.1	14.3	35.3	10.3	6.8
2003	5.07	53.9	136.1	50.8	140.3	15.3	41.7	78.4	132.9	43.9	6.3	6.6	23.0	1.7	8.1	13.9	39.3	13.8	7.9
2004	4.83	56.2	92.0	89.8	103.5	19.7	51.2	117.0	155.7	54.2	8.0	13.1	27.2	3.1	13.3	26.6	63.3	20.5	10.8
2005	4.82	35.5	38.0	49.2	85.8	11.5	29.2	54.5	70.8	48.8	4.3	9.7	29.6	2.4	10.2	16.2	34.7	11.2	14.5
2006	4.92	56.0	80.8	62.0	118.5	15.3	42.8	81.7	132.3	50.3	11.1	13.8	42.5	3.1	14.1	27.1	55.1	21.1	14.3
2007	4.94	39.3	63.6	71.0	70.0	13.0	32.7	89.4	97.0	36.4	8.1	13.4	25.6	2.7	11.5	26.0	52.2	18.1	10.0
2008	4.86	36.1	37.0	65.2	66.8	13.7	31.8	78.0	90.5	28.4	5.2	13.8	23.0	3.2	12.4	24.5	56.3	16.7	9.0
2009	4.86	42.5	77.9	51.2	68.1	14.3	39.9	55.1	150.9	31.3	6.7	8.0	15.5	2.2	8.8	13.1	55.4	17.7	6.4
2010	4.54	45.1	71.7	62.9	70.2	14.6	32.9	72.7	123.1	27.7	7.5	12.3	22.8	2.9	10.7	21.3	58.8	19.1	7.4
2011	4.89	41.8	113.6	40.4	74.5	12.3	27.1	55.6	142.9	28.0	8.3	6.4	19.9	2.0	7.2	13.2	52.6	18.4	5.4
2012	5.26	39.1	115.9	51.8	58.6	16.6	34.3	55.8	187.0	22.7	9.8	10.3	18.2	2.9	9.3	18.0	73.3	24.2	4.9
<b>Average</b>	<b>4.51</b>	<b>47.4</b>	<b>77.6</b>	<b>55.7</b>	<b>80.1</b>	<b>14.3</b>	<b>40.7</b>	<b>71.9</b>	<b>122.9</b>	<b>59.5</b>	<b>6.8</b>	<b>9.7</b>	<b>22.4</b>	<b>2.5</b>	<b>11.5</b>	<b>19.0</b>	<b>50.2</b>	<b>16.6</b>	<b>14.0</b>
STD	0.66	34.4	109.0	61.2	63.6	14.1	40.8	70.4	146.4	65.0	2.1	3.0	6.2	0.6	2.7	5.3	10.3	3.7	6.4
variation (%)	15	73	140	110	79	99	100	98	119	109	31.4	30.9	27.7	23.6	23.8	27.8	20.5	22.5	45.3
Max	7.05	250.0	900.0	959.4	595.0	155.9	320.0	1056.9	1950.0	505.5	11.1	14.5	42.5	3.9	16.7	27.1	73.3	24.2	27.9
Min	3.62	6.0	1.0	5.0	2.0	1.0	3.0	6.0	0.1	4.0	2.9	4.4	13.3	1.6	7.1	9.2	34.2	10.3	4.9
<b>TF-B</b>	<b>pH</b>	<b>Cond</b>	<b>NH4</b>	<b>Na</b>	<b>K</b>	<b>Mg</b>	<b>Ca</b>	<b>Cl</b>	<b>NO3</b>	<b>SO4</b>	<b>NH4</b>	<b>Na</b>	<b>K</b>	<b>Mg</b>	<b>Ca</b>	<b>Cl</b>	<b>NO3</b>	<b>N Tot</b>	<b>S</b>
1991	4.38	53.4	93.0	26.9	107.6	12.5	34.6	46.4	101.9	65.3	8.2	4.4	30.2	2.0	8.7	11.4	41.9	15.9	14.8
1992	4.69	32.7	45.8	29.3	89.4	6.1	14.8	38.6	44.9	42.5	6.8	7.4	30.6	1.4	5.0	14.4	28.0	11.6	14.8
1993	4.76	28.8	38.4	22.9	77.7	7.7	16.3	30.4	53.7	40.2	3.6	5.0	30.7	1.3	4.6	10.8	21.3	7.6	10.1
1994	4.71	33.3	41.7	25.2	84.9	8.0	18.9	30.7	49.2	39.0	5.7	7.9	28.9	1.9	6.9	14.7	31.8	11.6	13.5
1995	5.14	30.5	27.4	22.2	114.4	6.5	12.7	53.6	30.0	28.0	3.8	6.0	32.9	1.6	5.0	15.0	17.8	6.9	9.1
1996	4.50	52.0	102.3	23.7	78.3	7.4	18.7	31.8	79.6	53.7	9.7	3.2	24.0	1.3	4.9	6.7	26.3	13.5	10.5

1997	4.87	27.6	29.6	50.7	53.5	9.0	18.6	62.4	41.7	32.5	3.8	12.2	20.9	2.1	6.6	23.5	24.8	8.5	10.0
1998	4.73	29.0	36.0	39.6	46.5	9.0	22.9	44.9	42.3	35.2	3.7	7.7	15.8	1.7	7.2	13.7	20.8	7.5	8.6
1999	4.83	25.3	43.8	30.9	46.4	6.1	13.1	36.2	50.4	27.8	5.3	9.7	19.2	1.6	4.5	17.5	29.4	10.8	9.5
2000	4.88	29.4	62.7	34.8	66.3	8.1	17.5	41.2	57.5	29.2	9.1	9.0	28.3	2.1	7.1	16.8	35.4	15.1	10.0
2001	5.01	20.8	23.2	20.9	60.1	4.6	12.4	24.0	41.0	20.3	4.4	6.8	31.3	1.5	6.7	12.0	35.5	11.4	8.8
2002	5.17	22.0	31.6	29.3	75.6	6.9	11.3	32.8	33.7	20.5	4.2	6.5	24.3	1.5	4.2	10.9	20.2	7.8	6.1
2003	5.24	30.8	83.5	29.4	105.8	8.1	13.8	33.0	44.1	26.2	5.1	5.7	33.3	1.1	3.1	10.2	17.4	7.9	5.7
2004	4.94	34.2	30.9	40.1	152.9	9.1	12.9	49.7	35.4	24.4	2.7	7.4	55.5	1.8	4.1	14.7	16.8	5.9	6.3
2005	5.02	24.1	44.4	32.0	76.0	5.6	9.6	33.6	42.7	26.9	6.5	8.8	37.4	1.6	4.4	14.1	27.6	11.3	9.8
2006	4.89	24.8	36.7	22.6	87.4	5.7	10.9	25.4	38.1	21.9	5.6	5.5	29.3	1.3	3.8	9.4	26.5	10.3	7.2
2007	5.24	23.4	32.0	32.2	95.0	6.2	9.0	39.1	22.6	18.3	5.4	8.0	39.7	1.7	4.1	14.6	17.1	8.1	6.8
2008	5.15	19.9	19.8	30.3	71.8	5.8	9.5	34.3	28.0	15.8	2.8	8.4	36.3	1.6	4.2	14.8	19.5	6.6	6.2
2009	5.07	27.4	38.4	23.9	115.4	6.7	9.6	27.9	42.0	18.9	3.9	4.2	28.0	1.3	2.6	7.5	18.7	7.2	4.1
2010	5.25	28.3	50.0	27.9	119.3	7.1	13.0	35.3	69.7	19.6	5.2	5.3	42.2	1.2	3.5	10.0	28.0	10.4	5.4
2011	5.21	27.7	41.5	19.7	155.2	5.7	5.3	25.8	30.4	15.4	4.1	3.6	43.3	1.1	1.7	7.3	15.9	6.8	4.2
2012	5.42	24.6	71.9	25.5	83.1	3.8	6.1	32.2	36.9	15.2	7.3	5.9	32.7	0.8	1.7	11.6	15.4	9.1	3.8
<b>Average</b>	<b>5.56</b>	<b>28.9</b>	<b>45.6</b>	<b>29.3</b>	<b>89.1</b>	<b>7.0</b>	<b>13.6</b>	<b>36.5</b>	<b>45.1</b>	<b>27.7</b>	<b>5.3</b>	<b>6.8</b>	<b>31.6</b>	<b>1.5</b>	<b>4.8</b>	<b>12.8</b>	<b>24.4</b>	<b>9.6</b>	<b>8.4</b>
STD	0.84	23.6	76.1	32.8	124.4	7.4	17.2	47.1	57.4	25.5	1.9	2.2	8.8	0.3	1.8	3.8	7.3	2.8	3.2
variation (%)	15	82	140	141	142	143	144	145	146	147	36.5	32.1	27.8	22.3	38.2	30.0	30.1	28.9	38.1
Max	7.45	146.0	784.0	540.0	1060.0	60.0	161.0	744.0	695.0	220.0	9.7	12.2	55.5	2.1	8.7	23.5	41.9	15.9	14.8
Min	3.74	4.1	1.0	1.0	2.0	0.5	0.5	0.5	0.1	0.1	2.7	3.2	15.8	0.8	1.7	6.7	15.4	5.9	3.8

Table 2: Average annual values for pH (calculated on the basis of the average protons), conductivity and elemental concentrations of  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  for open field precipitation (OFP), throughfall under spruce (TF-S) and throughfall under beech (TF-B) for each hydrological year of the 1986-2012 period in the Strengbach catchment. The averages, standard deviations and deviations (%) have been calculated with the entire dataset (weekly and bi-weekly values). The annual fluxes have been calculated as described in 3.3. The statistical parameters have been determined based on the annual values. The Tot flux corresponded to the sum of nitrogen from both  $\text{NO}_3^-$  and  $\text{NH}_4^+$ .