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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

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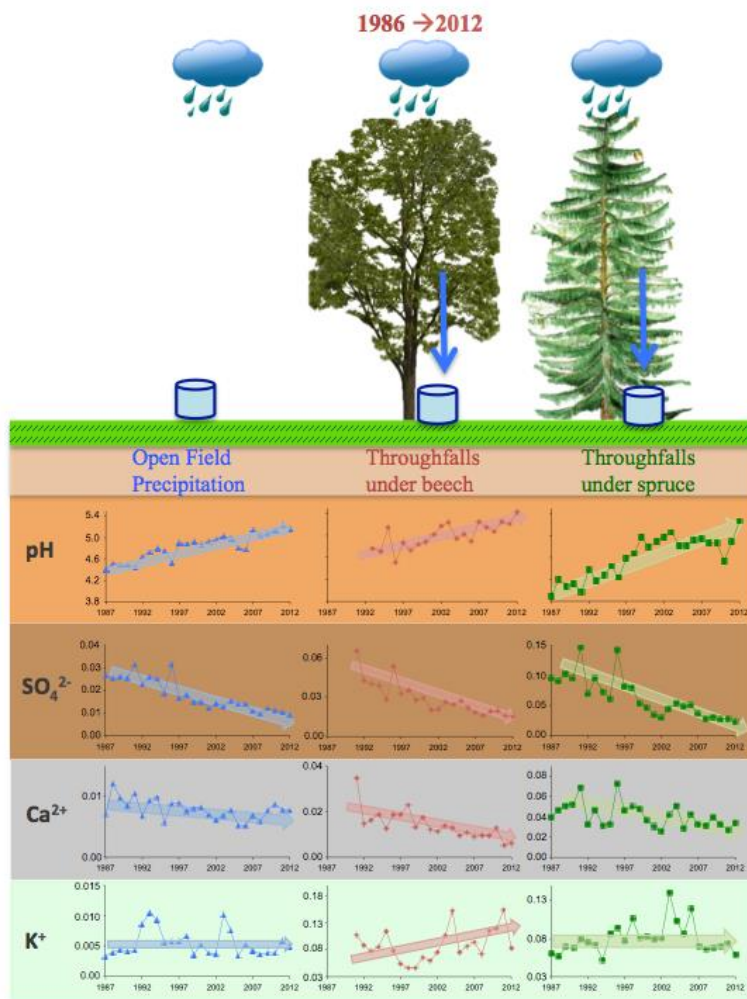
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17

18 **Graphical Abstract**

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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, SO_4^{2-} , Cl^- ,
29 NO_3^- , Ca^{2+} , Mg^{2+} , and K^+). Significant decreases in the concentrations and fluxes of several ions
30 were observed (H^+ and SO_4^{2-} , Cl^- , and Ca^{2+}) in open field precipitation and throughfalls. The regular
31 and strong decrease in protons and sulfate followed the decreases in anthropogenic SO_2 and NO_x
32 (proton precursors) since the 1980s. The decrease in 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⁻¹
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 SO₂ 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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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 (SO₂) and nitrogen oxide (NO_x) are the major sources of acid compounds in the
93 atmosphere contributing to acid precipitation. Anthropogenic SO₂ originates mainly from coal and
94 petroleum as energy sources (Smith et al., 2001; Sudalma et al., 2015). At the global scale, SO₂
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, SO₂ 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_x 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 SO₂, NO_x 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_x
107 emissions have almost doubled (70 Gt/yr in 1970 to 120 Gt/yr in 2005; EDGAR - July 2010).

108 NH₃ emission, mainly due to agricultural activities, globally still increased until now at a world
109 scale. In France, the annual NH₃ 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 SO₂ 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_x and SO₂ 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

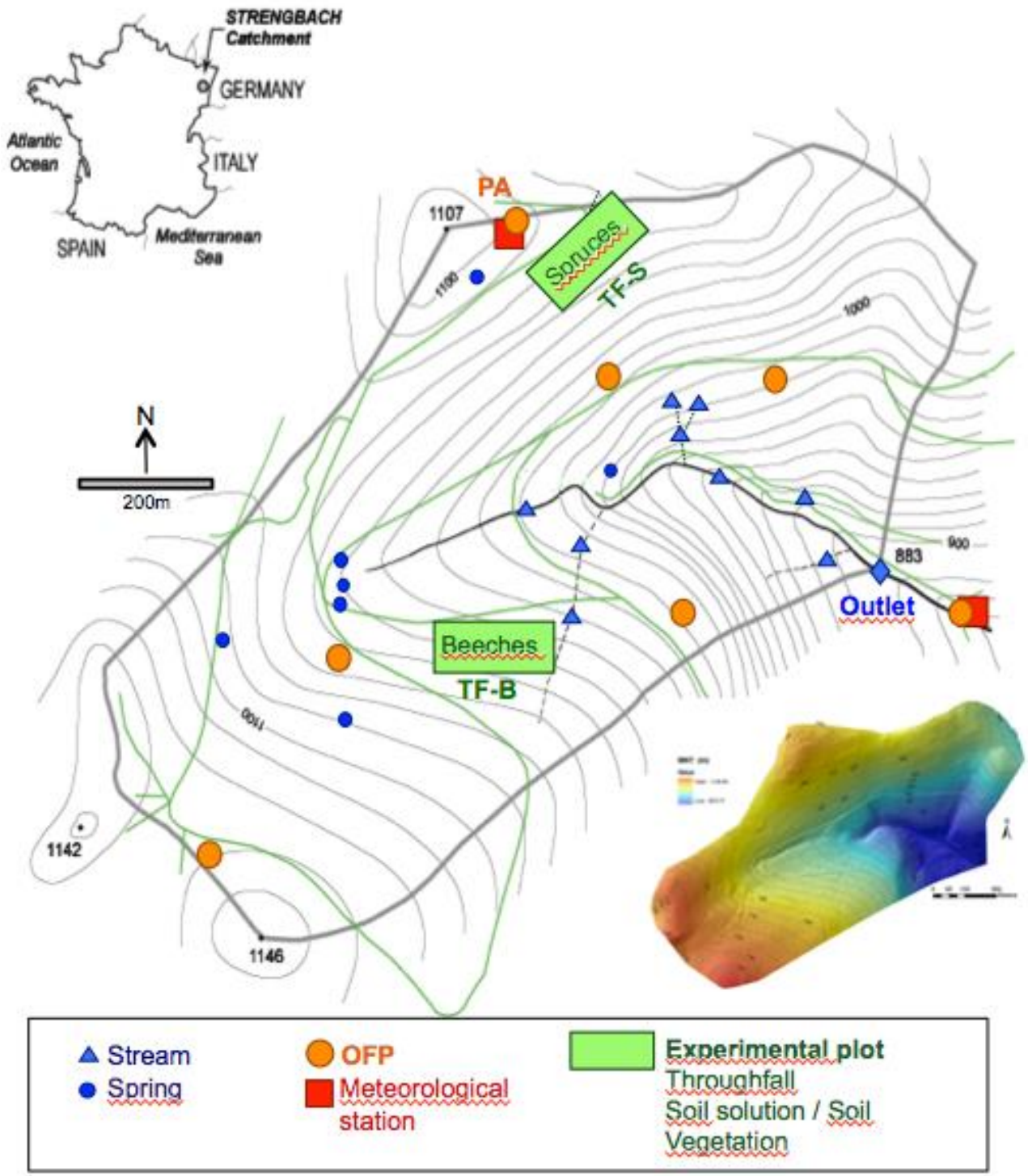
169 forest decline (Probst et al., 1990a; 1992a, b, Dambrine et al., 1991). The Vosges Mountains in
170 northeastern France are one of the areas in the country most sensitive to acid precipitation (Probst et
171 al., 1990b, 1992a, 1995a, Pascaud et al., 2016).

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⁻¹km⁻²) 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 km², 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 μm 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. NH_4^+ , Cl^- , NO_3^- and SO_4^{2-} were measured by automatic colorimetry
257 until 1990 and the 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 N-NO_3^- and 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^{th} and l^{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**

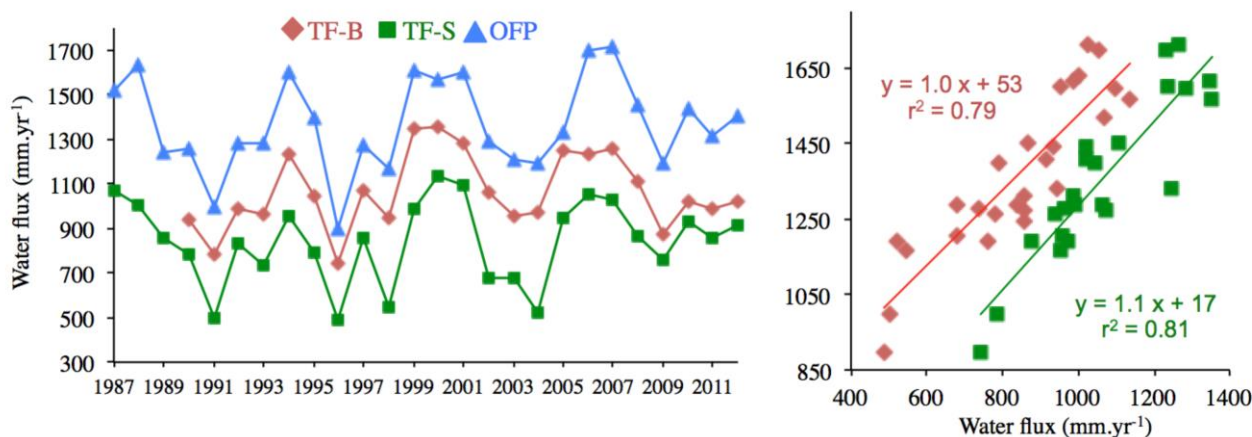
302 **4.1. Water fluxes**

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 (SO_4^{2-} , Cl^- , NO_3^- , Ca^{2+} , Mg^{2+} , K^+ , and 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 X_{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* X_{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 K^+ , Mg^{2+} , Ca^{2+} , Cl^- and 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 SO_4 , compared with the
370 studies noted above.

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

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 SO₄. 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, SO₄²⁻, and
 404 Ca²⁺ 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 ₄	Na	K	Mg	Ca	Cl	NO ₃	SO ₄	pH	H+
OFP	tau	-0.03	-0.12	-0.10	0.06	-0.05	-0.17	-0.11	-0.42	0.35	-0.37
	p	0.44	<0.01	<0.01	0.12	0.19	<0.01	<0.01	<0.01	<0.01	<0.01
TF-S	tau	0.04	0.06	0.04	0.03	-0.13	-0.04	0.02	-0.47	0.49	-0.51
	p	0.3	0.13	0.29	0.48	<0.01	0.32	0.65	<0.01	<0.01	<0.01
TF-B	tau	-0.09	-0.04	0.07	-0.15	-0.32	-0.1	-0.14	-0.42	0.30	-0.30
	p	0.03	0.35	0.12	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Theil Sen slope (mmol/year)											
OFP		0	-1.04E-04	0	0	0	-1.83E-04	-2.45E-04	-5.39E-04	3.37E-02	-7.1E-07
TF-S		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
TF-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

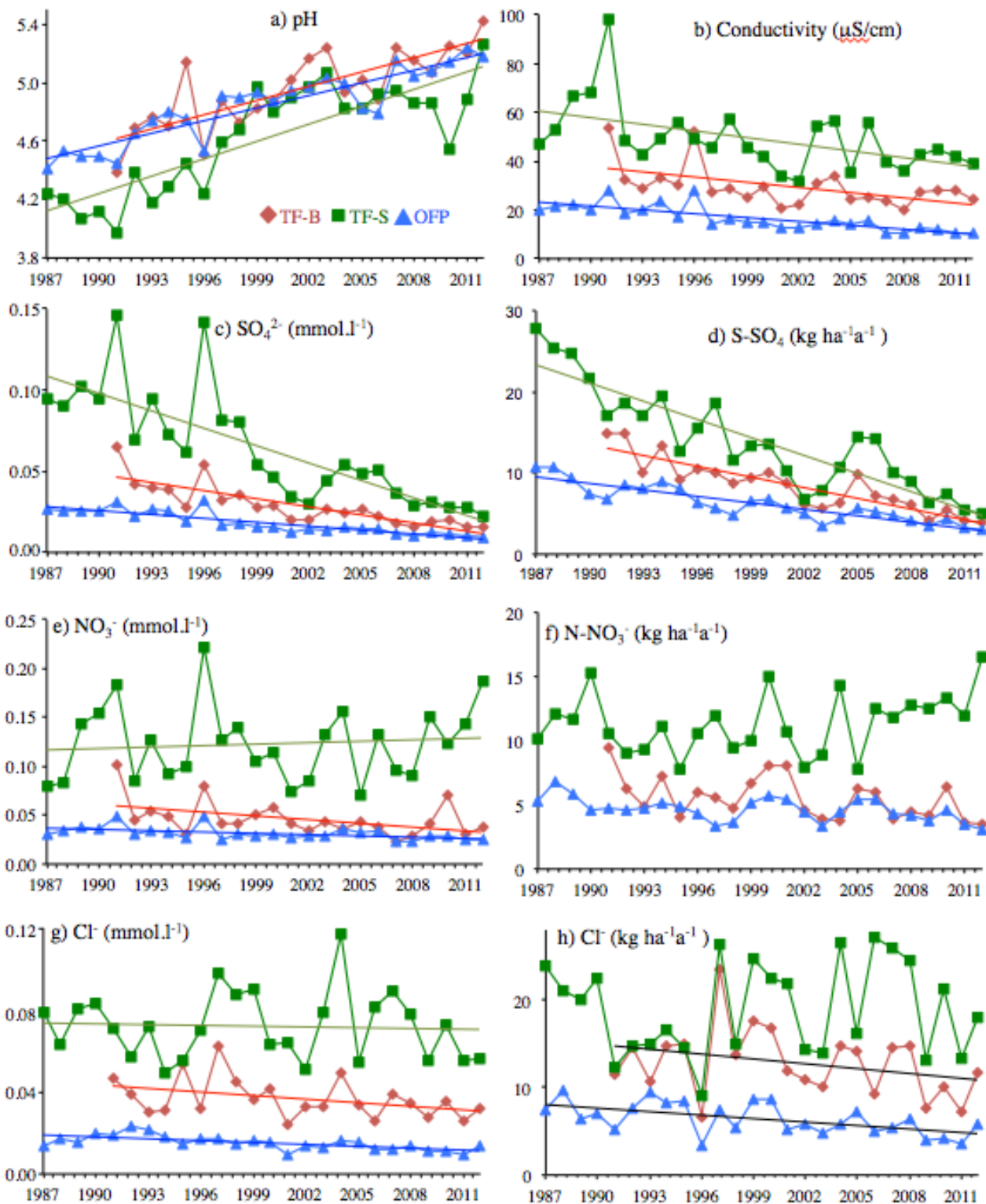
410 *Table 2: Results of the Seasonal Kendal Test (SKT) and the Teil Sen slope obtained for different*
411 *chemical elements with the 25 years data set of open field precipitation (OFP), spruce-throughfall*
412 *(TF-S) and beech-throughfall (TF-B).*

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.

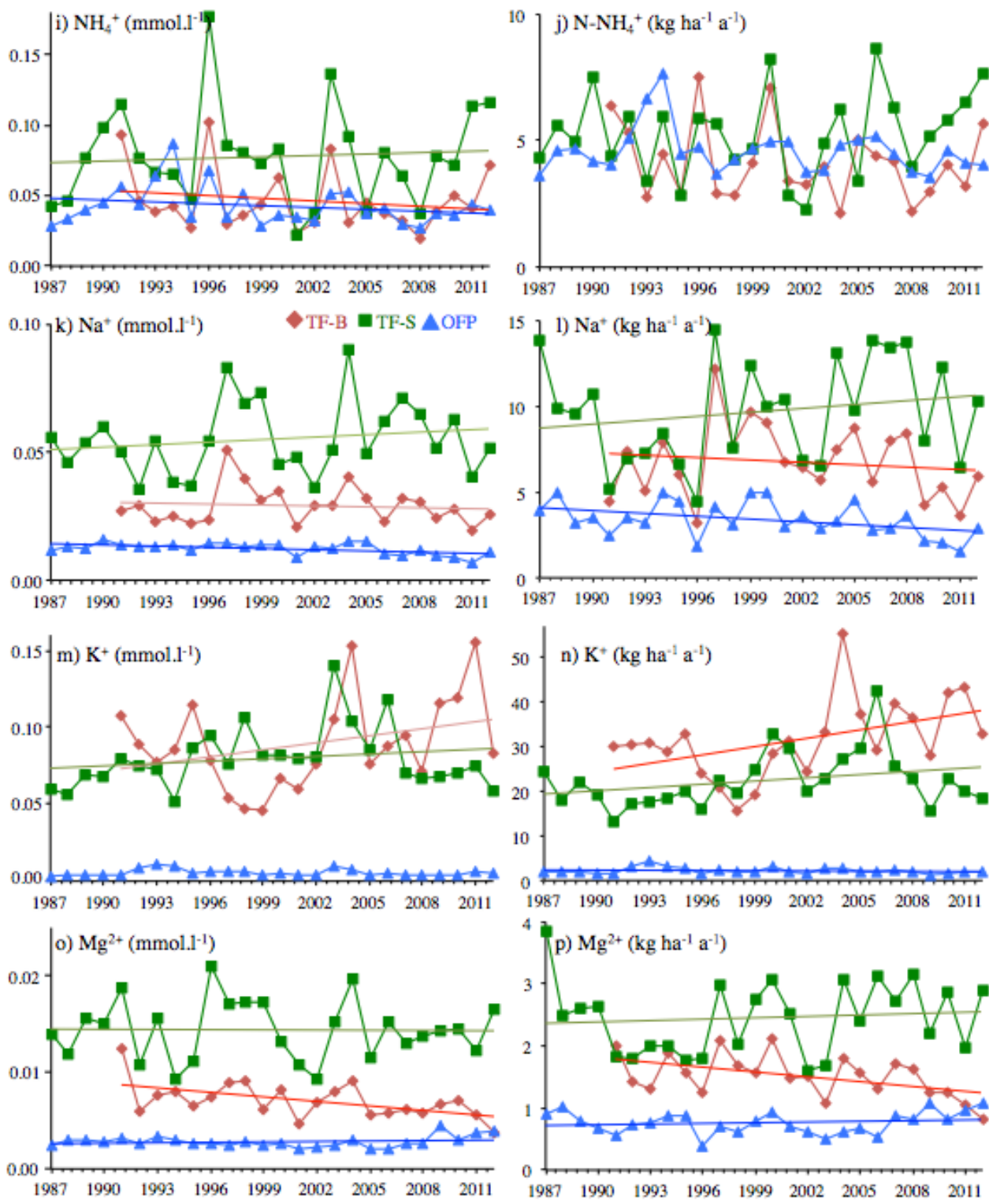
419 The mean annual SO₄²⁻ concentrations decreased from 27 to 9, 65 to 15 and 94 to 23 μmol l⁻¹ in
420 open field precipitation and throughfalls under beech and spruce, respectively, during the period
421 (Fig. 3; Table 2, Supplementary materials). The Theil-Sen mean slopes suggested reductions of 0.5,
422 1.1 and 2.2 10⁻³ mmol l⁻¹yr⁻¹ 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⁻¹a⁻¹ 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.

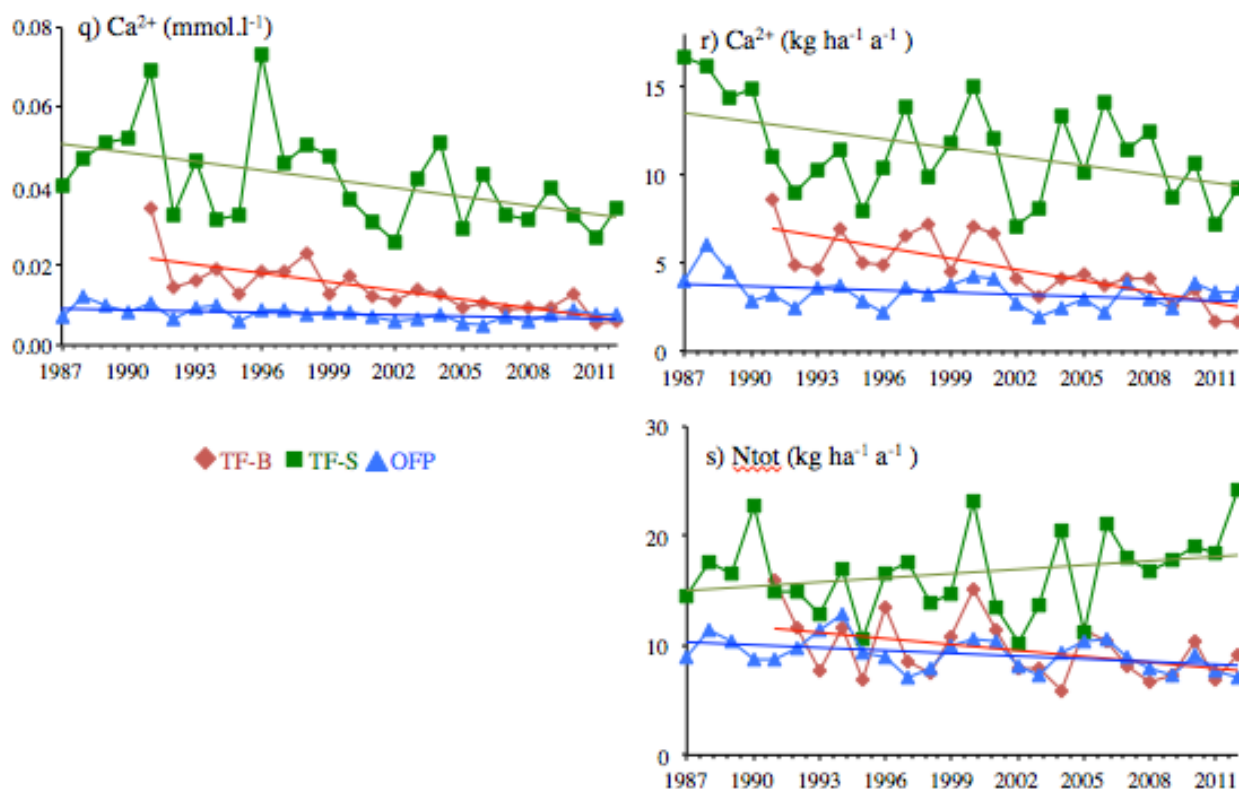
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429

430





432
 433 *Fig. 3: Evolution of the mean annual a) pH, b) conductivity ($\mu\text{S cm}^{-1}$), c) concentration of SO_4^{2-} in*
 434 *mmoles. l^{-1} , d) fluxes ($\text{kg ha}^{-1} \text{a}^{-1}$) of S- SO_4 , e) concentration of NO_3^- in mmoles. l^{-1} , f) fluxes (kg ha^{-1}*
 435 *a^{-1}) of N- NO_3 , g) concentration of Cl^- in mmoles. l^{-1} , h) fluxes ($\text{kg ha}^{-1} \text{a}^{-1}$) of Cl , i) concentration of*
 436 *NH_4^+ in mmoles. l^{-1} , j) fluxes ($\text{kg ha}^{-1} \text{a}^{-1}$) of N- NH_4 , k) concentration of Na^+ in mmoles. l^{-1} , l) fluxes*
 437 *($\text{kg ha}^{-1} \text{a}^{-1}$) of Na, m) concentration of K^+ in mmoles. l^{-1} , n) fluxes ($\text{kg ha}^{-1} \text{a}^{-1}$) of K, o)*
 438 *concentration of Mg^{2+} in mmoles. l^{-1} , p) fluxes ($\text{kg ha}^{-1} \text{a}^{-1}$) of Mg, q) concentration of Ca^{2+} in*
 439 *mmoles. l^{-1} , r) fluxes ($\text{kg ha}^{-1} \text{a}^{-1}$) of Ca, and s) fluxes ($\text{kg ha}^{-1} \text{a}^{-1}$) of Ntot 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, 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_{tot} fluxes ranged from 5.9 kg.ha⁻¹a⁻¹ (TF-B in 2004) to 24.2 kg.ha⁻¹a⁻¹ (TF-S in
451 2012) with the highest values systematically for TF-S (Table 2, Supplementary materials).
452 Concerning base cations other than Ca²⁺, concentrations decreased significantly for Na⁺ and K⁺
453 only in OFP and for Mg²⁺ in TF-B, with SKT p<0.01 (Table 2).
454 The highest cation fluxes in OFP were for Na⁺ and Ca²⁺ (3.4 and 3.3 kg.ha⁻¹a⁻¹, respectively, on
455 average for the 1986-2012 period), whereas the highest cation fluxes were for K⁺ in throughfall
456 (22.4 and 31.6 kg.ha⁻¹a⁻¹, 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 NH₄⁺ and to 20-fold for K⁺ (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⁺ (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⁺ (Fig. 3).

469

470 4.4. Correlations between chemical composition and fluxes

471 4.4.1. Relationship between elements

472

	NH₄	Na	K	Mg	Ca	H	Cl	NO₃	SO₄
	<i>vs SO₄</i>	<i>vs SO₄</i>	<i>vs SO₄</i>	<i>vs SO₄</i>	<i>vs SO₄</i>	<i>vs SO₄</i>	<i>vs SO₄</i>	<i>vs SO₄</i>	<i>vs SO₄</i>
OFP	0.65	0.28	0.26	0.39	0.48	0.62	0.31	0.82	1
TF-S	0.59	0.49	0.43	0.70	0.77	0.60	0.47	0.58	1
TF-B	0.59	0.38	0.16	0.63	0.63	0.63	0.33	0.68	1
	<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>
OFP	0.18	0.92	0.16	0.49	0.16	0.24	1	0.27	0.31
TF-S	0.34	0.95	0.45	0.76	0.61	0.11	1	0.40	0.47
TF-B	0.14	0.90	0.23	0.49	0.31	0.20	1	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>
OFP	0.42	0.13	0.33	0.55	1	-0.04	0.16	0.49	0.48
TF-S	0.68	0.61	0.65	0.91	1	0.37	0.61	0.81	0.77
TF-B	0.46	0.35	0.10	0.81	1	0.17	0.31	0.67	0.63
	<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>
OFP	0.07	0.25	-0.20	0.02	-0.04	1	0.24	0.54	0.62
TF-S	0.09	0.15	0.02	0.24	0.37	1	0.11	0.18	0.60

TF-B	0.21	0.26	-0.20	0.21	0.17	1	0.20	0.42	0.63
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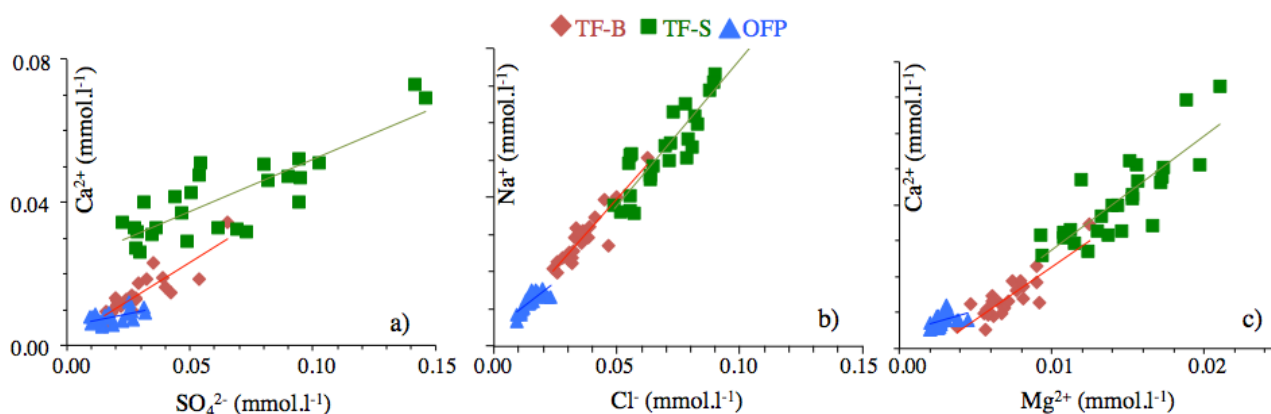
473 Table 3: Pearson correlation coefficients r between concentrations of some chemical elements in
 474 open field precipitation (OFP) and throughfalls under spruces (TF-S) and under beeches (TF-B)
 475 during the 1986-2012 period considering the entire sample dataset ($n=623$ for OFP, $n=591$ for TF-
 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 SO_4/H , SO_4/NO_3 , Mg/Ca and Na/Cl
 484 and for the two throughfalls (TF-S and TF-B) between Ca/ SO_4 , Mg/ SO_4 , Ca/ NO_3 and Mg/ SO_4
 485 (Table 3; Fig. 4). The correlations between Mg/Cl, Ca/Cl, NH_4/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. 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).

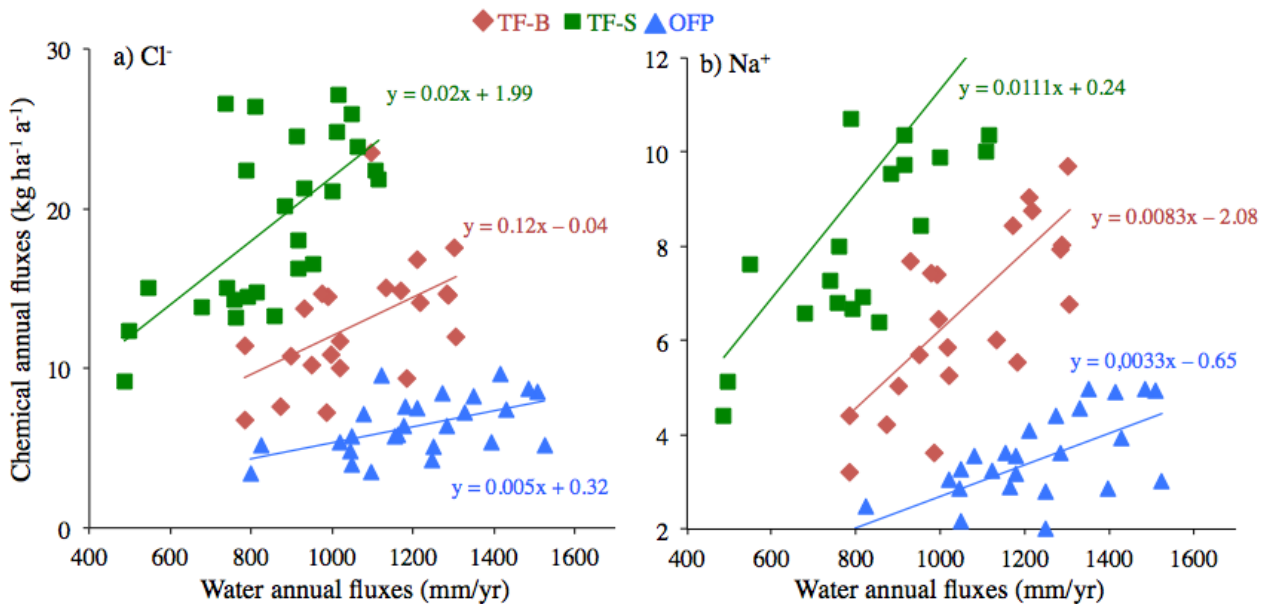
503

	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
OFP	0.21	0.64	0.15	0.48	0.59	0.53	0.55	0.29
TF-S	0.21	0.64	0.60	0.62	0.45	0.66	0.26	0.11
TF-B	-0.12	0.63	0.03	0.28	0.10	0.52	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: $r>0.5$.*

508



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⁻¹ and 30 kg ha⁻¹ 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 SO₂ 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 SO₄²⁻
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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ emissions were maximum
546 in 2006. Finally, the SO₂ 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 SO₂ 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 SO₂ 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 SO₂ 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, SO₂, as well as NO_x can be oxidized in the atmosphere as H₂SO₄ and HNO₃
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.

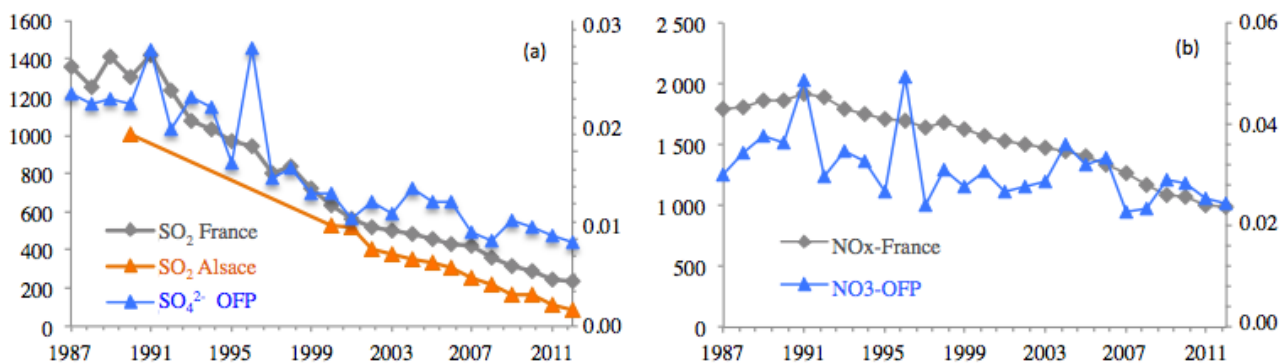
563 The increase in SO₄²⁻ concentrations observed in OFP and throughfalls during the period 2001-2008
564 (Fig. 3; 6) could be related to the SO₂ emitted in middle or long distance regions and transport as
565 SO₂ gaz or as degradation products and aerosols.

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 SO₄²⁻, NO₃⁻ and NH₄⁺ 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 SO₂ 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) SO₂ and b) NO_x 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 SO₂ and NO_x, 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 SO₄ 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 (SO₄²⁻) and (H⁺) are the sulfate and proton concentrations (mmole.l⁻¹), 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 SO₂.

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 SO₂ emissions had
616 strongly decreased during the past decades, the NO_x 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_x 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_x 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_x 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⁻¹ a⁻¹ in 1990 (Fig. 4). Similarly, NO₃ 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_x
640 emissions and the changes in NO₃ 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 NH₃ emissions
645 (NH₄ 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 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 SO_2
649 (Ferm and Hellsten, 2012) and then displayed a decrease. Consistently with nitrate, the increase in
650 NH_4 concentrations observed in throughfall under spruce could have been the result of vegetation
651 interactions. 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 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 SO_2 or 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 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⁻¹yr⁻¹ 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⁻¹a⁻¹ (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⁻¹a⁻¹ 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⁻¹a⁻¹) 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).

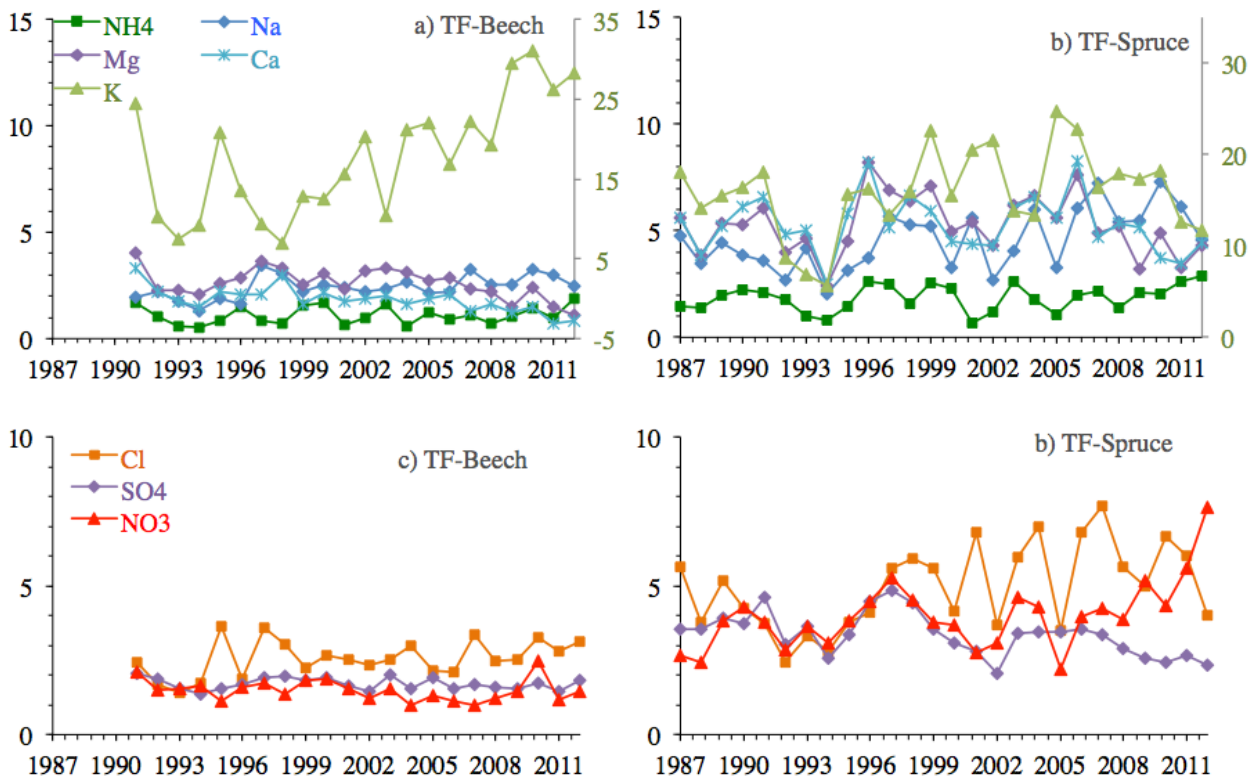
732 The processes of interaction between the rainwater and the canopy varied with the characteristics of
733 the forest stand (density, age, geometry, altitude, structure, height, density, LAI; e.g., Bréda, 1999;
734 2003; Erisman and Draaijers, 2003; Adriaenssens et al., 2012; Eaisalou et al., 2013; 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



755
 756
 757

758 *Fig. 7: Ratio of mean annual concentration in throughfall to open precipitation for NH₄, Na, K, Ca*
 759 *and Mg in a) beech and b) spruce stand and Cl, SO₄ and NO₃ 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 (NH₄⁺, Na⁺,
 762 Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻ and SO₄²⁻) 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 SO_4^{2-} , Cl^- and 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, 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 **Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and 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 Na^+ and 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 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 H_2O 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⁺ 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 NO₃⁻ and NH₄⁺ were similar in OFP with averages of
866 4.49 and 4.52 kg ha⁻¹ a⁻¹, respectively, for the 1986-2012 period. The results were also comparable
867 for throughfall under beech with 5.51 and 4.13 kg ha⁻¹ a⁻¹, 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⁻¹ a⁻¹ of N-NO₃ and N-NH₄, 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 NH₄⁺ 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 NO₃⁻ and NH₄⁺ in TF-S. However, in general NH₄⁺
885 was more efficiently retained in canopy than NO₃⁻ (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, SO₄²⁻, Cl⁻, NO₃⁻, Ca²⁺, Mg²⁺, and K⁺). The decrease in acidity and sulfate
897 concentration is likely related to the decrease in anthropogenic SO₂ and NO_x (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 Ca^{2+} and 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 (Na^+ , Cl^- , NO_3^- , Ca^{2+} , Mg^{2+} , SO_4^{2-} , and 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 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 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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962 **References:**

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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
Average		1368	1284	1433	837	1068	35	25
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⁻¹, 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 (1st October to 30th September) was considered.*

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	pH	Cond	NH ₄ ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	N-NH ₄	Na	K	Mg	Ca	Cl	N-NO ₃	N Tot	S-SO ₄	
OFP		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	
Average	4.78	16.4	42.0	12.3	5.3	2.8	7.9	15.0	31.2	18.0	5.9	3.4	2.2	0.8	3.3	6.4	20.6	9.2	6.2	
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	
TF-S	pH	Cond	NH4	Na	K	Mg	Ca	Cl	NO3	SO4	NH4	Na	K	Mg	Ca	Cl	NO3	N Tot	S	
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	
Average	4.51	47.4	77.6	55.7	80.1	14.3	40.7	71.9	122.9	59.5	6.8	9.7	22.4	2.5	11.5	19.0	50.2	16.6	14.0	
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	
TF-B	pH	Cond	NH4	Na	K	Mg	Ca	Cl	NO3	SO4	NH4	Na	K	Mg	Ca	Cl	NO3	N Tot	S	
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
Average	5.56	28.9	45.6	29.3	89.1	7.0	13.6	36.5	45.1	27.7	5.3	6.8	31.6	1.5	4.8	12.8	24.4	9.6	8.4
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 NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and 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 NO_3^- and NH_4^+ .