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

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18 **Graphical Abstract**

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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

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

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

Highlights:

- 1986-2012: a 2.5-decade survey of atmospheric deposition in the Vosges Mountains
- The sulfate decrease in precipitation and throughfall matched that of SO₂ emissions.
- The strong Ca decrease was related to changes in anthropogenic and natural sources.
- Beeches and spruces modified the atmospheric inputs to soil differently with time.
- N depositions decrease in OFP and under beech but increase under spruce.

1. Introduction

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

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

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

Sulfur dioxide (SO₂) and nitrogen oxide (NO_x) are the major sources of acid compounds in the atmosphere contributing to acid precipitation. Anthropogenic SO₂ originates mainly from coal and petroleum as energy sources (Smith et al., 2001; Sudalma et al., 2015). At the global scale, SO₂ emissions have strongly increased from 1850 (approximately 5 000 Gg/yr to the 1980s (approximately 150 000 Gg/yr) and then progressively decreased with a slight increase from 2000 (approximately 105 000 Gg/yr) to 2005/2007 (approximately 112 000 Gg/yr; Kopacek and Vesely, 2005, Stern, 2006; Smith et al., 2011; Klimont et al., 2013).

Due to implemented policies (Hettelingh et al., 2008) and economic factors, SO₂ emissions to the 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?

164 **2. Site description**

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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 $\pm$ 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.

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

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**

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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

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

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

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

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

where P is the precipitation amount.

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

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

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

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

3.2. Physico-chemical analysis

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

The pH and conductivity were measured, immediately after filtration, with a constant precision of ± 0.02 units.

The cations Ca, Mg, Na and K were measured by atomic absorption spectrometry until 2004 and then by ionic chromatography. NH_4^+ , Cl^- , NO_3^- and SO_4^{2-} were measured by automatic colorimetry until 1990 and then by ionic chromatography (Probst et al., 1990a, 1992a, 1995a, 2000; Pierret et al., 2014). Due to the changes in the analytical devices, the continuity of data and time series were controlled by ionic balance calculation for each sample, statistical and graphical tests, regular

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

3.3. Calculations

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

The fluxes of elements were calculated as the product of the sample concentration and the corresponding amount of water, and these fluxes were added to estimate the total annual flux, expressed in $\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$ (Table 2, Supplementary materials). The annual chemical fluxes were generally expressed as element flux (for instance, S for sulfate). The total N flux corresponded to the sum of N-NO_3^- and N-NH_4^+ fluxes (Table 2, Supplementary materials).

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

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

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

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

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

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

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

4. Results

4.1. Water fluxes

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

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

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

4.2. Chemical composition of precipitation

4.2.1 Chemical background

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

The mean annual electrical conductivity ranged from 10 to 28, 31 to 98 and 20 to 53 $\mu\text{S}/\text{cm}$ and the 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, respectively, illustrating the wide range of chemical characteristics of the samples. Similarly, the TF concentrations were 2 to 9 times greater than OP concentrations for the mean annual concentrations of major elements (SO_4^{2-} , Cl^- , NO_3^- , Ca^{2+} , Mg^{2+} , K^+ , and Na^+). The standard deviation calculated for the whole set of data and not only with the annual average illustrated the extremely large variability of the data set.

4.2.2 Sea-salt contribution

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

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

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

where X/Na_{precip} is the ratio between the element X and the concentration of Na in the corresponding sample of precipitation and $X/Na_{seawater}$ is the ratio between the element X and the concentration of Na in seawater.

The non-sea-salt concentration of X_{nss} can be calculated as

$$X_{nss} = (X)_{precip} - (X/Na)_{seawater} * (Na)_{precip}$$

where X_{precip} is the concentration of the element X in precipitation, $X/Na_{seawater}$ is the ratio between element X and the concentration of Na in seawater and X/Na_{precip} is the ratio between element X and the concentration of Na in the corresponding sample of precipitation.

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

The average EF and nss concentration values for K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} (with the $(X/Na)_{seawater}$ ratios from Singh et al., 2007; Mimura et al., 2016) were calculated for open field precipitation and throughfalls from the Strengbach catchment and summarized in Table 1. Open field precipitation and throughfalls exhibited higher EFs for Cl, ranging from 1.05 to 1.14 and with a very large dispersion (0.1 to 8), and even much higher for K, Ca and SO_4 , compared with the studies noted above.

The concentration corrected from sea-salt contribution (X_{nss}) was frequently negative for Cl and Mg, especially in throughfall samples, indicating that the correction was overestimated and inappropriate.

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

408

Seasonnal 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.

428

429

430

Fig. 3: Evolution of the mean annual a) pH, b) conductivity ($\mu\text{S cm}^{-1}$), c) concentration of SO_4^{2-} in 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 ($\text{kg ha}^{-1} \text{a}^{-1}$) 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 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 ($\text{kg ha}^{-1} \text{a}^{-1}$) of Na , m) concentration of K^+ in mmoles.l^{-1} , n) fluxes ($\text{kg ha}^{-1} \text{a}^{-1}$) of K , o) 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 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 (OFP), throughfall under spruce (TF-S) and under beech (TF-B) for the 1987-2012 period.

For the other elements, the trends were not always significant for the three types of precipitation.

The mean annual concentrations of nitrate ranged from 49-23, 100-23 and 221-71 $\mu\text{mol l}^{-1}$ in OFP, TF-B and TF-S, respectively (Fig. 3; Table 2, Supplementary materials), and the concentrations 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 by the SKT test, Table 2). No significant trend in nitrate was observed under spruces (TF-S). Similarly, NH_4^+ concentrations decreased in open field precipitation and throughfall under the beech stand and increased in throughfall under the spruce stand but with higher interannual variability and weaker SKT-tau for OFP and TF-S (Fig. 3; Table 2).

450 The mean annual Ntot 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).

470 4.4. Correlations between chemical composition and fluxes

471 4.4.1. Relationship between elements

472

	NH ₄	Na	K	Mg	Ca	H	Cl	NO ₃	SO ₄
	<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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Table 3: Pearson correlation coefficients r between concentrations of some chemical elements in open field precipitation (OFP) and throughfalls under spruces (TF-S) and under beeches (TF-B) during the 1986-2012 period considering the entire sample dataset ($n=623$ for OFP, $n=591$ for TF-S and $n=510$ for TF-B). In bold: $r>0.5$.

To discuss the comparison between TF-S and TF-B, we calculated the Pearson correlation coefficient between the elements and 1) sulfate, representing mainly the anthropogenic influence; 2) chloride, representing mainly the oceanic origin; 3) calcium from continental (natural and anthropogenic) sources; and 4) protons, representing global acid deposition (Table 3). The highest correlation coefficient was for the correlation between Na and Cl. Significant correlations were observed for OFP, TF-S and TF-B between SO_4/H , SO_4/NO_3 , Mg/Ca and Na/Cl and for the two throughfalls (TF-S and TF-B) between Ca/SO_4 , Mg/SO_4 , Ca/NO_3 and Mg/SO_4 (Table 3; Fig. 4). The correlations between Mg/Cl , Ca/Cl , NH_4/Ca , Na/Ca and K/Ca were significant only for TF-S (Table 3).

Fig. 4: Relationships between concentrations (mmol/l) of (a) Ca vs. SO_4 , (b) Na vs. Cl and (c) Mg vs. Ca for the open field precipitation (OFP) and throughfalls under beech (TF-B) and under spruce (TF-S) for the 1986-2012 period in the Strengbach catchment.

4.4.2. Relationships between fluxes of elements and water

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

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-](http://www.atmo-alsace.net)
 537 [alsace.net](http://www.atmo-alsace.net); 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

Fig. 6: a) SO_2 and b) NO_x emissions from 1987 to 2012 in France (in kt, CITEPA ordinate scale) and in Alsace (multiplied by a factor 50 in order to use the same scale, source: ASPA-<http://www.atmo-grandest.eu> (ordinate scale at the left), compared with the evolution of the mean annual a) sulfate and b) nitrate concentrations (mmol/l; ordinate scale at the right) in open field precipitation in the Strengbach catchment.

Protons

The increase in pH in atmospheric deposition (Fig. 4) was generally related to the decrease in anthropogenic emissions of the precursor gases of acid rain such as SO_2 and NO_x , as mandated by legislation (e.g., Likens et al., 1996; Norton et al., 2014; Pascaud et al., 2016). Nevertheless, the decrease in protons was mainly related to the decrease in SO_4 anions, both in open field precipitation and throughfalls. The linear relationships were as follows:

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

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

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

where (SO_4^{2-}) and (H^+) are the sulfate and proton concentrations (mmole.l^{-1}), respectively, r is the Pearson correlation coefficient and n is the number of samples in OFP, TF-B and TF-S.

At the global scale, Vet et al. (2014) observed that patterns of pH in wet deposition generally matched the emissions patterns of SO_2 .

The slopes of the pH trends for the period 1995-2007 (0.4, 0.5 and 0.5 obtained for OFP, TF-S and TF-B, respectively) were consistent with those observed for open field precipitation at 37 sampling sites throughout France (average pH increased 0.3 ± 0.1 over the period; Pascaud et al., 2016a). Similarly, between 1992 and 2005, in the bulk precipitation in Nacetin (forested site in the Czech 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

in 2012; CITEPA data). Nevertheless, Pascaud et al. (2016) observed a decrease in NH_4^+ concentration in precipitation from nine sampling sites (among the 37 French rural sites studied). Ammonium concentration could have been influenced by trends in atmospheric emissions of SO_2 (Ferm and Hellsten, 2012) and then displayed a decrease. Consistently with nitrate, the increase in NH_4 concentrations observed in throughfall under spruce could have been the result of vegetation interactions. NH_4^+ is not an acid compound but may generate acidity (during plant uptake or nitrification in soil, Van Bremen et al., 1983, Cui et al., 2015; Messenburg et al., 2016). Because of its strong influence on biogeochemical cycle in soils and forests, the decrease in NH_4 deposition and its long-term evolution should be addressed in the future.

5.1.2. Compounds with marine and continental origins

Chloride

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

The main source of chloride in the atmosphere was related to sea spray. The anthropogenic emissions were marginal in comparison to SO_2 or NO_x and might have resulted primarily from the combustion of coal and from accidental release during the incineration of chlorinated organic wastes but also in some places from road deicing salt (during winter).

Two hypotheses could be advanced to explain the slight reduction observed in Cl^- in open field precipitation (Fig. 3).

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

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

Calcium

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

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

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

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

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

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

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

725

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

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

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

The rainfall interceptions in TF-S were higher than in TF-B (Fig.2). The global explanation was that the small, needle-like structures of spruce are more efficient (acting as a comb) in collecting particles and cloud droplets compared with the larger leaf-like structures of deciduous trees as beech (Berger et al., 2008; Adriaenssens et al., 2012). The leaf area index (LAI), which expressed the foliar surface per surface unit, was often considered as an indicator (or proxy) of rainfall interception (Breda, 1999; 2003). The LAIs determined in the Strengbach catchment were 3.23 and 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 NH_4 , Na, K, Ca*
 759 *and Mg in a) beech and b) spruce stand and Cl, SO_4 and NO_3 in c) beech and d) spruce stands from*
 760 *the Strengbach catchment (period 1986-2012). Scale on the right corresponds to K concentrations.*

761

762 Similar to interception, the conductivity and most of the elemental concentrations (NH_4^+ , Na^+ ,
 763 Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-}) were higher in TF-S than in TF-B, and both were enriched
 764 compared with open field precipitation (Fig. 3, 4, 8). However, the chemical behavior and the
 765 interaction with the canopy depended on the nature and origin of the elements; some elements such

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 (Erisman and Draaijers, 2003; Adriaenssens et al., 2012;
862 Shen et al., 2013) and might explain the difference observed between the two stands. Meesenburg et
863 al. (2016) also observed higher nitrate concentrations in throughfalls under a spruce plot than under
864 a beech plot, with higher fluctuations in N input under spruce than under beech.

865 The annual fluxes of nitrogen derived from NO_3^- and NH_4^+ 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

though nitrogen from nitrate was slightly higher than that from ammonia. The throughfall under spruce showed various amounts, with 11.33 and 5.29 kg ha⁻¹ a⁻¹ of N-NO₃ and N-NH₄, respectively, on average for the 1986-2012 period (Table 2, Supplementary material). Thus, at first approximation, half of the atmospheric nitrogen inputs were derived from nitrate except under spruce where this proportion was approximately 70%.

Meesenburg et al. (2016) found that approximately 57% of N deposition was in the form of NH₄⁺ in beech and spruce plots from a forested plateau in Central Germany. In four Mediterranean forests with mainly oak trees, the nitrate dominated the total nitrogen atmospheric flux but with different percentage in agricultural, rural or urban site (58 to 80%; Avila et al., 2017), underlining the role played by the tree species, but also the site location (distance from urban or agricultural zone).

The nitrate concentration in throughfall was influenced by foliar activity (uptake *vs* excretion) but also by stress factors such as insects, fungi or water stress (Fischer et al., 2007). In addition, the age of the tree and its structure played roles in the atmospheric nitrate absorption. Wilson and Tiley (1998) showed that the branches of young spruces were more effective than needles for absorbing nitrate. One possible explanation might be that with aging and stand decline (which was the case for the considered spruce forest), the nitrogen nutrient requirements and thus the uptake by the spruce needles decreased, explaining the increase of NO₃⁻ and NH₄⁺ in TF-S. However, in general NH₄⁺ was more efficiently retained in canopy than NO₃⁻ (Avila et al., 2017), which could explain why the increase in nitrate is higher than that in ammonia in TF-S (Fig. 7b, 7d).

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

6. Conclusion

The long-term monitoring (several decades) of open field precipitation and throughfalls in the Strengbach catchment allowed the identification of some significant temporal trends (pH, conductivity, SO₄²⁻, Cl⁻, NO₃⁻, Ca²⁺, Mg²⁺, and K⁺). The decrease in acidity and sulfate concentration is likely related to the decrease in anthropogenic SO₂ and NO_x (proton precursors) emissions since the 80s in the Northern Hemisphere, whereas the worldwide emissions might have explained the increase during the late period, namely, in particulate form, and underlined the 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.

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

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

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

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References:

- Adrianssens S., Hansen K., Staelens J., Wuyts K., De Schrijver A., Baeten L., Boeckx P., Samson R. and Verheyens K., 2012. Throughfall deposition and canopy exchange processes along a vertical gradient within the canopy of beeches (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* (L.) Karst). *Science of the Total Environment* 420, 168-182.
- Akpo, A. B., Galy-Lacaux, C., Laouali, D., Delon, C., Liousse, C., Adon, M., Gardrat E., Mariscal A. and Darakpa, C., 2015. Precipitation chemistry and wet deposition in a remote wet savanna site in West Africa: Djougou (Benin). *Atmospheric Environment*, 115, 110-123.
- Asael S., 1990. Analyse structurale de quelques peuplements forestiers du bassin versant du Strengbach à Aubure (Haut-Rhin). DEA de biologie végétale et forestière. Université de nancy I. 91p.

973 Aubert, D., Stille, P., Probst, A., Gauthier-Lafaye, F., & Pourcelot, L., 2002. Characterization and migration
974 of atmospheric REE in soils and surface waters. *Geochimica et Cosmochimica Acta*, 66(19), 3339-3350.

975 Avila, A., Aguilhaume, L., Izquieta-Rojano, S., García-Gómez, H., Elustondo, D., Santamaría, J. M., and
976 Alonso, R., 2017. Quantitative study on nitrogen deposition and canopy retention in Mediterranean
977 evergreen forests. *Environmental Science and Pollution Research*, 24(34), 26213-26226.

978 Balestrini, R., Galli, L., and Tartari, G., 2000. Wet and dry atmospheric deposition at prealpine and alpine
979 sites in northern Italy. *Atmospheric Environment*, 34(9), 1455-1470.

980 Balestrini, R. and Tagliaferri, A., 2001. Atmospheric deposition and canopy exchange processes in alpine
981 forest ecosystems (northern Italy). *Atmospheric Environment*, 35(36), 6421-6433.

982 Balestrini, R., Arisci, S., Brizzio, M. C., Mosello, R., Rogora, M., and Tagliaferri, A., 2007. Dry deposition
983 of particles and canopy exchange: Comparison of wet, bulk and throughfall deposition at five forest sites
984 in Italy. *Atmospheric Environment*, 41(4), 745-756.

985 Biron, P., 1994. *Le cycle de l'eau en forêt de moyenne montagne: flux de sève et bilans hydriques*
986 *stationnels: bassin versant du Strengbach à Aubure, Hautes Vosges* (Doctoral dissertation, Université
987 Louis Pasteur (Strasbourg)).

988 Bonhomme M., 1967. Âge, par la méthode au strontium, des micas du granite des Crêtes (Vosges). 92e
989 congrès des Sociétés savantes.

990 Berger T.W., Untersteiner H., Schume H. and Jost G., 2008. Throughfall fluxes in a secondary spruce (*Picea*
991 *abies*), a beech (*Fagus sylvatica*) and a mixed spruce-beech stand. *Forest Ecology and Management*. 255,
992 605-618.

993 Bréda N.J.J., 1999. L'indice foliaire des couverts forestiers: mesure, variabilité et rôle fonctionnel. *Rev. For.*
994 *Fr* 2, 1999- p.135-150

995 Bréda N.J.J., 2003. Ground-based measurements of leaf area index: a review of methods, instruments and
996 current controversies. *Journal of experimental Botany*. 54, 2403-2417.

997 Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., ... and Emmett, B. 2010.
998 Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecological*
999 *applications*, 20, 30-59.

1000 Bultot, F., Dupriez, G. L., and Bodeux, A., 1972. Interception de la pluie par la végétation forestière
1001 estimation de l'interception journalière à l'aide d'un modèle mathématique. *Journal of Hydrology*, 17(3),
1002 193-223.

1003 Charlson, R. J., and Rodhe, H., 1982. Factors controlling the acidity of natural rainwater. *Nature*, 295, 683-
1004 685.

1005 Clarisse, L., Fromm, M., Ngadi, Y., Emmons, L., Clerbaux, C., Hurtmans, D. and Coheur, P. F., 2011.
1006 Intercontinental transport of anthropogenic sulfur dioxide and other pollutants: An infrared remote
1007 sensing case study. *Geophysical research letters*, 38(19).

1008 Coddeville, P., Pascaud, A., Sauvage, S., Nicolas, M., Mathias, E. and Probst, A., 2016. Évolution des
1009 émissions, de la qualité de l'air et des dépôts atmosphériques dans les espaces ruraux, notamment
1010 forestiers. Changes in atmospheric emissions, air quality and deposition in rural areas, especially in
1011 forests. *Pollution Atmosphérique*, (229-230).

1012 Cosby, B. J., Hornberger, G. M., Galloway, J. N., Wright, R. F., 1985. Modelling the effects of acid
1013 deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Water*
1014 *Resour. Res.* 21, 51-63.

1015 Crippa, M., Janssens-Maenhout, G., Dentener, F., Guizzardi, D., Sindelarova, K., Muntean, M., ... and
1016 Granier, C., 2016. Forty years of improvements in European air quality: regional policy-industry
1017 interactions with global impacts. *Atmospheric Chemistry and Physics*, 16(6), 3825-3841.

1018 Cui, J., Zhou, J., Peng, Y., Chan, A., and Mao, J., 2015. Effects of atmospheric deposition nitrogen flux and
1019 its composition on soil solution chemistry from a red soil farmland, southeast China. *Environmental*
1020 *Science: Processes & Impacts*, 17(12), 2082-2091.

1021 Dahire M., 1988. Granites et leucogranites péralumineux du Brézouard et du Bilstein (Vosges moyennes) :
1022 caractères pétrographiques, géochimiques et minéralogiques. Thèse de Doctorat. Université de Nancy,
1023 155p

1024 Dambrine E., Le Goaster S., Ranger J., 1991. Croissance et nutrition minérale d'un peuplement d'épicéa sur
1025 sol pauvre. II Prélèvement racinaire et transferts internes d'éléments minéraux au cours de la croissance.
1026 *Acta Oecologica*, 12, 791-808.

1027 Dambrine E., Carisey N., Pollier B., Granier A., Girard S., Lu P., Biron P. 1992. Dynamique des éléments
1028 minéraux dans la sève xylémique d'épicéas de 30 ans. *Ann. Sci. For.* 49, 489-510.

1029 Dambrine E., Pollier, Poszwa A., Ranger J., Probst A., Viville D., Biron P. and Granier A., 1998a. Evidence
1030 of current soil acidification in spruce (Strengbach catchment, Vosges mountains, North-Eastern France).
1031 *Water, Air and Soil Poll.* 105, 43-52.

1032 Dambrine E., Pollier B., Bonneau M. and Ignatova N., 1998b. Use of artificial trees to assess dry deposition
1033 in spruce stands. *Atmospheric Environment* 32, 1817-1824.

1034 Dambrine E., Probst A., Viville D., Biron P., Belgrand M.C., Paces T., Novak M., Buzey J., Cerny J. and
1035 Groscheova H., 2000. Spatial variability and long term trends in mass balance of N and S in central
1036 european forested catchments. In : *Ecological Studies*, E.-D. Schulze (ed.) Carbon and Nitrogen cycling
1037 in European Forested Ecosystems. Springer Verlag, Berlin, Heildelberg, vol. 142, Chap. 19, pp. 405-418.

1038 Delfs J., 1965. Interception and stemflow in stands of Norway spruce and beech in West Germany. In : W.E.
1039 Sopper and H.W. Lull (Editors), *Forest Hydrology, Proceedings of a National Science Advanced*
1040 *Seminar*, 29 August-10 September 1965, University Park PA. Pergamon Press, pp 179-185

1041 De Schrijver, A., Geudens, G., Augusto, L., Staelens, J., Mertens, J., Wuyts, K., Gielis L. and Verheyen, K.,
1042 2007. The effect of forest type on throughfall deposition and seepage flux: a review. *Oecologia*, 153(3), 663-
1043 674.

1044 De Vries, W., Dobbertin, M. H., Solberg, S., Van Dobben, H. F., and Schaub, M., 2014. Impacts of acid
1045 deposition, ozone exposure and weather conditions on forest ecosystems in Europe: an overview. *Plant*
1046 *and soil*, 380, 1-45.

1047 De Vries, W., Reinds, G.J., Vel, E., 2003. Intensive monitoring of forest ecosystems in Europe 2.
1048 Atmospheric deposition and its impacts on soil solution chemistry. *Forest Ecology and Management* 174,
1049 97-115.

1050 Draaijers, G. P. J., and Erisman, J. W., 1995. A canopy budget model to assess atmospheric deposition from
1051 throughfall measurements. *Water, Air, & Soil Pollution*, 85(4), 2253-2258.

1052 Eisolou H.K., Sengönül K., Gökbülak F., Serengil Y. and Uygur B., 2013. Effects of forest canopy cover and
1053 floor on chemical quality of water in Broad leaves and coniferous forests of Istanbul, Turkey. *Forest*
1054 *Ecology and Management*. 289, 371-377.

1055 Erisman JW, Draaijers G., 2003. Deposition to forests in Europe: most important factors influencing dry
1056 deposition and models used for generalisation. *Environ Pollut.* 124:379-88. [SEP]

1057 Evans C.D., Cullen J.M., Alewell C., Kopacek J., Marchetto A., Moldan F., Prechtel A., Rogora M. Vesely
1058 J. and Wright R.F., 2001. Recovery from acidification in European surface waters. *Hydrol. Earth Syst.*
1059 *Sci.* 5, 282-297.

1060 Evans C.D., Monteith D.T., Fowler D., Cape J.N. and Brayshaw S., 2011. Hydrochloric acid: an overlooked
1061 driver of environmental change. *Environ. Sci. Technol.*, 45, 1887-1894. doi: 10.1021/es103574u.

1062 Eyring, V., Isaksen, I.S.A., Berntsen, T., Collins, W.J., Corbett, J.J., Endresen, O., Grainger, R.G.,
1063 Moldanova, J., Schlager, H., Stevenson, D.S., 2010. Transport impacts on atmosphere and climate:
1064 Shipping. *Atmos. Environ.* 44 (37)

1065 Ferm, M., Hellsten, S., 2012. Trends in atmospheric ammonia and particulate ammonium concentrations in
1066 Sweden and its causes. *Atmos. Environ.* 61 (0), 30-39.

1067 Fioletov, V. E., McLinden, C. A., Krotkov, N., Li, C., Joiner, J., Theys, N. and Moran, M. D., 2016. A
1068 global catalogue of large SO2 sources and emissions derived from the Ozone Monitoring Instrument.
1069 *Atmospheric Chemistry & Physics*, 16(18).

1070 Fisher R., Mues V., Ulrich E., Becher G. and Lorenz M., 2007. Monitoring of atmospheric deposition in
1071 European forests and an overview on its implication on forest condition. *Applied Geochemistry* 2, 1129-
1072 1139.

1073 Fichter, J., Dambrine, E., Turpault, M. P., & Ranger, J., 1998. Base cation supply in spruce and beech
1074 ecosystems of the Strengbach catchment (Vosges mountains, NE France). *Water, Air, and Soil Pollution*,
1075 104(1-2), 125-148.

1076 Fuss, C. B., Driscoll, C. T., & Campbell, J. L., 2015. Recovery from chronic and snowmelt acidification:
1077 Long-term trends in stream and soil water chemistry at the Hubbard Brook Experimental Forest, New
1078 Hampshire, USA. *Journal of Geophysical Research: Biogeosciences*, 120(11), 2360-2374

1079 Galy-Lacaux, C., Laouali, D., Descroix, L., Gobron, N., and Lioussé, C., 2009. Long term precipitation
1080 chemistry and wet deposition in a remote dry savanna site in Africa (Niger). *Atmospheric Chemistry and*
1081 *Physics*, 9(5), 1579-1595.

1082 Gaudio N., Belyazid S., Gendre X., Mansat A., Rizzetto S., Nicolas M., Sverupt H. and Probst A., 2015.
1083 Combined effect of atmospheric nitrogen deposition and climate change on temperate forest soil
1084 biogeochemistry: a modelling approach. *Ecological Modelling*, 306, 24-34.

1085 Harrison, A.F., Schulze, E.D., Gebauer, G. and Bruckner, G., 2000. Canopy uptake and utilization
1086 of atmospheric pollutant nitrogen. In *Carbon and nitrogen cycling in European forest ecosystems*
1087 (pp. 171-188). Springer, Berlin, Heidelberg

1088 He, Z. B., Yang, J. J., Du, J., Zhao, W. Z., Liu, H., and Chang, X. X., 2014. Spatial variability of canopy
1089 interception in a spruce forest of the semiarid mountain regions of China. *Agricultural and forest*
1090 *meteorology*, 188, 58-63.

1091 Heijden G. Legoud A. Pollier B., Ranger P. and Dambrine E., 2014. The dynamics of calcium and
1092 magnesium inputs by throughfall in a forest ecosystem on base poor soil are very slow and conservative:
1093 evidence from an isotopic tracing experiment (^{26}Mg and ^{44}Ca). *Biogeochemistry* 118, 413-442.

1094 Heijden G., Legoud A., Nicolas M., Ulrich E., Johnson D.W. and Dambrine E., 2011. Long-term
1095 sustainability of forest ecosystems on sandstone in the Vosges Mountains (France) facing atmospheric
1096 deposition and silvicultural change. *Forest Ecology and Management*. 261, 730-740.

1097 Hettelingh, J. P., Posch, P., and Slootweg, J. 2008. Critical Load, Dynamic Modelling and Impact
1098 Assessment in Europe, CCE Status Report 2008, Report 500090003. *Coordination Center for Effects,*
1099 *Netherlands Environmental Assessment Agency, The Netherlands.*

1100 Hirsch, R. M., J. R. Slack, and R. A. Smith, 1982. Techniques of trend analysis for monthly water quality
1101 data, *Water Resour. Res.*, 18, 107–121.

1102 Hruska J. and Kram P. 2003. Modelling long-term changes in stream water and soil chemistry in catchments
1103 with contrasting vulnerability to acidification (Lysina and Pluhuv Bor, Czech republic). *Hydrology and*
1104 *earth Syst. Sci.* 7, 525-539

1105 Hunova, I., Maznova, J., Kurfürst, P., 2014. Trends in atmospheric deposition fluxes of sulphur and nitrogen
1106 in Czech forests. *Environ. Pollut.* 184, 668-675.

1107 Idir S., Probst A., Viville D. and Probst J.L., 1999. Contribution des surfaces saturées et des versants aux
1108 flux d'eau et d'éléments exportés en période de crue : tracage à l'aide du carbone organique dissous et de
1109 la silice. Cas du petit bassin versant du Strengbach (Vosges, France). *C.R. Acad Sci Paris*. 328, 89-96.

1110 Jenkins, A., Camarero, L., Cosby, B. J., Ferrier, R. C., Forsius, M., Helliwell, R. C., Kopáček, J., Majer, V.,
1111 Moldan, F., Posch, M., Rogora, M., Schöpp, W., Wright, R. F., 2003. A modelling assessment of
1112 acidification and recovery of European surface waters. *Hydrol. Earth Syst. Sci.* 2003, 7, 447–455.

1113 Johnson R.C., 1990, The interception, throughfall and stemflow in a forest in highland Scotland and the
1114 comparison with other upland forests in the U.K. *Journal of Hydrology* 118, 281–287.

1115 Kato, H., Onda, Y., Nanko, K., Gomi, T., Yamanaka, T., and Kawaguchi, S., 2013. Effect of canopy
1116 interception on spatial variability and isotopic composition of throughfall in Japanese cypress plantations.
1117 *Journal of hydrology*, 504, 1-11.

1118 Keene, W. C., Pszenny, A. A., Galloway, J. N., and Hawley, M. E., 1986. Sea-salt corrections and
1119 interpretation of constituent ratios in marine precipitation. *Journal of Geophysical Research:*
1120 *Atmospheres*, 91(D6), 6647-6658.

1121 Kendall M.G., 1975. Rank correlation methods, fourth ed. Charles Griffin, London.

1122 King H.B., Wang M.K., Zhuang S.Y., Hwang J.L., Liu C.P. and Kang M.J., 2006. Sorption of sulphate and
1123 retention of cations in forest soils of Lien-Hua-Chi watershed in central Taiwan. *Geoderma* 131, 143-153.

1124 Klimont Z., Smith S.J., Cofala J., 2013. The last decade of global anthropogenic sulphur dioxide 2000-2011
1125 emissions. *Environ. Res. Lett.* 8, 6pp.

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

- the Cascade Mountains of Oregon, USA. *Water Air and Soil Pollution* 42, 203-220.
- Mayewski, P. A., Lyons, W. B., Spencer, M. J., Twickler, M., Dansgaard, W., Koci, B. and Honrath, R. E., 1986. Sulfate and nitrate concentrations from a south Greenland ice core. *Science*, 232(4753), 975-977.
- McHale, M.R., Burns, D.A., Siemion, Jason, and Antidormi, M.R., 2017, The response of soil and stream chemistry to decreases in acid deposition in the Catskill Mountains, New York, USA: *Environmental Pollution*, v. 229, p. 607-620
- McLinden, C. A., Fioletov, V., Shephard, M. W., Krotkov, N., Li, C., Martin, R. V. and Joiner, J., 2016. Space-based detection of missing sulfur dioxide sources of global air pollution. *Nature Geoscience*, 9(7), 496–500. <https://doi.org/10.1038/ngeo2724>
- McDowell, W. H., Sánchez, C. G., Asbury, C. E. and Pérez, C. R. R., 1990. Influence of sea salt aerosols and long range transport on precipitation chemistry at El Verde, Puerto Rico. *Atmospheric Environment. Part A. General Topics*, 24(11), 2813-2821.
- Meesenburg, H., Ahrends, B., Fleck, S., Wagner, M., Fortmann, H., Scheler, B., and Meiwes, K. J. 2016. Long-term changes of ecosystem services at Solling, Germany: Recovery from acidification, but increasing nitrogen saturation?. *Ecological Indicators*, 65, 103-112.
- Mimura, A. M. S., Almeida, J. M., Vaz, F. A. S., de Oliveira, M. A. L., Ferreira, C. C. M., and Silva, J. C. J., 2016. Chemical composition monitoring of tropical rainwater during an atypical dry year. *Atmospheric Research*, 169, 391-399.
- Moldan B., Schnoor, J., 1992. Czechoslovakia: examining a critically ill environment. *Environmental Science and Technology* 26, 14–21.
- Moldan, F.; Kronnäs, V.; Wilander, A.; Karlun, E.; Cosby, B. J. 2004. Modelling acidification and recovery of Swedish lakes. *Water, Air, Soil Pollut.: Focus* 4, 139–160.
- Moore, J., Kekonen, T., Grinsted, A., & Isaksson, E., 2006. Sulfate source inventories from a Svalbard ice core record spanning the Industrial Revolution. *Journal of Geophysical Research: Atmospheres*, 111-D15, 1-13
- Nanus, L., McMurray, J. A., Clow, D. W., Saros, J. E., Blett, T., and Gurdak, J. J., (2017). Spatial variation of atmospheric nitrogen deposition and critical loads for aquatic ecosystems in the Greater Yellowstone Area. *Environmental Pollution*, 223, 644-656.
- Navratil T., Kurz D., Kram P., Hofmeister J. and Hruska J., 2007. Acidification and recovery of soil at a heavily impacted forest catchment (Lysina, Czech Republic)- SAFE modelling and field results. *Ecological modelling* 205, 464–474.
- Nihlgård, B., 1970. Precipitation, its chemical composition and effect on soil water in a beech and a spruce forest in south Sweden. *Oikos*, 208-217.
- Norton S.A., Wagai R., Navratil T., Kaste J.M. and Rissberger F.A., 2000. Response of a first-order stream in Maine to short-term in-stream acidification. *Hydrology and Earth System Sciences* 4, 383-391.
- Norton S.A., Kopáček J. and Fernandez I.J., 2014. Acid Rain – Acidification and Recovery. In: Holland H.D. and Turekian K.K. (eds.) *Treatise on Geochemistry*, Second Edition, vol. 11, pp. 379-414. Oxford: Elsevier.
- Oulehle F., Hofmeister J., Cudlin P. and Hruska J., 2006. The effect of reduced atmospheric deposition on soil and soil solution chemistry at a site subjected to long-term acidification, Nacetin, Czech Republic. *Science of the Total Environment* 370, 532-544.
- Oulehle F., Chuman T., Hruska J., Kram P., McDowell W.H., Myska O., Navratil T. and Tesar M., 2017. Recovery from acidification alters concentrations and fluxes of solutes from Czech catchments. *Biogeochemistry* 132, 251-272
- Paces T., 1985. Source of acidification in central Europe estimated from elemental budgets in small basins. *Nature* 315, 31-36
- Pallares C., 1993. Etude cinétique Etude cinétique de l'oxydation du dioxyde de soufre par des oxydants forts dans l'eau troposphérique. Thèse de doctorat, Université Louis Pasteur. Strasbourg

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

atmospheric influence (the Ringelbach catchment, Vosges Mountains, France): Lessons from a hydrogeochemical survey in the nineties. *Journal of Hydrology*. DOI :10.1016/j.jhydrol.2018.11.01

Prunier, J., Chabaux, F., Stille, P., Gangloff, S., Pierret, M. C., Viville, D., and Aubert, A., 2015. Geochemical and isotopic (Sr, U) monitoring of soil solutions from the Strengbach catchment (Vosges mountains, France): Evidence for recent weathering evolution. *Chemical Geology*, 417, 289-305.

Read, W. G., L. Froidevaux and J. W. Waters, Microwave limb sounder measurements of stratospheric SO₂ from the Mt. Pinatubo volcano (1993), *Geophys. Res. Lett.*, 20, 1299-1302.

Reinds, G. J., Posch, M., De Vries, W., Slootweg, J., and Hettelingh, J. P., 2008. Critical loads of sulphur and nitrogen for terrestrial ecosystems in Europe and Northern Asia using different soil chemical criteria. *Water, air, and soil pollution*, 193, 269.

Rizzetto S., Belyazid S., Gegout J.C., Nicolas M., Alard D., Corcket E., Gaudio N., Sverdrup H., Probst A., 2016. Modelling the impact of climate change and atmospheric N deposition on French forests biodiversity. *Env. Poll.*, 213, 1016-1027.

Rogora, M., R. Mosello, S. Arisci, M. Brizzio, A. Barbieri, R. Balestrini, P. Waldner, M. Schmitt, M. Stähli, A. Thimonier, M. Kalina, H. Puxbaum, U. Nickus, E. Ulrich and A. Probst, 2006. An overview of atmospheric deposition chemistry over the Alps: present status and long-term trends. *Hydrobiologia* 562, 17-40.

Rothe, A., Huber, C., Kreutzer, K., & Weis, W., 2002. Deposition and soil leaching in stands of Norway spruce and European beech: results from the Höglwald research in comparison with other European case studies. *Plant and soil*, 240(1), 33-45.

Schrumpf M., Axmacher J.C., Zech W., Lehmann J. and Lyaruu H.V.C., 2007. Long-term effect of rainforest disturbance on the nutrient composition of throughfall, organic layer percolate and soil solution At Mt Kilimanjaro., *Science of the Total Environment* 376, 241-254.

Schulze E.-D., 1989. Air pollution and forest decline in a spruce stand (*Picea abies*) forest. *Science* 244, 776-783.

Sequeira, R., 1993. On the large-scale impact of arid dust on precipitation chemistry of the continental northern hemisphere. *Atmospheric Environment. Part A. General Topics*, 27(10), 1553-1565.

Sen, P. K., 1968. Estimates of the regression coefficient based on Kendall's tau. *Journal of the American statistical association*, 63(324), 1379-1389.

Shen W., Ren H., Jenerette G.D., Hui D. and Ren H., 2013. Atmospheric deposition and canopy exchange of anions and cations in two plantation forests under acid rain influence. *Atmospheric Environment* 64, 242-250.

Singh, K. P., Singh, V. K., Malik, A., Sharma, N., Murthy, R. C. and Kumar, R., 2007. Hydrochemistry of wet atmospheric precipitation over an urban area in Northern Indo-Gangetic Plains. *Environmental monitoring and assessment*, 131(1-3), 237.

Skeffington R.A. and Hill T.J., 2012. The effects of a changing pollution climate on throughfall deposition and cycling in a forested area in southern England. *Science of the Total Environment*. 434, 28-38.

Smith S.J., Pitcher H. and Wigley T.M., 2001. Global and regional anthropogenic sulfure dioxides emissions. *Global planet Change* 29, 99-119.

Smith S J, van Aardenne J, Klimont Z, Andres R, Volke A C and Delgado Arias S 2011. Anthropogenic sulfur dioxide emissions: 1850–2005 *Atmos. Chem. Phys.* 11 1101–16

Staelens, J., De Schrijver, A., Verheyen, K., & Verhoest, N. E. (2008). Rainfall partitioning into throughfall, stemflow, and interception within a single beech (*Fagus sylvatica* L.) canopy: influence of foliation, rain event characteristics, and meteorology. *Hydrological Processes*, 22(1), 33-45.

Stern D.I., 2006. Reversal of the trend in global anthropogenic sulphur emissions. *Global Environmental Change*, 16, 207-220.

Sudalma, S., Purwanto, P., and Santoso, L. W., 2015. The effect of SO₂ and NO₂ from transportation and stationary emissions sources to SO₄²⁻ and NO₃⁻ in rain water in Semarang. *Procedia Environmental Sciences*, 23, 247-252.

Theil, H., 1950. A rank-invariant method of linear and polynomial regression analysis, I, II, and III, *Nederl. Akad. Wetensch. Proc.*, 53, 386-92, 521-5 and 1397-41

Thimonier, A., Dupouey, J. L., and Le Tacon, F., 2000. Recent losses of base cations from soils of *Fagus sylvatica* L. stands in northeastern France. *AMBIO: A Journal of the Human Environment*, 29, 314-321.

Thimonier, A., Schmitt, M., Waldner, P., and Rihm, B., 2005. Atmospheric deposition on Swiss long-term forest ecosystem research (LWF) plots. *Environmental monitoring and assessment*, 104(1-3), 81-118.

Thimonier A. Schmitt M., Waldner P. and Schleppi P., 2008. Seasonality of the Na/Cl ratio in precipitation and implications of canopy leaching in validating chemical analyses of throughfall samples. *Atmospheric Environment*, 42, 9106-9117.

Torseth, K., Aas, W., Breivik, K., Fjæraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre, C., Solberg, S., and Yttri, K. E., 2012. Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009. *Atmospheric Chemistry and Physics*, 12, 5447-5481.

Tu, F. H., Thornton, D. C., Bandy, A. R., Carmichael, G. R., Tang, Y., Thornhill, K. L., and Blake, D. R., 2004. Long-range transport of sulfur dioxide in the central Pacific. *Journal of Geophysical Research: Atmospheres*, 109(D15).

Turk, T.D., Schmidt, M.G., Roberts, N.J., 2008. The influence of bigleaf maple on forest floor and mineral properties in a coniferous forest in coastal British Columbia. *Forest Ecol. Manage.* 255, 1874–1882.

Ulrich B., 1981. 5. Soil processes B. ULRICH, P. BENECKE, WF HARRIS. PK KHANNA & R. MAYER. *Dynamic properties of forest ecosystems*, 23, 265.

Ulrich B., 1983. Interaction of forest canopies with atmospheric constituents: SO₂, alkali and earth alkali cations and chloride. In: Ulrich, B., Pankrath, J. (Eds.), *Effects of Accumulation of Air Pollutants in Forest Ecosystems*. Reidel, Dordrecht, pp. 33–45.

Ulrich B., 1984. Effects of air pollution on forest ecosystems and waters: the principles demonstrated at a case study in central Europe. *Atmosph Environ* 18, 621-628.

Van Breemen N, Mulder J. Driscoll CT, 1983. Acidification and alkalization of soil. *Plant and Soil* 75:283-308

Vanguelova E.I., Benham S., Pitman R., Moffat A.J., Broadmeadow M., Nisbet N., Durrant D., Barsoum N., Wilkinson M., Bocheureau F., Hutchings T., Broadmeadow S., Crow P., Taylor P., Durrant Houston T., 2010. Chemical fluxes in time through forest ecosystems in the UK – Soil response to pollution recovery. *Environmental Pollution*, 158, 1857-1869

Vet, R., Artz, R.S., Carou, S., Shaw, M., Ro, C.-U., Aas, W., Baker, A., Bowersox, V.C., Dentener, F., Galy-Lacaux, C., Hou, A., Pienaar, J.J., Gillett, R., Forti, M.C., Gromov, S., Hara, H., Khodzher, T., Mahowald, N.M., Nickovic, S., Rao, P.S.P., Reid, N.W., 2014. A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. *Atmospheric Environment* 93: 3-100

Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I.S.A., Tarrason, L., 2009. Evolution of NOX emissions in Europe with focus on road transport control measures. *Atmos. Chem. Phys.* 9 (4), 1506.

Vieno, M., Heal, M. R., Hallsworth, S., Famulari, D., Doherty, R. M., Dore, A. J., ... & Reis, S. (2014). The role of long-range transport and domestic emissions in determining atmospheric secondary inorganic particle concentrations across the UK. *Atmospheric Chemistry and Physics*, 14(16), 8435-8447.

Vogt, R. D., Seip, H. M., Larssen, T., Zhao, D., Xiang, R., Xiao, J., ... & Zhao, Y. (2006). Potential acidifying capacity of deposition: Experiences from regions with high NH₄⁺ and dry deposition in China. *Science of the Total Environment*, 367(1), 394-404.

Viville D., Biron P., Granier A., Dambrine E. and Probst A., 1993. Interception in a mountainous declining spruce stand in the Strengbach catchment (Vosges, France). *Journal of Hydrology*. 144, 273-282.

Viville D., Chabaux F., Stille P., Pierret M.C., Gangloff S., 2012. Erosion and weathering fluxes in granitic basins: The example of the Strengbach catchment (Vosges massif, eastern France). *Die Bodenkultur Journal for Land Management, Food and Environment*. 64, 121-126.

Vuorenmaa, J., Augustaitis, A., Beudert, B., Bochenek W., Clarke, N., de Wit, H. A., Dirnböck, T., Frey J., Hakola H., Kleemola S., Kobler, J., Kram P., Lindroos A-J., Lundin L., Löfgren S., Marchetto A., Pecka T., Schulte-Bisping H., Skotak K., Szybny A., Szpikowski J., Ukonmaanaho L., Ukonmaanaho L., Vana M., Akerblom S and Forsius M., 2018. Long-term changes (1990-2015) in the atmospheric deposition and

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

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

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

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

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

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

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

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

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

Yang, X., Wang, S., Zhang, W., Li, J., and Zou, Y., 2016. Impacts of energy consumption, energy structure, and treatment technology on SO₂ emissions: A multi-scale LMDI decomposition analysis in China. *Applied energy*, 184, 714-726.

Zeng G.M., Zhang G., Huang G.H., Jiang Y.M., Liu H.L., 2005. Exchange of Ca²⁺, Mg²⁺ and K⁺ and uptake of H⁺ and NH₄⁺ for the subtropical forest canopies influenced by acid rain in Shaoshan forest located in Central South China. *Plant Science* 168, 259-266.

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

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

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

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

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

	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 N_{Tot} flux corresponded to the sum of nitrogen from both NO_3^- and NH_4^+ .