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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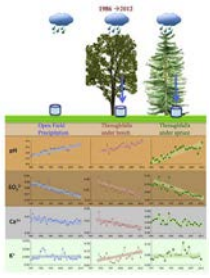
GRAPHICAL ABSTRACT



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ABSTRACT

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

The long-term monitoring evidenced some significant temporal trends (pH, conductivity, SO_4^{2-}, Cl^-, NO_3^-, Ca^{2+}, Mg^{2+}, and K^+). Significant decreases in the concentrations and fluxes of several ions were observed (H^+ and SO_4^{2-}, Cl^-, and Ca^{2+}) in open field precipitation and throughfalls. The regular and strong decrease in protons and sulfate followed the decreases in anthropogenic SO_2 and NO_x (proton precursors) since the 1980s. The decrease in Cl^- concentrations was weaker and could have 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

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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.

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; Oulehle 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 north-eastern 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; De Vries et al., 2014; Norton et al., 2014) and more recently in Asia (King et al., 2006; Zhang et al., 2007, 2012; Shen et al., 2013).

Sulfur dioxide (SO_2) and nitrogen oxide (NO_x) are the major sources of acid compounds in the atmosphere contributing to acid precipitation. Anthropogenic SO_2 originates mainly from coal and petroleum as energy sources (Smith et al., 2001; Sudalma et al., 2015). At the global scale, SO_2 emissions have strongly increased from 1850 (approximately 5000 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, SternD, 2006; Smith et al., 2011; Klimont et al., 2013).

Due to implemented policies (Hettelingh et al., 2008) and economic factors, SO_2 emissions to the atmosphere have been reduced since the 1980s by 50–85% in North America and Europe (Reinds et al., 2008; Norton et al., 2014; Kopacek et al., 2016; Fioletov et al., 2016) and by 90% in France since the 1990s (CITEPA: https://www.citepa.org/fr).

Anthropogenic NOx emissions reflect the dominant energy sector, and the major sources are high-temperature combustion processes (motor vehicles, electric power plants) and fuel combustion. Like SO_2, NOx emissions decreased in the early nineties but less significantly and were followed more swiftly by an increase of up to 6% in the newly industrialized countries. Since 1970, NOx emissions have almost doubled (70 Gt/yr in 1970 to 120 Gt/yr in 2005; EDGAR - July 2010).

NH_3 emission, mainly due to agricultural activities, globally still increased until now at a world scale. In France, the annual NH_3 emissions are almost stable since 1980 (CITEPA: https://www.citepa.org). By its acidifying and eutrophication role, the both forms of nitrogen has an impact on ecosystem safety and particularly on biodiversity, which remains a key problem to be solved (De Vries et al., 2003, Bobbink et al., 2010; Gaudio et al., 2015; Probst et al., 2015; Rizzetto et al., 2016).

Despite the decrease in the emissions of some precursors of acid rain such as SO_2 in some places around the world over the past three decades, the question of air pollution and ecosystem acidification remains a societal and scientific challenge. This situation occurs particularly because the emissions of such contaminants and their deposition remain significant, especially regarding nitrogen (Rogora et al., 2006; Nanus et al., 2017).

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

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

Because the measure of dry and occult deposition is very complicated (Lindberg and Garten, 1988a; Lindberg et al., 1988; Balestrini et al., 2007), the sampling and analysis of throughfall have been developed to estimate the entire atmospheric deposition of contaminants to forest ecosystems and thus indirectly determine the dry deposition. However, the main difficulty is that throughfall integrates various types of deposition and sorption processes when precipitation interacts with the trees: 1) wet deposition by rain or snow, 2) sedimentation of particles caught by the leaves during dry episodes and dissolution by the next rainfall, 3) impact of dry aerosols from fog and cloud droplets, 4) absorption of gases inside stomata and 5) recretion/absorption of elements by leaf cells following exchange processes with rainwater (Ulrich, 1983; Parker, 1983; De Vries et al., 2003; Probst et al., 1990a; Dambrine et al., 1998b; Thimonier et al., 2008; Berger et al., 2008; Kopacek et al., 2009; Adrianssens et al., 2012; Skeffington and Hill, 2012; Kato et al., 2013; Shen et al., 2013; Klos et al., 2014). Although throughfall result from a mixture of several processes, it currently remains an efficient way to estimate accurately the in-situ input flux of

most of the element deposition to forest ecosystems (e.g., Zimmermann and Zimmermann, 2014; Skeffington and Hill, 2012), except for a proportion of the nitrogen deposited which can be taken up by leaves and needle (Harrison et al., 2000).

Numerous publications have concerned acid precipitation and acidification processes. Nevertheless, few studies have examined in detail the long-term (several decades) evolution of atmospheric element inputs to ecosystems with different tree types, particularly in the context of the changes in pollutant emissions during the past decades. This study benefits from a 25-year record of chemical and water fluxes for

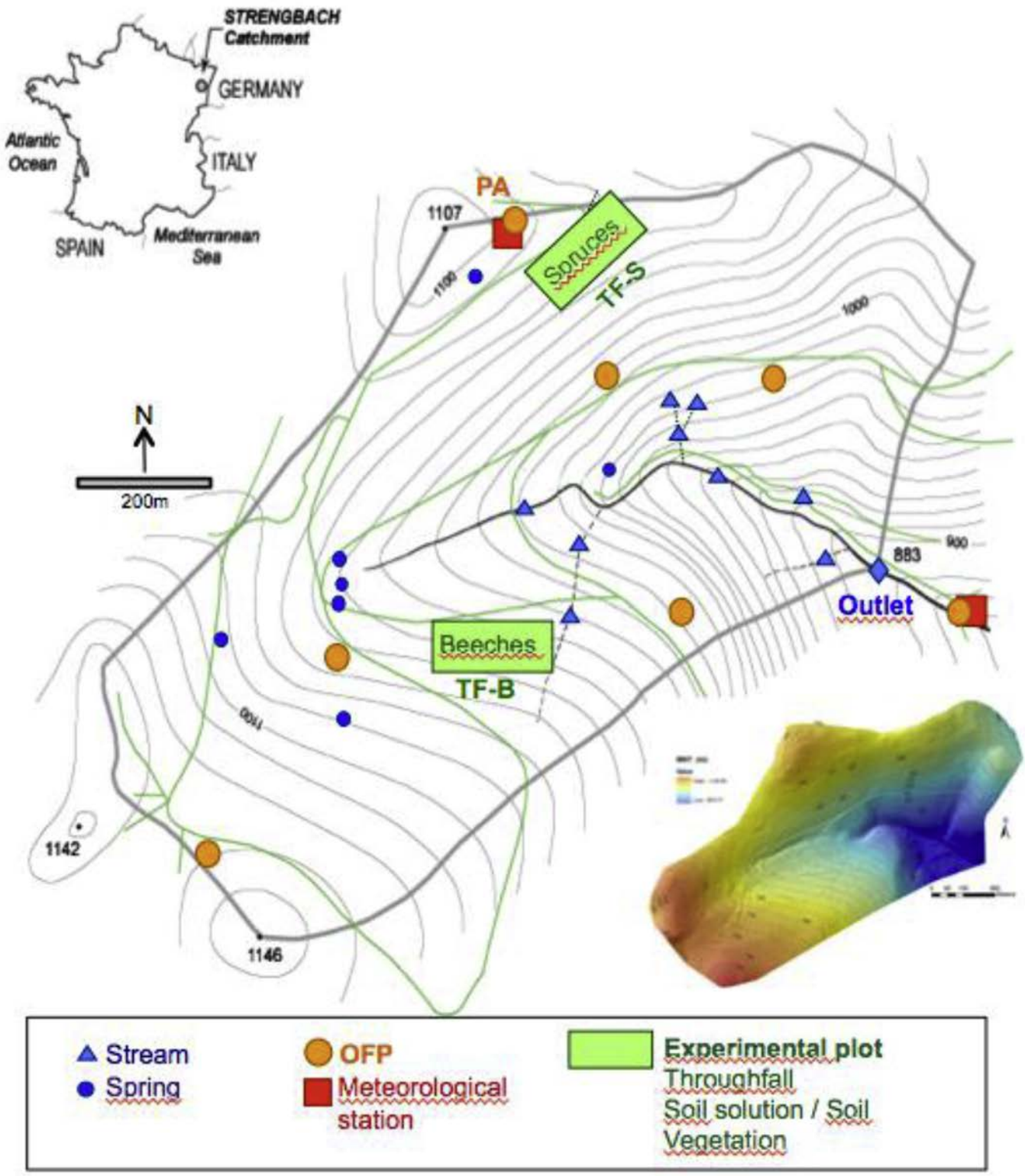

Fig. 1. Map of the Strengbach watershed with the locations of the outlet, rain gauges (OFP: open field precipitation), meteorological stations, and spruce and beech stands where throughfalls (TF-S and TF-B, respectively) are sampled for analyses. PA corresponds to the OFP site where the rain has been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

open field precipitation and throughfall in a mountainous granitic forested environment. Two contrasting types of trees (coniferous and deciduous) allowed study of the impact of tree species on contaminant and nutrient element inputs to soils.

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

- How did the global and local changes in NO_x and SO_2 emissions since the 1980s influence the sulfate and nitrate concentrations and fluxes in precipitation in a mountainous forest ecosystem?
- What are the respective long-term trends of the main cation and anion inputs in open field precipitation and in throughfall?
- How may tree species affect the atmospheric inputs by interception and canopy exchanges?

2. Site description

The symptoms of forest decline appeared in the mid-80s in the Vosges massif (France) at the same time as in other parts of northern Europe. Investigations in the Strengbach catchment have been developed in order to better understand the relationships between acid atmospheric deposition and forest decline (Probst et al., 1990a, 1992a, b, Dambrine et al., 1991). The Vosges Mountains in northeastern France are one of the areas in the country most sensitive to acid precipitation (Probst et al., 1990b, 1992a; 1995a; Pascaud et al., 2016).

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

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

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

The mean annual runoff for the corresponding period is 760 mm ($24.5\,l^{-1}km^{-2}$) ranging from 494 to 1132 mm/yr (Table 1, Suplementary materials). The precipitation is characterized by low intra-monthly variability due to the dominant westerly wind regime.

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

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

3. Methods

3.1. Sampling of open field precipitation and throughfall measurements

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

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

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

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

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

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, Suplementary materials).

Throughfall has been sampled using 2 gutters (2.0 × 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 did'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 aborption 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 the 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 ± 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 $kg.ha^{-1}a^{-1}$ (Table 2, Suplementary 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 $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ fluxes (Table 2, Suplementary 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 et al., 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 (Rogora 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).

$m = \text{Median}\left(\frac{x_j - x_l}{j - l}\right), \forall\, l < j$ where x_j and x_i were the jth and ith 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, Suplementary 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, Suplementary materials). The interception was systematically higher under the spruce stand than under the beech stand (Table 1, Suplementary materials). The average annual interceptions for the 1986–2012 period were 35% and 25% under spruce and beech stands, respectively (Table 1, Suplementary 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 (34–35%) and for the same beech plot (Biron, 1994; 25%) or with other similar spruce and beech plantations (Delfs, 1965; Nihlgård, 1970; Bultot et al., 1972; Johnson, 1990; Staelens et al., 2008; 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, Suplementary materials).

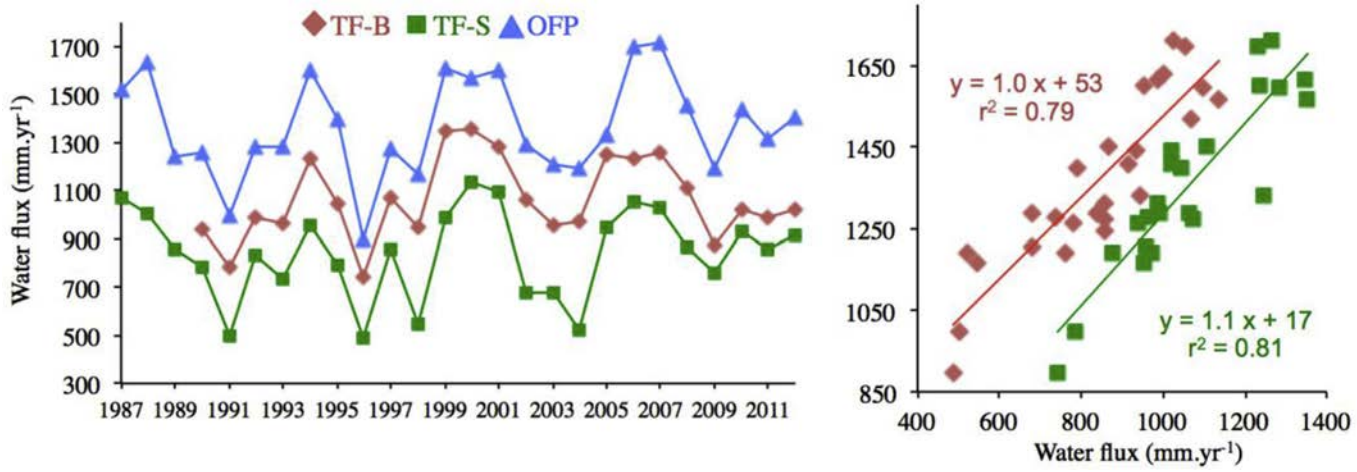

Fig. 2. a) Annual water fluxes in open field precipitation (OFP) and throughfalls under spruces (TF-S) and under beeches (TF-B) for the period 1987–2012; b) Open field precipitation (X axis) vs. throughfall (Y axis) under spruces (TF-S) or under beeches (TF-B) in the Strengbach catchment for the period 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 (Suplementary 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 µS/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 2–9 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; Laouali 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; Laouali 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 (0.1–8), 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 (70–150 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.

Indeed, for the anthropogenic-influenced elements, the sea-salt contribution was weak. For instance, for sulfate, the sea-salt fractions were on average 4, 5 and 9% in OFP, TF-S and TF-B, respectively. This result was confirmed by Pascaud (2013) and Pascaud et al. (2016) for a set of northeastern French stations. In the same way, the differences between the initial and nss concentrations for K and Ca were weak, which were confirmed by the high EF (Table 1)..

For all these reasons, the data and discussion in the following concern the bulk data, without any sea-salt corrections.

4.3. Trends in chemical composition and fluxes

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

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

The most obvious decreases in the concentrations and fluxes over time were for protons, SO_4^{2-}, and Ca^{2+} for the three types of precipitation (OFP, TF-B, and TF-S). The decreases in the acidity and sulfate concentration and fluxes were the highest, reaching 75% for sulfate concentration in TF-S (Table 2; Fig. 3; Table 2, Suplementary materials).

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

The mean annual SO_4^{2-} concentrations decreased from 27 to 9, 65 to 15 and 94 to 23 µmol l^{-1} in open field precipitation and throughfalls under beech and spruce, respectively, during the period (Fig. 3; Table 2, Suplementary materials). The Theil-Sen mean slopes suggested reductions of 0.5, 1.1 and 2.2 10^{-3} mmol $l^{-1}yr^{-1}$ for OFP, TF-B and TF-S, respectively (Table 2). Similarly, the mean annual S fluxes decreased from approximately 11 to 3, 15 to 4 and 28 to 5 kg $ha^{-1}a^{-1}$ in OFP, TF-B and TF-S, respectively (Fig. 3; Table 2, Suplementary materials). Considering that forest cover represents 90% of the catchment area (80 ha) with 80% spruce cover and 20% beech, the total sulfur atmospheric deposition can be calculated. At the Strengbach catchment scale, the annual sulfur deposition has decreased from 2 t of S in 1986 to 360 kg in 2012.

Table 1
Initial (non-corrected - nc) and non-sea-salt (nss) concentrations and enrichment factors (EF) in open field precipitation (OFP) and throughfalls under spruces (TF-S) and under beeches (TF-B) for K, Mg, Ca, Cl and SO_4. The data corresponded to the average values during the 1986–2012 period considering the entire sample data set (n = 623 for OFP; n = 591 for TF-S, and n = 510 for TF-B). The values in bold correspond to the non-sea-salt concentration.

	K	Mg	Ca	Cl	SO_4	K	Mg	Ca	Cl	SO_4
	concentration (µmol.l^{-1})					EF				
OFP- nc	*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**
TF-S nc	*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**
TF-B nc	*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**

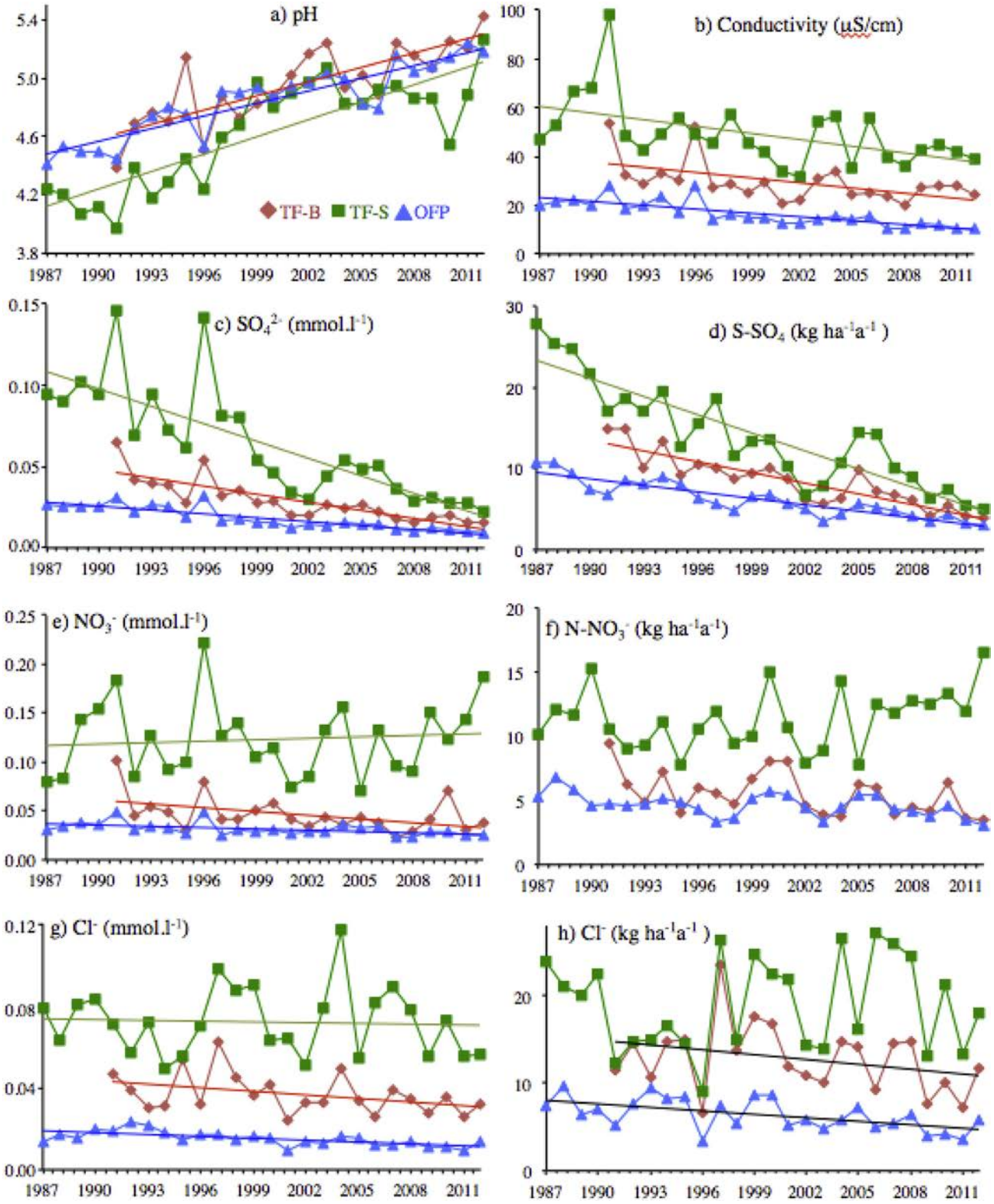

Fig. 3. Evolution of the mean annual a) pH, b) conductivity (µS cm^{-1}), c) concentration of SO_4^{2-} in mmoles.l^{-1}, d) fluxes (kg ha^{-1} a^{-1}) of S-SO_4, e) concentration of NO_3^- in mmoles.l^{-1}, f) fluxes (kg ha^{-1} a^{-1}) of N-NO_3, g) concentration of Cl^- in mmoles.l^{-1}, h) fluxes (kg ha^{-1} a^{-1}) of Cl, i) concentration of NH_4^+ in mmoles.l^{-1}, j) fluxes (kg ha^{-1} a^{-1}) of N-NH4, k) concentration of Na^+ in mmoles.l^{-1}, l) fluxes (kg ha^{-1} a^{-1}) of Na, m) concentration of K^+ in mmoles.l^{-1}, n) fluxes (kg ha^{-1} a^{-1}) of K, o) concentration of Mg^{2+} in mmoles.l^{-1}, p) fluxes (kg ha^{-1} a^{-1}) of Mg, q) concentration of Ca^{2+} in mmoles.l^{-1}, r) fluxes (kg ha^{-1} a^{-1}) of Ca, and s) fluxes (kg ha^{-1} 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 to 23, 100-23 and 221-71 µmol l^{-1} in OFP, TF-B and TF-S, respectively (Fig. 3; Table 2, Suplementary materials), and the concentrations decreased at an average of −0.4 and −1.3 mmol l^{-1}yr^{-1} in OFP and TF-B,

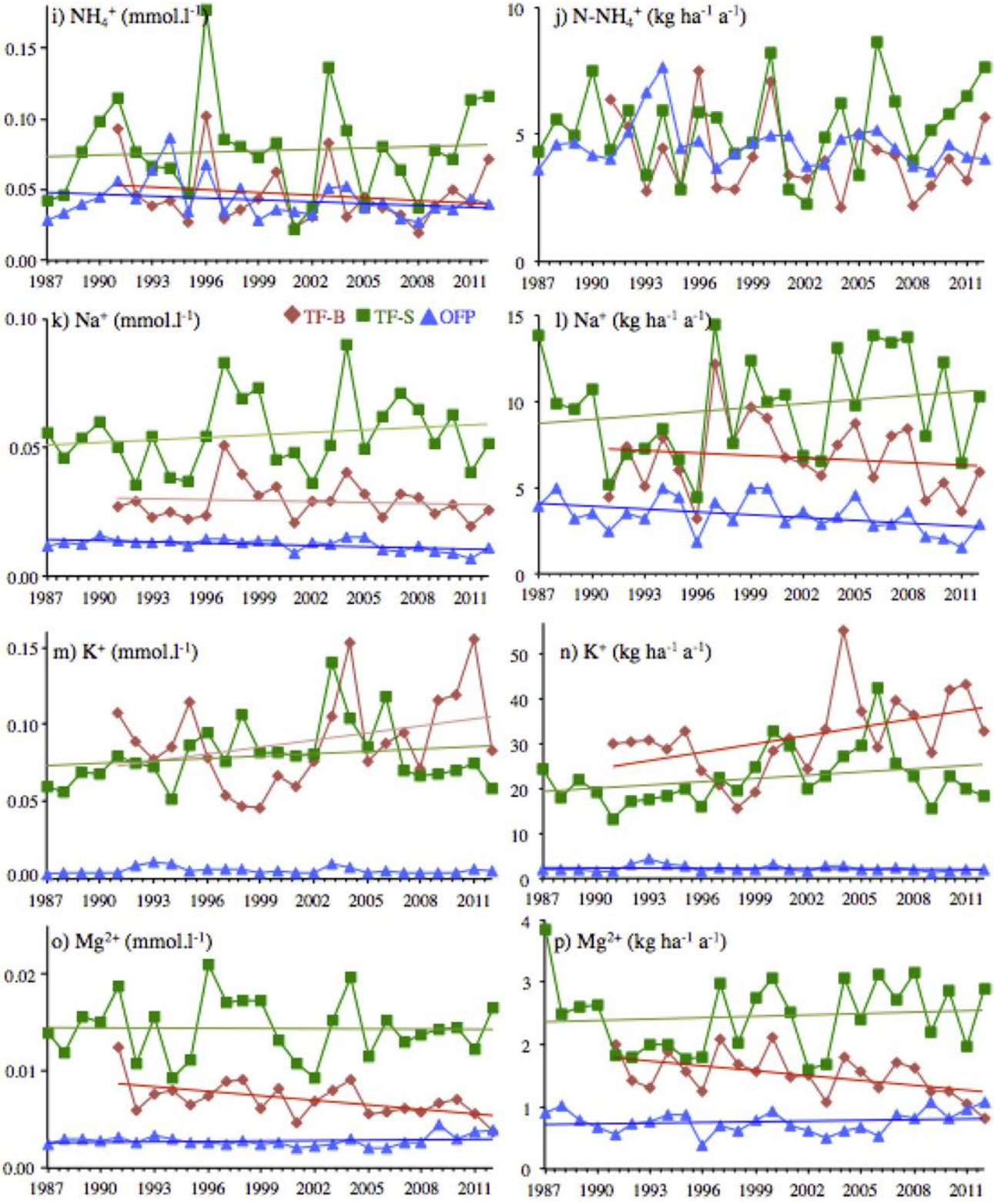

Fig. 3. (*continued*)

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).

The mean annual Ntot fluxes ranged from 5.9 kg ha^{-1}a^{-1} (TF-B in 2004) to 24.2 kg ha^{-1}a^{-1} (TF-S in 2012) with the highest values systematically for TF-S (Table 2, Suplementary materials).

Concerning base cations other than Ca^{2+}, concentrations decreased significantly for Na^+ and K^+ only in OFP and for Mg^{2+} in TF-B, with SKT $p < 0.01$ (Table 2).

The highest cation fluxes in OFP were for Na^+ and Ca^{2+} (3.4 and 3.3 kg ha^{-1}a^{-1}, respectively, on average for the 1986–2012 period),

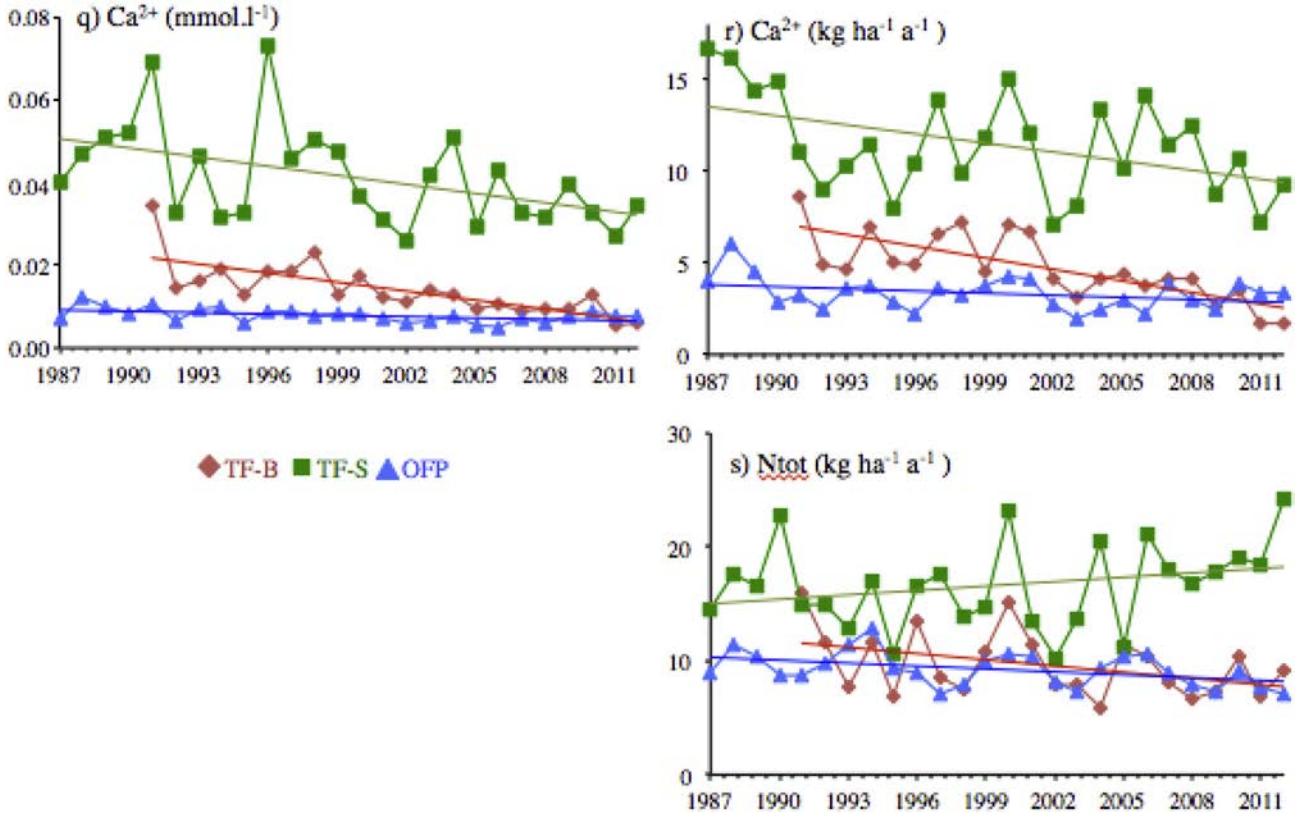

Fig. 3. (*continued*)

whereas the highest cation fluxes were for K^+ in throughfall (22.4 and 31.6 kg $ha^{-1}a^{-1}$, respectively, in TF-S and TF-B for the 1986–2012 period).

The precipitation composition was strongly modified after passing through the tree canopy. The element concentration in throughfall was systematically higher than in open field precipitation, with an increase of 1.25 for NH_4^+ and to 20-fold for K^+ (Table 2, Suplementary materials). These ratios were consistent with previous estimates in this area (Probst et al., 1990a, 1992a; 1995b) and were closely comparable to data published by Balestrini and Tagliaferri (2001) and Shen et al. (2013). The mean annual concentration was always higher in TF-S than in TF-B, except for K^+ (Table 2, Suplementary materials). Even if the long-term trends of pH in throughfall and precipitation increased in similar ways (Fig. 3a, Table 2), the modification of acidity by the canopy differed between the two types of plantation. The pH in throughfall under spruces was lower than that in open field precipitation, whereas the acidity decreased when rain passed through beeches (Fig. 3a, Table 2, Suplementary materials). The annual elemental fluxes followed the same trends as the elemental concentrations and were systematically the highest in TF-S, except for K^+ (Fig. 3).

4.4. Correlations between chemical composition and fluxes

4.4.1. Relationship between elements

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).

Table 2
Results of the Seasonal Kendal Test (SKT) and the Teil Sen slope obtained for different chemical elements with the 25 years data set of open field precipitation (OFP), spruce-throughfall (TF-S) and beech-throughfall (TF-B). The values in bold correspond to significant trend.

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

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. The values in bold correspond to correlation coefficient > 0.5.

	NH_4	Na	K	Mg	Ca	H	Cl	NO_3	SO_4
	vs SO_4	*vs SO_4*	*vs SO_4*	*vs SO_4*	*vs SO_4*	*vs SO_4*	*vs SO_4*	*vs SO_4*	*vs SO_4*
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**
	vs Cl	*vs Cl*	*vs Cl*	*vs Cl*	*vs Cl*	*vs Cl*	*vs Cl*	*vs Cl*	*vs Cl*
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
	vs Ca	*vs Ca*	*vs Ca*	*vs Ca*	*vs Ca*	*vs Ca*	*vs Ca*	*vs Ca*	*vs Ca*
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**
	vs H	*vs H*	*vs H*	*vs H*	*vs H*	*vs H*	*vs H*	*vs H*	*vs H*
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**

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).

A significant correlation was also observed for K^+ and Mg^{2+} in TF-S and for NO_3^- and Ca^{2+} in OFP. Except these two relations, no other flux of an element correlated significantly with the precipitation amount for TF-B (Table 4).

5. Discussion

5.1. Link between atmospheric deposition and emission trends

5.1.1. Anthropogenic compounds

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

As a comparison, the measured annual throughfall depositions of S in 1994 in spruce forests were approximately 20 kg ha^{-1} and 30 kg ha^{-1} in the Strengbach catchment and at Načetín in the Ore Mts, Czech Republic, respectively (Table 2, Suplementary materials; Dambrine et al., 2000; Oulehle et al., 2006). The differences between these two sites resulted from the intensities of SO_2 emissions, which were greater in Central Europe (Dambrine et al., 2000). On the basis of 37 sites located throughout France, Pascaud et al. (2016) identified a decline of 30–40% in SO_4^{2-} concentrations in wet open field precipitation from 1995 to 2007, close to that observed at the Strengbach catchment (30–45% in OFP, TF-S and TF-B). Similarly sulfate in rain and throughfall decreased significantly since 1990 in Europe or US (Balestrini et al., 2000; Pannatier et al., 2011; Thimonier et al., 2005; Rogora et al., 2006; Lehmann et al., 2007; Watmough et al., 2005; Oulehle et al., 2017; Vuorenmaa et al., 2017, 2018). By the 1980s, the rate of anthropogenic SO_2 emissions have decreased significantly (e.g., Klimont et al., 2013; Kopacek and Vesely, 2005, 2016; Fioletov et al., 2016). The European annual amounts of emitted SO_2 peaked in 1975 (60 000 t; Torseth et al., 2012; Hunova et al., 2014; Crippa et al., 2016). In France, the SO_2 emissions decreased from 3613 kT in 1973 to 232 kT in 2012 (−94%; Fig. 6; CITEPA: http://www.citepa.org). At a more local scale, the record of SO_2 emissions in the Alsace Region (ASPA:

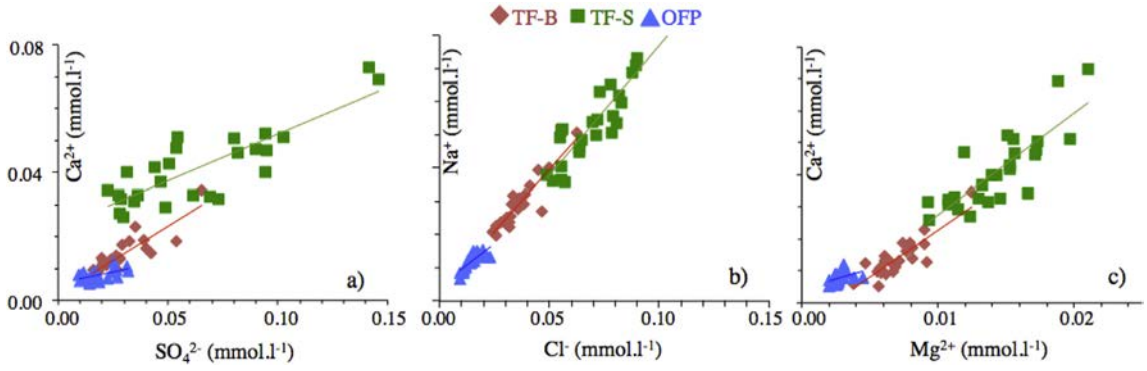

Fig. 4. Relationships between concentrations (mmol/l) of (a) Ca vs. SO_4, (b) Na vs. Cl and (c) Mg vs. Ca for the open field precipitation (OFP) and throughfalls under beech (TF-B) and under spruce (TF-S) for the 1986–2012 period in the Strengbach catchment.

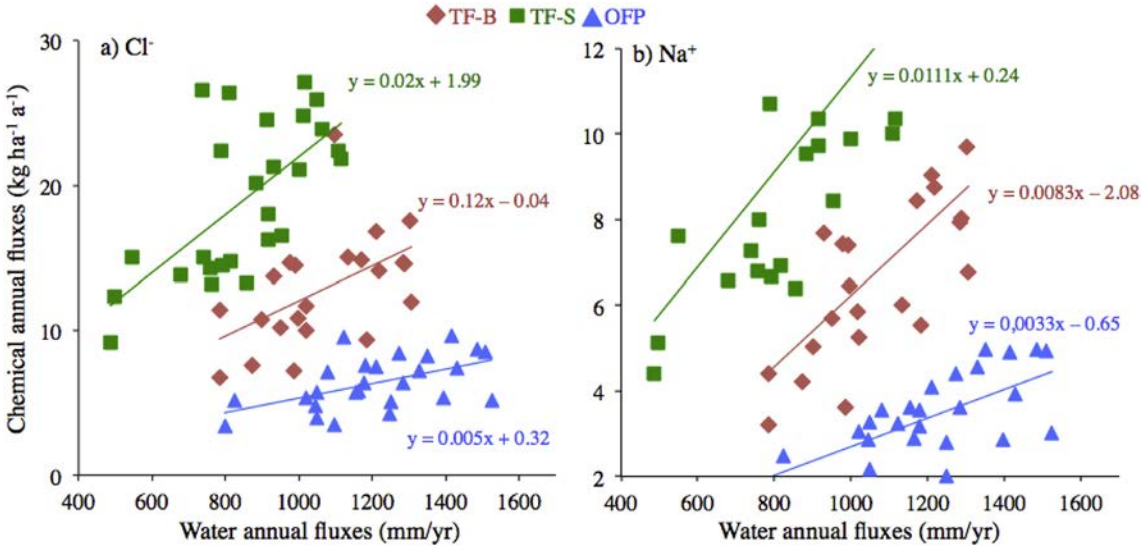

Fig. 5. Relationships between the annual chemical flux and the water flux (mm/yr) for contrasting and representative elements a) Cl^- and b) Na^+ for open field precipitation (OFP) and throughfalls under spruce (TF-S) and under beech (TF-B).

http://www.atmo-alsace.net; Fig. 7a) showed a similarly important decrease, explaining the global trend observed for the Strengbach catchment (Fig. 6).

However, starting in 2001, the global SO_2 emissions presented annual increases mainly caused by the economically emerging countries and regions such as China, India, the Middle East and Brazil (Smith et al., 2011; Klimont et al., 2013; Vet et al., 2014; McLinden et al., 2016; Li et al., 2017; EDGARV4.2 http://edgar.jrc.ec.europa.eu/background.php; Fig. 6). Fioletov et al. (2016) made an inventory of global SO_2 emissions for the period 2005–2014 and observed a maximum in 2007 mainly related with China emissions, which was consistent with our observations. Similarly, according to Yang et al. (2016) for the period 1995–2014, the China SO_2 emissions were maximum in 2006. Finally, the SO_2 emissions in several other countries increased, or stop to decrease, during the 2001/2008 period as Ukraine, Russia, Turkey and even United State (http://webdab1.umweltbundesamt.at).

According to different studies or models, the world SO_2 emissions have decreased again since 2008, (Klimont et al., 2013; Yang et al., 2016).

Until 2002, the sulfate concentration declined in open field precipitation and throughfalls in the Strengbach catchment, following the decrease in Alsace, French and worldwide SO_2 emissions as a whole (Fig. 6). However, the increase in sulfate deposition by 2001 (Fig. 3) cannot be related to regional influence of gaseous SO_2 emissions since no increase was observed in local and national emissions (Fig. 6). Intercontinental transports of anthropogenic sulfur dioxide have been observed and traced (Tu et al., 2004; Clarisse et al., 2011).

In addition, SO_2, as well as NO_x can be oxidized in the atmosphere as H_2SO_4 and HNO_3 respectively, which can move into the stratosphere and being transported over long-range scale (Read et al., 1993; Wilson et al., 1992). Anthropogenic sulfate have been recorded for example in ice cores in Greenland, in Svalbard or in alps glaciers and are attributed to long-range transport (Mayewski et al., 1986; Moore et al., 2006; Preunkert et al., 2001). Balestrini et al. (2007) estimated the dry distribution for sulfate from 43 to 47% in the canopy.

The increase in SO_4^{2-} concentrations observed in OFP and throughfalls during the period 2001–2008 (Figs. 3,6) could be related to the SO_2 emitted in middle or long distance regions and transport as SO_2 gaz or as degradation products and aerosols.

Two peaks in the mean annual concentrations of sulfate were recorded in 1991 and 1996, as well as in nitrate, ammonium, magnesium and calcium (Fig. 3). They can be related to very high concentrations during the spring season and more precisely from 01/03 to 15/05 (database OHGE). At the opposite, periods from 01/03 to 15/05 represented 15% and 4% of the annual water flux of for 1991 and 1996, respectively. Thus, contrary to the annual concentrations, the annual fluxes were not very much influenced by these high values (Fig. 3). No peaks were recorded for Cl, Na or K. Because SO_4^{2-}, NO_3^- and NH_4^+

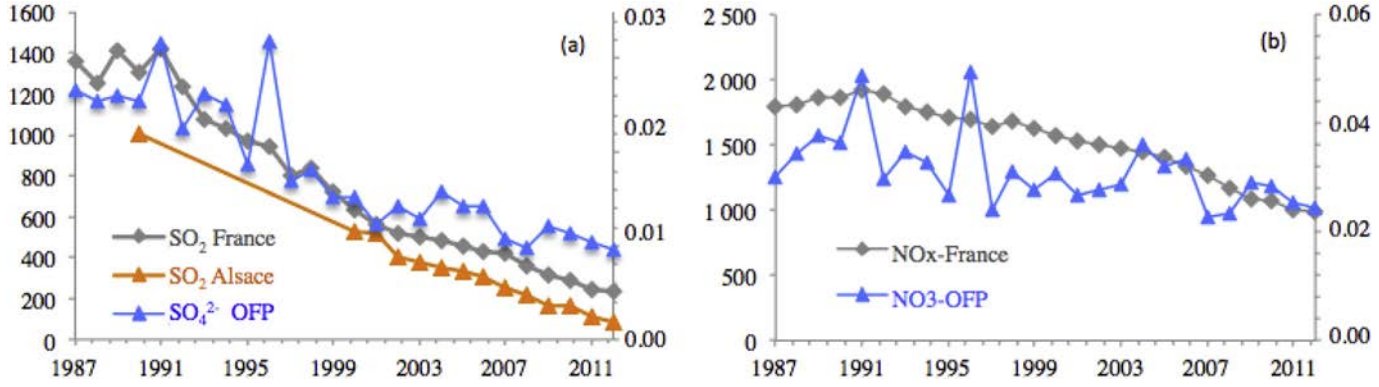

Fig. 6. a) SO_2 and b) NOx emissions from 1987 to 2012 in France (in kT, CITEPA ordinate scale) and in Alsace (multiplied by a factor 50 in order to use the same scale, source: ASPA-http://www.atmo-grandest.eu (ordinate scale at the left), compared with the evolution of the mean annual a) sulfate and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

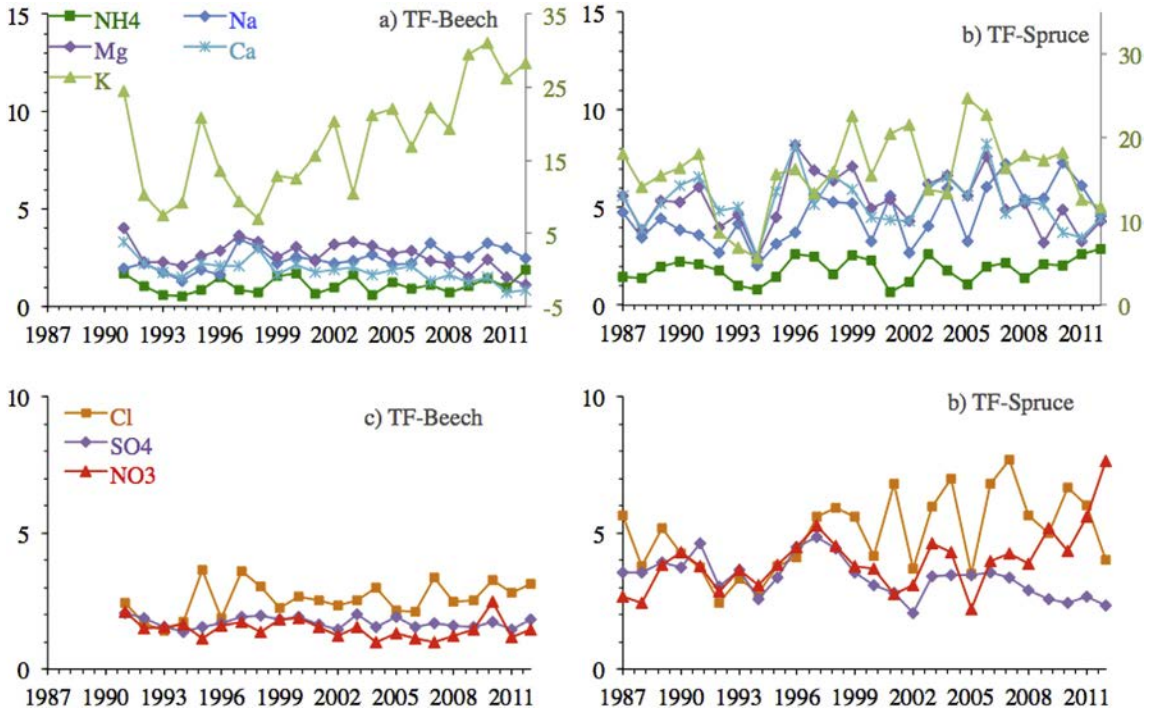

Fig. 7. Ratio of mean annual concentration in throughfall to open precipitation for NH_4, Na, K, Ca and Mg in a) beech and b) spruce stand and Cl, SO_4 and NO_3 in c) beech and d) spruce stands from the Strengbach catchment (period 1986–2012). Scale on the right corresponds to K concentrations.

were influenced by human activities, the high concentrations during spring for OFP, TF-S and TF-B could have been of anthropogenic origin from continental air masses (which would explain the absence of peaks for Na, Cl or K). Vieno et al. (2014) proposed that the primary cause of episodes of elevated nitrate and sulfate in atmospheric particulate matter was the meteorological conditions, i.e., persistent high-pressure system keeping air pollution.

In summary, the long-term sulfate concentrations in the precipitation trends could be explained by 1) mainly the global SO_2 gaseous emissions trend, 2) the long-distance transport of sulfur compounds, in agreement with the concept of long-range transport of atmospheric pollutants (Matejko et al., 2009; Posch et al., 2008; Hettelingh et al., 2008). and 3) local/regional conditions (climatic conditions, atmospheric gaseous and particulate concentrations) inducing specific seasonal variations within the global trend.

5.1.1.2. 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 NOx, 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:

$$(SO_4^{2-})_{OFP} = 633\ (H^+)_{OFP} + 0{,}075\ r = 0{,}62\ n = 623$$

$$(SO_4^{2-})_{TF\text{-}B} = 1343\ (H^+)_{TF\text{-}B} + 0{,}011\ r = 0{,}63\ n = 509$$

$$(SO_4^{2-})_{TF\text{-}S} = 835\ (H^+)_{TF\text{-}S} + 0{,}034\ r = 0{,}60\ n = 591$$

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).

The pH values of open field precipitation and throughfalls were still increasing, and the mean annual pH of rain in 2012 (5.18; Table 2, Suplementary materials) was still lower than the preindustrial pH value (estimated as 5.7 to 6; Pallares, 1993; Kopacek et al., 2016), which indicated that a steady-state, and recovery, had not yet been reached. Even if world SO_2 emissions had strongly decreased during the past decades, the NOx emissions were still higher than in 1960. These observations revealed that the pH of precipitation was still impacted by anthropogenic activities. Considering the trend observed in the precipitation data over the period from 1986 to 2012 and the annual concentrations (pH = 0.029 x year −52.41; r = 0,82; n = 25), the preindustrial pH of 5.7 could be reached in 2032 in the Strengbach catchment, if the emissions trends remain constant as at present and without any changes in environmental parameters.

5.1.1.3. Nitrogen (nitrate and ammonia). The NOx emissions have decreased since the 1990s in France and Europe (Fig. 6b), but they were still increasing at the global scale (Vet et al., 2014). The decrease in french NOx emissions could be estimated at 47% over the period 1985–2012 (CITEPA data; Fig. 6), but declines were less than those observed for sulfate because of the development of road transportation or international shipping (Vestreng et al., 2009; Eyring et al., 2010).

The decrease in nitrate observed in open field precipitation and beech throughfall in the Strengbach catchment could thus be related to the decrease in NOx anthropogenic gaseous emissions (Fig. 7b) in France or in Europe. However, surprisingly, the nitrate concentration in TF-S did not manifest a significant time-dependent evolution, with a large variability (Fig. 4a) of annual fluxes ranging from 19 in 2002 to 88 kg ha^{-1} a^{-1} in 1990 (Fig. 4). Similarly, NO_3 concentrations in throughfall under spruce (Nacetin site, Czech Republic; Oulehle et al., 2006) or under pine (Whitehead et al., 2002; Skeffington and Hill, 2012) had not changed significantly since the eighties or nineties. In contrast to sulfate, nitrate concentrations in throughfall were not only

the result of atmospheric deposits because of foliar uptake and biological excretions occurring at the water/leaf interfaces (Ulrich, 1983; Lovett and Lindberg, 1984; Skeffington and Hill, 2012).

Pascaud et al. (2016) highlighted the lack of a systematic relationship between the reduction in NOx emissions and the changes in NO_3 concentrations in open field precipitation from 37 French rural sites with both significant increasing and decreasing trends depending on the sites.

Ammonium concentrations, similarly to those of nitrate, decreased in OFP and TF-B but interestingly increased in TF-S. However, the trend was only statistically significant for the throughfall under beech ($-0{,}6$ mmol $l^{-1}yr^{-1}$), according to the SK Test (Table 2). The NH_3 emissions (NH_4 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 Breemen et al., 1983, Cui et al., 2015; Meesenburg 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

5.1.2.1. 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.

5.1.2.2. 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; Lovett-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 $l^{-1}yr^{-1}$ 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; Torseth et al., 2012).

The annual Ca flux produced in soils by mineral weathering at the Strengbach catchment was estimated as < 2 kg $ha^{-1}a^{-1}$ (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 $ha^{-1}a^{-1}$ 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 $ha^{-1}a^{-1}$) was almost equivalent to the input by precipitation (11.6 kg $ha^{-1}a^{-1}$) (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 kg $ha^{-1}a^{-1}$, respectively, under spruce and beech stands (Fig. 4i and j), which corresponded to a loss of 900 and 400 kg 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.

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, Suplementary materials, Fig. 7), as had already been observed in many places (Ulrich, 1983; Probst et al., 1990a,b; Draaijers and Erisman, 1995; Dambrine et al., 1998b; Balestrini and Tagliaferri, 2001; Balestrini et al., 2007; Vogt et al., 2006; Schrumpf et al., 2007; Berger et al., 2008; Staelens et al., 2008; Kopacek et al., 2009; Skeffington and Hill, 2012; Eisalou 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; Adrianssens et al., 2012; Eisalou 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; Adrianssens 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 (Bréda, 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 trees/ha), respectively (Asael, 1990), which was in agreement with the lower LAI measured for spruces (7.1–37% interception) than for beeches (7.9–25% interception) at the Kreisbach site (Lower Austria, Berger et al., 2008). However, LAI was probably not the best indicator to explain the differences in interception. The plant area index (PAI), referring to all the light-blocking elements (leaves, stems, twigs; He et al., 2014), seemed more appropriate to explain the variation in interception. The higher interception observed under spruces in the Strengbach catchment could thus be explained by the global geometry.

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

Similar to interception, the conductivity and most of the elemental concentrations (NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}) were higher in TF-S than in TF-B, and both were enriched compared with open field precipitation (Figs. 3, 4). However, the chemical behavior and the interaction with the canopy depended on the nature and origin of the elements; some elements such as SO_4^{2-}, Cl^- and Na^+ were not biologically reemitted or absorbed by the foliage, but they were mainly physically deposited as wet and dry atmospheric aerosols on the foliage area (Ulrich, 1983; Probst et al., 1992b; Dambrine et al., 1998b; Thimonier et al., 2008; Kopacek et al., 2009). In contrast, K^+ was strongly excreted by leaves, whereas Ca and Mg were weakly influenced by biological canopy exchange (e.g., Lovett and Lindberg, 1984; Kopacek et al., 2009; Adrianssens et al., 2012). The concentration ratio between throughfall and OFP was used to compare the atmospheric input under the two types of canopy (Fig. 7).

5.2.1. Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}

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

Na^+ and Cl^- were well correlated in open field precipitation and in throughfalls (Table 3; Fig. 5), underling their primary oceanic origin. Nevertheless, the decrease of Cl^- observed and discussed above (see 5.1.1) both in OFP and TF-B might have reflected the decrease of an anthropogenic fraction and/or changes in climatic influence. The significant and similarly increasing Cl and Na ratios over OFP (Fig. 7) observed in throughfall under spruce for the past years while these values remained constant in TF-B was questionable and lacked any consistent explanation. Na was generally considered inert with respect to the canopy (neither uptake nor excretion occurred; De Schrijver et al., 2007). Because of the good correlation of Cl with Na, chloride could also be considered inert. Moreover, the equilibrated Cl budget at the catchment scale confirmed the inert character of chloride in the Strengbach catchment (Probst et al., 1992a). The annual Cl and Na ratios over OFP were related to the annual H_2O flux, especially for the past decade with high values for the years 2001, 2007 and 2010. A modification of the rainfall regime and the wind mass origin, as discussed in 5.1.2, could have impacted the chemistry of the TF-S more deeply because of needles geometry and persistence, explaining why the variation was not significant for TF-B.

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

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

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

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

In contrast, the long-term evolution of K^+ in TF-B differed strongly

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

	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

from those of other cations, with higher variations and a significant increase since 2003 (Fig. 7). Potassium was a very mobile element in trees and was the most enriched cation in xylem sap (Dambrine et al., 1992). Adrianssens et al. (2012) observed that the ratio between K^+ concentrations in throughfall and bulk precipitation decreased with increasing canopy height and that this effect is more important in beech stands than in spruce stands. The K^+ concentrations in throughfalls thus seemed more influenced by the canopy structure under beeches than that under spruces. Indeed, with the beech stand aging, the canopy structure changed over time.

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

5.2.2. Protons

As suggested above, the geometry and persistence of spruce needles explained the higher concentration of acidic atmospheric-derived elements in the corresponding throughfall compared with OFP and TF-B (Fig. 3a). On the other hand, the throughfall under beeches was less acidic than in open field precipitation (Fig. 3a). Such a pattern had already been observed for coniferous and deciduous trees (Rothe et al., 2002; Berger et al., 2008; Draaijers and Erisman, 1995; Adrianssens et al., 2012; Eisalou et al., 2013). Indeed, some deciduous trees were able to partly neutralize the incoming atmospheric acidity by the uptake of H^+ through the canopy and the exchange with base cations or ammonium on the inner leaf surfaces (Zeng et al., 2005).

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

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

5.2.3. Nitrate and ammonium

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

The annual fluxes of nitrogen derived from NO_3^- and NH_4^+ were similar in OFP with averages of 4.49 and 4.52 kg ha^{-1} a^{-1}, respectively, for the 1986–2012 period. The results were also comparable 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-NO_3 and N-NH_4, respectively, on average for the 1986–2012 period (Table 2, Suplementary materials). 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 NH_4^+ 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 (58–80%; 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 (Fisher 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 NO_3^- and NH_4^+ in TF-S. However, in general NH_4^+ was more efficiently retained in canopy than NO_3^- (Avila et al., 2017), which could explain why the increase in nitrate is higher than that in ammonia in TF-S (Fig. 7b and d).

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, SO_4^{2-}, Cl^-, NO_3^-, Ca^{2+}, Mg^{2+}, and K^+). The decrease in acidity and sulfate concentration is likely related to the decrease in anthropogenic SO_2 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 displayed a decreasing trend in nitrate and ammonium concentrations. Considering the long-term trend slope, the preindustrial pH of 5.7 could be reached in 2032 in the Strengbach catchment.

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

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

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

As an illustration, the interception of water was two times more important under spruces than under beeches. Similarly, the concentrations of elements coming mainly or partly from atmospheric dry 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. For example, the annual Ca fluxes were on average half as important under beeches as under spruces, and during the period 1986–2012, they were reduced by 40 and 70%, from approximately 15 to 9 and approximately 6 to 2 kg $ha^{-1}a^{-1}$ under spruce and beech stands, respectively. These decreases could have been substantial in such an environment with Ca- and Mg-poor bedrock and participated in nutrient depletion in soils, which endangered soil fertility and might have contributed to forest decline.

Spruce needles accentuated the acidity and induced the intensification of acidification processes and consequently nutrient

leaching in soils, which led to forest decline. In contrast, beech leaves were able to neutralize a portion of the atmospheric protons, which minimized the negative effects of acid rain. Thus, the type of tree had a significant influence on the transfer of elements (nutrients and pollutants) in ecosystems.

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

Finally, a large proportion of K^+ in throughfall came from biological excretion with more than a factor of 15 between rain and throughfall fluxes. K was the chemical element the most influenced by the canopy. The increase in K^+ concentrations in beech throughfall could have been related to 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 sylvicultural 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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