Long-term additions of ammonium nitrate to montane forest ecosystems may cause limited soil acidification, even in presence of soil carbonate

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Abstract. In Europe, nitrogen (N) deposition to forest ecosystems decreased in the last decades, but remains in many cases higher than the critical loads, i.e. higher than what could be considered as safe. The main concerns about N deposition are eutrophication and acidification. In a long-term experiment in a montane (1200 m a.s.l.) coniferous forest in Alptal, central Switzerland, we simulated higher N deposition by adding NH_4NO_3 to rain water. This treatment represented 22 kg ha^{-1} y^{-1} of

15 N, compared to 12 kg ha^{-1} y^{-1} ambient bulk deposition. It was applied at the same time to a small catchment and to plots in a replicated block experiment (n=5). The site has a carbonate-rich parent material and is thus not particularly endangered by acidification. Nevertheless, while previous reports on this experiment concentrated on N as a nutrient, we examine here soil acidification processes as affected both by ambient and experimentally increased N deposition. In the last two and a half decades since study start in 1994, nitrate (NO_3^-) and especially sulfate (SO_4^{2-}) concentrations decreased in precipitation,

20 while pH increased by slightly more than 1 unit. In spite of these reduced acid inputs, the pH of the soil decreased. First, the exchangeable acidity in the soil increased, especially in the N-addition treatment. This was mainly observed on small mounds of the irregular topography of the site because they are less well buffered than the wet depressions. This trend, however, was also limited in time as exchangeable acidity later declined again, to reach values not much higher than 26 years before. This was also the case in the N-addition treatment and can be considered as a progressive recovery mainly due

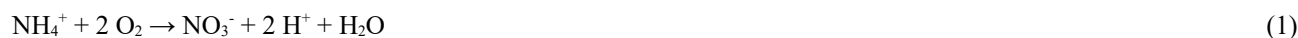
25 to the reduced acid inputs and, at this site with a carbonate-rich sub-soil, to the biological cycling of base cations. The pH of the runoff from the experimental catchments decreased by 0.3 units, both in the control and under N addition. Decreasing Ca^{2+} and increasing Al^{3+} and Fe^{2+} concentrations in runoff are also showing that the recovery observed in the exchangeable soil acidity is not yet able to stop the slow acidification of water leaving the catchments.

1 Introduction

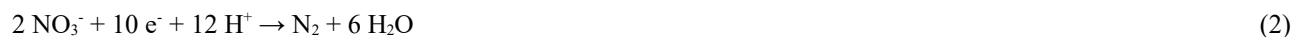
30   Due to anthropogenic activity, the transformation rate of inert N_2 into reactive N has been more than doubled compared to pre-industrial times (Vitousek et al., 1997). The reasons for this influx of reactive N are increases in combustion of fossil fuels, the widespread application of N fertilizer and the increased cultivation of N-fixing crops (Galloway et al., 2003). Globally, close to 80% of the emissions of NO_X and around 70% of the emissions of NH_4^+ are a result of human activity (Schlesinger & Hartley, 1992); (Delmas et al., 1997). A large share of the anthropogenic N emissions ends up in the

35   atmosphere and can be transported over long distances and deposited as a result of gravitation (dry deposition) or dissolved in atmospheric precipitation (wet deposition). Together with sulfate (SO_4^{2-}), NO_X compounds are responsible for the acidity in the atmospheric precipitation. As large regions of the terrestrial biosphere are N limited, increased N deposition can have significant effects on biological activity both below and above ground. In particular, forests in temperate regions are thought to be naturally N-limited (Vitousek & Howarth, 1991). Moderate increases of N deposition in forest soils have been shown

40   to be correlated with increased mineralization rates, nitrification as well as plant growth rates. Nitrification releases protons (H^+) into the soil solution (Equation 1).

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2\ H^+ + H_2O \tag{1}$$

NH_4^+ used by plants corresponds to an exchange of this cation with H+, which is then released into the soil (Galloway et al., 2003; Högberg et al., 2006). These biologically induced releases of H^+, together with the inflow of H^+ from the atmospheric

45   precipitation, mean that soil acidification is a possible consequence of increased N deposition. This has been observed in a wide range of studies (Boxman et al., 2008; Bowman et al., 2008; Lu et al., 2009; Högberg et al., 2006; Lieb et al., 2011). Losses of N from NO_3^- to atmospheric N_2, on the other hand, consume H^+ (Equation 2).

$$2\ NO_3^- + 10\ e^- + 12\ H^+ \rightarrow N_2 + 6\ H_2O \tag{2}$$

Decomposition of plant residues also leads to a consumption of H^+. Beside the balance between inputs and outputs, the rate

50   at which the soil acidifies depends on its buffering capacity. The dominant processes by which H^+ is buffered are either through biologically induced redox reactions, which can take place in decomposition of biomass, or through mineral weathering and cation exchange mechanisms on the surfaces of soil solids. These buffering mechanisms remove H^+ from the soil solution, reducing the acidity. Which type of buffering process dominates, depends on the soil pH and the mineralogy of the soil. The dissolution of calcium carbonates is the dominant buffering process in calcareous soils (Equation 3).

55    $$CaCO_3 + 2\ H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \tag{3}$$

The dissolution of silicates is a slower process and depends very much on the types of silicate minerals present in the soil. This buffering process usually only contributes substantially to the buffering systems at lower soil pH, as silicate dissolution rates increase logarithmically with decreasing pH (Amelung et al., 2018). At very low pH, hydrolysis and dissolution of Al and Fe complexes are the dominant buffering systems (Chadwick & Chorover, 2001).

60   If the rate of inflow of H^+ is higher than the rate of the buffering mechanisms, the soil will acidify. Soil acidification can be recognized by a number of factors including a reduction in soil pH over time indicating a higher concentration of H^+ in the

soil. A further indicator is an increase in the proportion of acidic cations compared with the proportion of base cations in the cation exchange capacity (CEC). As a consequence of the decreasing pH, cations such as H^+, aluminum (Al^{3+}), iron (Fe^{2+}) and manganese (Mn^{2+}) replace base cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+)

65 from the cation exchange sites on the surfaces of mineral particles and organic matter in the soil (Amelung et al., 2018). This leads to an overall reduction in the base saturation (BS) and a reduction of the buffering capacity. Cations, which are being replaced from exchange sites or stem from dissolution reactions of minerals, enter the soil solution and can leach from the soil. Runoff water from acidified soils shows higher concentrations of dissolved base cations and dissolved metals, especially Al^{3+} and Fe^{2+} (Warfvinge & Sverdrup, 1984). Soil acidifying processes can therefore be observed directly in the

70 soil or indirectly in the chemical composition of the runoff water.

Soil acidification due to increased N deposition can have adverse impacts on the biosphere and on the surrounding environment. Possible effects on plants can be Al toxicity as a result of increased Al loads in the soil solution and increased loads of Al adsorbed at the cation exchange sites. The depletion in base cations in the soil can also lead to nutrient imbalances affecting plant growth (Richter et al., 2007); (Göransson & Eldhuset, 1995). Furthermore, the increased leaching

75 of N, due to N saturation and increased nitrification rates can affect water bodies downstream by inducing eutrophication. Increased N deposition is not the only possible driver of soil acidification. Precipitation with low pH values, commonly known as acid rain, is another source of H^+ to the soil. The low pH is mainly caused by high concentrations of sulfate (SO_4^{2-}) and NO_X. Thanks to stringent emission regulations in Switzerland and in Europe in general, SO_4^{2-} concentrations in the precipitation have declined and the pH of precipitation has increased over the last 30 years. However, an abatement of

80 oxidized (NO_X) and especially reduced (NH_3) N emissions is more difficult. N concentrations have thus not decreased as much and N deposition continues to be an environmental problem. In Switzerland a large share of the natural ecosystems receive N deposition above the critical load (Rihm & Achermann, 2016). In large parts of the world, the deposition of reduced N also decreases less than that of oxidized N (Templer et al., 2022).

A considerable amount of research has been conducted on the effect of increased N deposition on weakly buffered soils such

85 as for example on alpine soils (Lieb et al., 2011), tropical soils (Lu et al., 2014), subtropical soils (Lu et al., 2009) and temperate non calcareous soils (Boxman et al., 2008). Soil acidification has been observed in all those cases. However, the effect of increased N deposition on the biogeochemistry of a well-buffered system, has not been examined to the same extent. This is probably due to the assumption that minimal effect is expected on soil pH of well-buffered soils. In the present study, the biogeochemical development of such a well-buffered forest soil in the Prealps of Switzerland was

90 analyzed. A long-term N-addition experiment has been conducted at that site, during which a catchment area in a coniferous forest was subjected to NH_4NO_3 additions at a rate of 22 kg ha^{-1} y^{-1} and compared to a control catchment receiving only ambient N deposition at a rate of 12 kg ha^{-1} y^{-1}. The chemistry of the runoff water from these catchments, as well as the atmospheric precipitation were regularly analyzed over the entire period of the experiment (Schleppi et al., 1998).

Despite the fact that the soil is well buffered, the question arises whether it might show signs of acidification as a result of

95   ambient N deposition, alone or in combination with N from the experimental addition of NH_4NO_3. Data of the precipitation

chemistry over time were used to test a first hypothesis:

1) Atmospheric precipitation becomes less acidic over time due to lower levels of pollution. This should be visible in an

increase in precipitation pH and should decrease the rate of soil acidification in the control.

The experimental N addition being almost twice the ambient deposition, soil samples from plots subjected to this N addition

100   were analyzed to examine a second hypothesis:

2) Relatively to the control, the N-treated soil (organic horizon and topsoil) experiences a stronger acidification, leading to

a lower pH and an increase of total acidity.

On this site, water movements through the soil occur mainly as preferential flow. This limits the contact between water and

the bulk of the well buffered Bw horizon. Soil acidification may thus affect the chemical composition of the runoff water.

105   Chemical data collected over more that 20 years from the experimental catchments were used to test a last hypothesis:

3) Soil acidification can affect the pH and the chemical composition of runoff water even on a site with a well buffered

subsoil.

2 Methods

2.1 Site description

110   The present study was conducted in the Alptal valley, in central Switzerland (47°03' N, 8°43' E), at 1200 m a.s.l. Flysch is

the parent rock material, which is composed of sedimentary conglomerates with clay-rich schists. The main soil types are

very heavy Gleysols. They contain on average 48% clay and have a low permeability, leading to a water table close to the

surface throughout the year (23 cm deep on average, Krause et al., 2013). The slope is about 20% with a west aspect. The

soil characteristics differ depending on the prevailing topography. At a scale of typically 10 m, the topography shows a

115   mosaic of mounds and depressions. The mounds are characterized by a lower lying water table and have a profile with mor

(raw humus), Ah and an oxidized or partly oxidized Bw horizon. The pH ranges from 3 to 4 at depths down to ~10 cm. In

the depressions, the water table can reach the surface, leading to waterlogged conditions. The profile consists of an anmoor

(muck humus) topsoil, and an almost permanently reduced Bg horizon (Hagedorn et al., 2001b). The pH lies between 4.5

and 6 at depths of 0 to ~10 cm. Depending on the locations, annual net nitrification rates (down to a depth of 15 cm) are

120   partly positive and partly negative (N immobilization). Overall, the net rate is not significantly different from zero

(Hagedorn et al., 2001b).

The climate of the study is cool and wet, with an average annual temperature of 6°C and average annual precipitation of

2300 mm, reaching a maximum of 270 mm in June and a minimum of 135 mm in October (averages from 1994 to 2015). A

naturally regenerating mature Norway spruce stand (*Picea abies* (L.) Karst. is present on the site, admixed with 15% silver

125   fir (*Abies alba* Mill.). The trees are up to 270 years old, have a dominant height around 30 m and a low leaf area index (LAI)

of 3.8 (Schleppi et al. 1999b). As waterlogged soil conditions inhibit their growth in depressions, the trees grow on the mounds, accompanied by a ground vegetation dominated by *Vaccinium myrtillus* and *Vaccinium vitis-idaea*. In the depressions, ground vegetation is dominated by *Caltha palustris*, *Petasites albus*, *Poa trivialis* and *Carex ferruginea*. Rooting depth of all plants is limited to 10–25 cm depending on the micro-topography (Schleppi et al., 1999b). Atmospheric

130 deposition of inorganic N in bulk and throughfall is 12 and 17 kg N ha^{-1} y^{-1}, respectively (Schleppi et al., 1998).

2.2 Experimental catchments and N addition

Two forested catchments, each approximately 1500 m^2 in area, were delimited by trenches dug one year before measurements began. These trenches reach into the gleyic sub-soil and capture the sub-surface water flow (Schleppi et al., 1998). No change of the vegetation along the trenches has been observed that would indicate an enhanced drainage of the

135 soil along the trenches. Both catchments feature a similar proportion of mounds (approx. 40%) and depressions (approx. 60%). Water level is measured continuously in V-notch weirs at the bottom of the catchments. Water discharge is calculated from these measurements and averaged over 10 min periods (Schleppi et al., 1998). Both catchments always showed a rapid response to rain events and exhibited similar runoff peaks (Schleppi et al., 2004).

One year of measurements with weekly water analyses served as a calibration period. Increased N deposition was then

140 simulated in one of the catchments by sprinkling NH$_4$NO$_3$ dissolved in rain water collected into a water tank (2000 L) from a polyethylene sheet (300 m^2) spread outside the forest. N addition occurred automatically when the tank was full, i.e., in small but frequent amounts: approximately 200 times per year for an average of 22 kg N ha^{-1} y^{-1}. In a paired-catchment design, the other catchment served as a control and received the same amount of rain water without any added N. During winter, N treatment was done with a backpack sprayer as occasional applications of a concentrated NH$_4$NO$_3$ solution on the snow

145 cover.

In June 2009, 15 trees per forested catchment, all with a diameter at breast height >20 cm, were girdled by removing bark and cambium around the stem (Krause et al., 2013). One year later, the girdled trees became infested by bark beetles (*Ips typographus*). To prevent spreading of the infestation, trees were felled in August 2010. This represented a heavy selective cutting by 38% of the total basal area of all trees >10 cm at breast height. The branches (with needles still attached) were left

150 on site, while the boles were removed by helicopter. Within 2 years after girdling, neither soil temperatures (7.1°C on average) nor soil water depths (23 cm on average) were affected. (Krause et al., 2013).

2.3 Sampling and analyses

Precipitation was measured and sampled weekly from an open area. Two 0.05 m^2 rain gauges were used, except in the winter when only one was heated in order to let the snow melt. Water samples were proportionally combined fortnightly and

155 filtered (0.45 μm). NH$_4^+$ was analyzed by flow injection, anions by ion chromatography and cations by induced-coupled plasma atomic emission spectrometry (ICP-AES) (Schleppi et al., 1998). The pH was measured with a Metrohm 654 pH-meter. Its electrode was filled with a low-concentration electrolyte (0.55 M KCl) to adapt to the low ionic strength of

precipitation samples. Further, 10% of the same 0.55 M KCl were added to each sample prior to measurement. Stable readings were difficult to achieve with precipitation water. For this reason, samples were bubbled with N_2 to favor degassing and readings taken after a fixed time of 6 minutes. In order to check the long-term consistency of the pH measurements, precipitation samples were proportionally pooled over periods of 3 months and frozen. After 21 years of collection, these samples were melted, measured again and compared to values calculated from the H^+ concentrations derived (by weighted averages) from the measurements done just after collection.

Runoff water was collected proportionally to the discharge (an aliquot per 200 or 300 L discharge) and bulked over 2 weeks (Schleppi et al., 1998; Schleppi et al. 2006). These samples were analyzed with the same methods as for precipitation water. For their pH measurement, a Metrohm 691 pH-meter was used, with a (normal) KCl 3 M electrolyte.

Soil samples were taken in a replicated block design (n=5) from plots located around and receiving the same treatment as the headwater catchments. See Hagedorn et al. (2001a) for a schematic map of the entire experiment. Each plot had a sprinkler at its center, spraying either rain water (control) or rain water with added NH_4NO_3 (N-addition treatment). Blocks (pairs of plots) were located so as to cover the variability of the topographical features: two blocks were set on mounds and three in depressions. Samples were taken as 3 cores per plot (5 cm diameter) at irregular intervals of several years. They were immediately refrigerated, brought to the lab, separated by soil layer and bulked over the 3 cores per plot. Stones and roots were removed and the samples then dried at 65°C. Samples taken in 1996 had been frozen and were dried and measured only in 2017. Samples taken in 2007 had been dried and were measured also in 2017. In other years, measurement followed drying within one month at most. The O and A horizon were included in our analyses. The Bw horizon receives almost no N from the experimental addition, as shown by ^{15}N labelling (Providoli et al., 2006). It is further well buffered by the presence of carbonate and was thus not included in our analyses on acidification.

In general, 10 g of each soil sample was suspended in 20 ml 0.01 M $CaCl_2$ for half an hour. For soil samples high in organic matter content, only 5 or 2.5 g was used. The pH was subsequently measured with a Hamilton 9.99 electrode on a Metrohm 691 pH-meter. The effect of the soil amount was assessed by weighing 2, 4, 6 and 8 g from each horizon and suspending all in 20 ml 0.01 M $CaCl_2$. The H^+ concentration varied less than 3 % between the different soil amounts, which means that the difference in pH due to varying weight of soil was negligible. For this reason, no pH correction for soil weight was needed. Total soil acidity (defined as the sum of exchangeable Al^{3+} and H^+) was extracted by suspending 5 g of each soil sample (in duplicate) in 50 ml 1 M KCl and mixing them in an overhead stirrer for one hour. If the soil had a high organic matter content, or if only a small amount of soil sample was available, only 2.5g was used instead of 5 g. The extract was then filtered through 5893 pleated filters. Total acidity and exchangeable Al^{3+} were measured using an automated sampler (814 USB Sample Processor, Metrohm). The exchangeable H+ was calculated by subtracting the amount of exchangeable Al^{3+} from the total acidity. Reference samples were measured at regular intervals, in order to check for drift. The samples were measured in sequence from highest to lowest pH, in order to minimize possible carry over between the single measurements. The samples with pH 3.55 and below were diluted with the equal volume of 1 M KCl. Samples with pH larger than six were not measured for soil acidity. The resulting acidity values were then corrected for weight and dilution wherever necessary.

Exchangeable cations were extracted with 1 M NH_4Cl (soil:solution ratio: 1:10) during 1 hour and measured by ICP-AES. The effective cation exchange capacity (CEC_{eff}) was calculated by summing up the charge equivalents of exchangeable H, K, Ca, Mg, Al, and Fe. The base saturation (BS) equaled the relative fraction of K, Ca, and Mg of the CEC_{eff}.

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2.4 Statistics

Changes in precipitation chemistry were estimated using linear models with the lm function in R, with time and seasonality as explanatory variables. Seasonality was tested using a sinusoidal approach, testing for both the sine and the cosine of the yearly cycle.

200 Linear mixed-effects models were used to estimate the effects of the N treatment, time, and their interaction on soil acidity. Models were fitted with the lme function from the nlme R package version 3.1-162 (Pinheiro et al., 2023). Treatment (control or N addition) and time were used as fixed effects as well as a second-degree polynomial for time to allow for slopes changing during the course of the experiment. Replications (pairs of plots) were considered a random effect allowing for random intercepts and slopes by treatment, as the same locations were sampled over the years and cannot be assumed to be

205 independent. The interaction between treatment and time was also tested for, but was subsequently removed as no significance could be shown. The dependent variable soil acidity was log-transformed to correct for the unequal variance between replications due to the topography. To test differences in total acidity between topography three fixed effects were used: treatment, topography (mound or depression) and interaction between the treatment and topography. Allowing for random slopes for treatment did not let the model converge, for which reason only random intercepts was tested. Separate

210 linear mixed-effects models (with identical structures) were fitted for the A and the O soil horizon.

Runoff water chemistry changes were estimated using the same approach as with the precipitation with two extra explanatory variables: Treatment (control or N addition) and interaction between treatment and time. The interaction was tested by introducing a pseudo variable for both treatments, accounting for reference period during the first year before treatment start and then increasing for N treatment and decreasing for control. In order to represent only the interaction, the

215 sum of the pseudo variable had to be zero across treatments and also across time points.

3. Results

3.1 Precipitation chemistry

Overall the precipitation rates in the Alptal showed no significant change over time between the beginning of the experiment in April 1994 and the last data presented here (2019). The annual precipitation averaged at 2130 mm. The bulk precipitation

220 data showed a highly significant increase in pH of the atmospheric precipitation ($P < 0.001$; Table S1, Fig. 2). At the beginning of the project, the pH averaged above 5 and increased to an average of almost 6.8 by the end of 2019. The increase

in pH took place at an average rate of 0.068 per year. Single very high values (up to pH 8) were observed after weather events bringing Sahara dust over the Alps.

During the same time period the SO_4^{2-} and the NO_3^- concentration in the precipitation both showed a significant decrease(P < 0.001; Table S1, Fig. 2). Since 1994, the average SO_4^{2-} concentration had more than halved at a rate of 0.028 mg l^{-1} per year. The NO_3^- concentration did decrease over time, however not as strongly as the S deposition. The concentrations of NH_4^+ did not change significantly during the years of monitoring and remained at an average level around 0.3 mg l^{-1}. All measured variables showed a significant seasonality (P < 0.001; Table S1, Fig. 2) with pH showing a minimum around July and SO_4^{2-}, NO_3^- and NH_4^+ showing the maximum values in June, May and April respectively.

3.2 Soil

Soil pH decreased significantly over time for both the N-treated soil as well as the control soil (p < 0.001; Fig. 3, Table S2). Neither the rates of decrease in pH nor the average values differed between the two treatments significantly. The O horizon showed higher pH values with a stronger decrease in pH over time than the A horizon.

The results from the linear mixed effects model for total acidity showed a significant (p < 0.001; Fig. 3, Table S2) non-linear change over time for both the control and N-treated soil. The total acidity showed an increase over time, peaking around 2012 and then decreasing continuously. The same characteristics for total acidity were observed for both soil horizons, however with lower values for the A compared to the O horizon.

The variance in total acidity between replications (measured values) can partly be explained by topography. There were 5 replications for each of the sampling campaigns in the years 1996, 2007, 2014, 2016 and 2022 as described in the methods. Two of the replications are located on mounds and three replications are in depressions. The total acidity on the mounds differ significantly from the total acidity from the depressions (p =0.006 / 0.012 for O and A horizon respectively; Fig. 4, Table S2). The interaction between topography and treatment is marginally significant as well for the O horizon and significant of the A horizon (p = 0.070 / 0.023 for O and A horizon respectively).

A difference in proportions of exchangeable cations between the control and N-treated soil was observed, when examining the soil from the mounds and depressions separately for both the O and the A horizon (Fig. 5). The N-treated soil showed a higher percentage in acidic exchangeable cations (shown in red in Fig. 5), mainly Fe^{2+}, Al^{3+} and H^+, than the control. The control accordingly exhibited a higher percentage of exchangeable base cations (shown in blue in Fig. 5), mainly Ca^{2+} and Mg^{2+}. The acidic exchangeable cations in the N-treated soil make up close to 40 % and 50 % in the O and A horizons respectively, whereas in the control soil they only make up ~ 15 % and ~ 10 %. The difference in exchangeable cations between the depressions and the mounds were observed, with the depressions showing less than 10% of the exchangeable acidic cations. Ca^{2+}/Al^{3+} ratios ranged from over a 1000 in the depressions to about 1.4 on the mounds.

3.3 Runoff water

The concentrations in the runoff water of all anions and cations except for Fe^{2+} changed significantly over time (p = <0.001) for the control catchment. Al^{3+} and pH showed marginally significant and Fe^{2+}, SO_4^{2-} and Ca^{2+} showed significant

250 interactions between treatment and time (Table S3 and Fig. 5). The pH decreased for both catchments with two distinct periods of relative higher pH from 2010 to 2012 and 2017 to 2020. Al^{3+} and NO_3^- increased in concentration in the runoff water from both catchments, while showing a significantly higher rate of increase for the N-treated catchment (Fig. 6 and Table S4). Fe^{2+} concentrations increased significantly in the runoff from the N-treated catchment, but stayed stable in the control. A significant decrease in concentration of SO_4^{2-} and Ca^{2+} was observed for both catchments. The decrease in

260 concentration in the runoff water from the N-treated catchment was significantly lower compared to that of the control catchment. All anion and cation concentration showed significant seasonal trends (Fig. 6 and Table S4).

The observed NO_3^- concentration showed a distinct non-linearity in the runoff water from the N-treated catchment. For this reason a 5th order polynomial was included in the linear model to capture the non-linearity. The water from the N-treated catchment showed a sudden increase in concentration of NO_3^- starting around 1995 and increasing constantly till reaching a

265 maxima in 2010, after which a decrease sets in. At the end of 2018 the concentration reaches a minimum, after which it increases at a low rate. In comparison, the control does not show much variation over time, other than a slight decrease after 2010. Two dates are highlighted in the NO_3^- plot in Figure 5. March 1995 indicating the beginning of the NH_4NO_3 additions to the N-treated catchment and June 2009 which indicates the girdling of select trees prior to their felling in August 2010.

4 Discussion

270 Considering trends reported elsewhere in the last decades, our first hypothesis was that our experimental site is subjected to decreasing atmospheric acid inputs. From 1994 to 2019, the precipitation sampled at the Alptal site has indeed become significantly less acidic. This was clearly visible in the increase in pH and in the decreasing concentrations of SO_4^{2-} and, to a lesser extent, NO_3^-. The NH_4^+ concentrations showed no significant change over time. These findings are consistent with other sites in Switzerland (Thimonier et al., 2019). These authors reported, since the mid-1990's, partly significant decreases

275 in NH_4^+ depending on the measurement site, and mostly significant decreases in NO_3^- deposition. Data from our research site are also in line with average decreases measured since 1988 by the national air pollution monitoring in wet deposition of SO_4^{2-} (-79%), NO_3^- (-36%) and NH_4^+ (-20%) (BAFU, 2022). These trends are obviously the result of measures taken to reduce anthropogenic emissions of SO_4^{2-}, NO_X and NH_3, respectively. Similar trends are generally observed in Europe (EMEP, 2021). In a world-wide study of time series from forest and grassland watersheds, Templer et al. (2022) also found a

280 general reduction in bulk NH_4^+, and especially NO_3^- deposition. This means that reduced N compounds become progressively more important relative to oxidised N in atmospheric deposition.

The observed increase in precipitation pH is strong. As a linear trend of measurements done from 1994 until 2019, it increased by 1.63. Measuring again frozen samples gave higher pH values for old samples. If we take this fact into account, there is an increase of 1.18 in the same 25 years. It is not possible to tell if one of these numbers is closer to reality than the

285   other. In spite of calibrating the pH-meter before every fortnightly measurements, we cannot completely exclude that there could be a long-time trend due to the aging of pH-meter and electrodes. We cannot either exclude that a slow degassing took place in the frozen samples, leading to a loss of dissolved CO_2 and thus to a slight pH increase, even if the size of the bottles (mostly 250 - 1000 mL) does not so much favour degassing. Further, some buffering effects may lead to losses of H^+ during the mixing of fortnightly samples into quarterly composites, resulting in some differences compared to the pH calculated out

290   of the fortnightly measurements (by the weighted average of H^+ concentrations). Even with these uncertainties on the precise numbers, we can conservatively conclude that H^+ inputs by precipitation decreased by one order of magnitude within 25 years. This is also in line with the trends observed over Switzerland, with a gain of more than 1 pH unit over the last 35 years (BAFU, 2022). As stated in this national report, the cause of this pH increase has to be sought in the above-mentioned decrease in emissions of N and especially S oxides.

295   The soil acidifying effect of precipitation is not limited to its pH, i.e. to its H^+ concentration. Soil acidification as a consequence of increased N deposition has been established in a wide range of studies (e.g. Lu et al., 2014; Lieb et al., 2011; Bowman et al., 2008). This lead to our second hypothesis that our N-addition treatment contributes to soil acidification. NO_3^- can have an acidifying effect if leached together with base cations, leading to their replacement by H^+ or Al^{3+} on the exchange complexes. NH_4^+ has also an acidifying effect if it is nitrified (Eq. 1) or taken up by plants in exchange with H^+.

300   These two N ions represent nowadays the main potential of soil acidification from ambient precipitation. Adding them as N treatment represented a strong increase of this potential in our experiment. Since NO_3^- leaching increased in the N-addition treatment (Fig. 6; see also Schleppi et al., 2017), part of the potential acidification is realized. This can explain the stronger increase in soil acidity observed on the mounds under N-addition compared to the control (Fig. 4, 5). The contribution of NH_4^+ is more questionable because the slightly increased N uptake by the trees (Krause et al., 2012) can also be in the form

305   of NO_3^-. Further, net nitrification is small or partly even negative in the Alptal soil. The added NH_4^+ is well retained in the ecosystem and abiotic fixation is believed to be a major process of retention (Providoli et al., 2006), which can limit its acidifying effect.

It is quite surprising that the total acidity appears to decrease in the N-addition treatment at the same time as in the control, in spite of the much higher load of NO_3^- and NH_4^+. The only explanation that we have is that most of the acidifying potential of

310   these ions is not expressed on this site. NO_3^- leaching occurs, but also in the control (Fig. 6) and mostly by preferential flow of precipitation NO_3^- rather than by leaching of NO_3^- from nitrification in the soil (Hagedorn et al., 1999). And, as explained above, nitrification and plant uptake of NH_4^+ are limited by the (partly abiotic) immobilization of this ion in the soil. This can explain that we observe a recovery after roughly 2010, with a decrease of the exchangeable acidity ($H^+ + Al^{3+}$). This tendency is not reflected in the pH, but this is understandable considering that the exchange complexes lost acid cations into the solution during the last decade. Even if the soil pH does not yet show signs of recovery, our first hypothesis of a decrease

315

in acid inputs and in soil acidification is confirmed, and even surpassed considering the observed recovery in exchangeable acidity.

As shown by our measurements (Fig. 5), the topsoil of the depressions is buffered by a high saturation in base cations. On the mounds, however, the saturation is lower, which can be explained by an increased leaching of base cations as water

320   moves deeper into the soil and laterally towards the depressions. The lower buffering capacity of the mounds was then partly consumed by N-addition treatment. This is in line with our second hypothesis of an acidifying effect of the added NH_4NO_3. With time, however, the exchangeable acidity decreased again. Besides the increase in pH in precipitation and the fact that NO_3^- and NH_4^+ only partly express their acidifying potential, biological element recycling certainly also plays a role in the observed recovery. Most studies on soil acidification were conducted on soils that have no, or no longer any carbonate. In

325   contrast, the subsoil of our site contains carbonate. It is thus a large source of base cations for plant roots. With the uptake of base cations from the lower soil horizons and their restitution as litter on the forest floor, this biological cycling acts against acidification and can be considered as a further buffering mechanism. This appears to be effective enough even if the gley horizon of our site features reducing conditions (Hagedorn et al., 2001b), making it unfavorable for deep rooting. Base cations in plant litter are also a mechanism by which they can be redistributed between topographical features, presumably

330   from the base-cation richer depressions onto the mounds. Also because of the low redox potential of the soil, denitrification can be measured at this site (Mohn et al., 1999). With a rate in the order of magnitude of 1 kg N ha^{-1} y^{-1}, denitrification acts against acidification (see Equation 3).

Beside the replicated plots, our N-addition experiment is also conducted in a paired-catchment design. As expected, the most prominent effect of the treatment was to increase NO_3^- leaching out the N-addition catchment. A leaching peak over

335   approximately 5 years after girdling then cutting part of the trees in 2009/2010. A smaller peak was also measured in the control, where the same girdling and cutting also took place. These results were discussed in detail in Schleppi et al. (2017) and the peak following girdling and curring was interpreted as a result of a reduced root uptake. For the present study, our third hypothesis was that other ions than just NO_3^- exhibit changes over time and be affected by the N addition. At the beginning of the experiment, water sampled at the weirs of the small catchments showed a higher pH around 7.5. With time,

340   it decreased to approximately 7.2. Two relatively sudden increases occurred at the beginning of the years 2010 and 2017. They could not be brought into relation with a change of electrodes or any other change in the measurements. For the first period (2010-2011), the higher pH may be an effect of the reduced uptake of base cations by tree roots, which means less release of H$^+$ by these roots after they had used up their starch reserves within a few months (Krause et al., 2013). In the years 2017 to 2019, the pH measured in precipitation (with a different pH-meter) were also higher than the long-term trend.

345   We did not find any other explanation for this period of high pH values in runoff water. This overall tendency of declining pH was accompanied by a decrease in Ca^{2+} and an increase in Al^{3+} and Fe^{2+} concentrations. This shift from base cations to acid cations is a clear sign of a progressive acidification of the soil, more precisely of the hydrologically active layers of the soil, since the bulk of the Bw horizon is practically impermeable. Unlike the exchangeable acidity in the soil, but similarly to the soil pH, no sign of recovery was observed in the composition of runoff water. Since the exchange complexes of the soil

350   lost acid cations during the last decade, it is understandable that recovery processes are not synchronous. Overall, the signals
        confirm our third hypothesis that soil acidification translates into the composition of runoff water even on a site with a well
        buffered subsoil. The sequence of recovery, however, is not the same as often observed in forests that were subjected to
        strong soil acidification after high S deposition. In such highly impacted systems, the storage and subsequent release of
        sulfur plays a dominant role and can delay the recovery of the soil (Ahrends et al., 2022) more than that of surface waters
355   (Lawrence et al., 2015).

5 Conclusions

The Flysch parent material of the Alptal soil contains calcium (and magnesium) carbonate. When an N-addition experiment
was started in 1995, we did not expect to see any acidification effects of the supplementary NH_4NO_3. After years of
monitoring the pH both in precipitation and in runoff water from our small experimental catchments, we noticed opposite
360   trends: less acid precipitation but a declining pH in the runoff. For the present study, we used older and newer soil samples to
        try understanding the underlying processes. The results show that the observed trends can be interpreted as a timely shift in a
        recovery process initiated by the (legally imposed) abatement of N and especially S oxides. The first effect is a reduction of
        the acidity in precipitation. First, the weakly buffered mounds of our site first continued to acidify. The N treatment (addition
        of roughly twice as much N as in the ambient deposition) has a significant effect here. Later, the reduced acid inputs allowed
365   base cations to replace again part of the exchangeable acid cations, even under continuing N addition. This process, certainly
        linked to the biological cycling of base cations, also takes time but may later lead to a recovery of the soil pH. A pH decline
        is also still observed in the runoff water of our small experimental catchment, but with a value still above 7, this trend is not
        alarming for water quality or for the health of water bodies. A future monitoring will be necessary to see if and when a
        recovery takes place in the soil and runoff pH.

370

Author contribution

As a principal investigator, PS was significantly involved in the set-up and running of the field experiment. TB provided
most soil analyses as well as the re-measurement of pH from frozen samples for the present study. TB and PS wrote the
manuscript with contributions of the other authors.

375   ## Competing interests

The authors declare no competing interests.

Data availability

Upon request, data obtained during the present study are available from the corresponding author.

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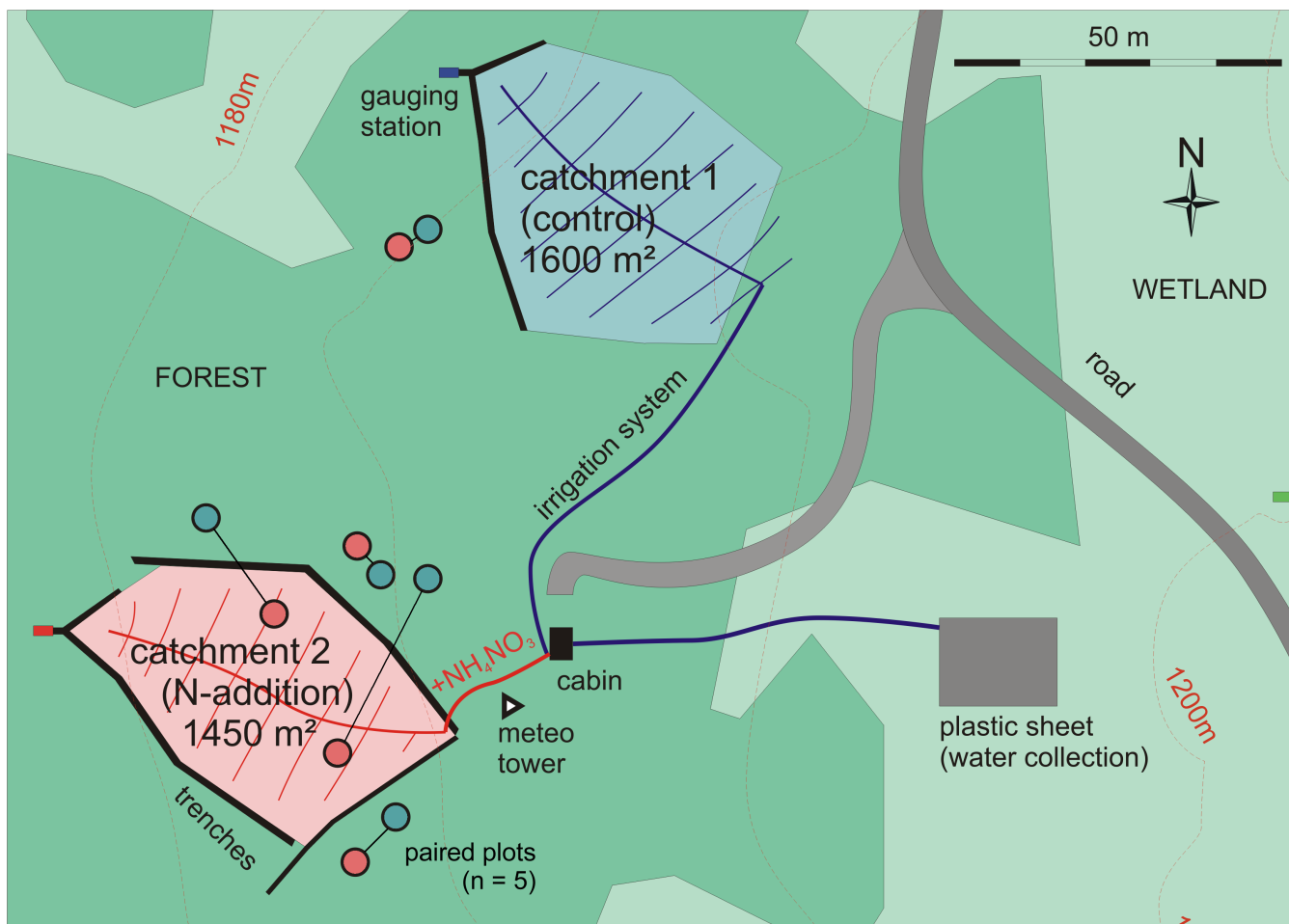

475 **Figure 1: Map of the experimental setup showing the small experimental catchments in the Alptal forest. The same treatments as in the catchments (control or N addition) were also applied to small plots in a replicated design (n=5). The location of each plot was chosen so as to minimize the differences (topography, vegetation, light) within the pairs (replications) but to cover the variability of the site between them.**

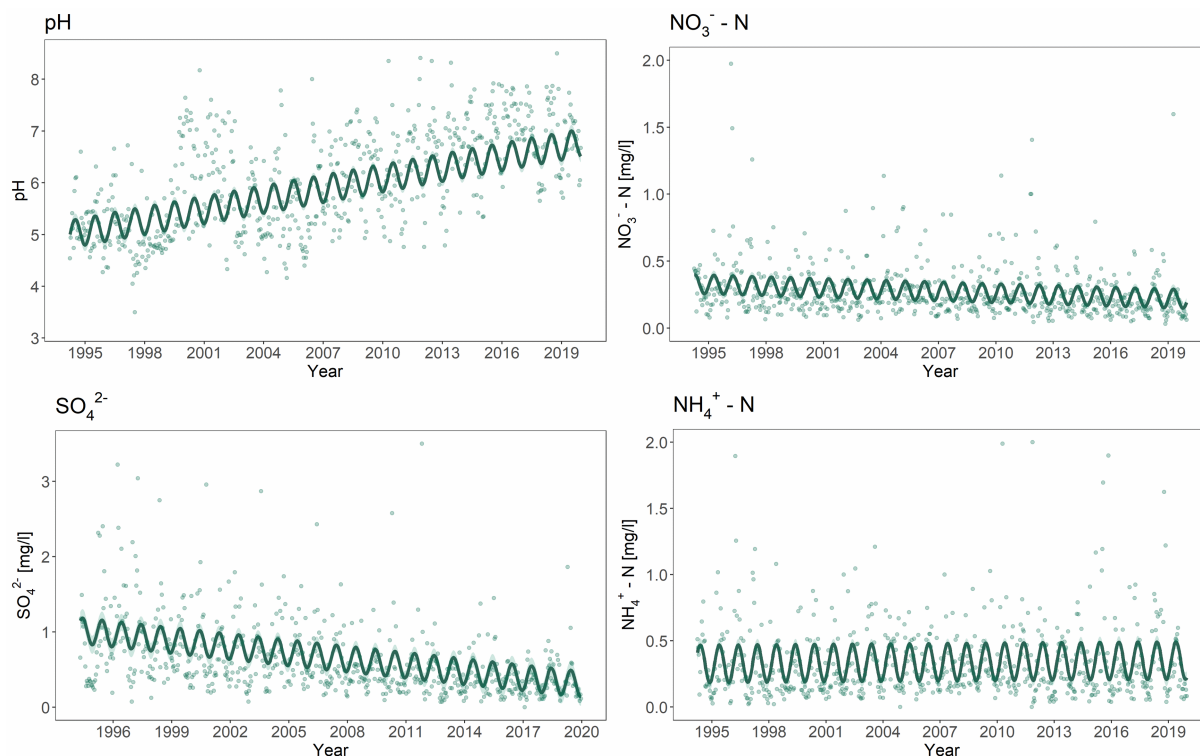



Figure 2: Cation and anion concentration in precipitation from the study site in the Alptal as a function of time. The points are measured values with a timestep of 2 weeks. The continuous solid lines are the predicted values calculated with linear models. 8 and 2 outliers were excluded from the graphs for SO_4^{2-} and NH_4^+ respectively.

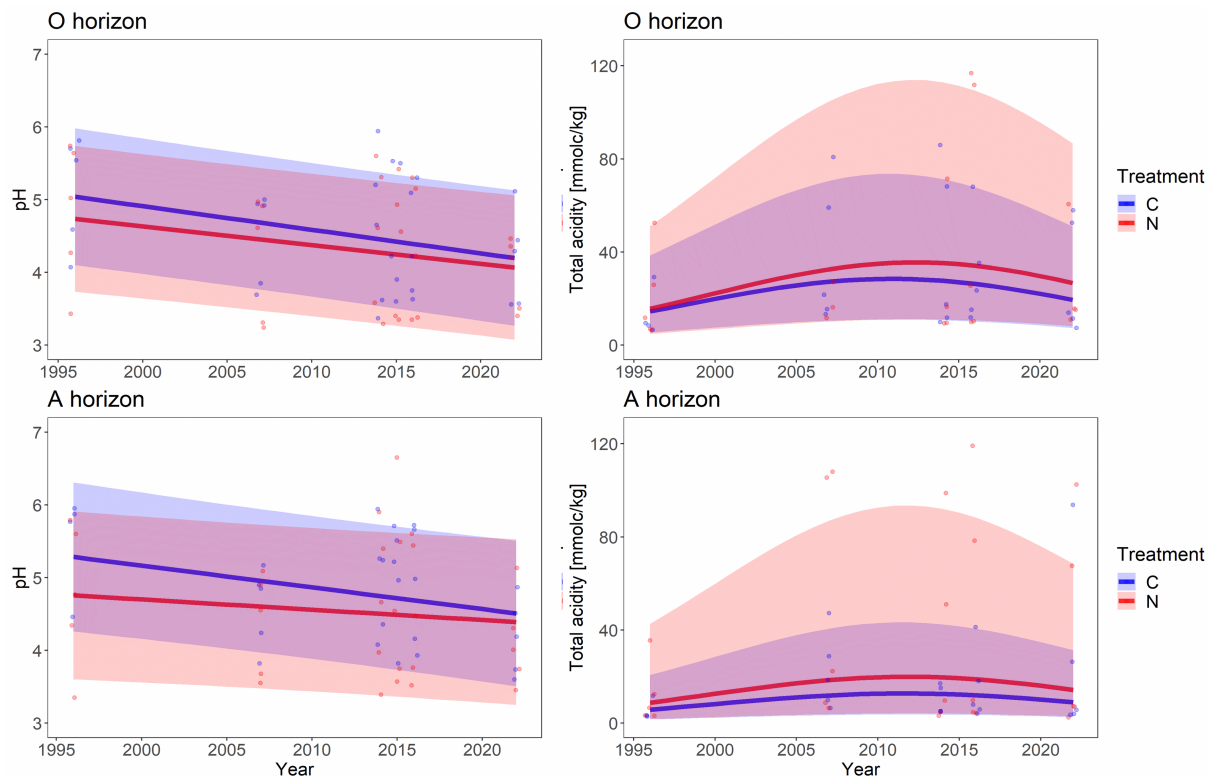
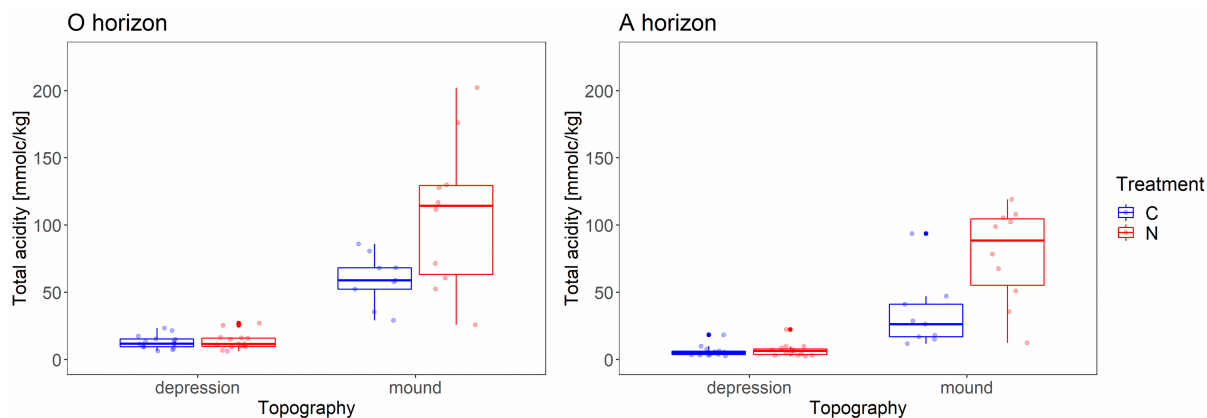



Figure 3: Soil pH and total acidity predictions for O and A horizon based on linear mixed effects model (continuous line with
485   confidence intervals) as a function of time, calculated with measured values from the years 1996, 2007, 2014, 2016 and 2022
(individual points). 4 highest points were excluded from pH plot for O horizon. Modeled total acidity values were back
transformed from log scale. 2 outliers were excluded from O horizon plot for total acidity.

490   Figure 4: Observed total soil acidity values from all years for O and A horizon for both topographical features (mounds and
depressions).

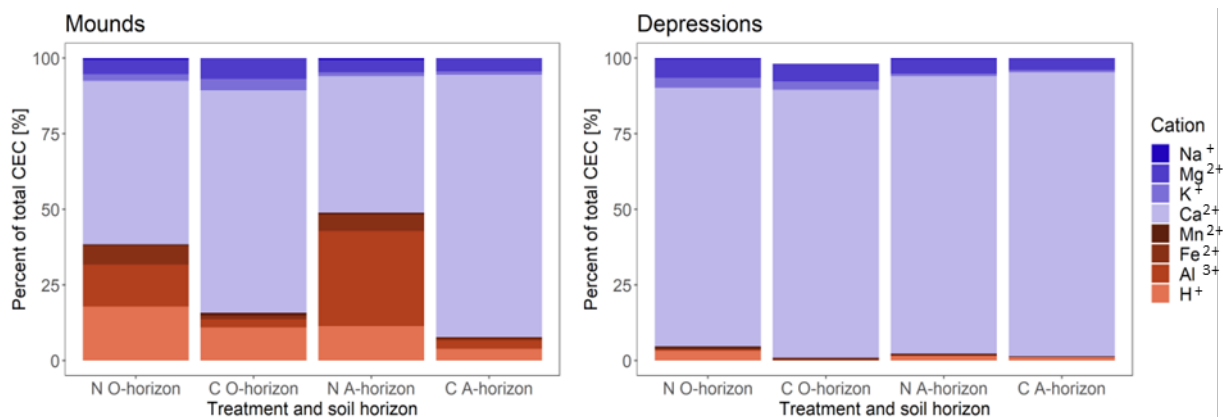



Figure 5: Exchangeable cations in proportions of total cation exchange capacity (CEC) for the year 2016. (Pb an Zn were excluded as their concentrations was negligibly small or zero for most replications). Acidic cations are indicated by the color red and base cations are blue.

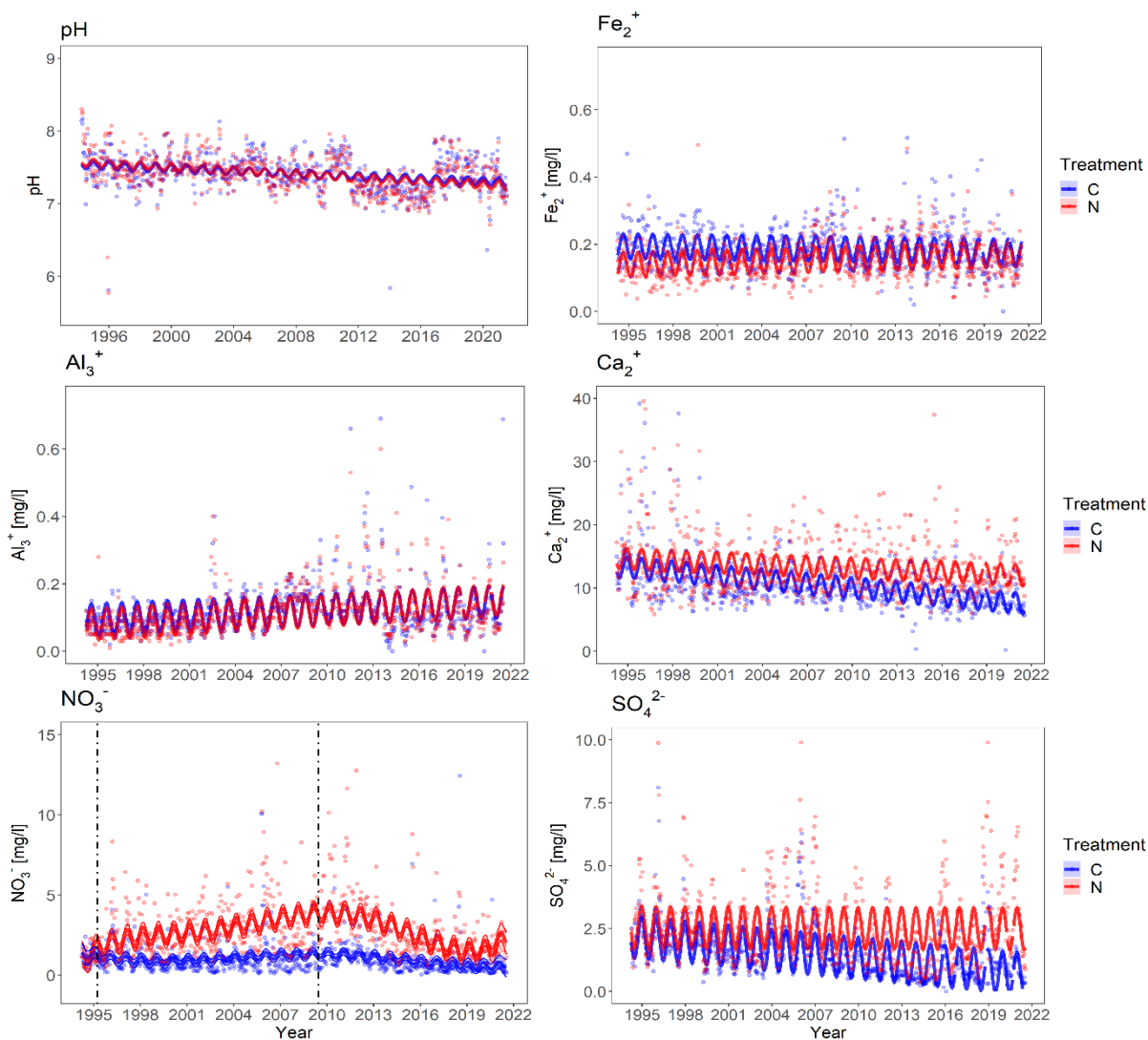



Figure 6: Cation and anion concentrations in soil runoff water from the control (blue) and N-treated (red) catchment as a function of time. The points are measured values with a time step of 2 weeks. The continuous solid lines are the predicted values from the linear models with confidence intervals. 4 highest points were excluded from pH plot for O horizon. For the NO$_3^-$ a 5th order polynomial was included in the lm model to capture the non-linearity of the data. The first dashed line indicates the beginning of the addition of NH$_4$NO$_3$ to the N-treated catchment. The second dashed line indicates the date of ringing of trees prior to felling. For Fe$^+$, Ca$^+$, NO$_3^-$ and pH, 1 outlier was excluded each from the plot and for SO$_4^{2-}$ 4 outliers were excluded.