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

5   Thomas Baer[1], Gerhard Furrer[2], Stephan Zimmermann[1], Patrick Schleppi[1]

[1]Forest Soils and Biogeochemistry, Swiss Federal Research Institute for Forest, Snow and Landscape Research (WSL), CH-8903 Birmensdorf, Switzerland
[2]Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, CH-8092 Zürich, Switzerland

Correspondence to: Patrick Schleppi (patrick.schleppi@wsl.ch)

Abstract. Nitrogen (N) deposition ~~to forest ecosystems~~ decreased in the last decades in Europe, but in many cases remains higher than the critical loads, i.e. higher than what could be considered safe for biodiversity and ecosystem functioning ~~for biodiversity and ecosystem functioning for specified sensitive receptors of the environment~~. The main concerns about N deposition are eutrophication and acidification. In a long-term experiment (1994 to present) in a montane (1200 m a.s.l.)

15   coniferous forest in Alptal, central Switzerland, we simulated increased N deposition by adding NH_4NO_3 to rainwater. This treatment consisted of an additional N input of 22 kg ha^{-1} y^{-1} to the 12 kg ha^{-1} y^{-1} ambient bulk deposition rate or 17 kg N ha^{-1} y^{-1} throughfall rate. The treatment was applied simultaneously to a small catchment area and to plots in a replicated block experiment (n=5). The site has a carbonate-rich parent material and is thus not particularly at risk of acidification. Nevertheless, ~~while previous reports on this experiment concentrated on N as a nutrient,~~ we examined soil acidification

20   ~~processes~~ as affected both by ambient and experimentally increased N deposition. In the two and a half decades since the beginning of the study, nitrate (NO_3^-) and especially sulfate (SO_4^{2-}) concentrations decreased in precipitation, while pH increased by slightly more than 1 unit. ~~In spite of these reduced acid inputs~~In the same time period a reduction in ~~, the~~ pH of the soil was measured ~~decreased. First, t~~The exchangeable acidity in the soil increased, especially in the N-addition treatment. This was mainly observed on small mounds because ~~they~~ the drier mounds are less well buffered than wet

25   depressions. This trend, however, was 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 a progressive recovery mainly due 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

30   exchangeable soil acidity is not yet able to stop the slow acidification of water leaving the catchments. However, with the

runoff water pH remaining above 7, this trend is not alarming for water quality or for the health of water bodies. Future monitoring will be necessary to see if and when a recovery takes place in the soil and runoff pH.

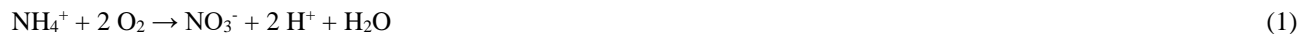
1 Introduction

35 Due to anthropogenic activity, the transformation rate of inert N_2 into reactive N has ~~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, widespread application of N fertilizer and 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~~ from human activity (Schlesinger & Hartley, 1992; Delmas et al., 1997). A large share of anthropogenic N emissions ends up in the atmosphere and can be

40 transported over long distances and deposited ~~as a result of gravitation (dry deposition) or dissolved in atmospheric precipitation (wet deposition)~~ in dry or wet form. Together with sulfate (SO_4^{2-}), NO_X compounds are responsible for the acidity in 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

45 (Vitousek & Howarth, 1991). Moderate increases of N deposition in forest soils have been shown to be correlated with increased mineralization rates, nitrification, and 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^+ taken up by plants corresponds to an exchange of this cation with H^+, which is then released into the soil (Galloway et

50 al., 2003; Högberg et al., 2006). These biologically induced releases of H^+, together with the increased deposition of H^+ caused in part by NO_X from the atmospheric 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).

Denitrification, i.e. transformation of N from NO_3^- to atmospheric N_2, on the other hand, is a sink for H^+ (Equation 2).

55 $$2\ NO_3^- + 10\ e^- + 12\ H^+ \rightarrow N_2 + 6\ H_2O \tag{2}$$

~~A further sink of H^+ is the decomposition of plant matter.~~ Besides the balance between inputs and outputs, the rate at which the soil acidifies depends on its buffering capacity. The dominant processes by which H^+ is buffered is 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,

60 reducing its acidity. Soil pH and the mineralogy of the soil determine which type of buffering process dominates. The dissolution of calcium carbonates is the dominant buffering process in calcareous soils (Equation 3).

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

At very low pH, hydrolysis and dissolution of Al
and Fe complexes are the dominant buffering systems (Chadwick & Chorover, 2001).

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 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^+) 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
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
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 (Convention on Long-Range
Transboundary Air Pollution), SO_4^{2-} concentrations in precipitation have declined and the pH of precipitation has increased
over the last 30 years. However, achieving reduction in oxidized (NO_X) and especially reduced (NH_3) N emissions is more
difficult, and N deposition continues to be an environmental problem. In Switzerland, a large share of the natural ecosystems
receive N deposition above their 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 effects of increased N deposition on weakly buffered soils
such as 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. In the
present study, the biogeochemical development of such a well-buffered forest soil in the Prealps of Switzerland was
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} compared to a control catchment receiving only ambient N deposition or throughfall at a rate of 12 kg ha^{-1} y^{-1} or 17 kg N ha^{-1} y^{-1} respectively. Atmospheric precipitation and runoff water from these catchments were regularly analyzed over the entire period of the experiment (Schleppi et al., 1998).

100   In this study we investigate the acidifying effects on the soil as a result of ambient N deposition in combination with N from the experimental addition of NH_4NO_3. Precipitation chemistry over time was used to test a first hypothesis:

1) Atmospheric precipitation became less acidic over time due to lower levels of pollution. This should be observable as an increase in precipitation pH and a lower rate of soil acidification in the control.

To test the effect of experimental N addition on the soil, samples from plots subjected to the increased N inputs as well as the

105   controls were analyzed to examine a second hypothesis:

2) Relative to the control, the N-treated soil (organic horizon and topsoil) experienced a stronger acidification, measured as a lower pH and an increase in total acidity.

The site shows water movements through the soil 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 runoff water. Chemical

110   data collected over more than 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 at~~on~~ a site with a well-buffered subsoil.

2 Methods

2.1 Site description

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

120   mounds and depressions. The mounds are characterized by a ~~lower lying~~deeper 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

125   partly positive and partly negative (N immobilization). Overall, the net nitrification 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, mixed with 15% silver fir

130   (*Abies alba* Mill.). The trees are up to 270 years old, have a dominant height of ca. 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). At the beginning of the

135   experiment Aatmospheric deposition of inorganic N in bulk and throughfall is was 12 and 17 kg N ha^{-1} y^{-1}, respectively

(Schleppi et al., 1998).

2.2 Experimental catchments and N addition

An N addition experiment was conducted at the Alptal site to assess the effects of atmospheric N deposition. The design of

the experiment (Fig. 1) was two-fold. First, NH_4NO_3 dissolved in rain water was added by sprinklers to a small headwater

140   catchment and compared to a control catchment in a paired-catchment design (Schleppi et al., 1998). The added rainwater to

both catchments only leads to a mild increase of 7% on average to the annual ambient precipitation.

Second, small plots received the same treatment as the catchments at the same time but in a replicated block design (n=5)

(Hagedorn et al., 2001a). 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

145   features: two blocks were set on mounds and three in depressions. The small plots were mostly just outside the catchments,

but in two cases N-addition plots were inside the corresponding catchment (Fig. 1). Combining both designs enabled us to

study soil processes in more detail in the replicated plots while we could also obtain an integration of relevant processes at

the larger scale of the catchments, encompassing the different topographic features as well as a larger number of trees.

The twowo forested catchments, each approximately 1500 m^2 in area, were delimited by trenches leading to the gauging

150   stations.dug one year before measurements began. These trenches were dug one year before measurements began and reach

into the gleyic sub-soil and while capturinge the sub-surface water flow (Schleppi et al., 1998). No change of the vegetation

along the trenches has been observed that would indicate enhanced drainage from the soil along the trenches. Catchment 1

(control) has a convex shape in the upper region and did thus not require trenches there (Fig. 1). Both catchments feature a

similar topography with similar proportions of mounds (approx. 40%) and depressions (approx. 60%). Water level is

155   measured continuously in V-notch weirs (custom made) at the bottom of the catchments. Water discharge is calculated from

these measurements and is 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 before N-addition treatment began.

Increased N deposition was then simulated in one of the catchments by applying NH_4NO_3 dissolved in rainwater with

160   permanently deployed sprinklers. Rainwater was collected on a polyethylene sheet (300 m^2) spread outside the forest and

channeled into a water tank (2000 L). N addition occurred automatically when the tank was full, in small but frequent

amounts: approximately 200 times per year for an average of 22 kg N ha^{-1} y^{-1} additional N input to the ambient deposition rate of 12 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 resulting in a N input of 12 kg N ha^{-1} y^{-1}. During winter, N treatment was done with a backpack sprayer as occasional applications of a concentrated NH$_4$NO$_3$ solution on the snow cover.

In June 2009, 15 trees per forested catchment, all with a diameter at breast height of >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*) and were felled in August 2010 to prevent the spread. This represented a heavy selective cutting (38% of the total basal area of all trees >10 cm diameter at breast height) affecting both catchments equally. The branches (with needles still attached) were left on site, while the boles were removed by helicopter. This disturbance did not affect soil temperatures (7.1°C on average) nor soil water depths (23 cm on average) (Krause et al., 2013).

2.3 Sampling and analyses

Precipitation was measured and sampled weekly from an open area approximately 150 m west of the forested catchments. Two 0.05 m^2 rain gauges (custom made) were used, except in the winter when only one was heated in order to let the snow melt. These gauges consist of a polypropylene funnel mounted on top of an opaque PVC tube with a polyethylene 5-L collection bottle inside. Water samples were proportionally combined fortnightly and 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 (Metrohm, Herisau, Switzerland). 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. To check the long-term consistency of the pH measurements, precipitation samples were proportionally pooled over periods of 3 months and frozen during the entire experiment. After 21 years of collection,In 2016 these samples were melted, measured again with the current 654 pH-meter (Metrohm, Herisau, Switzerland) and compared to values calculated from the H$^+$ concentrations derived (by weighted averages) from the original measurements done just after collection during the experiment.

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 (Metrohm, Herisau, Switzerland) 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$_4$NO$_3$ (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

195 ~~depressions.~~ Soil samples were taken from the 10 plots (Fig. 1) at irregular intervals of several years (1996, 2007, 2014, 2015, 2016 and 2022). 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 were 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

200 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). As the Bw horizon ~~It~~ is ~~further~~ well buffered by the presence of carbonate, it ~~and~~ was ~~thus~~ not included in our analyses on acidification. ~~In general,~~ 10 g of each soil sample were 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 were used. The pH was subsequently measured with a Hamilton 9.99 electrode on a Metrohm

205 691 pH-meter (Metrohm, Herisau, Switzerland). 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 by 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

210 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 were 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

215 measured in sequence from highest to lowest pH, in order to minimize possible carry over between the single measurements. Samples with a pH of 3.55 and below were diluted with the equal volume of 1 M KCl. Samples with a pH higher than 6.0 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$_4$Cl (soil:solution ratio: 1:10) during 1 hour and measured by ICP-AES.

220 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$_{eff}$.

2.4 Statistics

Changes in precipitation chemistry were estimated using linear models with the lm function in R, with time and seasonality as

225 explanatory variables. Seasonality was tested using a sinusoidal approach, testing for both the sine and the cosine of the yearly cycle.

Linear mixed-effects models were used to estimate the effects of the N treatment, time, and their interaction on soil acidity and pH. 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 independent. The interaction between treatment and time was also tested, 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 for 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, so only random intercepts were used. Separate 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 precipitation with ~~two extra additional~~the following explanatory variables: time, seasonality, t~~T~~reatment (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 sum of the pseudo variable had to be zero across treatments and also across time points.

~~to~~The time series of pH in precipitation and in runoff were available in fortnightly steps. In a first approach, we tested these series for auto-regression with the acf function from the stats package (R Core Team, 2013) of R (version 4.1.2).

We further tested the short-term correlation between pH in precipitation and runoff. For this purpose, we filtered for data between 21 May and 28 October, to avoid data obtained in the presence of snow cover. For each year, we calculated the deviations compared to the average of that year, thus removing the long-term trends and keeping only the short-term variations. Based on this data, correlations were calculated with a shift between zero and nine time steps from the first to the second series.

3. Results

3.1 Precipitation chemistry

Overall, precipitation rates in the Alptal showed no significant change over time between the beginning of the experiment in April 1994 and the latest available measurements (2019). Annual precipitation averaged 2130 mm. The bulk precipitation data showed a ~~highly~~ significant increase in pH of the ~~atmospheric~~ precipitation ($P < 0.001$; Table S1, Fig. 2). At the start of the experiment~~At the beginning of the project~~, average pH was above 5 and increased to ~~almost~~ 6.8 by the end of 2019. The increase in pH took place at an average rate of 0.068 per year (SE ± 0.003). Occasional very high values (up to pH 8) were

observed, which are linked to atmospheric conditions that result in dust originating from the Sahara being transported over the Alps ~~after weather events bringing Sahara dust over the Alps~~.

260 In the same time period, SO_4^{2-} and 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 more than halved at a rate of 0.029~~8~~ mg l^{-1} per year (SE ± 0.003). The NO_3^- concentration also decreased over time, but not as strongly as the S deposition (Table S1, Fig. 2). The concentration of NH_4^+ did not change significantly during the years of monitoring and remained at an average level of ca. 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

265 and SO_4^{2-}, NO_3^- and NH_4^+ showing maximum values in June, May and April respectively.

3.2 Soil

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

270 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. It initially increased 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 variation in total acidity between ~~replications~~ replicates (measured values) can partly be explained by topography. There were 5 ~~replications~~ replicates for each of the sampling campaigns in the years 1996, 2007, 2014, 2016 and 2022 as described

275 in the methods. Two of the ~~replications~~ replicates ~~are~~ were located on mounds and three in depressions. Total acidity on the mounds differ~~ed~~s significantly from total acidity in the depressions (p =0.006 / 0.012 for O and A horizon respectively; Fig. 4, Table S2). The interaction between topography and treatment ~~i~~was~~s~~ marginally significant for the O horizon and significant ~~of~~ for the A horizon (p = 0.070 / 0.023 for O and A horizon respectively), so that N-treated mounds were the most acidic.

A difference in proportions of exchangeable cations between the control and N-treated soil was observed when examining the

280 soil from 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 depressions

285 and 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 of all anions and cations (except for Fe^{2+}) in the runoff water changed significantly over time (p = <0.001) for the control catchment. Al^{3+} and pH showed marginally significant interactions (p = 0.073 and p = 0.092) and Fe^{2+}, SO_4^{2-}

and Ca^{2+} showed highly significant 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 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 model. 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 maximum in 2010, after which it started to decreased. At the end of 2018 the concentration reached a minimum, then started to increase slowly again. In comparison, the control did 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.

The auto regression between precipitation and runoff showed mainly that correlations decreased from 0.6 (precipitation) or 0.5 (runoff) at a lag of 1 fortnightly period to reach a first minimum at a lag of 12-14 fortnightly periods, then increasing again up to 22-27 fortnightly periods, corresponding to a yearly cycle.

The pH in the runoffRunoff water pH and precipitation pH showed no significant short term correlation to each other for the same time period for botheither the control andor the N-treated catchment, with correlation coefficients of -–0.081 and -0.078 respectively. The correlation was also not significant when the time periods were offset by 1 to 9 timesteps (1 timestep equals 2 weeks), with the correlation coefficients ranging from -0.184 to 0.090 for the control and -0.108 to 0.122 for the N--treated catchment.

4 Discussion

4.1 Atmospheric deposition

Based on general trends in the last decades, our first hypothesis was that our experimental site is subjected to decreasing atmospheric acid inputs. From 1994 to 2019, 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^-. of precipitation water. The NH_4^+ concentrations showed no significant change over time. These findings are consistent with other sites in Switzerland which have reported, since the mid-1990's, partly significant decreases in NH_4^+ and mostly significant decreases in NO_3^- deposition (Thimonier et al., 2019). 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 clearly 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 general reduction in bulk NH_4^+, and especially NO_3^- deposition. This means that reduced N compounds become progressively more important relative to oxidized N in atmospheric deposition.

The observed increase in pH in our precipitation samples was strong. As a linear trend of measurements from 1994 until 2019, pH~~it~~ increased by 1.63. Re-measuring frozen samples gave higher pH values for old samples, resulting in a weaker increase . ~~If we take this fact into account, there is an increase~~ of 1.18 in the same 25 years. The observed trends over time in pH from original samples and from the measurements of the frozen samples were not identical but also not significantly different (p = 0.075). It is not possible to determine which of these values is more accurate. Despite calibrating the pH-meter before every fortnightly measurement, we cannot completely exclude that there could be a long-time trend due to the aging of the 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 ~~likely~~ favor 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 from the fortnightly measurements (by the weighted average of H^+ concentrations). Even with these uncertainties, we can conservatively conclude that H^+ inputs by precipitation decreased by one order of magnitude within the last 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.

4.2 Soil acidification

The pH of precipitation, i.e. its H^+ concentration, is not the only factor leading to soil acidification.~~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 leads 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 in the soil. NH_4^+ also has an acidifying effect if it is nitrified (Eq. 1) or taken up by plants in exchange with H^+. These two N ions represent the main potential of soil acidification from ambient precipitation. Adding them as N treatment simulated a strong increase of this potential in our experiment. As explained in a previous article (Schleppi et al., 2017), NO_3^- leaching quickly increased as a result of the N-addition. This was interpreted as a short-term effect linked to fast, preferential water flow through the top-soil, leading to the loss of approximately 10% of the added N. After several years of treatment, we observed a further reduction of NO_3^- retention, down to approximately 70%, which we consider a sign of progressive N saturation of the ecosystem. Finally, a peak of NO_3^- leaching was observed in the 5-6 years after girdling and subsequent felling of part of

the trees. This peak was clearly more pronounced in the N-treated catchment than in the control and this was interpreted as a

355   result of the decreased N demand of the trees. Since NO_3^- leaching increased in the N-addition treatment (Fig. 6; see also Schleppi et al., 2017), we can ascertain that acidification occurred in part due to the acidifying potential of NO_3^-. This can explain the stronger increase in soil acidity observed on the mounds under N-addition compared to the control (Fig. 4, 5) and can also partly explain that Ca^{2+} concentrations decreased less (as a result of buffering processes) in N-treated catchment than in the controlCa^{2+} concentrations decreased less in N-treated catchment than in the control (Fig. 6). The contribution of

360   NH_4^+ is more questionable because the slightly increased N uptake by the trees (Krause et al., 2012) can also be in the form of NO_3^-. Further, net nitrification rate is minimal or even negative at times in the soil at our site (Hagedorn et al., 2001b). 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 appeared to decrease in the N-addition treatment at the same time as in the control,

365   in spite of the much higher load of NO_3^- and NH_4^+. We suggest that most of the acidifying potential of these ions is not expressed on this site. NO_3^- leaching occurred, but also in the control (Fig. 6) and mostly by preferential flow of NO_3^- in precipitation 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 the observed recovery after 2010, with a decrease of the exchangeable acidity ($H^+ + Al^{3+}$). This tendency is not

370   reflected in the pH, but this can be explained by the losses of acidic cations from the exchange complexes into the solution during the last decade. Even if soil pH does not yet show signs of recovery, our first hypothesis of a decrease in acid inputs and in soil acidification was confirmed, and even surpassed considering the observed recovery in exchangeable acidity. As shown by our measurements (Fig. 5), the cation exchange sites of the topsoil of the depressions is buffered by a high saturation in base cations. However, on the mounds the saturation is lower, which can be explained by an increased leaching

375   of base cations as water moves deeper into the soil and laterally towards the depressions. As a result, the lower buffering capacity of the mounds was further reduced 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 pH increase 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

380   conducted on soils that lack, or no longer contain carbonate (See historical review by Grennfelt et al. (2020) and, for a Swiss perspective, Blaser et al. (2008)). In 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 return to the forest floor as litter, this biological recycling 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),

385   which makes making it the soil unfavorable for deep rooting, i.e. for the ability of plants to access deep soil layers rich with base cations. This biological recycling of base cations from tree roots to canopy and back to the forest soil as plant litter is

also a mechanism by which base cations can be redistributed between topographical features, i.e. from the base-cation richer depressions onto the more base-cation depleted mounds.

A further mechanism acting against soil acidification is denitrification (see Equation 3). Due to the low redox potential of the

390 soil at our site, denitrification could be measured (Mohn et al., 1999) and showed a rate in the order of magnitude of 1 kg N ha^{-1} y^{-1}. ~~Base cations in plant litter are also a mechanism by which they can be redistributed between topographical features, presumably 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).~~

395 **4.3 Runoff water chemistry**

Besides 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 an increase of NO$_3^-$ leaching out the N-addition catchment. We found that~~A~~ leaching peak~~ed~~ ~~over~~during -approximately 5 years after the girdling and subsequent cutting of some of the trees in 2009/2010. A smaller peak was also measured in the control, where the same girdling and cutting was performed. These

400 results were discussed in detail in Schleppi et al. (2017) and the peak following girdling and cutting was interpreted as a result of reduced root uptake. For the present study, our third hypothesis was that ions other than just NO$_3^-$ would 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 pH around 7.5. With time, it decreased to approximately 7.2. Two relatively sudden increases occurred at the beginning of 2010 and 2017. They could

405 not be traced to any change in the measurements such as a change of electrodes. For the first period (2010-2011), the higher pH may be an effect of the reduced uptake of base cations by roots after girdling some trees on both catchments~~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. The two periods of higher pH values also did not correlate

410 with soil frost, which occasionally occurs at this site (Stähli, 2017). Furthermore, the absence of any short-term correlation between runoff pH and precipitation pH in the same or in the previous 2-week periods is in contrast with what was previously observed for NO$_3^-$ concentrations (Schleppi et al., 2017). While the NO$_3^-$ signal is partly transmitted through the soil by preferential water flow, the different behavior of the pH can be explained by buffering reactions in the soil. Cation exchange especially is much more efficient than anion-exchange, thus completely decoupling these two time-series.

415 The decrease in pH was also measured in a third catchment nearby, which showed a decrease in pH of approx. -0.018 per year. This third catchment was not included in this study as it consists of fallow land and thus is not comparable from a vegetation point of view to the N treated and control catchment areas in the forest.

The 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, no sign of recovery was observed in the chemical composition of runoff water. Since the exchange complexes of the soil 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 (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 as a result of the added NH_4NO_3. After years of monitoring the pH both in precipitation and in runoff water from our small experimental catchments, we noticed opposite trends: less acid precipitation but a declining pH in the runoff. For the present study, we used older and newer soil samples to examine the underlying processes. The results show that the observed trends can be interpreted as a temporal shift in a recovery process initiated by the (legally imposed) abatement of emissions of N and especially S oxides. The first effect is a reduction of the acidity in precipitation. At first the weakly buffered mounds of our site acidified. The N treatment (addition of roughly twice as much N as in the ambient deposition) had a significant effect on the acidification. Later, the reduction in acid inputs from precipitation allowed base cations to replace part of the exchangeable acid cations in the soil, even under continuing N addition. This process, which is certainly linked to the biological cycling of base cations, takes time but may lead to a recovery of the soil pH in the future. A pH decline was also observed in the runoff water of our small experimental catchment. However, the pH remained above 7 and this trend is not alarming for water quality or for the health of water bodies. Future monitoring will be necessary to see if and when a recovery takes place in the soil and runoff pH.

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.

Competing interests

The authors declare no competing interests.

Data availability

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

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455 direction of Daniele Pezzotta. We also thank Sandra Angers-Blondin for support and advice with R programming and modeling and for proofreading the manuscript for final submission.

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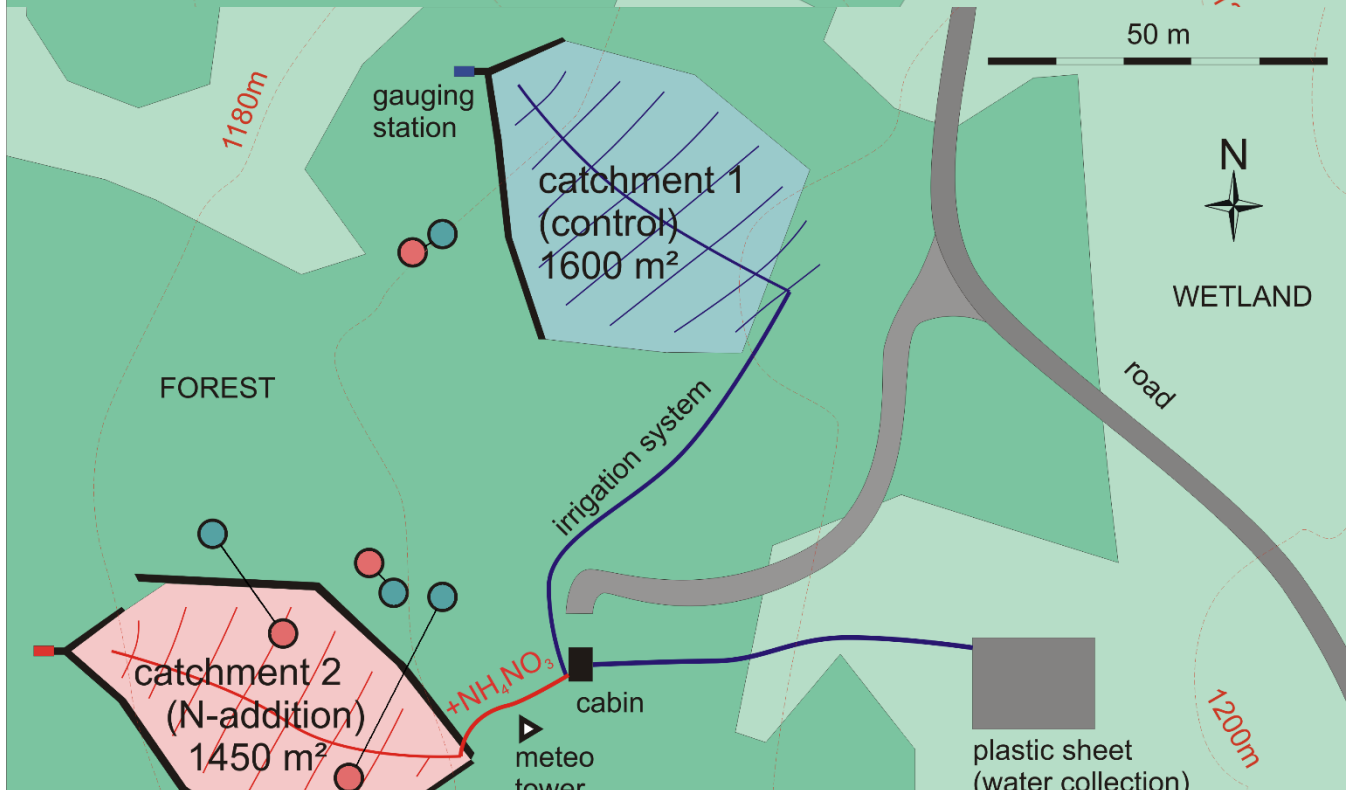
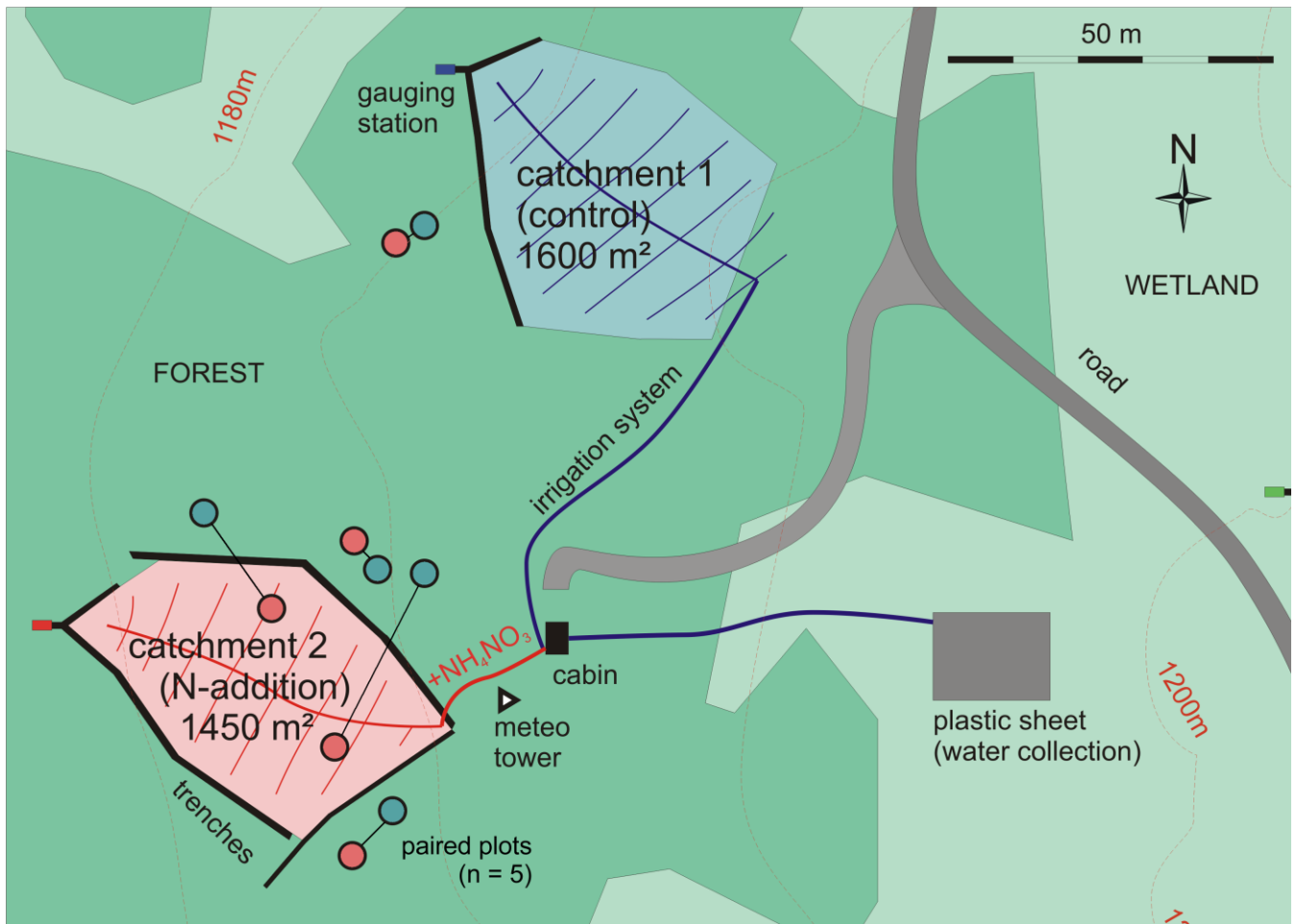
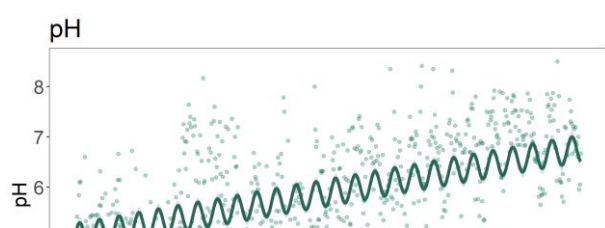
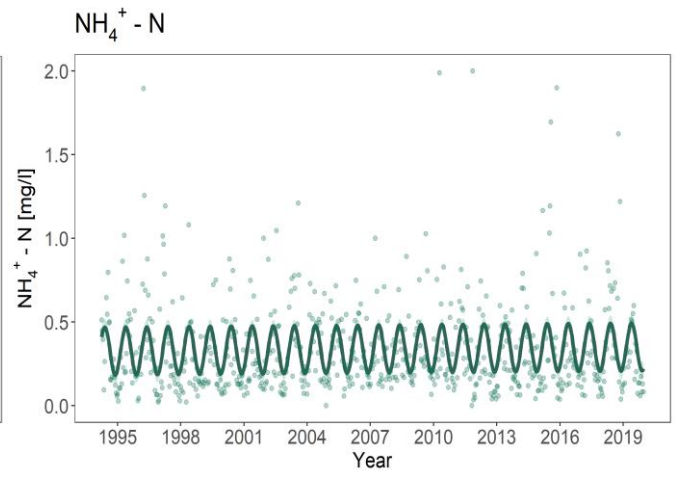
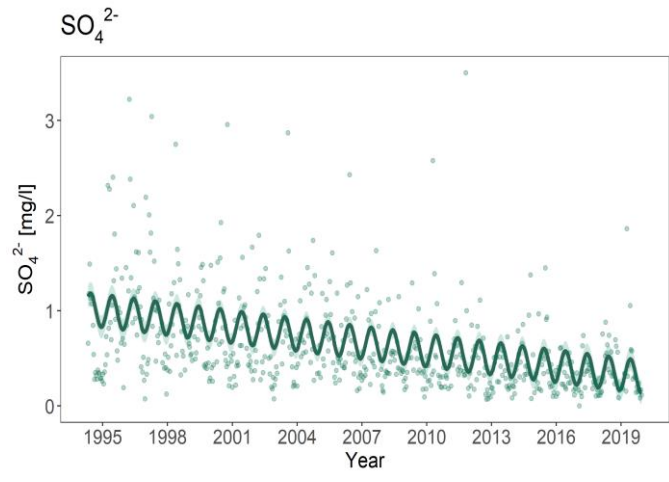
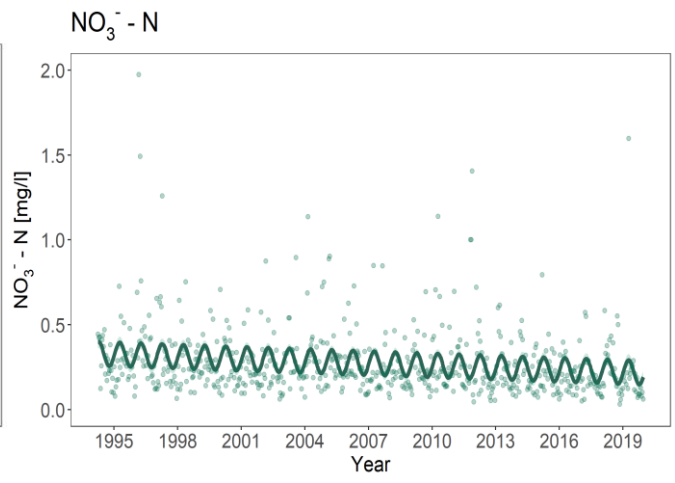
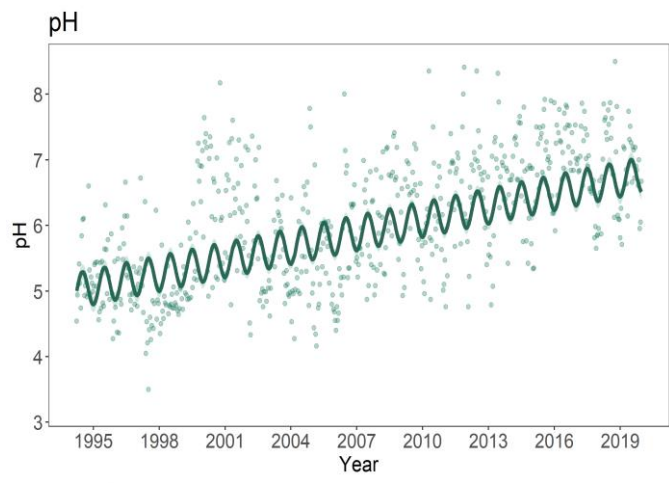


Figure 1: Map of the experimental setup showing the small experimental catchments in the Alptal forest. Catchment 1 has a convex shape in the upper region and did thus not require trenches there. The same treatments as in the catchments (control or N addition) were also applied to small plots in a replicated design (n=5). Blue circles indicate control plots and red circles indicate N addition plots (replications, shown here as lines connecting plots). 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.

565 **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.**

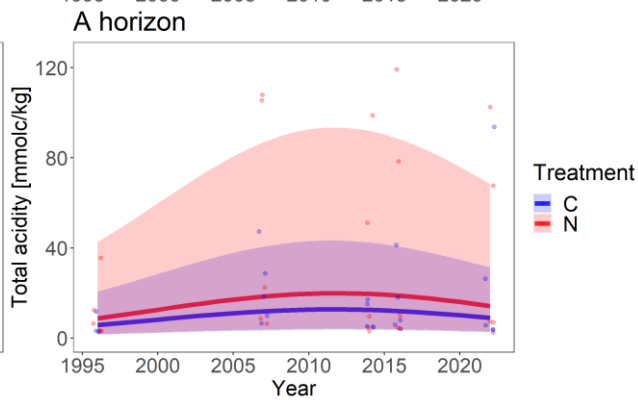
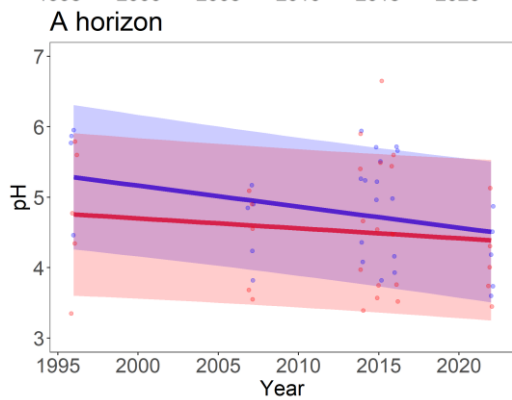
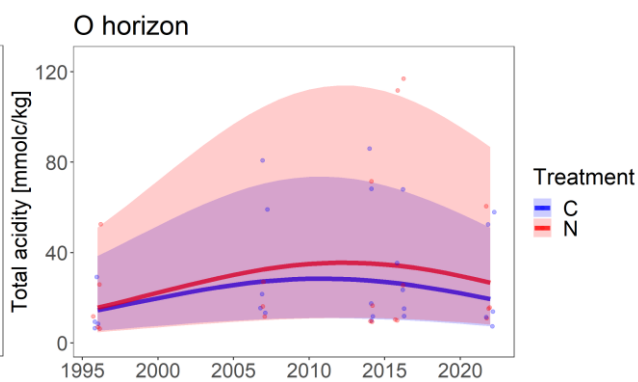
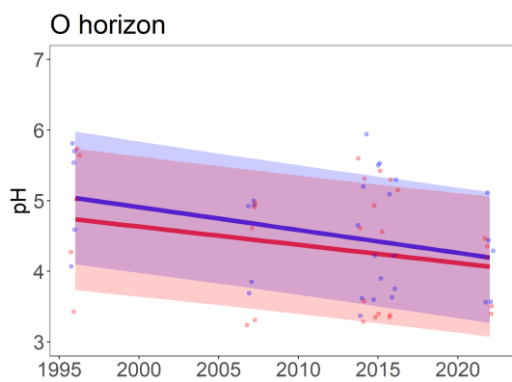
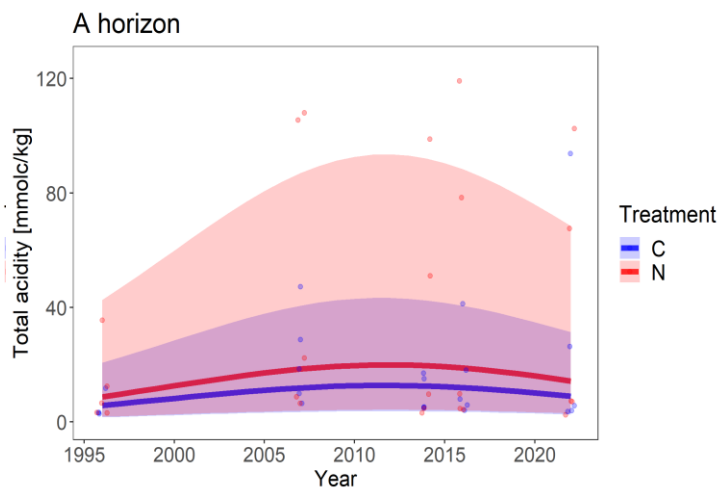
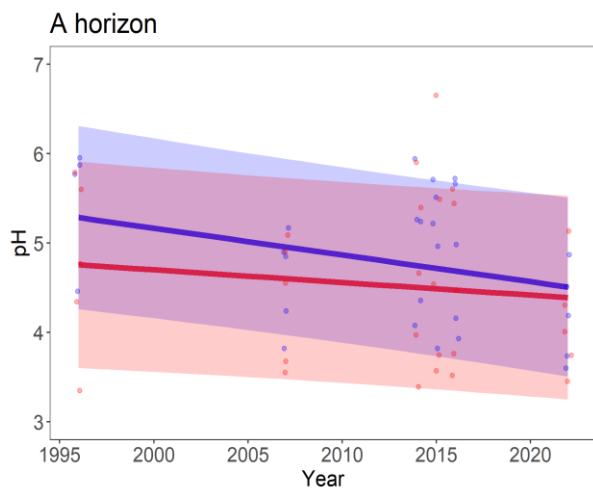
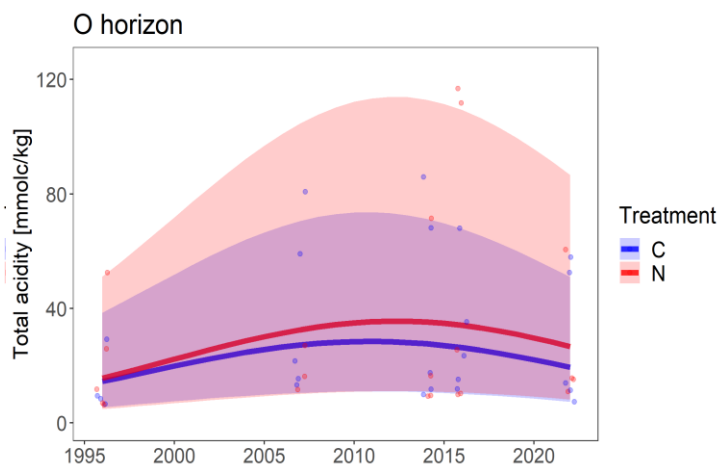
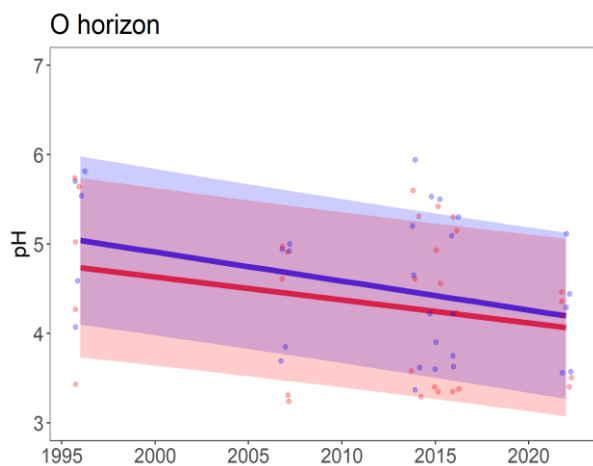



Figure 3: Soil pH and total acidity predictions for O and A horizon based on linear mixed effects model (continuous line with confidence intervals) as a function of time, calculated with measured values from the years 1996, 2007, 2014, 2016 and 2022 (individual points). 4 highest points were excluded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

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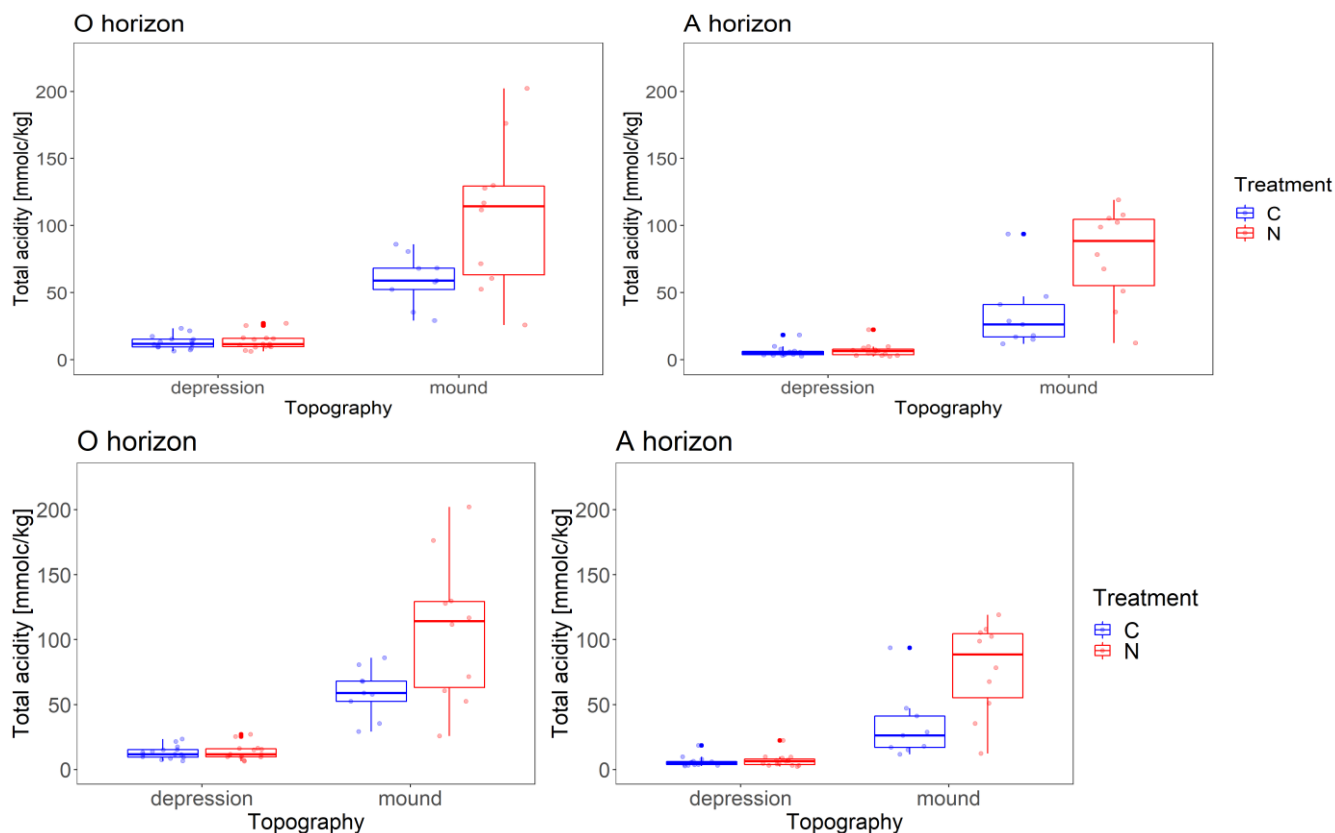
Figure 4: Observed total soil acidity values from all years for O and A horizon for both topographical features (mounds and depressions).
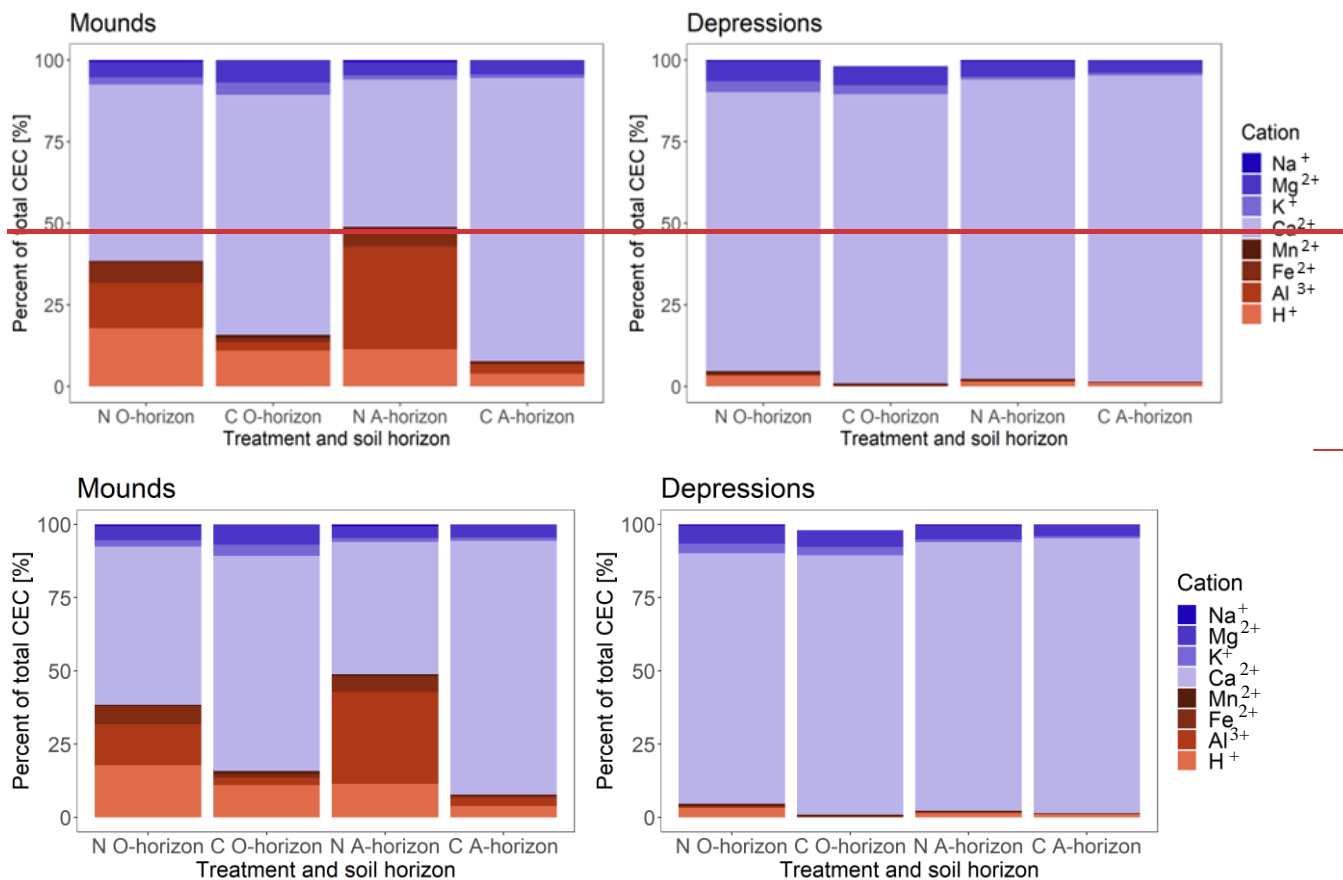
Figure 5: Exchangeable cations in proportions of total cation exchange capacity (CEC) for the year 2016. (Pb an Zn were excluded as their concentrations was negligibly small or zero for most replications). Acidic cations are indicated by the color red and base cations are blue.
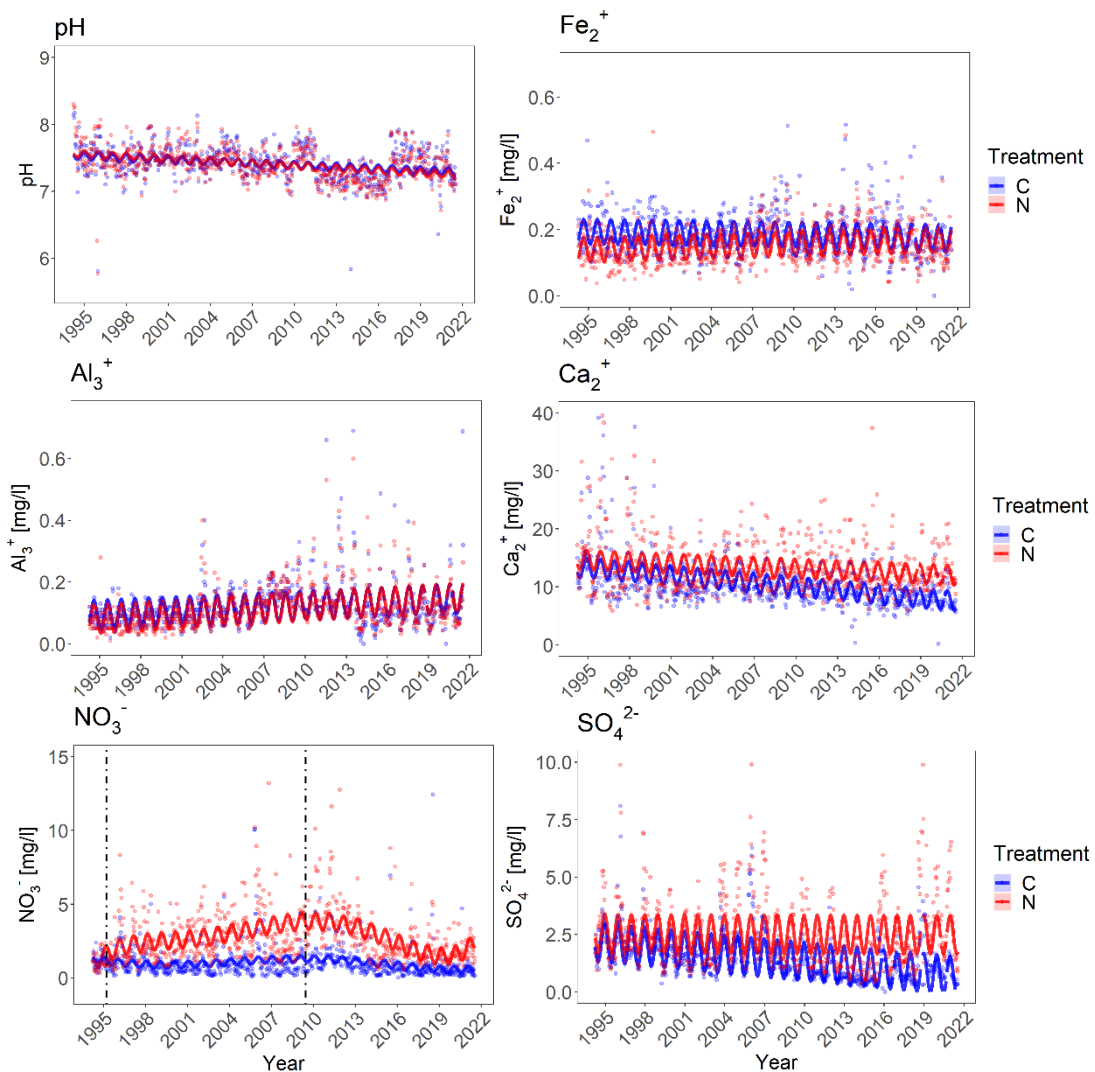
Figure 6: Cation and anion concentrations in soil runoff water from the control (blue) and N-treated (red) catchment as a function of time. The points are measured values with a time step of 2 weeks. The continuous solid lines are the predicted values from the linear models with confidence intervals. 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_4NO_3 to the N-treated catchment. The second dashed line indicates the date of ringing of trees prior to felling. For Fe_2^+, Ca_2^+, NO_3^- and pH, 1 outlier was excluded each from the plot and for SO_4^{2-} 4 outliers were excluded.

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