Heathland ecosystems, human impacts and time: A long term heathland trial investigating ecosystem changes that occur after exposure to climate change, elevated N deposition and traditional vegetation management practices

Kopittke, G.R.

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Chapter 5

Soil Acidification Occurs Under Ambient Conditions but is Retarded by Repeated Drought: Results of a Field-Scale Climate Manipulation Experiment

GR Kopittke, A Tietema and JM Verstraten
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Abstract

Acid atmospheric emissions within Europe and North America have decreased strongly since 1985 and most recent acidification studies have focused on the changes occurring within ecosystems as a result of this decreased deposition. This current study documents a soil acidification trend under ambient N deposition conditions over a 13\(^4\) year period, suggesting that acidification continues to be a process of concern at this *Calluna vulgaris* dominated heathland with an acidic sandy soil. The annual manipulation of climatic conditions on this heathland simulated the predicted summer rainfall reduction (drought) and resulted in a long term retardation of the soil acidification trend. The pH of the soil solution significantly decreased over the course of the trial for both treatments, however, in the final two years the decline continued only in the Control treatment. This retardation is primarily associated with the reduction in rainfall leading to lower drainage rates, reduced loss of cations and therefore reduced lowering of the soil acid neutralizing capacity (ANC). However, a change in the underlying mechanisms also indicated that N transformations became less important in the Drought treatment. This change corresponded to an increase in groundcover of an air-pollution tolerant moss species and it is hypothesized that this increasing moss cover filtered an increasing quantity of deposited N, thus reducing the N available for transformation. A soil acidification lag time is expected to increase between the two treatments due to the cumulative disparity in cation retention and rates of proton formation. To the authors’ knowledge, this is the first study in which such acidification trends have been demonstrated in a field-scale climate manipulation experiment.

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\(^{4}\) This chapter presents results after 13 annual drought treatments, whereas the remainder of the thesis presents results after 14 annual drought treatments.

Photo (left) Site soil profile with a ceramic soil-solution-sampler. Photographer Gillian Kopittke 2012.
1 Introduction

Predicted climate change is likely to affect key ecosystem functions such as carbon storage, nutrient cycling and species composition (IPCC 2007b, Wessel et al. 2004). Therefore, many of the recent climate change research studies have focused on carbon (C) and nitrogen (N) cycling in relation to altered temperature and precipitation patterns. This has been important to predict reliably the effect of climate change on net ecosystem C sequestration, particularly in ecosystems where N was historically limited and atmospheric N deposition is likely to contribute to increased C production / accumulation in plants and soils (Beier et al. 2008, Beier et al. 2009, de Vries et al. 2009, Gorissen et al. 2004, Oulehle et al. 2011, Treseder 2008). However, on sites that are N saturated from elevated N deposition, there may be other processes occurring such as long-term soil pH (acidification) changes. These acidification processes have not, so far, been investigated in relation to the IPCC predicted climate changes for altered rainfall patterns in Europe, e.g. increased extreme events, decreased summer precipitation and increased winter precipitation (IPCC 2007a).

Accelerated soil acidification resulting from elevated atmospheric deposition is a well-studied topic (Reuss et al. 1987, van Breemen et al. 1983) having been investigated through numerous studies, including soil solution trend analysis, soil sampling studies and determination of N or sulphur (S) budgets and proton cycles (e.g. De Schrijver et al. 2006, Neiryck et al. 2002, Tietema and Verstraten 1991, Verstraten et al. 1990). Acid atmospheric emissions within Europe reached a peak between the mid-1960s to 1980s with deposition rates in the order of 40 to 80 kg N ha\(^{-1}\) year\(^{-1}\) recorded in the Netherlands (van Breemen and van Dijk 1988). Between 1985 and 1995, strong reductions in acidifying emissions were observed (particularly for SO\(_2\)) as a result of the introduction of air pollution abatements (Fowler et al. 2007, Jaarsveld and Bleeker 2004). Emissions have continued to decline in Europe, with European Union (EU) countries reducing N (NO\(_x\)+ NH\(_3\)) output by 42% (22,162 Gg year\(^{-1}\) to 12,753 Gg year\(^{-1}\)) and SO\(_x\) output by 82% (24,857 Gg year\(^{-1}\) to 4,575 Gg year\(^{-1}\)) between 1990 and 2010 (EEA 2012). In some countries, such as the Netherlands, even greater reductions have been observed, with a 57% reduction of N emissions between 1990 and 2010 (EEA 2012).

With this significant reduction in anthropogenic acid emissions and subsequent deposition in Europe and North America, questions have been posed on whether acidification is still an ecological threat (Alewell et al. 2000). Most recent acidification studies have focused on the changes occurring within ecosystems as a result of decreased N and S deposition. These studies have found signs of recovery but have also observed that as S deposition decreases there is increased dissolved organic carbon (DOC) solubility leaching into waterways, or that previously deposited sulfate was stored in the soil and it is released over time leading to cation leaching and continued acidification (e.g. Armbruster et al. 2003, Cai et al. 2012, Evans et al. 2006, Hruška et al. 2009, Monteith et al. 2007, Oulehle 2008).
et al. 2011). However, to the authors’ knowledge, there have been no detailed studies that link investigations of soil acidification under the current reduced N deposition rates with the interaction of changed climatic conditions.

A long term climate manipulation trial established on a heathland in the Netherlands provided a unique opportunity to monitor the development of soils under ambient N deposition conditions and to investigate the interaction of a drought manipulation on acidification trends. This climate trial was part of a network of sites established in Europe that aims to investigate the effect of the IPCC predicted climate change of altered rainfall patterns, in particular a decreased summer precipitation (Beier et al. 2004). Heathlands have large nutrient pools bound in the ectorganic (O) horizon which may potentially be mobilized if climatic conditions change (Nielsen et al. 1999, Schmidt et al. 2004). These ecosystems have conservative element cycles and it was hypothesized that changes in seepage water chemistry would be early indicators of changes in soil processes in the topsoil in response to climate change. Therefore, soil solution data from the 13 year study was used to investigate pH, element concentrations and element fluxes of the heathland haplic podzol soil.

Early results published for this Dutch heathland indicated that the soil was N saturated and wet N deposition exceeded critical loads of 15–20 kg N ha\(^{-1}\) year\(^{-1}\) for over half a century (Schmidt et al. 2004). Under these elevated acid deposition conditions, anthropogenic protons enter the soil system and soil acidification occurs through a proton transfer process (van Breemen et al. 1983). In soils that are already acidic, such as in this study, the proton participates in one of two important transfer processes: (1) cation exchange reactions with the soil complex, and (2) reactions of protons with the relatively quickly soluble amorphous components of the soil, such as the release of inorganic Al species by dissolution of soil constituents (Reuss et al. 1987). These are also the primary neutralizing processes in sandy soils where infiltrated water has a short residence time and where only the rapid buffering reactions are able to occur prior to solute leaching (Verstraten et al. 1989). The leaching of these metal ions (e.g. the base cations) is irreversible and once they are leached they are unavailable for any future neutralizing reactions. This leads to a permanent change in pH (van Breemen et al. 1983).

Therefore, if the previously recorded high N deposition rates continued, it was hypothesized that the soil pH would reduce over time. However, if site deposition rates followed the decreasing trend observed in Europe, then acidification trends were hypothesized to be retarded or reversed. This paper reports the results of a long-term experiment that investigated these acidification trends both under ambient conditions and under the altered precipitation pattern of repeated annual drought in a heathland on an acid sandy soil with a low acid buffering capacity.

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5 The remainder of the thesis presents results after 14 annual drought treatments.
2 Materials and Methods

2.1 Study Site

Investigation was undertaken at a dry heathland, located approximately 25 m a.s.l. at Oldebroek, The Netherlands. Heathlands are mostly cultural landscapes that have been formed by human activities, where organic matter is exported from the heathlands to improve other arable lands by methods such as grazing, burning, mowing or sod removal (Diemont and Heil 1984). The dominant vascular species at the site is *Calluna vulgaris* (L.) Hull which grows to a maximum height of 75 cm and provides approximately 95% of the groundcover, with some *Deschampsia flexuosa* and *Molinia caerulea*. The Calluna community was relatively old as it was last cut in 1984 and was in a net-biomass-loss phase of growth (Gimingham 1985, van Meeteren et al. 2008). The dominant non-vascular species is *Hypnum cupressiforme* Hedw. with two ecological phenotypes, one growing under Calluna protection and the other adapted to more light between Calluna plants. The soil is a nutrient-poor, well drained, acid sandy *Haplic Podzol*. Wet deposition rates were high for both bulk N (10.7–37.4 kg N ha\(^{-1}\) year\(^{-1}\)) between 1998 and 2012 and SO\(_4\) (4.2–6.2 kg S ha\(^{-1}\) year\(^{-1}\)) between 2008 and 2011. Further information about the site location, species composition and climate is provided in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Description of the Oldebroek Trial Location (Van Meeteren et al. 2007).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Location</strong></td>
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<tr>
<td><strong>Co-ordinates</strong></td>
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<tr>
<td><strong>Elevation</strong></td>
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<tr>
<td><strong>Slope</strong></td>
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<tr>
<td><strong>Climate</strong></td>
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<tr>
<td><strong>Rainfall</strong></td>
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<td><strong>Temperature</strong></td>
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<tr>
<td><strong>Soil</strong></td>
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<tr>
<td><strong>Parent Material</strong></td>
</tr>
</tbody>
</table>

2.2 Experimental Design

Six experimental plots of 5 m x 4 m (with a 0.5 m buffer strip around the perimeter) were established in a homogeneous area of the heathland in 1998. Two treatments were allocated randomly: Control (n=3) and Drought (n=3). Light scaffold structures were built over all the plots, to ensure that any impact from the scaffolding (e.g. shading and sheltering) occurred in all plots. The scaffolding structure was built of galvanized steel
tubes and was covered by thin plastic sleeves to prevent contaminants from leaching into the plot (Beier et al. 2004).

Over the Drought plots, the frame supports a retractable curtain made of transparent polyethylene plastic. Rain sensors activate the motor to extend this cover over the plots when rain is detected and to retract the cover when the rain stops. When the curtain is extended in these Drought plots to exclude the rain, wind sensors again retract the curtain to prevent damage during periods of high wind (>10 m s\textsuperscript{−1}). Outside this period, no manipulation treatment was applied to the Drought plots and all plots received the same precipitation amount as the Control during non-drought periods.

The Drought treatment was applied each year in the growing season, which occurs from April to October. Precipitation was excluded for two to three months within this growing season and overall the treatment reduced precipitation by 6–29%. The specific timing of the drought periods, as well as the reduction in rainfall the Drought plots received, are included in Table 2. The experimental treatments began in May 1999 and the results detailed in this paper covered the time period 1998–2012. Further details on the design of the treatment manipulations can be found in Beier et al. (2004).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Year} & \textbf{Site Annual Precipitation (mm)} & \textbf{Drought Treatment Dates} & \textbf{Drought Precipitation Reduction (\%)} & \textbf{Soil Moisture Content after Drought} \\
& & & & \\
& & & \textbf{Control (m\textsuperscript{3} m\textsuperscript{−3})} & \textbf{Drought (m\textsuperscript{3} m\textsuperscript{−3})} \\
\hline
1999 & 891 & 26 May – 10 Aug & 8.2\% & 0.141 & 0.097 \\
2000 & 1142 & 24 May – 25 July & 18.8\% & 0.184 & 0.062 \\
2001 & 1030 & 28 May – 14 Aug & 28.6\% & 0.222 & 0.044 \\
2002 & 1032 & 3 Jul – 16 Aug & 23.0\% & 0.191 & 0.044 \\
2003 & 836 & 3 Jun – 12 Aug & 17.9\% & 0.082 & 0.037 \\
2004 & 1220 & 25 May – 28 Jul & 23.0\% & 0.202 & 0.041 \\
2005 & 1196 & 16 Jun – 12 Aug & 26.6\% & 0.236 & 0.050 \\
2006 & 1233 & 30 May – 7 Aug & 20.1\% & 0.134 & 0.042 \\
2007 & 1018 & 13 Jul – 14 Sep & 21.0\% & 0.118 & 0.049 \\
2008 & 874 & 2 Jun – 29 Jul & 20.1\% & No data & No data \\
2009 & 820 & 27 May – 28 Jul & 29.0\% & No data & No data \\
2010 & 1007 & 22 Apr – 30 May & 5.9\% & 0.164 & 0.150 \\
2011 & 887 & 5 Apr – 10 Jun & 7.3\% & 0.194 & 0.089 \\
\hline
\end{tabular}
\caption{Drought Treatment Effects.}
\end{table}
2.3 Sampling and Analysis

2.3.1 Soil Solution

Soil solution was sampled at the base of the rooting zone (30 cm below soil surface, approximately at the lower boundary of the BC horizon) by using ceramic tension soil-solution-samplers (Soilmoisture Corp., Goleta, CA, USA). Three soil-solution-samplers were installed in each plot in 1998, approximately 6 months prior to the start of the experimental treatments (n=9 per treatment). The samples were collected on an approximately monthly basis although no samples were collected during frost periods.

Soil solution samples were measured for pH prior to filtration. From 2007 onwards, Electrical Conductivity was also determined prior to filtration (0.2 µm membrane filter). All samples were analyzed for NO$_3^-$, NH$_4^+$, SO$_4^{2-}$ (after 2007), PO$_4^{3-}$, dissolved organic N (DON) and Cl$^-$ concentrations using an Skalar autoanalyzer. Note: NO$_2^-$ was also analyzed but was not detected in any sample and therefore is not included in further discussion. Cation concentrations (Al, Ca$^{2+}$, Fe, K$^+$, Mg$^{2+}$, Mn$^{2+}$ and Na$^+$) were determined in 1999, 2002, 2010 and 2011 using Inductively Coupled Plasma-Optical Emission Spectroscopy (PerkinElmer ICP-OES).

Precipitation amount was monitored by rain gauges located both outside the experimental plots and inside each plot to record water input to the different treatments. The gauges were placed under the curtains at approximately one meter above ground level. The precipitation water from outside the plots was analyzed following the same methods used for soil solution samples.

The mean solution pH values were determined from the calculated molar H$^+$ concentrations of the pH measurements and are presented using negative log transformed data. The DOC was used to calculate the concentration of organic anionic sites (DOC$^-$) using the dissociation constant (pK) / pH relationship for fulvic acid (Oliver et al. 1983, van Wesemael and Verstraten 1993). The sum of cations ($\Sigma$ H$^+$ + NH$_4^+$ + Al$^{3+}$ + Ca$^{2+}$ + Fe$^{2+}$ + K$^+$ + Mg$^{2+}$ + Mn$^{2+}$ + Na$^+$) and sum of anions ($\Sigma$ DOC$^-$ + NO$_3^-$ + PO$_4^{3-}$ + Cl$^-$) were calculated where full data sets were available. Note: SO$_4^{2-}$ concentrations were excluded from the sum of anions calculation as they were not analyzed prior to 2007. Where SO$_4^{2-}$ concentrations prior to 2007 are referenced, they were calculated using the difference between the sum of cations and sum of anions (‘calculated SO$_4^{2-}$’), as the soil solution has electrical neutrality. These calculated values were compared to the analytical SO$_4^{2-}$ concentrations obtained between 2007 and 2012 and were found to be a good approximation.

2.3.2 Calculation of Element Fluxes

Water balances were estimated for each treatment using the chloride mass balance (CMB) method (Wood 1999). The CMB method of estimating soil water drainage is based on an assumption the water mass flux can be calculated if the chloride in the soil solution originates only from precipitation, the chloride is conserved in the system, the chloride-
mass flux has not changed over time and there is no recycling or concentration of chloride within the soil solution (Wood 1999). Once these conditions are met, the flux can be expressed as:

\[
\text{Drainage Value} = \frac{(P)(\text{Cl}_p)}{\text{Cl}_{sw}}
\]  

(1)

where for a specified period of time (t): Drainage Value is the soil water flux (mm t\(^{-1}\)), P is the precipitation for the measurement period (mm t\(^{-1}\)), Cl\(_p\) is the precipitation chloride concentration (µmol L\(^{-1}\) t\(^{-1}\)) and Cl\(_{sw}\) is the chloride concentration of the soil water (µmol L\(^{-1}\) t\(^{-1}\)). The element output was calculated by multiplying the soil solution concentrations by the Drainage Value. Element input was calculated by multiplying the rainfall concentrations by the rainfall flux (mm t\(^{-1}\)) for the same time period and are represented as Drought\(_{\text{rainfall}}\) and Control\(_{\text{rainfall}}\). The rainfall fluxes represent wet deposition and so the actual deposition rates may be slightly higher when considering dry deposition.

When the Drainage Values for the Control and Drought treatments were compared to the Cl\(^-\) influx in the precipitation, there a good approximation between Cl\(^-\) input and Cl\(^-\) output (data not shown). This indicated that the chloride in the soil solution originated only from precipitation and that the CMB method was suitable for calculating the water balance of this system. Fluxes of other elements were then calculated based on the Drainage Values for each lysimeter location.

Mobilization or retention of cations was estimated as the difference between atmospheric input from precipitation and leaching loss beneath the root zone using the element flux. The retention (positive values) or mobilization (negative values) relative to the input was calculated as:

\[
\% \text{ Retention} = \left( \frac{(\text{Input}_{\text{rainfall}}) - (\text{Output}_{\text{fluxes}})}{\text{Input}_{\text{rainfall}}} \right) \times 100
\]  

(2)

Net proton flux attributed to N transformations were determined by net output of ammonium less net output of nitrate to the system (Tietema and Verstraten 1991):

\[
(NH_4^+_{\text{input}} - NH_4^+_{\text{output}}) - (NO_3^-_{\text{input}} - NO_3^-_{\text{output}})
\]  

(3)

and assumes a negligible change in storage of NH\(_4^+\) and NO\(_3^-\).

2.3.3 Soil Samples

Soil samples were obtained to a depth of 30 cm during the installation of the soil-solution-samplers in 1998. Analysis was undertaken on the three main horizons encountered (LF, Ae and BC). The C and N concentrations were analyzed on a CNS analyzer (Vario EL Analyzer, Elementar). Organic samples were extracted with water (1:10) and 0.125M BaCl\(_2\) (1.25 w/v) and mineral samples were extracted with H\(_2\)O (1:1) and 0.125M BaCl\(_2\) (1:50 w/v) to determine anion and cation concentrations and the available acidity. The Effective Cation Exchange Capacity (ECEC) was calculated and soil cation pools were calculated using the exchangeable cation (molar charge) concentrations, the known horizon thicknesses and the horizon dry bulk densities.
In 2005, a soil pit was excavated outside the control plots and samples obtained from each of the mineral soil horizons (Ae, Bhs, Bhs/BC and BC) to 30 cm depth. Soil pH was measured in H$_2$O, 0.01M CaCl$_2$ and 1.0M KCl (1:2.5 w/v). Selective extraction analyses were performed to determine the pools of Al and Fe fractions present at the site and included total metals (HCl solution after a HF/H$_2$SO$_4$ destruction), total free metals (0.54M Na dithionite-citrate); total amorphous metals (NH$_4$Ox/Ox, pH 3.0 in the dark); organic fraction of amorphous metals (0.1M Na pyrophosphate/NaOH; pH 9.7); mobile fraction of amorphous metals (0.056M Na tetraborate; pH 9.5); reactive metals (0.5M CuCl$_2$) and weakly exchangeable cations (1.0M NH$_4$Cl$_2$) (Bruckert 1982, Holmgren 1967, Juo and Kamprath 1979, McKeague and Sheldrick 1977, Schwertmann 1964).

The fast (exchangeable) and reactive soil Acid Neutralizing Capacities (ANC) were calculated using the following equations:

\[
\text{ANC}_{(ex)} = \text{ECEC} - \text{adsorbed H}^+ \tag{4}
\]

\[
\text{ANC}_{(r)} = [6(\text{Al}_2\text{O}_3) + 6(\text{Fe}_2\text{O}_3) + 4(\text{MnO}_2) \text{ ammonium oxalate}] + \text{adsorbed bases} \tag{5}
\]

where ANC$_{(ex)}$ is a measure of the acid buffering that occurs primarily by adsorbed (and water soluble) ‘exchangeable’ cations and ANC$_{(r)}$ is a measure of the adsorption by reactions of protons with relatively quickly soluble soil constituents (the amorphous material) (Verstraten et al. 1989). Due to the very low content of easily weatherable minerals, the total ANC of the soil horizons was not taken into account.

### 2.4 Data Analysis

Only years in which a continuous 12 months of data was available were used in the analysis. These periods are listed below and are hereafter abbreviated to a single year number, based on the year in which the majority of samples were obtained.

- ‘2002’: August 2001 – August 2002 (22 sampling events)
- ‘2003’: May 2003 – April 2004 (16 sampling events)
- ‘2008’: June 2008 – July 2009 (9 sampling events)
- ‘2010’: March 2010 – March 2011 (10 sampling events)
- ‘2011’: April 2011 – April 2012 (12 sampling events)

Within the results and discussion sections, the ‘early years’ of the study refers to years 1999 and 2000, and the ‘final years’ of the study refers to years 2010 and 2011.

The effect of climate treatment on soil chemical properties was investigated by pairwise t tests (using the Bonferroni correction factor) whereby an effect is considered as significant if its associated p-value is ≤0.05. The effect of climate treatment on soil solution pH, on
the sum of anions and on the sum of cations was investigated using a linear mixed effects model (Pinheiro and Bates 2000). Where the response variable was the soil solution measurement (a repeated measurement per location), the trial treatments formed the fixed effects and the measurement locations formed the random effects. A simple linear regression was used within each climate treatment to assess the relationships of cations in the soil solution. Where mean results are referenced, the standard errors of the mean are provided in both text and graphics.

For the statistical analyses, the R statistical computing program was used (R Development Core Team 2008).

3 Results

3.1 Soil

The soil pH was acidic and results at 30 cm depth (BC horizon) corresponded to the soil solution pH obtained at the same depth in the first year of the trial (pH: 4.53). The ECEC and ANC\(_{(ex)}\) were greatest in the organic LF horizon and reduced with depth. The ANC\(_{(r)}\), which is much greater than the ANC\(_{(ex)}\) in the mineral horizons, showed minor increases with increasing depth (Figure 1). There were no significant differences at any depth horizon between the Control treatment and the Drought treatment.

Analysis of the soil metal pools indicated that total Al concentrations were significantly greater than total Fe concentrations (Table 3). The majority of the metals were associated
with the inorganic pools, with approximately 95% of the aluminium bound to silicate minerals and 40% of the iron present as free crystalline (inorganic) iron. All the amorphous Fe and Al was organically bound with a dominant part of the Al in the reactive form.

### Table 3 Mineral Soil Pools of Iron and Aluminium (mmol kg\(^{-1}\)) for the Control treatment.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth</th>
<th>Total Metals (a)</th>
<th>Total Free Metals (b)</th>
<th>Silicate Bound Metals</th>
<th>Total Amorphous Metals (c)</th>
<th>Organic Amorphous Metals (d)</th>
<th>Mobile Amorphous Metals (e)</th>
<th>Reactive Metals (f)</th>
<th>Exchangeable Metals (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Iron (mmol kg(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AE 0–4/8</td>
<td>22.7</td>
<td>17.0</td>
<td>5.7</td>
<td>6.84</td>
<td>7.04</td>
<td>4.75</td>
<td>n.d.</td>
<td>0.264</td>
</tr>
<tr>
<td></td>
<td>B(_{hs}) 4/8–10/16</td>
<td>28.9</td>
<td>21.9</td>
<td>6.9</td>
<td>10.6</td>
<td>12.7</td>
<td>7.38</td>
<td>n.d.</td>
<td>0.274</td>
</tr>
<tr>
<td></td>
<td>B(_{nh})/BC 10/16–22</td>
<td>27.8</td>
<td>18.2</td>
<td>9.5</td>
<td>6.58</td>
<td>5.91</td>
<td>2.93</td>
<td>n.d.</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td>BC 22–30</td>
<td>25.2</td>
<td>15.2</td>
<td>10.0</td>
<td>4.51</td>
<td>3.49</td>
<td>1.07</td>
<td>n.d.</td>
<td>0.093</td>
</tr>
<tr>
<td></td>
<td>Aluminium (mmol kg(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AE 0–4/8</td>
<td>229</td>
<td>13.3</td>
<td>216</td>
<td>8.57</td>
<td>9.80</td>
<td>8.46</td>
<td>6.56</td>
<td>3.8</td>
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<tr>
<td></td>
<td>B(_{hs}) 4/8–10/16</td>
<td>220</td>
<td>17.2</td>
<td>202</td>
<td>7.75</td>
<td>11.1</td>
<td>9.99</td>
<td>6.08</td>
<td>3.3</td>
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<tr>
<td></td>
<td>B(_{nh})/BC 10/16–22</td>
<td>253</td>
<td>24.8</td>
<td>229</td>
<td>14.6</td>
<td>15.3</td>
<td>12.4</td>
<td>7.75</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>BC 22–30</td>
<td>237</td>
<td>26.6</td>
<td>211</td>
<td>17.1</td>
<td>20.5</td>
<td>13.6</td>
<td>7.52</td>
<td>2.3</td>
</tr>
</tbody>
</table>

(a) HF / H\(_2\)SO\(_4\) destruction; (b) Na dithionite-citrate extractable; (c) NH\(_4\)Ox/Ox pH 3.0 exchangeable; (d) Na pyrophosphate / NaOH pH 9.7 extractable; (e) Na tetraborate / NaOH pH 9.5 extractable; (f) CuCl\(_2\) extractable; and (g) NH\(_4\)Cl extractable. The n.d. indicates concentrations were not determined.

### 3.2 Soil Solution pH

Soil solution pH significantly decreased over time for all treatments (p <0.0001). The pH consistently decreased prior to 2010 in both the Control and Drought treatments, with the mean pH decreasing from 4.50 and 4.55, respectively in 1999 to 4.29 and 4.19, respectively in 2008 (Figure 2). From 2010 to 2011, the pH declined to 3.85 in the Control treatment, whilst the Drought treatment pH remained relatively stable at 4.12.

Assessment of the pH prior to 2010 indicated there was a significant decrease in pH from 1999 to 2008 (p<0.0001) but there was no significant effect of treatment on the pH (p=0.11). In 2011, the soil solution pH in the Control treatment was significantly more acidic than in the Drought treatment (p 0.0013).

The results for the input precipitation (Rainfall) have been included in Figure 2 for comparison to the soil solution. Mean input pH increased from 5.13 in 1999/2002 to 5.35 in 2003 and then decreased to 4.59 in 2010/2011.
3.3 Soil Solution Anions / Cations

The sum of cations in soil solution significantly increased between 1999 and 2011 (p<0.0001) and there was a significant effect of the Drought treatment (p=0.004; Figure 3).

Figure 2 Annual mean pH of the soil solution in the Control and Drought treatments for 1999 to 2011. Site precipitation data (Rainfall) is shown for comparison. The annual means are calculated from a minimum of nine soil solution sampling events (in 2008), with a maximum of 25 sampling events (in 2000), from an available nine sampling locations per treatment. The bars represent the standard error of the mean.

Figure 3 Mean Sum of Anions (lines) and Sum of Cations (symbols) for the Control and Drought treatments, with Rainfall input shown for comparison. The difference observed between the sum of anions and sum of cations is attributed to SO$_4^{2-}$. The annual means for Drought and Control are calculated from a minimum of nine sampling events (in 2008), with a maximum of 25 sampling events (in 2000) from an available nine sampling locations per treatment. The bars represent the standard error of the mean.
At the start of the trial in 1999, there was no difference between the treatments (p=0.159). However, after 13 years of repeated Drought treatments the sum of cations was significantly greater in the Drought treatment than the Control treatment (p=0.0096; 2010/11). The cations were not assessed in each year and so, once the calculated SO₄ was included, the anions concentrations in solution could be used as an indication of the cation concentrations in soil solution in the intermediate years. The overall trend of the anion concentrations supported the trend observed in the cations. The mean anion sums and cation sums in the Drought and Control treatment soil solutions were greater than the Rainfall concentration in every year.

Assessment of individual cation and anion relationships showed that there was no relationship for either Al or Fe with DOC in the soil solution (data not shown). Fe²⁺ concentrations in the soil solution were low in all years (annual mean Fe²⁺ <10.5 µmol L⁻¹) and did not have significant relationships with any anion. In contrast, Al³⁺ was linearly related to NO₃⁻ for both the Control and Drought treatments in 1999/2000 (r²=0.58 and r²=0.66, respectively; Figure 4a and 4b). A similar relationship remained in later years (2010/2011) for the Control treatment, however this relationship no longer existed for the Drought treatment. There was no relationship between Al³⁺ and SO₄²⁻ in either 1999/2000 or 2010/2011 for the either the Control or Drought treatments (Figure 4c and 4d). Summing the SO₄²⁻ and NO₃⁻ concentrations can indicate if there is joint importance of S and N transformations in the acidification reactions. However, this joint concentration did not improve the relationship with Al³⁺ in either 1999/2000 or 2010/2011 (for example 2010/2011: Drought p=0.045 and Control p=0.61) when compared to the relationship of Al³⁺ with NO₃⁻ (data not shown).

Relationships between base cations (Σ Ca²⁺ + Mg²⁺ + K⁺ + Na⁺) and NO₃⁻ existed for both the Control treatment (r²=0.73) and the Drought treatment (r²=0.68) in 1999/2000. By 2010/2011, this relationship had weakened in the Control treatment and did not exist for the Drought treatment (Figure 5a and 5b). In contrast, there was initially no relationship between base cations and SO₄²⁻ for either treatment but by 2010/2011, base cation concentrations were linearly related to SO₄²⁻ in the Drought treatment (r²=0.74).

### 3.4 Element Pools

The output of cations in the soil solution at 30 cm were lower in the Drought treatment than in the Control treatment for all years, with the exception of NH₄⁺ and K⁺ in 1999/2002 and Mg²⁺ in 2010/2011 (Table 4). The cation fluxes did not include soil mineral weathering rates and so total cation balances could not be calculated. However, the general cation balance between cation input and cation output was calculated through the Mobilization and Retention values. In the initial years (1999/2002), high mobilization of Al³⁺ and moderate mobilization of base cations was observed in both treatments. In the final years (2010/2011), base cations and Al³⁺ continued to be mobilized in the Control treatment. However, a different pattern was observed in the Drought treatment where base cations were retained and there was a reduction in Al³⁺ mobilization. A change in the proportion
of NH$_4^+$ retention was also observed, with greater retention on the Drought treatment than on the Control.

The relationships of individual base cations with anions were examined and the only relationships found were for K$^+$ with NO$_3^-$ (Control and Drought in all years), Na$^+$ with NO$_3^-$ (weak relationships for Control and Drought in 1999/2000) and individually for Ca$^{2+}$, Mg$^{2+}$ and Na$^+$ with SO$_4^{2-}$ (Drought in 2010/2011; data not shown). There were no relationships between any base cation concentration and SO$_4^{2-}$ concentrations in the Control treatment for any year.

**Figure 4** Relationship of Al$^{3+}$ and (a) NO$_3^-$ in the Control treatment, (b) NO$_3^-$ in the Drought treatment, (c) SO$_4^{2-}$ in the Control treatment, and (d) SO$_4^{2-}$ in the Drought treatment (µmol L$^{-1}$). The data and regression lines for 1999/2000 and 2010/2011 periods are shown in each plot with * indicating the value of the slope is significant (p<0.01) or ** indicating it is highly significant (p<0.001).
Figure 5 Relationship of the base cations (sum of Ca$^{2+}$, Mg$^{2+}$, K$^+$ and Na$^+$) and (a) NO$_3^-$ in the Control treatment, (b) NO$_3^-$ in the Drought treatment, (c) SO$_4^{2-}$ in the Control treatment, and (d) SO$_4^{2-}$ in the Drought treatment ($\mu$mol L$^{-1}$). The data and regression lines for 1999/2000 and 2010/2011 periods are shown in each plot, with * indicating the p-value of the slope is significant (p<0.01) or ** indicating it is highly significant (p<0.001). Four points that were included in the regression calculation but not displayed in graphs (b) and (d) had cation concentrations that exceeded 2000.

The N budget indicated that in 1999/2000, NO$_3^-$ output from the soil was greater than the input, with approximately 298% (Control) and 230% (Drought) of the rainfall NO$_3^-$ measured in the soil solution output (Table 5). Calculation of the N transformations indicated that protons were generated in both treatments, although there was 25% less proton formation in the Drought treatment than in the Control.

In 2010/2011, the NO$_3^-$ output was still greater than the input on the Control treatment (158% output). However, the Drought treatment showed a different pattern with less NO$_3^-$ in the drainage than in the rainfall (65% output), indicating a reduction in nitrification. The
positive net proton fluxes indicated that protons were formed from N transformations in 2010/2011 although production in both treatments had decreased since 1999/2000. The proton formation in 2010/2011 was 60% less in the Drought treatment than in the Control treatment.

### Table 4: Cation Budget for the Control and Drought treatments, showing mean soil pools in 1998 and the mean annual rainfall input and soil solution output at 30 cm (mmol cm⁻² year⁻¹) for the periods 1999–2002 and 2010–2011. Rainfall input and soil solution output were calculated using the site water balance model and do not include cation inputs from dry deposition. Soil pools were calculated from the ECEC of the soil removed during soil-solution sampler installation.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Control Treatment</th>
<th>Drought Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{NH}_4^+ )</td>
<td>( \text{Al}^{3+} )</td>
</tr>
<tr>
<td>Initial Years (1999–2002)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Input (mmol m⁻² year⁻¹)</td>
<td>76.9 ± 13.3</td>
<td>2.2 ± 0.3</td>
</tr>
<tr>
<td>Output (mmol m⁻² year⁻¹)</td>
<td>43.5 ± 13.3</td>
<td>127.8 ± 13.0</td>
</tr>
<tr>
<td>Balance (mmol m⁻² year⁻¹)</td>
<td>33.5 ± 125.6</td>
<td>-126.2 ± -26.6</td>
</tr>
<tr>
<td>Retention / Mobilization</td>
<td>43%</td>
<td>-5709%</td>
</tr>
<tr>
<td>Final Years (2010–2011)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Input (mmol m⁻² year⁻¹)</td>
<td>70.9 ± 36.2</td>
<td>2.6 ± 0.6</td>
</tr>
<tr>
<td>Output (mmol m⁻² year⁻¹)</td>
<td>10.4 ± 6.8</td>
<td>109 ± 61.4</td>
</tr>
<tr>
<td>Balance (mmol m⁻² year⁻¹)</td>
<td>60.5 ± -106.4</td>
<td>19.5 ± -4.9</td>
</tr>
<tr>
<td>Retention / Mobilization</td>
<td>85%</td>
<td>-4092%</td>
</tr>
</tbody>
</table>
Table 5 Nitrogen Budget for the Control and Drought treatments for the periods 1999–2000 and 2010–2011, showing annual mean rainfall input and soil solution output at 30 cm (mmol c m⁻²). Rainfall and soil solution balances were calculated using the site water balance model. Proton formation from N transformations was calculated by \((NH_4^+ \text{input} - NH_4^+ \text{output}) - (NO_3^- \text{input} - NO_3^- \text{output})\), assuming a negligible change in storage of NH₄⁺ and NO₃⁻.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Control Treatment (mmol c m⁻² year⁻¹)</th>
<th>Drought Treatment (mmol c m⁻² year⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH₄⁺</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>Rainfall Input</td>
<td></td>
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<tr>
<td>1999–2000</td>
<td>114.0</td>
<td>66.4</td>
</tr>
<tr>
<td>Annual Mean</td>
<td>± 25.2</td>
<td>± 0.7</td>
</tr>
<tr>
<td>2010–2011</td>
<td>70.9</td>
<td>74.6</td>
</tr>
<tr>
<td>Annual Mean</td>
<td>± 36.2</td>
<td>± 26.8</td>
</tr>
<tr>
<td>Solution Output</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1999–2000</td>
<td>84.3</td>
<td>197.9</td>
</tr>
<tr>
<td>Annual Mean</td>
<td>± 21.5</td>
<td>± 58.5</td>
</tr>
<tr>
<td>2010–2011</td>
<td>10.4</td>
<td>117.9</td>
</tr>
<tr>
<td>Annual Mean</td>
<td>± 6.8</td>
<td>± 70.4</td>
</tr>
<tr>
<td>Proton Formation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1999–2000</td>
<td>161.2</td>
<td></td>
</tr>
<tr>
<td>Annual Mean</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010–2011</td>
<td>103.8</td>
<td></td>
</tr>
</tbody>
</table>

4 Discussion

Soil solution acidified over time for both Control and Drought treatments. However, after 13 years of sequential droughts, the soil solution pH was higher in the Drought treatment compared to the Control, indicating that the Drought retarded the acidification process. Acidification of soils occurs through the input of protons (e.g. acidic deposition) and subsequent proton transfer between the soil and the soil solution (van Breemen et al. 1983). Therefore, the extent to which soil acidification occurs is determined by the quantity of protons generated, and the capacity of the soil to buffer this acidification is broadly determined by the soil ANC. Thus, changes in soil pH can be interpreted through understanding the changes that occur in proton generation rates, cation balances and cation relationships in the soil solution. Therefore, the observed soil acidification will be discussed in terms of the underlying soil and soil solution relationships that existed at the beginning of the trial (the early years) and the changed conditions that existed later in 2010/2010 (the later years).

4.1 Relationships in the Early Years of the Field Study

The initial soil characterization at the study site indicated that there was a relatively low ANC₁ in the subsoil compared to the ANCᵢ. The release of Al from amorphous particles is
the dominant weathering process in acidic sandy podzols and can account for 60–90% of the acid neutralization (van der Salm et al. 2000). Therefore, although overall weathering rates were not investigated as part of this study, it is expected that a proportionally greater quantity of amorphous Al and Fe than base cations were available for fast buffering neutralization reactions. However, weathering rates of amorphous Al differ between compounds and the inorganic amorphous compounds have a faster dissolution rate than the organic amorphous compounds (van der Salm et al. 2000). The dominant amorphous Al compounds present in the trial site soil were organic compounds, indicating that relatively slower dissolution rates occurred. Therefore, the longer the residence time of infiltrated water (and associated protons) in the soil matrix, the more time available for dissolution of organic amorphous Al$^{3+}$ and acid buffering reactions.

An investigation of the relationship of Al$^{3+}$ to anions in the soil solution indicated that metal availability was not reduced by complexation with organic acids (DOC$^-$) and therefore metal concentrations were associated with inorganic acids in soil solution (Lundström et al. 2000). Inorganic acids can be generated through mineralization / nitrification of organic N or the mineralization / oxidation of organic S, which results in neutralization reactions in the soil solution such as the cation exchange or mineral dissolution reactions described previously (Reuss et al. 1987, van Breemen et al. 1983). The net effect of such processes is a net removal of protons and a net release of base cations and aluminium to soil solution.

This net release of base cations and aluminium in response to inorganic acids was observed in soil solution in 1999/2000, where both Al$^{3+}$ and base cation concentrations were significantly related to NO$_3^-$, which indicated that N transformations rather than S transformations were generating the majority of the protons in the soil for both treatments. The importance of nitrification was confirmed both by the N budget, which showed that NO$_3^-$ output was greater than input (indicating nitrification), and by the calculated positive proton fluxes. These processes occurred for both the Control and Drought treatments in 1999/2000, although there was 25% less proton formation in the Drought treatment than in the Control treatment, which approximately corresponded to the 23% lower ‘drought’ rainfall rate and therefore lower wet deposition rates in 2000.

The net release of base cations and aluminium into solution was followed by the leaching of these elements to below the root zone for both the Control and Drought treatments (as shown by the cation budget). However, the percentage of cations mobilized was generally lower in the Drought treatment and this is attributed to the reduced water flow observed in these plots.

### 4.2 Relationships After 13 Years of Ambient Conditions

Soil pH declined over the 13 year period for the Control treatment, but the rate of decline was more rapid in the final years. This indicated that an ANC buffering threshold may have
been reached in 2010 for the Control treatment, where the continuous addition of protons had protonated the conjugate bases at the previous proton levels (van Breemen et al. 1983). More acidic rainfall in 2010 and 2011 may have also accelerated the acidification trend in the Control treatment, with increased addition of H\(^+\) protons resulting in more proton transfers occurring and increased leaching of metal ions from the soil. However, it is important to note that the pH values are represented in a log scale and so the H\(^+\) concentration in soil solution has increased exponentially more than the H\(^+\) increase observed in the rainfall.

Investigation of the underlying relationships in 2010/2011 indicated that the relationships of Al\(^{3+}\) and base cations to NO\(_3^−\) still existed but had weakened. Additionally, the NO\(_3^−\) output for the Control treatment also still exceeded the input and the generation of protons through N transformations still occurred, although at reduced rates. This evidence of acidification corresponded to the observed decline in soil pH under ambient environmental conditions in the Control treatment.

Questions have previously been posed on whether acidification is still an ecological threat, considering the significant reduction in anthropogenic acid deposition in Europe and North America (Alewell et al. 2000). In this study we have identified that soil acidification is still occurring under ambient conditions in the Netherlands, suggesting that acidification continues to be of ecological concern, not only when considering the rate of ecosystem recovery. The sandy podzols of south-eastern Netherlands have low S storage capacity (Alewell 2001) and so the acidification trends identified at the study site are most likely associated with current deposition conditions rather than release of stored SO\(_4^{2−}\). Ambient N deposition conditions during this study ranged between 10.7 and 37.4 kg N year\(^{-1}\) and, although this is less than historical deposition rates, the rates in some years still exceeded the critical loads of 15–20 kg N year\(^{-1}\) described for dry heathlands (Bobbink and Roelofs 1995).

Only one other recent detailed field study has identified a continuing acidification trend under ambient deposition conditions (Boxman et al. 2008). This soil solution study was also conducted in the Netherlands but in a pine forest ecosystem over a 17 year period. This study showed that the soil solution pH at 10 cm depth had significantly decreased by 0.2 units to pH 3.0 in 2006, indicating a net formation of acid. However, soil solution at 90 cm depth had a reduced leaching of base cations over the same time period, indicating that recovery may have started at depth. The throughfall (wet + dry deposition) rates reported in the Boxman et al. (2008) study decreased by 25% for bulk N and by 65% for S between 1984 and 2006. Although these throughfall deposition values cannot be directly compared to the Oldebroek bulk deposition rates (no dry deposition rates measured), a similar rate of decrease is likely to have occurred across the country. The study concluded that further decreases in atmospheric deposition were required before the ecosystem could recover (Boxman et al. 2008).
A contrasting result was identified at another pine forest ecosystem located in the Czech Republic where soil solution pH trends were studied in conjunction with a 70% reduction in SO$_2$ emissions between 1994 and 2005 (Oulehle et al. 2006). It was observed that soil solution pH did not significantly change over time (i.e. no further acidification) and soil solution ANC increased during the study period. However, the system pH also did not show a recovery from the previous soil acidification, which was attributed to the desorption of previously stored sulfur leading to continued enhanced leaching of base cations. It is noted that throughfall bulk N deposition did not significantly decrease or increase during the Ouhehle et al. (2006) trial period (23 kg N ha$^{-1}$ year$^{-1}$), however, the rates were approximately half that recorded for the Boxman et al. (2008) study in the Netherlands in 2006 (46 kg N ha$^{-1}$ year$^{-1}$). This relative difference in N deposition between the Netherlands and other European regions corresponded to other reported observations, such as where wet N deposition at our Oldebroek site was between 1.6 and 2.8 times greater than other European shrubland sites (Schmidt et al. 2004).

4.3 Relationships After 13 Years of Repeated Annual Drought

In contrast to the ambient conditions, 13 years of repeated annual drought retarded the pH decline even under the more acidic rainfall recorded in 2010/2011. The repeated drought treatment resulted in a long-term change in the underlying mechanisms. The Al$^{3+}$ and base cations relationships with NO$_3^-$ no longer existed and concurrently, a relationship was observed between the base cations and SO$_4^{2-}$. This indicated that N transformations had become less important and the reduction of the role of N was reflected in the N budget, where NO$_3^-$ output and proton formation was greatly reduced between 1999/2000 and 2010/2011. With this decrease in the importance of N, the generation of protons from S transformations became relatively more important (or more observable) in the Drought treatment and / or the S atmospheric deposition had increased. Although the S deposition was not recorded in each year and changes to S input cannot be determined, the Boxman et al. (2008) study in the south-east of the Netherlands recorded co-deposition of NH$_4^+$ and SO$_4^{2-}$, with decreases in wet + dry S deposition between 1998 (25 kg S ha$^{-1}$ year$^{-1}$) and 2006 (20 kg S ha$^{-1}$ year$^{-1}$). Since deposition of NH$_4^+$ decreased at Oldebroek over the study period, it is unlikely that SO$_4^{2-}$ deposition increased. Therefore, it is hypothesized that the S transformations became relatively more observable with the decreasing importance of N transformations.

No other published studies have been found where an acidification trend is investigated with an interaction of changed climate conditions. The acidification retardation by the Drought treatment is hypothesized to be primarily associated with the reduction in rainfall resulting in lower drainage rates. The lower drainage rates have led to greater retention (or reduced mobilization) of base cations and Al$^{3+}$, thus resulting in a long term reduced lowering of the long term ANC of the soil. A secondary cause of lower drainage rates may be associated with the development of soil hydrophobicity in the Drought treatment which has been observed at this site as part of other investigations (Sowerby et al. 2008).
This hydrophobicity may have resulted in lower infiltration rates and subsequently lower drainage.

In the Drought treatment, the exclusion of rainfall led to the exclusion of a portion of the associated wet N deposition. This resulted in less N input and less N transformations / proton formation occurring within the soil. However, proton formation in 2010/2011 was reduced by 60%, which is more than can be explained by a 7% reduction in rainfall. This reduction may be because either (a) the N measured in the rainfall did not enter the soil and did not form protons, or (b) the N output did not reach the collection depth at 30 cm.

Atmospheric N may not be available for N transformations if it is intercepted by plant roots within the soil or intercepted by mosses prior to reaching the soil. Increases in plant biomass would indicate if a net N uptake from the soil had increased. Annual non-destructive estimates of Calluna biomass and the known N content of Calluna allowed for approximations of N storage to be calculated. These results indicated that N storage generally increased from 1999 to 2002 (Control: 72 kg N ha\(^{-1}\) to 120 kg N ha\(^{-1}\)) when the plant community was aged between 14 and 18 years and was in a ‘net biomass gain’ phase of growth (Kopittke et al. 2012b). This Calluna N accumulation rate was marginally less in the Drought treatment. As the Calluna plants aged, a more open plant form with larger woody stems developed and the total Calluna cover decreased (with greater decrease in Drought) but there was no overall change in Calluna biomass or N storage. This indicated there was negligible change in the N uptake by Calluna plants in either the Control or Drought treatments for the majority of the study period and therefore (from 2002 onwards) increased N was available in the soil for transformation.

Mosses were also present on the treatment plots and grew under and in between the Calluna plants. Mosses are known to be highly efficient at N filtration and some mosses have been shown to increase N uptake with increasing atmospheric N deposition e.g. up to a peak of 18 kg ha\(^{-1}\) year\(^{-1}\) in Sphagnum spp (Lamers et al. 2000, Liu et al. 2012, Pitcairn et al. 1998). Total moss cover increased from 1999/2000 to 2010/2011 on both the Control (58% to 73% cover) and Drought treatments (48% to 83% cover). The dominant moss species identified was *Hypnum cupressiforme*: a pollution tolerant species (Hallingbäck 1992). In the UK, the cover and occurrence of *H. cupressiforme* has been shown to increase at high N deposition sites, while other species adapted to poor nutrient soils, such as Calluna, concurrently decreased in cover and occurrence (Stevens et al. 2004). The increasing *H. cupressiforme* cover is likely to have intercepted more deposited N and reduced the N available for transformation reactions in the soil, explaining the lower number of proton formed over time in both Control and Drought treatments. Moss cover increased much more on the Drought treatment (34% increase) than on the Control treatment (15% increase). To equate these cover values to the quantity of N being filtered from atmospheric deposition by moss, N storage values were approximated from moss biomass values (estimated from non-destructive vegetation measurements) and the known N content of the moss. In 1999/2000, the N stored in moss was estimated to be 33
kg N ha\(^{-1}\) and 30 kg N ha\(^{-1}\) for the Control and Drought treatments, respectively. In 2010/2011, the N stored had increased to approximately 120 kg N ha\(^{-1}\) and 163 kg N ha\(^{-1}\) for the Control and Drought treatments, respectively. This indicated that the moss layer filtered the N from atmospheric deposition at a rate of approximately 8 kg ha\(^{-1}\) year\(^{-1}\) (Control) and 12 kg ha\(^{-1}\) year\(^{-1}\) (Drought). This additional N filtration in the Drought treatment is likely to explain part of the much lower proton formation observed in that treatment.

Within the soil, drought periods may lead to other processes that affect the N and cation balance. Drying and rewetting cycling can enhance nitrification in surface soils but result in nitrification inhibition in the subsurface soil (Xiang et al. 2008). Under repeated drought conditions, there would be less rewetting cycles, which would reduce the N transformations within the soil and is likely to reduce the number of protons generated during the drought period. Water deficits can also promote greater relative allocation of photosynthate to root growth in woody plant species, ultimately resulting in higher root:shoot ratios and a greater capacity to absorb water and nutrients (Kozlowski and Pallardy 2002). This would cycle the cations and retain some potential ANC in the ecosystem. However, this ability to capture nutrients may differ between species due to reductions in root phosphatase activity (Sardans et al. 2008) and the response of Calluna root systems to repeated annual drought is unknown.

Other processes in the soil are well recognized to reduce the N availability, such as the negative association of increasing anionic DOC\(^{-}\) concentrations with decreasing NO\(_3\)\(^{-}\) concentrations (Weyhenmeyer and Jeppesen 2010). Although not reported within this study, the DOC concentrations in each soil solution sample were analyzed and DOC fluxes calculated. These results showed that there was no overall DOC flux change over time in either the Control or the Drought treatment. In addition, there was no relationship within the soil solution between anionic DOC\(^{-}\) and NO\(_3\)\(^{-}\) concentrations. Therefore, it is unlikely that the decreased NO\(_3\)\(^{-}\) output is associated with DOC\(^{-}\) concentrations in this case.

### 4.4 Future Considerations

Overall, proton generation continues to occur and, without external input of cations, the soil acidification processes are expected to continue under ambient conditions. The acidification lag time is expected to increase between the two treatments due to the cumulative disparity in cation retention and rates of proton formation. However, heathlands are normally managed through removal of aboveground vegetation (i.e. cutting) on a 7–8 year cycle, which did not occur at this site. If this cycle had continued, the biomass removal would also remove stored base cations from the system. Removal of woody biomass has been identified as an important acidifying factor in forest ecosystems (Hruška and Cienciala (2003) in Dahlgren and Driscoll 1994, Hédl et al. 2011) and although heathlands have less biomass than forests, its removal would result in loss of an important source of cations in both Control and Drought treatments and accelerate acidification.
This study investigated the scenario of a repeated annual drought i.e. decreased rainfall in the growing season every year. However, if the predicted change in precipitation patterns led to increased rainfall rates in Europe rather than reduced rainfall as tested here, the underlying mechanisms found in this study allow us to hypothesize that the soil acidification trend would increase at this site. Although the inputs of N wet deposition would be diluted, the total N input would remain the same and the overall output in the soil solution would increase leading to increased loss of cations (and therefore acid neutralizing capacity) from the soil.

5 Conclusion

Soil acidification has occurred on a N-saturated heathland community where ambient N deposition rates were lower than historical deposition rates, but still exceeded critical loads in some years. This soil acidification trend was retarded when the heathland was subjected to 13 years of repeated annual drought conditions. The Drought treatment reduced rainfall input, which lead to lower drainage rates, less cations leached from the system and a reduced lowering of the soil ANC. However, N transformations became less important in the Drought treatment over time and this is hypothesized to be associated with the observed increase in groundcover of a pollution tolerant moss species. Moss layers filter N from the available precipitation and as the moss cover increases, there would be increasing N removal from the rainfall and less N available for transformation in the soil. In the future, the acidification lag time is expected to increase between the two treatments due to the cumulative difference in cation retention and rates of proton formation. If the change in global precipitation patterns led to increased rainfall rates, rather than a reduction as tested here, it is hypothesized that the soil acidification trend would increase due to increased leaching of cations and the subsequent reduction of soil ANC.