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Experimental field estimation of organic nitrogen formation in tree canopies.

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Abstract

The content of organic N has been shown in many studies to increase during the passage of rain water through forest canopies. The source of this organic N is unknown, but generally assumed to come from canopy processing of wet or dry deposited inorganic N. There have been very few experimental studies in the field to address the canopy formation or loss of organic N. We report two studies: a Scots pine canopy exposed to ammonia gas, and a Sitka spruce canopy exposed to ammonium and nitrate as wet deposition. In both cases, organic N deposition in throughfall was increased, but only represented a small fraction (<10%) of the additional inorganic N supplied, suggesting a limited capacity for net organic N production, similar in both conifer canopies under Scottish summertime conditions, of less than $1.6 \text{ mmol N m}^{-2} \text{ mth}^{-1}$ (equivalent to $3 \text{ kg N ha}^{-1} \text{ y}^{-1}$).

Keywords

Organic nitrogen; wet deposition; dry deposition; throughfall; nitrogen budget.

Capsule

Experimental addition of inorganic N to conifer canopies shows limited production of organic N in throughfall

Introduction

Nitrogen compounds, deposited from the atmosphere to vegetation as gases and particles, or in precipitation, interact with plant surfaces before reaching the soil. Although some N is retained by vegetation, and only reaches the soil when the plant dies or sheds its leaves, most passes through the canopy fairly quickly and enters the soil as throughfall (TF = canopy drip) or stem flow (SF = water running down tree stems). Canopy uptake or retention of inorganic N (ammonium or nitrate) and organic N has long been recognised as an important fate for N in forests, where it is relatively simple to measure TF and SF for comparison with wet deposition, although its dependence on dry deposition is less easily established (Parker, 1983, Schaefer and Reinert, 1990, Tukey, 1970). It is not clear, however, what happens to the N that is retained in the canopy. Potential fates include: uptake by leaves or stems followed by use as nutrient N (Raven, 1988, Rennenberg and Gessler, 1999); uptake and use by epiphytic organisms (Endres and Mercier, 2001, Knops et al., 1996, Leith et al., 2008); chemical retention in or on bark (Dail et al., 2009); volatilisation as surface water evaporates; and chemical or biological transformation of inorganic N to organic N, followed by deposition in TF or SF (Ferm, 1993, Zimmermann et al., 2007).

Although the chemical composition of organic N in TF is rarely characterised, one study has shown a significant contribution (17%) of amino acids (Forsum et al., 2006), and the chemical composition is likely to affect the subsequent fate of organic N in soil (Michalzik and Matzner, 1999, Möller et al., 2005, Qualls and Haines, 1991a, 1991b). Organic N may also have canopy sources similar to those that lead to increases in dissolved organic matter (DOM) in TF compared to precipitation, such as insect frass, leaf exudates, leaf damage or dry deposition of water-soluble organic compounds from the atmosphere. For example, large changes in DOM have been measured in TF in response to aphid infestations at the Deepsyke site described below (Stadler et al., 2001).

Several analytical techniques have been used to measure organic N in TF and precipitation; the variety of chemical techniques used historically for measuring ‘total soluble N’ has led to some debate as to the comparability of different studies (Cornell et al., 2003). However, the sampling of wet-only or bulk precipitation for inorganic N, and the range of sampling methods for TF and SF, also introduce quantitative uncertainties into the values of inorganic N reported, whether through the contribution of dry-deposited material on the collectors (González Benítez et al., 2009), or losses of material through biological or chemical activity in the sample in the field prior to collection and preservation by cooling, freezing or addition of biocide (Cape et al., 2001b, Michalzik et al., 1997). Consequently, the estimation of ‘organic N’ as the difference between ‘total N’ and the sum of the inorganic ions (ammonium and nitrate) is inevitably less precise than for many other constituents of wet deposition. These variations may lead to differences in interpretation, and quantitative understanding of the processes involved may be difficult. This approach also only includes water-soluble organic N; there may also be particulate organic N removed from canopies in TF which is not included in measurements of ‘water-soluble’ organic N. However, in practice, the ‘water-soluble’ fraction is effectively defined by the size and type of filter used prior to chemical analysis, and this is not always reported.

In many cases, the overall deposition of N measured in TF and SF exceeds that measured in wet deposition, i.e. ‘net throughfall’ (NTF) = TF + SF – wet deposition, is positive. In a meta-analysis of data up to 1983, the average ratio of deposition in TF to wet deposition was $1.6 (\pm 1.3)$ for NH_4^+ , $1.3 (\pm 0.9)$ for NO_3^- and $1.9 (\pm 1.5)$ for total N (including organic N) (Parker, 1983). The increase in overall N deposition below the canopy relative to wet deposition is most probably caused by dry deposition of N on the canopy, which is not measured (over annual time scales) but may be estimated using measured or modelled air concentrations and an appropriate inferential model (Butler and Likens, 1995). In such cases the measured increase in N deposition in NTF (i.e. measured deposition below canopy, less wet deposition above canopy) gives a lower bound to the dry deposition on the canopy. The assumption is that most plant canopies are not sources of N, i.e. that vegetation conserves N and that this is therefore unlikely to be removed from a canopy by leaching or ion exchange.

Organic nitrogen in throughfall

Although many studies report changes (usually increases) in organic N concentrations in TF compared with incident precipitation, not all report the relevant fluxes, so that net uptake of inorganic or organic N cannot be estimated. A review of temperate forests showed a range of dissolved organic N (DON) in bulk precipitation in the range 1-4 kg N ha⁻¹ y⁻¹, with the associated DON fluxes in TF in the range 1-12 kg N ha⁻¹ y⁻¹ (Michalzik et al., 2001). Where studies have reported fluxes, deposition of organic N in TF can sometimes be less than in precipitation, implying net uptake or retention of organic N in the canopy. Some studies that provide flux data (as opposed to simply concentrations) are summarised in Table 1. This is a relatively small subset of all the data on N deposition above and below forest canopies, but in most such studies no measurements have been made of the organic N content and deposition of both incident precipitation and throughfall.

TABLE 1 near here

There have been few experiments in which canopy transformations of deposited N, including organic N, have been studied through experimental manipulation. Changing the nutrient status of trees can change canopy processes. For example, a soil fertilizer treatment (with and without irrigation) of *Pinus radiata* in Australia showed net uptake of NH₄⁺ and release of organic N in TF from the control trees, but release of NH₄⁺ and increased release of NO₃⁻ and organic N in TF from fertilized trees, with the size of the effect being magnified in the irrigated treatment (Crockford and Khanna, 1997). Although it is possible that the additional N measured in TF was cycled from the roots through the canopy, it is more likely that the higher N status of the canopy led to lower retention of wet-deposited N. Direct manipulations of forest canopies, as opposed to the soil, are even rarer. One recent study, using helicopter addition of NH₄NO₃ to a mature conifer forest canopy (Gaige et al., 2007) showed conversion of both NH₄⁺ and NO₃⁻ to organic N in throughfall, by the use of ¹⁵N isotopic labelling, in a forest where organic N made up 80% of the total N below canopy in untreated areas (i.e. where canopy transformation processes were apparently very active). Conversion of the treatment-applied inorganic N was rapid, and essentially complete within a few days of the application to the canopy.

We present here data from two large-scale field experiments where, as part of the main experiment, measurements were made of both inorganic and total N in precipitation, treatments and TF. The objective was to estimate the extent to which canopy additions of inorganic N lead to net formation of organic N in TF under the climatic and growing conditions of the trees in the experiments. In the first experiment, trees were exposed to additional ammonia gas; in the second, several different N-containing solutions were applied to the canopy.

Experimental methods

Ammonia fumigation – AMBER experiment

The AMBER experiment (Ammonia Mitigation By Enhanced Recapture) was designed to study the use of woodland planting around agricultural point sources of ammonia, such as intensive livestock units, to trap emissions close to source and prevent transport away from the farm (Theobald et al., 2001). A schematic diagram of the experiment is shown in Figure 1. The site was located in south-east Scotland (lat. 55°42' N, long. 3°21' W, elevation 250 m). Ammonia gas was released into a 40 m long ventilated manifold using a mass-flow controller from a cylinder of pure NH₃ (BOC Ltd.) when the prevailing south-westerly wind was blowing towards a shelter belt of trees (mostly mature Scots pine, about 12 m high, with a closed canopy and LAI estimated as 2 (Theobald, 2004)). Ammonia gas concentrations and TF deposition were measured across the 60 m wide woodland. Measurements started in autumn 2000 for one year. The data presented here are from summer (1 May - 13 September) 2001, and from TF samplers between 20 and 25 m from the edge of the woodland, which were most directly comparable in terms of canopy and exposure to the TF 'control' plots (see below).

Rain and TF samples were preserved in the field using thymol (2-isopropyl-5-methylphenol), to prevent microbial degradation during and after collection (Ayers et al., 1998, Cape et al., 2001b, Hadi and Cape, 1995), and were collected approximately weekly, depending on rainfall amounts. Rain was sampled (in triplicate) using 20 cm diameter polyethylene funnels mounted 1.5 m above ground, draining to black polyethylene bottles. Throughfall was sampled using gutters mounted above the ground vegetation at fixed distances from the woodland edge, draining to black polyethylene bottles containing thymol. 'Control' TF gutters were placed to the north-west of the main experiment, away from the influence of the ammonia source. Ammonia gas concentrations were measured upwind, and within the woodland, using passive samplers of ALPHA design (Tang et al., 2001) at 1.5 m above ground, with occasional measurements of the vertical profile from the ground to above the canopy using a continuous wet annular denuder (Theobald et al., 2001).

FIGURE 1 near here

Canopy treatment with simulated rainfall – Deepsyke forest

This major field experiment was designed to study the effects of nitrogen and sulphur-containing pollutants in wet deposition on a plantation forest (planted 1986, at 2m spacing) of Sitka spruce (*Picea sitchensis* (Bong.) Carr). The forest (Deepsyke) is in southern Scotland in an area remote from gaseous pollutants and with relatively low levels of N deposition (8-10 kg N ha⁻¹ y⁻¹), lat. 55°46'N, long. 3°17'W, elevation 290 m. Four replicate blocks, each containing 10 trees, were established for each of 6 different experimental treatments. A canopy spraying system was built around each experimental block, to deliver the treatment solutions, which were made up on site from concentrated solutions using collected rainwater, and sprayed onto the canopy

from above on average 6 times weekly, at a rate of 2 mm rain equivalent per application. At the time of the measurements presented below (summer 2001), the trees had closed canopy, were ca. 7 m high with an average stem basal area of ca. 0.015 m², and with an estimated leaf area index up to 10 m² m⁻². The canopy density was markedly smaller in response to treatments containing H₂SO₄, which caused a doubling of litter fall, but with no significant effect on tree growth (Sheppard et al., 2001). The trees had been receiving the treatments (A-F) shown in Table 2 for the previous 5 years. In 2001 the treatment regime was modified, with different numbers of replicated blocks receiving the same 6 treatments. Spraying was carried out early in the morning on days when conditions were calm with minimal sunshine. Further details of the experiment have been published elsewhere (Sheppard and Crossley, 2000, Sheppard et al., 2004).

TABLE 2 near here

Rain was sampled within a clearing in the forest using three collectors, each comprising a 20cm diameter polyethylene funnel mounted 1.5m from the ground attached to a five litre black polyethylene bottle. A small quantity (ca. 5 g) of thymol was added prior to collection to suppress any microbial action during and after collection. Filtered (0.45 µm, cellulose nitrate membrane) sub-samples were stored prior to analysis in polyethylene bottles at < 5°C.

Each of the 24 experimental plots contained a linked framework of guttering with an overall area of 1 m². The guttering was arranged to give the steepest permissible incline, thereby reducing the TF residence time and minimising compositional changes. It was arranged in a 'herring bone' structure drawing TF from the whole plot into a central collecting vessel. A small permeable container with ca. 5 g solid thymol biocide was added to the collecting tanks at the start of each TF sampling period. Samples were collected twice monthly through the course of the summer and stored (after filtration through 0.45 µm membrane) in a cold room (< 5 °C) whilst awaiting analysis. Results from measurements of rain and TF chemistry in 1999 and 2000 showed retention by the canopy of 20-40% of the additional applied N (Cape et al., 2001a, Chiwa et al., 2004). In 2001, the continuing measurements of rain and TF chemistry were used to investigate the fate of organic N.

Because of retention and exchange of N in the canopy, a quantitative budget can only be calculated if the amount of material applied to the canopy is accurately known. Variation in spray application, and spray drift, led to smaller amounts of deposition than calculated simply on the basis of the known concentration and amounts applied during treatments. Consequently, the sulphate and sodium ions in TF were used as conservative tracers of deposition. In the 'single dose' treatments the average deposition of sulphate and sodium ions in TF was 75% of the total amounts applied; for the 'double dose' treatment the fraction of the applied spray treatment recovered in

TF was 60%. These ‘capture efficiencies’ have been used to calculate the amounts of N actually applied to the canopy in the different treatments. The data presented here are the summed deposition values for the period 17 May to 14 August 2001. During this period the rainfall was 334 ± 3 mm (mean and standard deviation of 3 collectors). Input of N in rainfall was 8.2 ± 0.8 mmol $\text{NH}_4\text{-N m}^{-2}$, 6.9 ± 0.2 mmol $\text{NO}_3\text{-N m}^{-2}$, and 2 ± 2 mmol organic N m^{-2} . The ‘background’ treatments (E) contained additional 5 μM $\text{NH}_4\text{NO}_3 + \text{H}_2\text{SO}_4$ (Table 2) and provided (including incident rainfall) 8.7 ± 0.8 mmol $\text{NH}_4\text{-N m}^{-2}$, 7.6 ± 0.2 mmol $\text{NO}_3\text{-N m}^{-2}$, and 2 ± 2 mmol organic N m^{-2} ; the small additional organic N input came from the N content of the stored rain water used to make up the spray solution. Inputs of N in treatments A, C and D were 150 ± 40 nmol N m^{-2} , 250 ± 50 nmol N m^{-2} , and 160 ± 1 nmol N m^{-2} , respectively, where the uncertainties are standard deviations of the plot means within each treatment.

For both studies, total water-soluble N was analysed in triplicate using an ANTEK8060 analyzer in flow injection mode. The carrier (water) and filtered (0.45 μm) sample was nebulised into a furnace at 1050 °C in an oxygen/helium flow, where all nitrogen-containing solutes were converted quantitatively to nitric oxide (NO) which was then quantified by chemiluminescent reaction with ozone. Nitrate and ammonium concentrations were determined by ion chromatography (Metrohm) of filtered samples. Water-soluble organic N was calculated as the difference between total N and the sum of inorganic N (ammonium and nitrate). Analysis methods are described in more detail elsewhere (González Benítez et al., 2009).

Results

Dry deposition of ammonia – AMBER experiment

Figure 2 shows the deposition of inorganic and organic N in rainfall, in the ‘control’ TF, and in the TF from the centre of the treated woodland, averaged over the 2 sets of TF samplers between 20 and 25 m from the edge, for the 7 sample collections during the period. The integrated deposition over the 18 weeks is shown in Figure 3. Comparison of the ‘control’ TF data with the rainfall data shows that around 25% of the total wet-deposited N was retained by the canopy (Figure 3). However, this calculation does not include any contribution from dry deposited material. Although there was only a small difference in NH_4^+ deposited in rain and TF (Figure 2a), there would have been significant deposition of NH_3 gas even at the ‘control’ site, in the absence of exposure to the fumigation treatment. Average background NH_3 concentrations upwind of the release point were $4 \mu\text{g NH}_3 \text{ m}^{-3}$, leading to an estimated additional dry deposition of NH_3 to the canopy of around 50 mmol N m^{-2} over the period (based on an assumed deposition velocity of 0.02 m s^{-1} to the woodland canopy), and implying retention of a similar amount in the canopy. Almost all the NO_3^- in rain was retained by the canopy (Figure 2b), and there was a small net increase in organic N in TF compared with rain (Figure 2c). These results are similar to reported behaviour for other coniferous forests (see Table 1), in which there is often a net increase in organic N in TF, and retention of inorganic N.

FIGURES 2 & 3 near here

In the fumigated plot, however, the total deposition in TF was dominated by NH_4^+ , and even this is likely to be much less than the overall deposition of NH_3 gas and NH_4^+ in solution to the canopy. Dry deposition of NH_3 was probably more than $100 \text{ mmol N m}^{-2}$ over the period, based on the NH_3 concentrations measured below the canopy during NH_3 fumigations, which were around $45 \mu\text{g NH}_3 \text{ m}^{-3}$, and the observation that concentrations above the canopy were around 20% of those measured below (Theobald et al., 2001). The capacity of the canopy to retain NH_3 was exceeded, leading to a net increase in NH_4^+ deposition in TF relative to the ‘control’ of $27 \pm 6 \text{ mmol m}^{-2}$ over the period (Figure 2a). The deposition of NO_3^- in TF ($8 \pm 2 \text{ mmol m}^{-2}$) was similar to that in rainfall ($8.7 \pm 0.6 \text{ mmol m}^{-2}$), and greater than in the ‘control’ plot ($2.1 \pm 0.6 \text{ mmol m}^{-2}$), implying no net retention of NO_3^- in the canopy, although there was some variability throughout the period (Figure 2b). This could be interpreted either that NO_3^- was not retained because of the high availability of NH_4^+ in the canopy, or because nitrification of NH_4^+ to NO_3^- in the canopy matched the uptake of NO_3^- in the canopy. There was a large increase in deposition of organic N compared to the ‘control’ TF (Figure 2c), but this was still equivalent to only around 10% of the NH_3 likely to have been retained in the canopy, although this estimate is very uncertain. The net increase in organic N deposition in TF in the fumigated area over the period ($11 \pm 1 \text{ mmol m}^{-2}$ cf. $4 \pm 2 \text{ mmol m}^{-2}$ in the ‘control’ area; $P=0.01$ for two-tailed paired t-test over 7 sample dates) is equivalent to a net formation rate in the canopy of $1.6 \pm 0.6 \text{ mmol m}^{-2} \text{ mth}^{-1}$.

Additional wet deposition – Deepsyke experiment

The uptake/release of water-soluble N from plots that received no (or small additional) N in the spray treatment (rainfall, 17 mmol m^{-2} ; ‘background’, 18 mmol m^{-2}) is shown in Figure 4. There was net uptake of both NH_4^+ and of NO_3^- , and net production of organic N in the canopy, although not at a rate that balanced the uptake of inorganic N, so that there was a small net uptake of total N.

FIGURE 4 near here

The uptake/release of water-soluble N from plots that received additional N in the spray treatment (NH_4NO_3 (D), 160 mmol m^{-2} ; $\text{NH}_4\text{NO}_3+\text{H}_2\text{SO}_4$, 150 (A) or 250 (C) mmol m^{-2}) is shown in Figure 5. There was net uptake of NH_4^+ from NH_4NO_3 solution, but this was suppressed in the presence of H_2SO_4 (‘acid’ at pH2.5: A, C) at both treatment rates. Uptake of NO_3^- was enhanced by the presence of acidity (treatment A), but only increased slightly with the double dose acid treatment (treatment C). For both ions the net retention was only a small proportion (ca. 20% for A, D and 12% for C) of the additional N supplied to the canopy. There was net production of organic N in the canopy; over the period the total deposition in TF with ‘single’ N additions (A, D) was $8 \pm 2 \text{ mmol m}^{-2}$ compared with $4.0 \pm 0.5 \text{ mmol m}^{-2}$ in the ‘no spray’ treatments (F), and $5 \pm 2 \text{ mmol m}^{-2}$ in the ‘background’ treatment with

added spray (E). The difference relative to the 'background' treatment equates to a net formation rate in the canopy of $1 \pm 3 \text{ mmol m}^{-2} \text{ mth}^{-1}$. Although not statistically significant (paired t-test, $n = 5$) the net production in the N treatments was greater than in the 'background' on 4 of the 5 sampling dates.

FIGURE 5 near here

Discussion

Review of previous data

The summary data in Table 1 show some general features that have been identified before (Parker, 1983). For inorganic N, deposition in TF on average is similar to wet deposition, but with considerable scatter across sites. However, for sites where dry deposition has been estimated, inorganic N in TF represents only around half of the estimated (wet + dry) input from the atmosphere, implying that half is retained in the canopy. Total N deposition (inorganic + organic) in TF (and SF where measured) is similar on average to total N deposition in precipitation, with smaller deviations above and below a 1:1 ratio than for inorganic N. However, for those sites at which dry deposition has been estimated, total N in TF+SF is only around 80% of estimated inputs (on average), with net retention of N at almost all sites. For organic N, below-canopy deposition in TF is on average 24% of total (wet + dry) N input, and accounts for 36% of total N in TF. Large enhancement of organic N deposition in TF compared to wet deposition occurs particularly where wet deposition of organic N is small. At a few sites there is net retention of organic N in the canopy, implying that leaves or epiphytic organisms can utilise organic N, or that organic N is removed from solution by adsorption or absorption by canopy surfaces. Because of the lack of information on the chemical composition of organic N, we do not know whether the 'organic N' measured in precipitation is chemically modified before being measured as 'organic N' in TF. There is also no information on the contribution of dry deposition of organic N to canopies, although it undoubtedly occurs (González Benítez et al., 2009), so that retention of organic N by canopies may be systematically underestimated.

Conclusions from field manipulation experiments

Experimental manipulations can be used to determine the potential for systems to respond to changes in N inputs, although they do not necessarily provide a good indication of long-term behaviour. They can, however, be very useful in identifying pathways and processes. The use of stable isotopes to study the rate of exchange of material with plant canopies has already been mentioned (Dail et al., 2009, Gaige et al., 2007) in a study where a large input of N was applied to a forest with relatively low N deposition. This study demonstrated that exchange processes occurred rapidly, and generated significant transformation of inorganic to organic N in the process. We do not know, however, whether the canopy itself or the epiphytes it supported would have produced the same response under sustained inputs at the same level over many years, when the greater availability of N might have led to profound changes in the canopy structure and composition.

The AMBER experiment described above showed that short-term exposure to NH_3 led to changes in canopy behaviour, particularly with respect to nitrate, although, because ^{15}N was not used, we could not determine whether the apparent change in nitrate behaviour (from retention to no retention) was attributable to nitrification of deposited NH_3 in the canopy, as has been reported elsewhere after chronic exposure to high NH_3 concentrations over many years, albeit within leaves rather than on leaf surfaces (Papen et al., 2002). Although the dry deposition of NH_3 and other inorganic N components (aerosol ammonium and nitrate, nitric acid) could only be crudely estimated, a large quantity of NH_3 relative to the ‘control’ plots (27 mmol m^{-2}) was deposited in TF as NH_4^+ , presumably washed from the canopy surfaces by rain. What was significant, though, was the small fraction of dry deposited NH_3 that was transformed to organic N, indicating a finite capacity for transformation of inorganic N in this canopy of around $1.6 \text{ mmol m}^{-2} \text{ mth}^{-1}$ under summer conditions.

The Deepsyke experiment followed 5 years of treatment, so the surface epiphytes and microbial populations may have already adapted somewhat to the additional N inputs. Moreover, the N additions were made in small increments between May and November each year, more frequently and with much smaller solution concentrations than the 5 applications during the growing season in the helicopter experiment (Gaige et al., 2007). As observed at the AMBER site, albeit with a different tree species, the net amount of organic N measured below the canopy was a very small fraction of the total N applied to the canopy, again suggesting a finite capacity to transform additional inorganic N, in this case around $1 \text{ mmol m}^{-2} \text{ mth}^{-1}$ under the same summer conditions (the same year). There is also some evidence (Figure 5) that additional acidity may inhibit NH_4^+ retention and enhance NO_3^- retention (Cape et al., 2001a, Chiwa et al., 2004). Comparison of the A (acid) and D (no acid) treatments showed 19 ± 9 ($n = 4$ plots) $\text{mmol m}^{-2} \text{ NH}_4^+$ retained in the absence of acid, and 6 ± 7 ($n = 2$) mmol m^{-2} with acid. The equivalent figures for NO_3^- are $10 \pm 13 \text{ mmol m}^{-2}$ without acid and $26 \pm 1 \text{ mmol m}^{-2}$ with acid. The latter may include losses of gaseous HNO_3 from the canopy, rather than retention. For organic N, no effect of acid was observed, with net formation of $6 \pm 2 \text{ mmol m}^{-2}$ in both treatments.

Conclusions

The fate of organic N in the transformation and utilisation of atmospheric N deposition in plant canopies is important, because it may have implications for the subsequent transformation and utilisation of N in forest soils and reuse by plants. The capacity of forest canopies to generate organic N from inorganic N has been shown to be limited, but of sufficient size to make measurable changes to the organic N content of TF for most forests, which have ambient inputs in the range of $5\text{--}30 \text{ kg N ha}^{-1} \text{ y}^{-1}$ ($35\text{--}200 \text{ mmol N m}^{-2} \text{ y}^{-1}$). The experimentally determined upper limit to the capacity for net organic N production in summer months in southern Scotland was similar for both conifer species, despite the differences in species, age, size and canopy structure, at up to $1.6 \text{ mmol N m}^{-2} \text{ mth}^{-1}$, based on assumed limiting production rates in the

presence of a large excess of inorganic N deposition to the canopy. This may be contrasted with results for a mature conifer forest in eastern North America (Gaige et al., 2007), where canopy retention of experimentally applied inorganic N was up to 80% or $20 \text{ mmol N m}^{-2} \text{ mth}^{-1}$ during the growing season. This very large % retention was ascribed to the canopy architecture and the means of delivery, as small droplets of 0.48M NH_4NO_3 solution from a helicopter. Some of the apparent retention (estimated as 5-10% of input) was loss from the canopy of gaseous HNO_3 during the first 24h after application (Dail et al., 2009). However the authors did not estimate the potential loss of deposited NH_4NO_3 as gaseous NH_3 and HNO_3 following dissociation of the salt during deposition, or over a longer period on the canopy surface (Stelson and Seinfeld, 2007).

The transformations that occur in canopies also appear to be strongly dependent on the N status of the forest (Crockford and Khanna, 1997), and not simply on the atmospheric inputs. It is possible that the increased organic N in TF observed in the experiments presented above was mediated through the roots, as a response to increased TF deposition. At both sites, there had been exposure to enhanced N deposition for at least a year prior to the TF measurements of organic N. At the AMBER experiment there are no data on leaf N status, but at Deepsyke leaf N status was closely followed; when leaf tissue N concentrations were measured in 2000 there was no significant difference in needle N concentrations across treatments (except for the double-dose N + acid treatment) (Sheppard et al., 2004). For many forests that have been exposed to air pollution for decades, however, the N status may be well correlated with the deposition, making interpretation more difficult. However, given the magnitude of the in-canopy N transformations that can occur under low to moderate N inputs and the potential role of the different components of organic N in soil processes, the importance of the canopy in modifying the chemical composition of organic N should not be ignored.

The experiments described here show that the quantitative transformation between inorganic and organic N in these forest canopies in a Scottish summer is probably not important relative to the large additions of N provided in the experimental treatments. However, the data show that the organic N deposition flux can increase or decrease as water moves through the canopy, depending on the availability of inorganic N. The implied (bio)chemical conversion has implications for the fate of TF nitrogen in the soil; processing of organic N in soil has been studied in more detail, taking as inputs to the soil surface the TF and SF that can be relatively simply measured below the forest canopy (Michalzik and Matzner, 1999, Möller et al., 2005, Qualls, 2000, Qualls and Haines, 1992). Attempts to estimate the complete budget of N inputs to forests for comparison with eventual drainage outputs, however, need to explicitly include not only the wet deposition of organic N (as recorded in Table 1), but the dry deposition of inorganic N (for which approximate estimates can be derived from measured air concentrations of gases and particles) and of organic N, for which no relevant data are yet available. Unfortunately, the simple use of TF data in estimating N inputs misses

the direct uptake of N in the canopy, which can inhibit root uptake and therefore influence below-ground processing of N (Rennenberg and Gessler, 1999). Moreover, the use of only inorganic N deposition as input for risk assessments, e.g. in the Critical Loads approach used widely in Europe (Achermann and Bobbink, 2003), means that the importance of organic N deposition from the atmosphere and its subsequent progress through canopies and soils is effectively ignored.

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Table 1. Measurements of N deposition in throughfall from studies in which both inorganic and organic N deposition was measured. ‘net TF’ = TF (+ SF) - wet deposition, for total (inorganic + organic) N; ‘net org N’ = TF - wet deposition, for organic N only. All data are in deposition units of kg N ha⁻¹ y⁻¹. ‘na’ indicates no data available.

Location	forest type	wet inorg N	wet org N	dry N	net TF(wet)	net TF (wet+dry)	net org N	Reference
Germany	<i>Picea abies</i>	12.8	1.0	na	10.3	na	2.4	(Michalzik and Matzner, 1999)
Adirondacks, NY	spruce-fir	13.0	0	3.4	-5.2	-8.6	3.5	(Friedland et al., 1991)
USA	Integrated Forest Study							(Lovett and Lindberg, 1993)
site	ST	15.1	0.61	13	8.3	-4.7	7.7	
	CP	4.0	0.13	3.1	3.5	0.4	3.8	
	LP	5.5	0.14	4.5	3.9	-0.6	2.3	
	WF	13.5	0	2.5	-3.5	-6.0	3.2	
	HF	4.5	1.7	3.5	2.2	-1.3	0.1	
	DF	2.7	0.1	2.1	-0.7	-2.8	0.7	
	RA	2.7	0.2	2.0	0.6	-1.4	1.6	
	NS	9.0	1.4	1.9	-5.6	-7.5	0.6	
Ithaca, NY	hardwood	7.8	0	3.6	4.6	1.0	1.4	(Butler and Likens, 1995)
California	<i>Quercus douglasii</i> + lichens	0.51	0.73	na	0.7	na	1.2	(Knops et al., 1996)
	<i>Quercus douglasii</i> - lichens				0.5		1.0	
Eastern Finland	<i>Picea abies</i>	2.3	1.6	1.2	-0.9	-2.1	0.3	(Pirainen et al., 1998)
S Sweden	<i>Picea abies</i>	9.4	0.5	5.8	4.1	-1.7	2.1	(Ferm and Hultberg, 1999)
N Spain	<i>Pinus radiata</i> Manzanal	11.4	6.7	na	6.3	na	0	(Gonzalez-Arias et al., 2000)
	<i>P. radiata</i> Posadero	9.4	5.2	na	2.7	na	-0.6	
Switzerland	<i>Picea abies</i>	11	1	na	6	na	5	(Hagedorn et al., 2001)
Central Japan	<i>Pinus densiflora</i>	20.2	0.8	na	30	na	1.6	(Wakamatsu et al., 2005)
Central Japan	mixed forest	19	7.9	na	5.3	na	1.3	(Ham et al., 2007)
South China	subtropical pine	32	18	na	-5	na	0.4	(Fang et al., 2008)
	subtropical mixed				-12	na	-3.2	
	subtropical old growth				2	na	2.3	
Poland	<i>Betula pubescens</i> (Apr-Oct)	6.4	4.2	na	-6.1	na	-2.4	(Kram, 2008)
Belgium	<i>Betula pendula</i> (Overheide)	14.2	6.4	na	3.9	na	-1.0	(Sleutel et al., 2009)
	<i>Pinus nigra</i> (Overheide)	14.2	6.4	na	16.5	na	-0.1	
	<i>Pinus nigra</i> (Tulderse Heide)	16.4	7.1	na	23.0	na	1.6	

Table 2. Experimental treatments applied to Deepsyke forest, southern Scotland, as a spray above the forest canopy in 2001. Each treatment was applied to between 2 and 8 replicate blocks of 10 trees, following a change in the experimental regime at the end of 2000, after 5 years of prior treatment with 4 replicate blocks per treatment. Two plots were also treated with a double dose of NH_4NO_3 (D) but data are not reported because of a fault in one of the distribution lines. Data from treatment B are not discussed further but are shown for completeness.

Treatment	No. of replicate blocks	Composition	Concentration	Frequency (nominal) x 2 mm wk⁻¹
A	2	$\text{NH}_4\text{NO}_3 + \text{H}_2\text{SO}_4$	1.6 mM (3.2 mM N, H^+)	6
B	2	Na_2SO_4	1.6 mM (3.2 mM Na^+)	6
C	2	$\text{NH}_4\text{NO}_3 + \text{H}_2\text{SO}_4$	1.6 mM (3.2 mM N, H^+)	12
D	4	NH_4NO_3	1.6 mM (3.2 mM N)	6
E	8	$(\text{NH}_4\text{NO}_3 + \text{H}_2\text{SO}_4)$	0.005 mM (0.01 mM N)	6
F	4	No spray (control)		

Captions to Figures

Figure 1: schematic diagram of the AMBER experiment (Theobald et al., 2001); the prevailing SW wind (from left to right) carried ammonia gas into the woodland from the source manifold.

Figure 2: Deposition at each sampling date of a: NH_4^+ , b: NO_3^- , c: organic N, in rainfall (thin line), in throughfall from the control plots (thick line – control TF), and in throughfall from the centre of the woodland (dashed line – treatment TF), about 25 m downwind of the NH_3 source. Error bars show standard deviations of replicate samplers (3 for rain, 4 each for throughfall).

Figure 3: Overall N deposition (mmol N m^{-2}) at the AMBER site for the 7 sampling dates between 1 May and 13 September 2001. Throughfall was measured under Scots pine trees in a control area (away from NH_3 release) and in the centre of the treated plot, about 25 m downwind of the NH_3 source (Treatment TF). Error bars show standard deviations of replicate samplers (3 for rain, 4 each for throughfall)

Figure 4: Net exchange of N in a Sitka spruce canopy to which experimental additions of ions were made in spray treatments between May and August 2001. Treatments were: ‘no spray’ (i.e. rainfall only), or ‘background’ spray containing $5 \mu\text{M}$ ($\text{NH}_4\text{NO}_3 + \text{H}_2\text{SO}_4$) = ($10 \mu\text{M N}$) (see Table 2).

Figure 5: Net exchange of N in a Sitka spruce canopy to which experimental additions of ions were made in spray treatments between May and August 2001. Treatments were: ‘N only’ - spray delivering NH_4NO_3 ($160 \text{ mmol N m}^{-2}$); ‘NSAcid’ - spray delivering $\text{NH}_4\text{NO}_3 + \text{H}_2\text{SO}_4$ ($150 \text{ mmol N m}^{-2}$, 75 mmol S m^{-2}) and ‘2NSAcid’ - spray delivering $\text{NH}_4\text{NO}_3 + \text{H}_2\text{SO}_4$ ($250 \text{ mmol N m}^{-2}$, $125 \text{ mmol S m}^{-2}$)

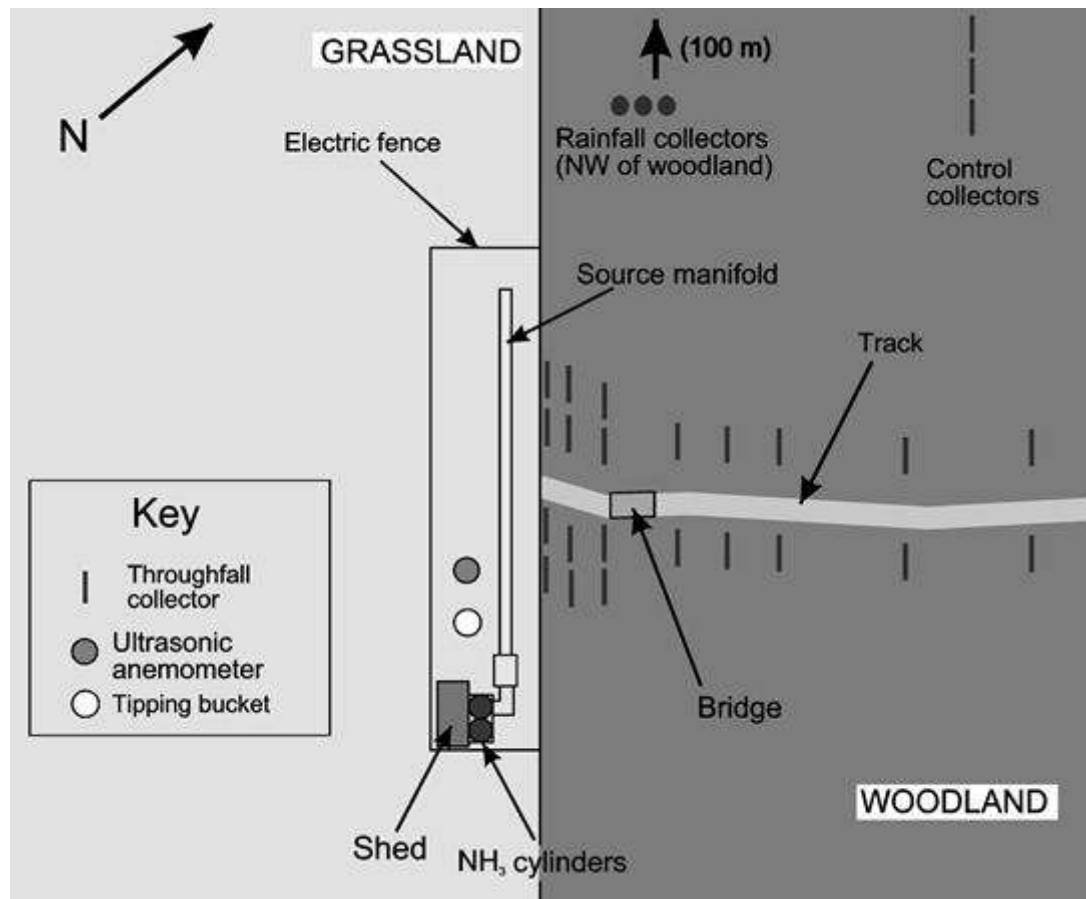


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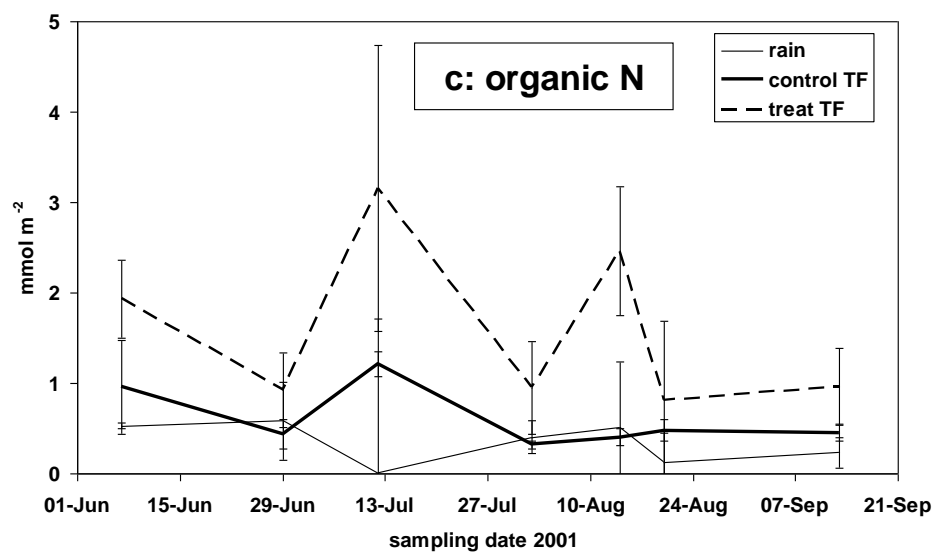
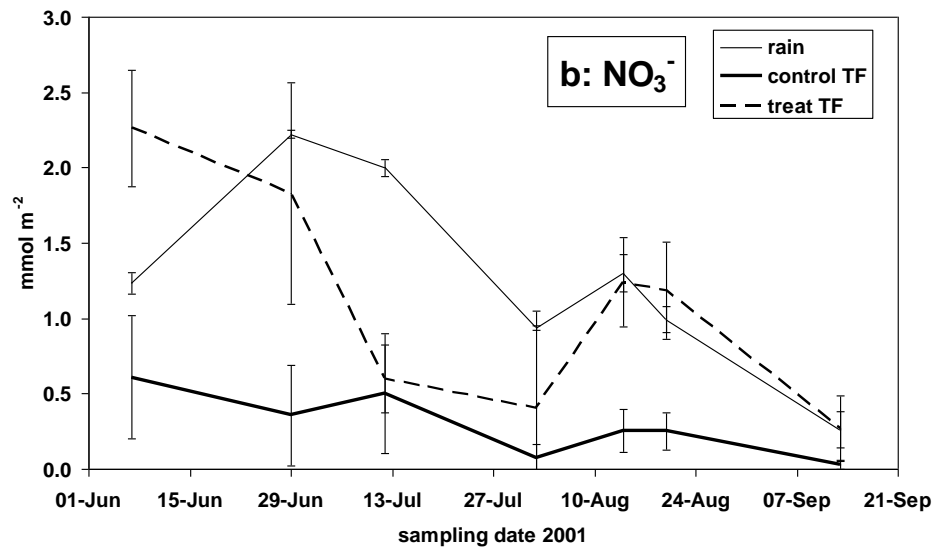
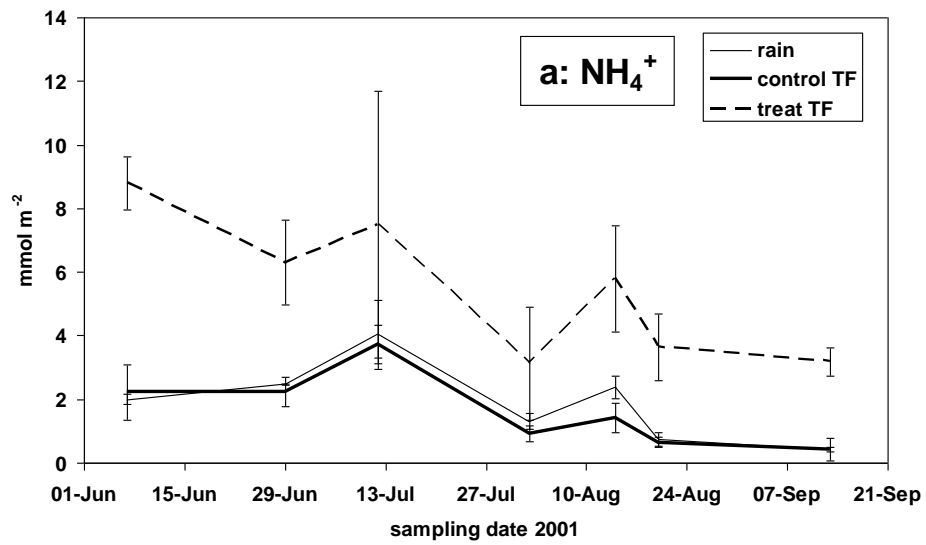


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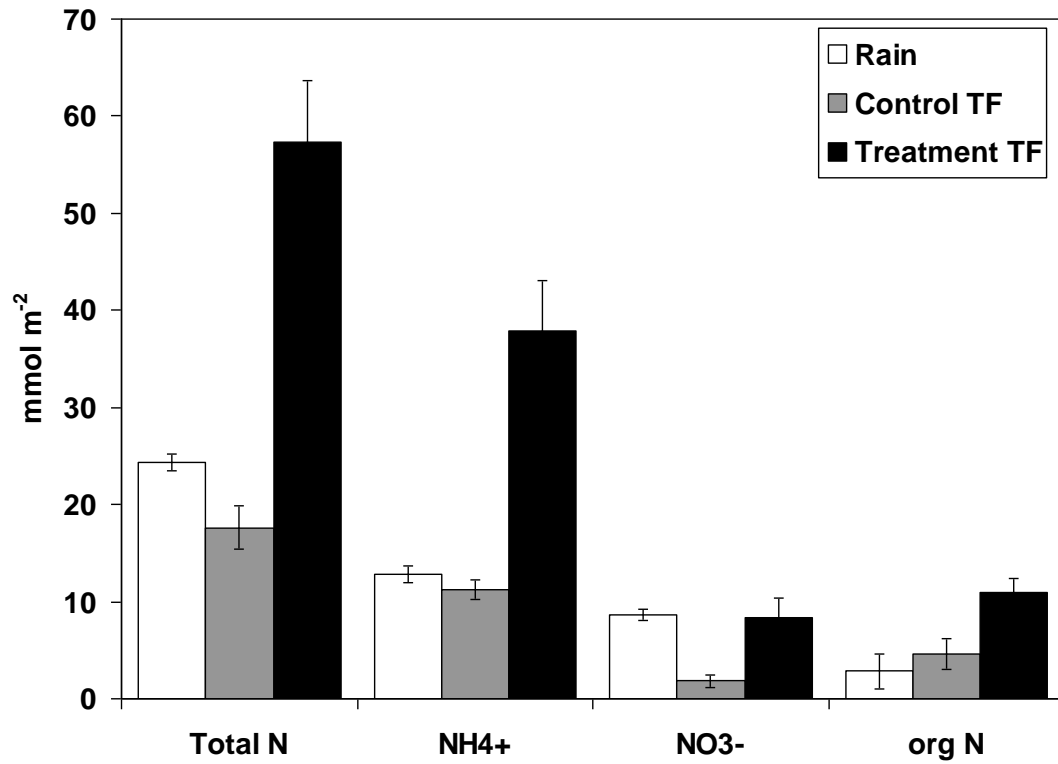


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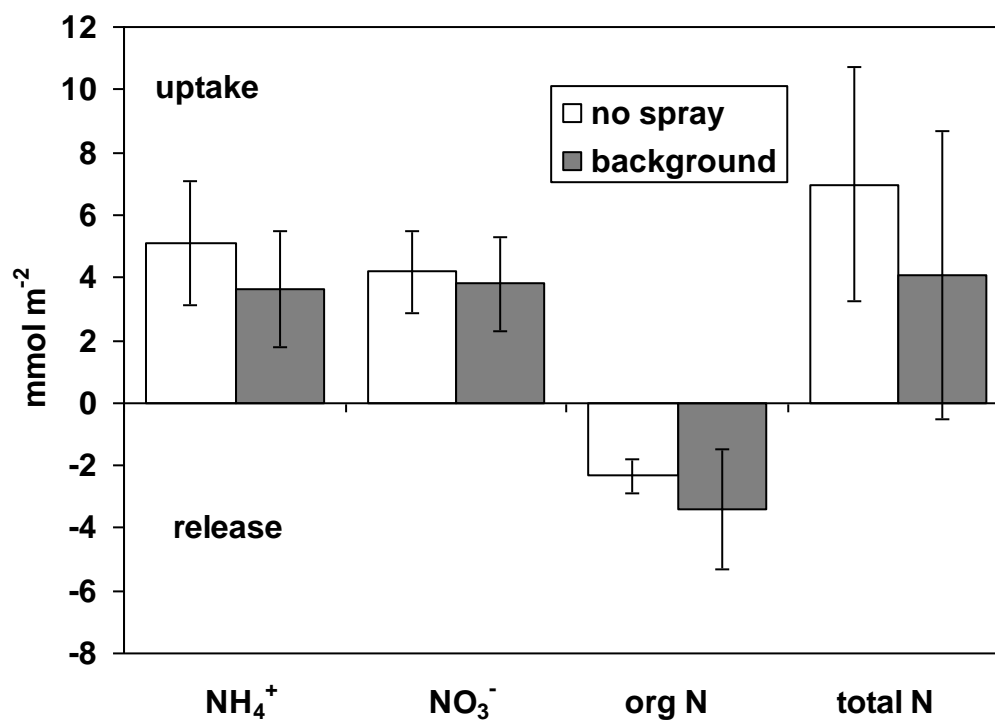


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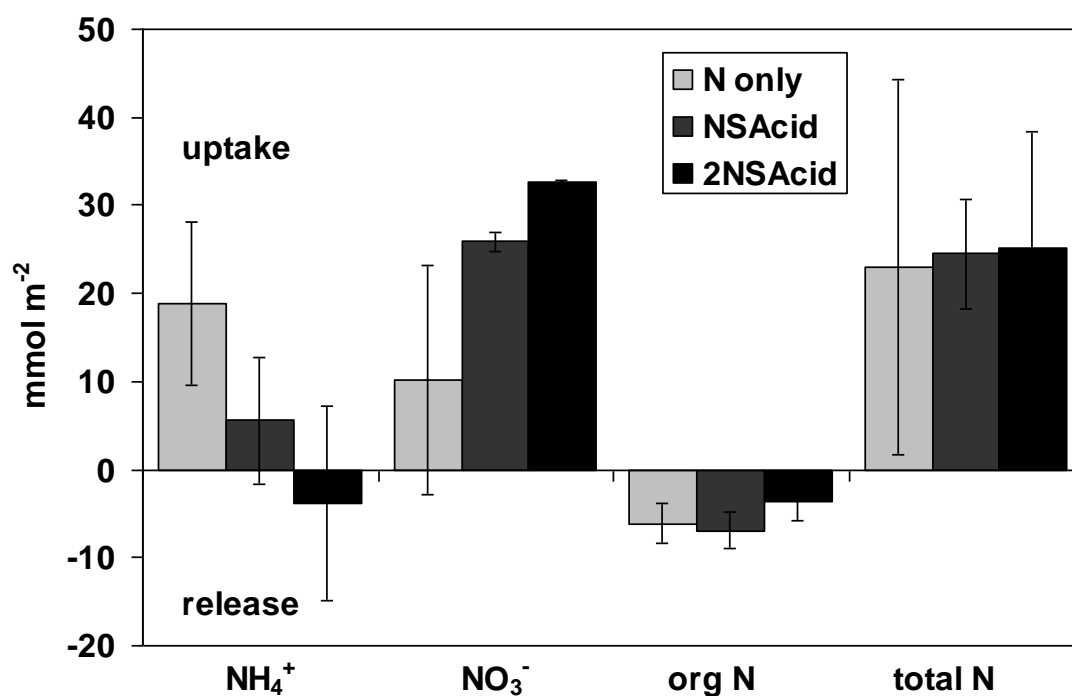


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