

**Fluxes of nitrogen in a semi-natural ecosystem**

A thesis submitted to The University of Manchester for the degree of  
Doctor of Philosophy  
in the Faculty of Engineering and Physical Sciences.

**2013**

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## Abstract

Nitrogen (N) is known to be a limiting factor in peatlands and as such, the vegetation present has adapted to living in low N conditions. This makes such ecosystems particularly vulnerable to increases in the deposition of reactive N ( $N_r$ ), which may result in significant changes to its biodiversity and biogeochemistry. Since the industrial revolution, the amount of anthropogenic  $N_r$  globally has increased from  $\sim 15 \text{ Tg N yr}^{-1}$  in the 1860's to  $\sim 187 \text{ Tg N yr}^{-1}$  in 2005, and is estimated to reach  $\sim 267 \text{ Tg N yr}^{-1}$  by 2050 (Galloway et al. 2004, Galloway et al. 2008). Consequences include acidification, loss of biodiversity, changes in vegetation, N-saturation, eutrophication, health impacts and the release of greenhouse gases.

Objectives of this thesis were (i) to measure key components of the N-budget at Auchencorth Moss, a Scottish moorland, for a two year period (Jan 2009 – Dec 2010) and (ii) to compare current deposition rates with those measured 14/15 years previously. Annual fluxes of N inputs were estimated from measurements of wet only deposition, estimates of N-fixation deposition and from atmospheric deposition modelled from hourly concentrations of N containing gases and aerosols. Exports were estimated from stream measurements and from atmospheric emissions modelled from hourly concentrations.

Organic N is often an underreported part of the N-cycle, but the results presented here suggest it is an important part of the N story. An attempt to identify (dissolved organic nitrogen) DON compounds in both precipitation and stream water was made using GC $\times$ GC-NCD. Ten unique compounds were detected, of which only five could be identified: pyrrole, benzonitrile, dodecylamine, N-nitrosodipropylamine and decylamine. Pyrrole, benzonitrile and three unknown compounds were present in both precipitation and stream samples.

Ammonia ( $\text{NH}_3$ ) fluxes were measured over a 7 month period in 2009 using a wet-chemistry gradient system with online analysis and calculated with the aerodynamic gradient method. The results were used to refine a bi-directional dynamic exchange model. Several parameters were updated, including an increased stomatal emission potential from 180 to 350, a reduction of the minimum cuticular resistance ( $R_{w,\min}$ ) used to calculate  $R_w$  from  $20 \text{ s m}^{-1}$  to  $15 \text{ s m}^{-1}$  and an increase in the leaching rate ( $K_l$ ) from the leaf surfaces from  $-0.01$  to  $-0.1 \text{ s}^{-1}$ . The exchange parameterisations used to estimate  $\text{HNO}_3$ , HONO and the aerosol compounds were taken from the literature and earlier studies at the site.

Overall, Auchencorth was found to accumulate N, with deposition exceeding export by  $-1.61 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . The main N deposition was from  $\text{NH}_3$ , followed by wet deposition of ammonium. DON, which is not routinely included in N budgets, contributed 6.5% of total deposition. The largest loss of N was as DON via the stream with N losses of  $-5.31 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  or 71.8% of total export. Between 1995 and 2009/2010, deposition decreased by  $0.81 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , with the wet deposition of inorganic nitrogen decreasing by 25.2%, but dry deposition increasing by 12.5%. DON,  $\text{N}_2\text{O}$  and N-fixation were not included in the comparison as they were not measured in 1995.

This thesis has demonstrated that DON is an important parameter in the overall N budget, and should be routinely measured when assessing the N status of ecosystems.



**Declaration**

No portion of work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Rebecca McKenzie

4<sup>th</sup> July 2013



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## **Acknowledgements**

This work was funded by the UK Natural Environment Research Council (NERC) through PhD studentship grant number NE/H526351/1. The work was carried out jointly between the Centre for Ecology and Hydrology (CEH), Edinburgh, Scotland and the University of Manchester, School of Earth, Atmospheric and Environmental Sciences.

I would like to thank my supervisors Dr Ute Skiba, Dr Eiko Nemitz and Professor Mark Sutton of CEH and Dr Martin Gallagher of The University of Manchester for their encouragement and invaluable advice throughout this study.

Many thanks to Dr Mustafa Öze1 and Dr Jacky Hamilton of The University of York, for assistance with the GC×GC-NCD and helping with data analysis.

I would like to thank the landowner at Auchencorth Moss for access to the fieldsite and Ian Leith (CEH), Netty Van Dijk (CEH), Sarah Leeson (CEH) and Ivan Simmons (CEH) for managing the site measurements. Thanks also to the numerous staff at CEH for helping me with field work, laboratory analysis and data analysis: Dr Kerry Dinsmore, Dr Julia Drewer, Dr Stephanie Jones (CEH/Scotland's Rural College), Dr Marsailiidh Twigg, Professor Neil Cape, Dr Juan Gonzalez-Benitez, Dr Mhairi Coyle, Sim Tang and Margaret Anderson.

Last but certainly not least, I would like to thank my parents, my sister Helen and numerous friends for their enduring support. A special thank you to Lena Boukelia, for her assistance and advice throughout my PhD; to Laura Bolan and my Mum Rachel for braving the Scottish weather at weekends to assist with fieldwork; to my mentor Sue Owen, for keeping things in perspective; to my aunts Sarah, Caroline and Hilary for their words of wisdom, and finally to my Gran for just being there, I always enjoyed our visits.



## **Author's contribution to the papers**

### **Paper I: The import and export of organic nitrogen species at a Scottish Moorland**

R. McKenzie analysed the stream and wet only samples herself for nitrate, ammonium and total nitrogen. She collected and filtered the stream samples and filtered the wet only samples after collection. She shared the responsibility of collecting, filtering and analysing the soil water. She shared responsibility of collecting soil samples for extraction by KCl, but carried out all the extractions. Analysis of the extracts was carried out elsewhere. The GC×GC-NCD was operated by M. Özel, but all sample preparation and data analysis was carried out by R. McKenzie. The manuscript was written by R. McKenzie in cooperation with the co-authors.

### **Paper II: Dry deposition of inorganic nitrogen compounds to a Scottish moorland**

R. McKenzie took part in planning the field experiment and was responsible for setting it up, collecting data and equipment maintenance. She processed the data, assessed the model and wrote the manuscript in cooperation with the co-authors.

### **Paper III: The import and export of reactive nitrogen compounds from a Scottish moorland**

R. McKenzie developed the idea of this paper in cooperation with the co-authors. She calculated/inferred most of the fluxes herself, with the exception of the NO and NO<sub>2</sub> fluxes which were supplied to her by Mhairi Coyle. She wrote the manuscript in cooperation with the co-authors.



## **1. Introduction**

Nitrogen (N) is an important and essential component of all life; it is the fourth most common chemical element found in living tissue (Vitousek et al. 1997). In its most common form, dinitrogen ( $N_2$ ), N is an inert gas which makes up approximately 78% of the earth's atmosphere (Schlesinger 1997, Vitousek et al. 1997). Its triple bonded nature makes it unavailable to most organisms due to the large amount of energy required to break these bonds (Galloway et al. 2003). A further ~20% of N is trapped as sedimentary rock, which requires extraction, or soil organic matter, which must be decomposed by soil microbes, in order for the N to be released into a useable form (Vitousek et al. 1997, Galloway 1998). These restraints in the availability of N have made it a limiting factor in many ecosystems (Schlesinger 1997, Vitousek et al. 1997, Vitousek et al. 2002). Peatlands are one such ecosystem. Due to the harsh conditions typical of peatlands, they are often nutrient-poor, and thus nitrogen limited. This has led to the presence of plants adapted to low N conditions and plants with a nitrogen-fixing ability in the peatland setting.

In the last 150 years the amount of reactive nitrogen ( $N_r$ ) available has increased significantly (Galloway et al. 2004), and if this continues, it may result in an imbalance in the way in which N moves amongst ecosystems. Across Europe, changes in species composition has been attributed to an increase in N deposition in a variety of habitats, including heathlands, grasslands and moorlands (Pitcairn et al. 1998). In nitrogen limited ecosystems, this could cause unprecedented changes over time and may even lead to the destruction of such ecosystems. It is therefore important to gain a better understanding of how nitrogen is cycled in natural, clean ecosystems in order to fully appreciate the consequences of increasing the reactive N supply.



## 1.1 The Nitrogen Cycle

The N cycle describes the movement of N from one pool of N to another. It is a complex and balanced system but our understanding of it is limited and there are many processes and exchanges which are not yet well understood. Uncertainties in rates of major processes such as denitrification and biological N fixation make quantifying N fluxes and the effects of anthropogenically produced N difficult (Galloway et al. 2004). Many of the processes associated with the terrestrial N cycle require a source of carbon, making both the N and C cycles closely linked (Killham 1994, Gruber and Galloway 2008). Other processes and cycles may also be affected by the transformations of N.

### 1.1.1 The Terrestrial Nitrogen Cycle

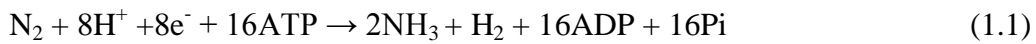
Below are the descriptions of the major N processes of the terrestrial N cycle which need to be considered for the purpose of this study (see also Fig. 1.1):

#### 1.1.1.1 N-fixation

In order for  $N_2$  in the atmosphere to become available to organisms, it must first be “fixed” to create N compounds containing hydrogen (H) or oxygen (O) (Vitousek et al. 1997). N-fixation is the term used to describe the breakdown of the triple bonds in atmospheric  $N_2$  and the subsequent formation of N compounds which are then biologically available ( $N_r$ ) (van Egmond et al. 2001). In nature, this is achieved through two main processes: lightning strikes, which produce  $3\text{--}5 \text{ Tg N y}^{-1}$  and biological nitrogen fixation, which naturally produces  $90\text{--}130 \text{ Tg N y}^{-1}$  (Galloway 1998, Galloway et al. 2003). The high temperatures produced during a lightning strike, enables NO to be formed from molecular oxygen and nitrogen. The NO is then oxidized to  $NO_2$  and then to the biologically available  $HNO_3$ , where it is subsequently removed from the atmosphere and deposited on land or sea (Nieder and Benbi 2008).

Biological nitrogen fixation (BNF) is restricted to a few species of algae and bacteria (known as diazotrophs). These include both free-living and symbiotic cyanobacteria; actinomycetes associated with non-leguminous angiosperms; free-living bacteria such as *Clostridium* and *Bacillus* and the most significant, *Rhizobium*, a type of bacteria found in the root nodules of leguminous plants (Killham 1994). Under optimal conditions the chemical equation for BNF is:





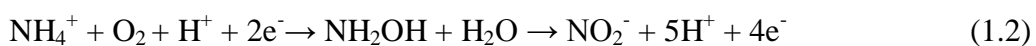
where Pi is inorganic phosphate, liberated when ATP (adenosine triphosphate) is hydrolysed to ADP (adenosine diphosphate) (Leigh 2004).

The symbiotic relationship formed between plant and diazotroph allows the plant to obtain the N it requires, whilst supplying the diazotroph with carbon; usually in the form of sugars such as glucose (Leigh 2004). This process is only possible because of the presence of the enzyme nitrogenase within the bacteria which acts as a catalysis, allowing atmospheric N<sub>2</sub> to be converted into NH<sub>3</sub> (Schlesinger 1997). It is highly sensitive to the presence of oxygen but can be either an aerobic or anaerobic process depending on the type of N-fixer present (Killham 1994). Soil acidity can also be an inhibiting factor: in the case of *Rhizobium* bacteria, a pH of less than 4.3 can mobilise aluminium to which the bacteria is highly sensitive (Killham 1994). High temperatures can affect the rate of photosynthesis of the plant host, which in turn, affects the amount of C available to the bacteria. Most free-living N-fixers are heterotrophs (excluding cyanobacteria) and the supply of C available in the soil is often a limiting factor (Killham 1994). An overabundance of inorganic N in the soil can also suppress the rate of fixation; with the high energy requirement for N-fixation (equation 1.1), more readily available N will be taken up in preference to atmospherically fixed N. However in natural N limited ecosystems, the small rates of heterotrophic N fixation (<1-5 kg N ha<sup>-1</sup> y<sup>-1</sup>) may contribute significantly to the total N budget (Vitousek et al. 2002).

#### 1.1.1.2 Nitrification

Nitrification is the oxidation of ammonium (NH<sub>4</sub><sup>+</sup>) to nitrate (NO<sub>3</sub><sup>-</sup>) via nitrite (NO<sub>2</sub><sup>-</sup>). It is a two-step process carried out by specific microorganisms under aerobic conditions. Autotrophic nitrification is the dominant form in most soils and is typically facilitated by bacteria such as *Nitrosomonas europaea* (first step) and *Nitrobacter winogradskyi* (second step) (Wrage et al. 2001).

The first stage involves the oxidation of ammonium to nitrite via hydroxylamine (NH<sub>2</sub>OH) (Killham 1994):





The second stage involves the oxidation of nitrite to nitrate (Killham 1994):



Both processes produce energy and the bacteria use  $\text{CO}_2$  as a carbon source (Wrage et al. 2001).

Heterotrophic nitrification is less well understood, but it has been suggested that under the right conditions some types of fungi (rather than bacteria) can nitrify organic N without it first being mineralised into  $\text{NH}_4^+$  (Wrage et al. 2001). Organic C is used as a source of C, but the overall products are the same as for autotrophic nitrification.

Both autotrophic and heterotrophic nitrification are inhibited by low temperature, low pH and poorly oxygenated soils. When oxygen becomes too short in supply, it is possible for NO or  $\text{N}_2\text{O}$  to be produced instead of  $\text{NO}_3^-$  (Wrage et al. 2001).

#### 1.1.1.3 Denitrification

Denitrification is the main route by which N is returned to the atmosphere, and is one of the most important nitrogen processes. Complete denitrification is an anaerobic process and produces  $\text{N}_2$ . However, in the presence of low levels of  $\text{O}_2$  partial denitrification occurs, releasing one of the intermediary products,  $\text{NO}_x$  or more commonly  $\text{N}_2\text{O}$ , a powerful greenhouse gas (Nieder and Benbi 2008). NO produced by denitrifiers is more likely to be consumed by denitrifiers than be emitted to the atmosphere (Davidson et al. 1993). This is mostly as a result of optimal conditions of denitrification inhibiting gaseous diffusion, preventing the release of NO and encouraging consumption (Davidson et al. 1993).

Denitrification can be carried out by a large variety of heterotrophic bacteria but only if the basic requirements of low oxygen levels, a C source and an N source are available (Skiba et al. 2008).

There are several pathways of denitrification; the most commonly presented being heterotrophic denitrification. This involves the reduction of  $\text{NO}_3^-$  by heterotrophic microorganisms to either  $\text{N}_2\text{O}$  or  $\text{N}_2$  depending on the aerobicity of the soil (Wrage et al. 2001, Skiba et al. 2008):

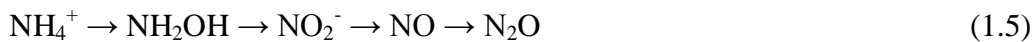




Each step is catalysed by an enzyme:  $\text{NO}_3^-$  to  $\text{NO}_2^-$  by nitrate reductase;  $\text{NO}_2^-$  to  $\text{NO}$  by nitrite reductase;  $\text{NO}$  to  $\text{N}_2\text{O}$  by nitric oxide reductase and  $\text{N}_2\text{O}$  to  $\text{N}_2$  by nitrous oxide reductase (Wrage et al. 2001). If conditions are not optimal, the enzymes cannot catalyse the reaction preventing complete denitrification. For example, at low pH the nitrous oxide reductase is inhibited resulting in  $\text{N}_2\text{O}$  to be released instead of  $\text{N}_2$ . The same occurs if some  $\text{O}_2$  is present as the nitrous oxide reductase is affected more by the presence of  $\text{O}_2$  than the other reductases (Wrage et al. 2001). These denitrifiers live both aerobically and anaerobically but will only use  $\text{NO}_3^-$  as an electron acceptor for respiration once oxygen levels have fallen low enough (Wrage et al. 2001). For heterotrophic denitrification an organic C supply is essential (Skiba et al. 2008).

The best conditions for denitrification to occur are depleted  $\text{O}_2$ , warm temperatures, high  $\text{NO}_3^-$  concentrations, a carbon source, and high soil water content (Simek et al. 2002, Nieder and Benbi 2008).

Nitrifier denitrification involves (mainly) the autotrophic bacteria which carry out the first step in nitrification. It requires a carbon source of  $\text{CO}_2$  as opposed to organic C needed for heterotrophic denitrification (Skiba et al. 2008).  $\text{NH}_4^+$  is oxidised to  $\text{NO}_2^-$  but instead of being further oxidised to  $\text{NO}_3^-$ , it is reduced into  $\text{NO}$  or  $\text{N}_2\text{O}$  (Skiba et al. 2008):



This process is responsible for most of the soil  $\text{NO}$  emissions and for some of the  $\text{N}_2\text{O}$  emissions (Davidson 1991, Davidson and Verchot 2000).

#### 1.1.1.4 Mineralisation/Immobilisation

Mineralisation refers to the breakdown of organic N ( $\text{N}_{\text{org}}$ ) into available forms of N, such as  $\text{NH}_4^+$  and  $\text{NO}_3^-$  and is achieved by microbial biomass present in the soil. Immobilisation is the reverse reaction and refers to the processes by which  $\text{NH}_4^+$  and  $\text{NO}_3^-$  is converted to  $\text{N}_{\text{org}}$  by soil microbes, soil fauna and plants (Killham 1994). Both reactions can occur at the same time and the amount of  $\text{N}_r$  in the soil depends on which of these two processes dominates (Cabrera et al. 2005). For example, if immobilisation



was the dominant process, the soils would be poor in available N and the vegetation would need to find an alternative source of  $N_r$ .

Plants absorb  $NH_4^+$  or  $NO_3^-$  from the soil via their root hairs. The uptake of  $NH_4^+$  can be restricted by the presence of negatively charged soil particles to which the  $NH_4^+$  is attracted, resulting in the preferential utilisation of  $NO_3^-$  (Killham 1994).  $NH_4^+$  incorporated in this way can make up to 8% of the N in surface soils and up to 45% in deeper soils (Smil 1997). The type of nitrogen taken up by a plant affects its internal charge balance, resulting in the release of substances which are either acidic (if  $NH_4^+$  is utilised) or alkali (if  $NO_3^-$  is utilised) in order to maintain this balance (Killham 1994, Schlesinger 1997). Immobilisation therefore has an important impact on the pH of the soil.

#### 1.1.1.5 Ammonification

Refers specifically to the release of  $NH_3$  or  $NH_4^+$  from the breakdown of organic matter by microbes (Schlesinger 1997).  $NH_3$  is emitted to the atmosphere, whereas  $NH_4^+$  remains in the soil/water body and can be utilised by vegetation; immobilised by microbes; fixed by clay minerals or used in nitrification (Schlesinger 1997).

#### 1.1.1.6 N Leaching

N leaching is the process by which mobile N compounds are transported out of the soil by water. The most common type of leaching is  $NO_3^-$  leaching due to its negative charge allowing free movement with the soil water. The positively charged  $NH_4^+$  is not commonly leached from temperate soils due to the charge being held in the soil within the clay lattice, by bonds with negatively charged surfaces on organic material or rapid microbial uptake (Killham 1994, Schlesinger 1997, Nieder and Benbi 2008). The leaching of  $NO_3^-$  from the soil has become a rising problem due to increased fertiliser use. Not all the N from fertilisers is utilised, leading to an accumulation of N in soil which can be subsequently washed out into aquatic ecosystems. As an often limited nutrient,  $NO_3^-$  accumulating in streams, lake, rivers etc. may result in eutrophication and potentially pollute groundwater. The World Health Organisation Standards states that the presence of more than 10 mg of  $NO_3^-$ -N  $L^{-1}$  renders the water unhealthy to drink. Such is the problem that nitrate vulnerable zones (NVZ) have cropped up across Europe, restricting the use of fertilisers and monitoring sites at risk of breaching WHO standards.



Less is known about the leaching of dissolved organic N (DON) as it is only relatively recently that measurements have started. The movement of DON depends on its chemical composition and various hydrological factors e.g. the dissolution kinetics of humic substances and flow paths of water through the soil (Nieder and Benbi 2008). DON leaching may result in increasing the bioavailability of N in the aquatic systems to which it is transported, and conversely, reduce the accumulation of N from whence it came (Nieder and Benbi 2008).

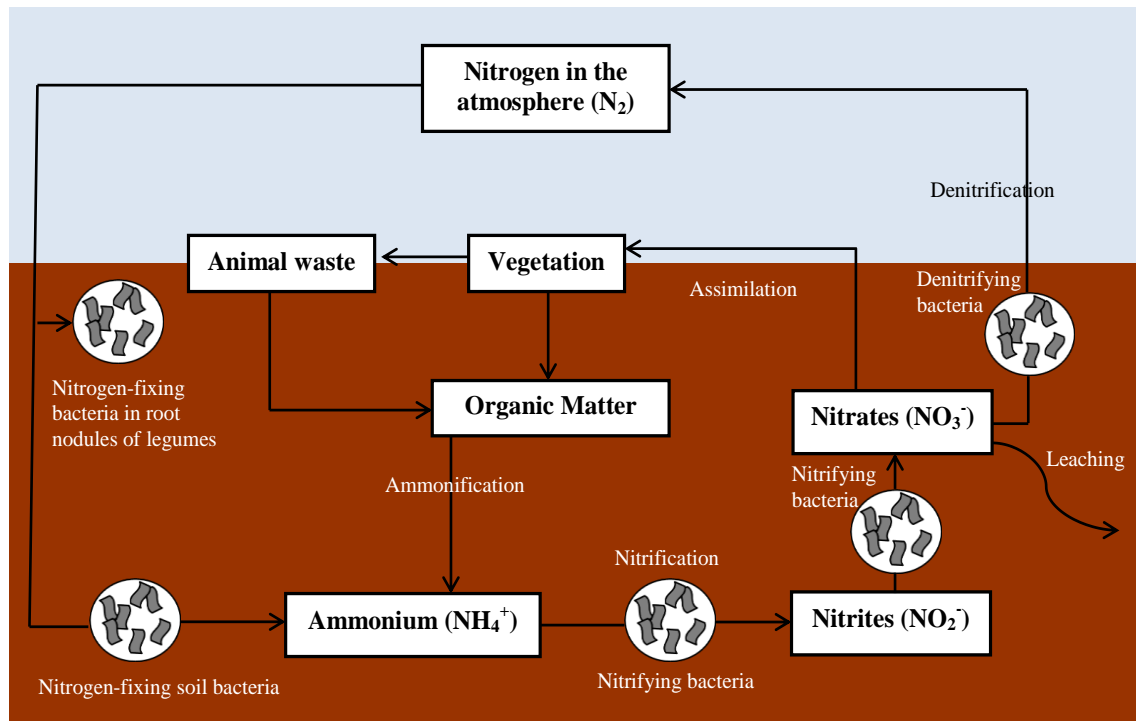


Figure 1.1. The nitrogen cycle, showing the major nitrogen processes in a terrestrial setting.

### 1.1.2 Atmospheric Chemistry

Although  $N_2$  is the most common form of N in the atmosphere, its inert nature means it is not commonly involved in atmospheric chemistry (Seinfeld and Pandis 2006). Its main input into the reactive N pool is via N-fixation (section 1.2.1.1). The primary source of  $N_2$  released into the atmosphere is from denitrification. It is difficult to measure the  $N_2$  flux to and from the atmosphere due to large background concentrations –  $N_2$  makes up 78% of the atmosphere. Many of the methods developed so far are inadequate as some are solely laboratory based, require high levels of  $^{15}N$  input, expensive, or difficult to evenly distribute through the soil resulting in unreliable data



(Fowler et al. 2009). There are however, a number of trace species important to the chemistry of the atmosphere which are outlined below.

#### 1.1.2.1 Reduced N

Approximately 60% of the total deposited N in the UK is in reduced forms of N ( $\text{NH}_3 + \text{NH}_4^+$ ) (Pitcairn, 1998).  $\text{NH}_3$  is an important gas due to the pollution effects on vegetation. It is a reactive gas, resulting in a relatively short lifetime – around 10 days - and therefore its impact tends to be localised.  $\text{NH}_3$  is deposited either directly by turbulent transfer, or by dissolution into  $\text{NH}_4^+$  and wet deposited as precipitation.  $\text{NH}_4^+$  makes up a large fraction of atmospheric aerosols and unlike  $\text{NH}_3$ , the impact tends to be further downwind of its source (Nieder and Benbi 2008).  $\text{NH}_3$  is a major neutralising gas, which reacts with acidic products such as  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  reducing the acidity of the atmosphere and subsequently of precipitation (Spindler et al. 2001). The dissolution of  $\text{NH}_3$  in rainwater produces  $\text{OH}^-$  making it a source of alkalinity for rainwater:



Approximately 22% of atmospheric acidity is believed to be neutralised by  $\text{NH}_3$  (Schlesinger 1997). In contrast, the deposition of  $\text{NH}_4^+$  can result in acidification of soils as a result of microbial nitrification. During the first stage of nitrification, where  $\text{NH}_4^+$  is oxidised to  $\text{NO}_2^-$ ,  $\text{H}^+$  molecules are released resulting in acidification of the surrounding soils (section 1.1.1.2; reaction 1.3) (Flechard and Fowler 1998).  $\text{NH}_4^+$  is an important nutrient, and increased deposition in nutrient-poor ecosystems can lead to eutrophication. This can lead to N saturation - where there is more N available than needed by plants and/or microbial communities - resulting in changes in vegetation and leaching into nearby water bodies (Adamson et al. 1998, Flechard and Fowler 1998, Trebs et al. 2006).

By far the largest sources of  $\text{NH}_3$  are from agriculture which contributes ~85% of UK emissions; including emissions from animal houses, manure storage, decomposition of animal waste products (both urea and excrement), from the mineralization of organic matter in soils and from the use of fertilisers (both mineral and manure) (Shallcross 2009, Hertel et al. 2011). Globally approximately  $44.3 \text{ Tg N y}^{-1}$  of the  $58.2 \text{ Tg N y}^{-1}$  of  $\text{NH}_3$  emitted is from agricultural activities (Galloway et al. 2004). Other sources



include energy production (2.9 Tg N y<sup>-1</sup>) and natural processes such as natural forest fires and soil/vegetation emissions (11 Tg N y<sup>-1</sup>) (Galloway et al. 2004). Since 1860, the deposition of NH<sub>3</sub> has increased from ~18.8 Tg N y<sup>-1</sup> to ~56.7 Tg N y<sup>-1</sup> and is expected to increase to ~116 Tg N y<sup>-1</sup> by 2050 (Galloway et al. 2004).

#### 1.1.2.2 Nitrous oxide

Nitrous oxide (N<sub>2</sub>O) is a powerful greenhouse gas with a global warming potential 298 times that of CO<sub>2</sub> (IPCC 2007). It contributes ~6% towards global warming by absorbing outgoing radiation not captured by other greenhouse gases. Tropospheric N<sub>2</sub>O has a low reactivity which results in a long lifetime (~120 years) (IPCC 2007). Overtime it is transported to the stratosphere where it is destroyed by photolysis ( $h\nu$ ) and reactions with excited oxygen atoms (O(<sup>1</sup>D)) (Shallcross 2009):



The NO produced as a result of the above reaction provides a major input of NO into the stratosphere (Seinfeld and Pandis 2006) and facilitates the reactions which destroy ozone, causing the ozone layer to thin (Killham 1994, Schlesinger 1997). Due to the decline in fluorocarbon compounds N<sub>2</sub>O is now the most important ozone-depleting molecule in the stratosphere (Ravishankara et al. 2009).

Since the industrial revolution the amount of N<sub>2</sub>O released into the atmosphere has increased from 270 ppb to 319 ppb (1750-2005) IPCC (IPCC 2007, Dalal and Allen 2008). Emissions have increased due to an increase in the use of N fertilisers and an increase in atmospheric N deposition (Skiba et al. 2000). On the global scale, soils, particularly fertilised arable and grasslands, are a major source of N<sub>2</sub>O (Stolk et al. 2009). Over 80% of anthropogenically produced N<sub>2</sub>O comes from agriculture, with crop production accounting for 50% of this figure (Nieder and Benbi 2008).



### 1.1.2.3 Total Reactive N

Total Reactive N (also known as Reactive Odd N) ( $\text{NO}_y$ ) is the term used to describe nitrogen oxides ( $\text{NO}_x$ ), and the compounds derived from the atmospheric oxidation of  $\text{NO}_x$ . These compounds consist of nitric acid ( $\text{HNO}_3$ ), nitrous acid ( $\text{HONO}$ ), the nitrate radical ( $\text{NO}_3$ ), peroxyacetylnitrate (PAN;  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ), nitrate aerosol, alkyl nitrates ( $\text{RONO}_2$ ), dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) and peroxyntitric acid ( $\text{HNO}_4$ ) (Seinfeld and Pandis 2006, Monks and Leigh 2009).

Globally,  $\text{NO}_y$  contributes approximately 33% of the N deposited in terrestrial ecosystems (Galloway, 2004). Since 1860 the amount of  $\text{NO}_y$  deposited from the atmosphere to terrestrial ecosystems has increased from  $6.6 \text{ Tg N y}^{-1}$  to  $24.8 \text{ Tg N y}^{-1}$  and is expected to reach  $42.2 \text{ Tg N y}^{-1}$  by 2050 (Galloway, 2004). These increases have been attributed to various man-made activities, primarily agriculture and the burning of fossil fuels. Below, the compounds of  $\text{NO}_y$  considered in this study are discussed further.

#### 1.1.2.3.1 Nitrogen oxides

Nitrogen Oxides ( $\text{NO}_x$ ) is the collective term used to describe NO and  $\text{NO}_2$  and are significant contributors of atmospheric chemistry.  $\text{NO}_x$  has a short residence time ranging from 1-2 days in the lower troposphere to around 4-14 days in the upper troposphere (Neff et al. 2002, Seinfeld and Pandis 2006). The major sources of  $\text{NO}_x$  are from industrial and vehicle emissions i.e. the burning of fuel, but small amounts are produced naturally from lightening, forest fires and microbial soil emissions (Schlesinger 1997). NO is a by-product of nitrification and can be produced rather than  $\text{NO}_3^-$  if oxygen levels are slightly reduced. It is also a substrate and product of denitrification but this is very rarely a source of emitted NO (Davidson et al. 1993). In urban areas,  $\text{NO}_x$  is a major contributor to photochemical smog (Jaffe 1992). In the stratosphere, NO is produced from the photolysis of  $\text{N}_2\text{O}$  and contributes to the destruction of ozone (reactions 1.7-1.9).

The main losses of  $\text{NO}_x$  from the atmosphere during daylight is via the wet deposition of  $\text{HNO}_3$  (reaction 1.18) with only small amount in long-distance transport (Schlesinger 1997, Shallcross 2009).  $\text{NO}_x$  is also lost by dry deposition.

The concentration of  $\text{NO}_x$  has an important effect on tropospheric processes as they have a significant effect on  $\text{O}_3$  production and destruction (Shallcross 2009). For



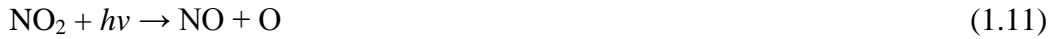
example, with regards to the presence of the peroxy radical  $\text{HO}_2$  (produced from reactions between the hydroxyl radical (OH) and methane or carbon monoxide), low levels of  $\text{NO}_x$  allows  $\text{HO}_2$  to take part in  $\text{O}_3$  destroying processes. However, at high levels of  $\text{NO}_x$ ,  $\text{HO}_2$  acts as a catalyst for the oxidation of NO to  $\text{NO}_2$ :



thus contributing to the production of  $\text{O}_3$  through further reactions involving  $\text{NO}_2$  and its photoproducts (reactions 1.11 and 1.12) (Monks and Leigh 2009).

In the troposphere, NO is formed by lightening N-fixation (section 1.2.1.1) and can be further oxidised to  $\text{NO}_2$ .  $\text{NO}_2$  absorbs over the entire range of the UV and visible solar spectrum and is dissociated by sunlight to form NO and O (reaction 1.11) (Seinfeld and Pandis 2006).

During daylight, NO +  $\text{NO}_2$  are closely coupled and quickly interconverted in the presence of  $\text{O}_3$  (Seinfeld and Pandis 2006, Shallcross 2009):



M represents an atmospheric molecule which acts as a heat sink for the reaction between O and  $\text{O}_2$ , preventing the disintegration of any newly formed  $\text{O}_3$  molecules (Monks and Leigh 2009). Reactions 1.11 and 1.12 are the only known processes which produce  $\text{O}_3$  in the troposphere (Monks and Leigh 2009).

At night,  $\text{NO}_2$  does not photolyse, consequently any NO present at night that is converted to  $\text{NO}_2$ , is not converted back. During the day, NO/ $\text{NO}_2$  ratios in air near the surface range from 0.2 to 0.5, but at night this falls to 0 (Monks and Leigh 2009).  $\text{NO}_2$  is then slowly oxidised by  $\text{O}_3$  to form the nitrate radical  $\text{NO}_3$ :





#### 1.1.2.3.2 Nitrate Radical and Dinitrogen Pentoxide

The nitrate radical ( $\text{NO}_3$ ) is believed to be the main oxidant in night-time atmospheric chemistry (Monks and Leigh 2009).  $\text{NO}_3$  during the day is rapidly photolysed and has a lifetime of approximately 5 s in the presence of sunlight (Seinfeld and Pandis 2006). It also reacts with  $\text{NO}$  with such speed that the two compounds cannot coexist in significant quantities. At night, when  $\text{NO}$  concentrations are small,  $\text{NO}_3$  is able to take part in other reactions.

At night,  $\text{NO}_3$  reacts with  $\text{NO}_2$  forming dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ):



Reaction 1.15 can be reversed by the thermal decomposition of  $\text{N}_2\text{O}_5$  back into  $\text{NO}_2$  and  $\text{NO}_3$ :



$\text{N}_2\text{O}_5$  also reacts with water to form nitric acid ( $\text{HNO}_3$ ):



and is an important reaction for the removal of  $\text{NO}_x$  from the atmosphere (Seinfeld and Pandis 2006).

#### 1.1.2.3.3 Nitric acid

In the troposphere,  $\text{HNO}_3$  is formed as a result of a reaction between  $\text{NO}_2$  and  $\text{OH}$ :



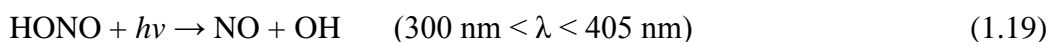
It is also formed during lightning strikes (section 1.2.1.1) and through a reaction between  $\text{N}_2\text{O}_2$  and water (reaction 1.17). The  $\text{HNO}_3$  is then quickly (within days) washed out of the atmosphere or neutralised by  $\text{NH}_3$  to form  $\text{NH}_4\text{NO}_3$  (Erisman et al. 1988, Galloway et al. 2004). As it is an acid, the presence of  $\text{HNO}_3$  in water droplets reduces the pH of the rain, making  $\text{HNO}_3$  an important constituent of acid rain. It is



biologically available making it a source of  $N_r$ . Nitric acid is also produced industrially for use in the production of explosives and fertilisers (Jaffe 1992).

#### 1.1.2.3.4 Nitrous acid

HONO is an important source of the hydroxyl radical (OH), an oxidising species which produces pollutants such as ozone ( $O_3$ ) in the troposphere, via the following reaction (Stutz et al. 2002, Acker and Moller 2007):



In polluted areas, HONO has been found to produce up to 34% of the total OH formed during the day (Alicke et al. 2002).

HONO is a secondary pollutant and its sources and formation are not well understood (Schimang et al. 2006, Trebs et al. 2006). It is generally believed that HONO is formed during the night via heterogeneous reaction of  $\text{NO}_2$  and water on surfaces such as plant cuticles, soil surfaces or aerosols (Acker et al. 2004, Schimang et al. 2006):



This reaction is thought to be of minor importance to HONO formation during sunny conditions (Acker and Moller 2007).

HONO can also be formed homogeneously during times of the day when concentrations of OH and NO are high (Stutz et al. 2002):



During daylight, HONO is rapidly broken down by photolysis, resulting in a typical residence time of 15 min (Stutz et al. 2002). This results in lower concentrations of HONO during the day than at night.



### 1.1.3 Other Key Compounds of the N Cycle

Most of the important N containing compounds considered in this study are outlined in sections 1.1.1 and 1.1.2. Below are descriptions of compounds also to be considered but not mentioned previously.

#### 1.1.3.1 Organic N

Organic N ( $N_{\text{org}}$ ) can be described as nitrogen containing compounds which originated in living matter and includes complex compounds such as organic nitrates, amines, amides, proteins and other amino acids (Jaffe 1992, Neff et al. 2002). These compounds have a variety of different properties and atmospheric lifetime can vary from seconds to weeks depending on the compound (Neff et al. 2002).  $N_{\text{org}}$  is often a neglected or underreported part of the nitrogen cycle due to the difficulties in measuring it. The complexities arise from the numerous fractions which constitute  $N_{\text{org}}$ , making it difficult to give an accurate concentration of total  $N_{\text{org}}$ . As a result,  $N_{\text{org}}$  is calculated by subtracting inorganic N ( $\text{NH}_4^+ + \text{NO}_3^-$ ) from total N, which can lead to over/under estimates depending on the accuracy of the measurements of the inorganic and total N fractions. However, studies that have been done have suggested the  $N_{\text{org}}$  can be an important component of atmospheric emissions and deposition, with estimates of 10-50 Tg N  $\text{y}^{-1}$  being emitted and deposited (Galloway et al. 2004). It is also believed to be an important fraction of both soil and water chemistry. For example, a UK wide study into water-soluble  $N_{\text{org}}$  found it made up between 24% and 40% of the wet deposition of nitrogen (Cape et al. 2004). The N in  $N_{\text{org}}$  is not readily available and must first be broken down into  $N_r$  compounds by microbial mineralization. Due to a lack of data, the anthropogenic quantification of  $N_{\text{org}}$  is currently not possible (Galloway et al. 2004).

#### 1.1.3.2 Nitrate

$\text{NO}_3^-$  can be deposited either dry deposited as an aerosol or wet deposited when the aerosol is washed out by precipitation. The  $\text{NO}_3^-$  aerosols, can be transported downwind from its source. As an important nutrient  $\text{NO}_3^-$  is often in demand and is required as a plant nutrient and in the first stage of heterotrophic denitrification (Eq. 1.4). As with  $\text{NH}_4^+$ , increased deposition of  $\text{NO}_3^-$  can lead to eutrophication and acidification of sensitive ecosystems, which may result in changes to species composition (Flechar et



al. 1998). It can also lead to an increase in  $\text{NO}_3^-$  leaching due to elevated levels in the soil.

## 1.2 Nitrogen, pollution and climate change

The nitrogen cycle is a complex but balanced process. However, in the last 150 years, the amount of anthropogenic  $\text{N}_r$  has increased by a factor of 12.5; from  $\sim 15 \text{ Tg N y}^{-1}$  in the 1860s, to  $\sim 140 \text{ Tg N y}^{-1}$  in the 1990s and  $\sim 187 \text{ Tg N y}^{-1}$  in 2005 (Galloway et al. 2004, Galloway et al. 2008, Sutton et al. 2011), threatening to disrupt this balance. Many of these nitrogen compounds being emitted can be health hazards in large quantities, and can also add to the problems of climate change and ecosystem destruction/alteration. Food production is responsible for approximately 70% of total N emissions (Nieder and Benbi 2008), the other main source being energy production.

By far the biggest impact on the availability of  $\text{N}_r$  has come from the development of the Haber-Bosch process. It was a breakthrough in crop production, enabling humans to fix nitrogen from the atmosphere into ammonia (Schlesinger 1997):



Approximately 86% of the  $\text{NH}_3$  produced was processed into fertilisers (Galloway et al. 2004), leading to a huge increase in the production of food and thus led to an explosion in the global population, which otherwise would not have been able to happen (Gruber and Galloway 2008). Prior to the 1930s, the only way to fertilise the ground was via natural fertilisers, such as manure, which resulted in the recycling of existing  $\text{N}_r$ . With a growing population there is a higher demand for food resulting in more intensive agriculture and the need for more fertiliser. It is believed that the Haber-Bosch process has resulted in an increase of the availability of  $\text{N}_r$  by  $\sim 100 \text{ Tg N y}^{-1}$ , and this figure is expected to increase to  $\sim 165 \text{ Tg N y}^{-1}$  by 2050 (Galloway et al. 2004).

Another growing source of anthropogenic  $\text{N}_r$  is biological nitrogen fixation (BNF). Whilst BNF is a natural process, the growth of leguminous plants, has increased considerably as a result of human intervention. For thousands of years crops such as soya beans, rice and cereals have been grown for food but in recent times the crop yield



has increased significantly to help feed the ever-growing population. Leguminous plants such as the soya bean, create  $N_r$  via a symbiotic relationship with *Rhizobia* which is able to fix N whereas rice paddies provide an optimal environment for N fixation by free-living cyanobacteria under anaerobic conditions (Galloway et al. 2004). It is believed that the amount of  $N_r$  created in this manner has increased from  $\sim 15 \text{ Tg N y}^{-1}$  in 1860s to  $\sim 31.5 \text{ Tg N y}^{-1}$  and will in future increase to  $\sim 50 \text{ Tg N yr}^{-1}$  by 2050 (Galloway et al. 2004).

As well as crop agriculture increasing, the amount of livestock being reared has also increased as a result of the population boom and increased meat consumption per person. Livestock, particularly intensive cattle and chicken farming are responsible for increased release of  $\text{NH}_3$  into the atmosphere from their manure, and through an increase in demand for animal feed.

Energy combustion involving the burning of fossil fuels results in  $N_r$  that has been trapped in long-term geological reservoirs to be released into the atmosphere. Some high-temperature processes may result in a small amount of atmosphere  $\text{N}_2$  being fixed. Up to  $20 \text{ Tg N y}^{-1}$  of N is emitted to the atmosphere as a result of energy combustion, mostly as NO (Vitousek et al. 1997) and increase in demand for energy and personal transport is likely to result in this figure rising. The increase of NO and  $\text{NO}_2$  as a result of pollution has led to an increase in the levels of ozone ( $\text{O}_3$ ) in the troposphere, which is a powerful greenhouse gas but can also adversely affect human and plant health. IPCC (2001) suggest that by 2050,  $38.8 \text{ Tg N y}^{-1}$  to  $94.9 \text{ Tg N y}^{-1}$  of  $N_r$  will be created as a result of fossil fuel combustion.

### 1.3 The Role of Nitrogen in Different Ecosystems

#### 1.3.1 Peatlands

Peatlands are unique ecosystems renowned for their harsh conditions. They are characterised by acidic soil, high water tables and poor oxygenation. These factors, along with low temperatures, slow down the decomposition of litter, leading to an accumulation of organic matter (Bragazza et al. 2007). It is believed that peatlands make up only 2-3% of the earth's surface but stores around one third of the world's carbon, making peatlands an import part of the global carbon story (Bragazza et al. 2007). Although carbon-rich, peatlands tend to be nutrient-poor; resulting in a specialist



plant species to be able to live in these conditions. Nitrogen (N) is often a limiting nutrient so plants present are adapted to low N conditions.

Peatlands are often divided into two main groups; ombrotrophic bogs and minerotrophic fens. Ombrotrophic bogs gain nutrients from atmospheric deposition only, resulting in the characteristic high acidity. In contrast, minerotrophic fens receive nutrients from groundwater as well as precipitation. Litter studies have shown that the litter from ombrotrophic peatlands decomposes at a slower rate than litter from minerotrophic peatlands. This is believed to be as a result of the presence of a larger proportion of vascular plants in minerotrophic peatlands as conditions tend to be more hospitable (Bragazza et al. 2007). N deposition by precipitation onto semi-natural peatlands tends to be small in most areas, ( $< 10 \text{ kg N ha}^{-1} \text{ y}^{-1}$ ) but the effects can be extensive (Phoenix et al. 2012). Typically, N deposited in precipitation exceeds N exported out in to stream water as drainage losses tend to be minimal (Hayden and Ross 2005). Most of the N deposited is inorganic with  $N_{\text{org}}$  representing small but significant proportion of the total N deposited. However, output fluxes of N in the stream water tend to have greater concentrations of  $N_{\text{org}}$  than inorganic N (Adamson et al. 1998). Low rainfall years are notable for producing high levels of  $\text{NO}_3^-$  in the soil and streams (Adamson et al. 1998). Removal of  $\text{NO}_3^-$  by denitrification is often the dominant process in peatlands due to their low redox potentials (Charman 2002). An increase in the availability of  $\text{NO}_3^-$  is likely to result in increased denitrification which may result in an increase in  $\text{N}_2\text{O}$  emissions, especially in acid soils (Skiba et al. 1998, Skiba et al. 2013).

An increase in nitrogen deposition in peatland settings may result in an overabundance of  $N_r$ , eventually resulting in “N saturation” and significant export of N out of the soil and into nearby streams (Adamson et al. 1998). It may also cause the species composition of peatland plants to be changed, and more vigorous N loving species may move in to take advantage of the surplus nitrogen (Pitcairn et al. 1995). Some studies have suggested that as an indirect effect of increased N deposition, microbial decomposition of litter may be speeded up (Bragazza et al. 2007), thus reducing the accumulation rate of the peat. Increased temperatures, evaporation rates and lower rainfall rates due to climate change will increase soil mineralisation rates, increasing gaseous emissions of N and C. These issues, along with the potentially higher temperatures as a result of global warming, could see a huge change in the dynamics of



peatlands and may result in the loss of a major carbon store, exacerbating the problem of climate change.

### 1.3.2 Grassland

Grasslands are dominated by grasses and other herbaceous plants with little natural tree or shrub cover (less than 10%). On a global scale, grasslands make up ~20% of the land mass (Di Marco 2005) and are typically used for grazing livestock. Grasslands are an important source of  $\text{N}_2\text{O}$  which is emitted as a result of nitrification and/or denitrification depending on factors such as soil temperature, soil wetness and N availability. The increase in the use of fertilisers has resulted in an increase in  $\text{N}_2\text{O}$  emissions and  $\text{NO}_3^-$  leaching adding to atmospheric and water pollution issues. Non-fertilised agricultural grasslands often contain clover to act as a natural N replenisher due to the N fixing ability of clover (Jaffe 1992).

### 1.3.3 Forests

Forested areas make up approximately 30% of the total global land mass (Nieder and Benbi 2008) and are characterised by the high density of trees present. Forests are scavengers of pollutants and N deposition rates underneath forests is usually larger than in open areas as a result of a larger canopy surface area (Fowler et al. 1989). They are also the largest natural source of NO emissions from soils (Pilegaard et al. 2006). Soils tend to be acidic and N limited due to a prevalence of N immobilisation in areas where N deposition is small. However, the current position of N in forested ecosystems is changing from N-limited to N-saturated as a result of increased  $\text{N}_r$  deposition (Pilegaard et al. 2006). The consequences of this may result in increased acidification as a result of increased nitrification, increased  $\text{NO}_3^-$  leaching, changes in ground vegetation and soil chemistry and increases in emissions of greenhouse gases to the atmosphere (Pilegaard et al. 2006).

### 1.3.4 Arable

Arable land is land used in crop production and is a major source of  $\text{N}_2\text{O}$  (Stolk et al. 2009). The cycle is dominated by fertilisation (input of N) and removal of biomass N (harvest and livestock). Emissions of NO,  $\text{N}_2\text{O}$  and/or  $\text{N}_2$  and leaching of  $\text{NO}_3^-$  can be large, depending on crop rotation, fertiliser application rates and timing, soil and meteorological conditions (Fowler et al. 2009).



## **2. Materials and Methods**

### **2.1 The Study Site**

Auchencorth Moss is an ombrotrophic peat bog located in south Scotland, approximately 18 km southwest of Edinburgh (National Grid Reference NT221562; lat. 55°47'30N; long. 03°14'20W; Fig. 2.1). It has been an active field site for the monitoring of trace gas and particle concentrations/fluxes by Centre for Ecology and Hydrology since 1995 and part of the site has been designated a Site of Special Scientific Interest (SSSI) by Scottish Natural Heritage. The volume of peat in the catchment is estimated to be ~50 million m<sup>3</sup>, with depths up to 5 m, and an average depth of 50 cm. The total peat coverage is ~1214 ha, of which approximately 170 ha is extracted (located 1.75 - 3.4 km W-SW of the monitoring station) (Mitchell and Mykura 1962, Dinsmore 2008). The site is used primarily for low intensity sheep grazing (less than one livestock unit km<sup>-2</sup>) and in 2009 a small herd of cows (15-20) also grazed on the site.

The Black Burn has a catchment area of approximately 335 ha and runs SW to NE of the CEH atmospheric monitoring station at Auchencorth. It drains into the river North Esk and is fed by numerous tributaries, including one which originates in the area of peat extraction. There are a number of overgrown ditches laid out in parallel which is evidence of the drainage activities of the 1900s and 1960s. The elevation of the catchment is approximately 250-300 m and the main soil type is Histosols (85% coverage); with Gleysol (9%), Humic Gleysol (3%) and Cambisols (3%) present mostly at the margins of the catchment (Billett et al. 2004).



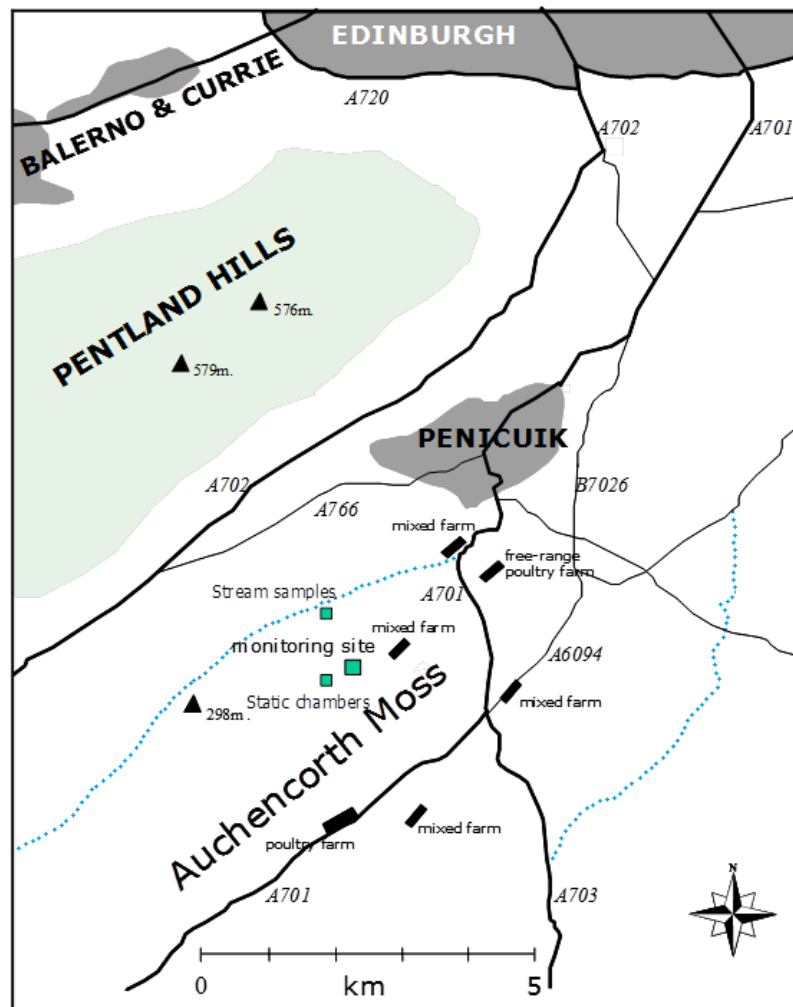


Figure 2.1. Schematic map of the sampling sites at Auchencorth Moss. The green squares indicate the location of the stream site, static chamber site and monitoring station. The black boxes indicate the location of surrounding farms and the blue dotted line indicates a stream.

### 2.1.1 Vegetation

The vegetation consists of numerous hummocks and hollows typically associated with a peatland setting. The hollows are depressions up to 30 cm deep and are dominated by blankets of *Sphagnum* mosses, with various sedges, monocotyledons and other bryophytes also present. The hummocks can be up to 30 cm high, although *Sphagnum* mosses are present, there is a larger density of vascular plants, with the dominant species being *Deschampsia flexuosa*, *Eriophorum vaginatum* and *Juncus effusus*. Further information with regards to vegetation at Auchencorth Moss can be found in Flechard and Fowler (1998) and Dinsmore (2008).



### 2.1.2 Meteorology

Temperature and precipitation data for the field site between January 2009 and December 2010 are shown in Figure 2.2. Precipitation was measured using a precipitation tipping bucket (Campbell instruments, UK) and air temperature was measured using a Humitter probe (Humitter 50YC, Vaisala Inst., USA). In 2009 the mean annual rainfall was 989 mm and the mean annual air temperature was 7.6 °C; in 2010 the mean annual rainfall was 649 mm and the mean annual air temperature was 6.6 °C. In 2010, a significant amount of snow fell, interfering with the tipping bucket, and resulting in no measurements for the months of January to the beginning of March. There was no precipitation at the end of March. It is estimated that an additional 423 mm of precipitation fell during this period, making the total precipitation for 2010 approximately 1072 mm. This additional precipitation was estimated from the ratio of discharge and precipitation, measured at the stream sampling site by the Black Burn (Fig 2.1) (Skiba et al. 2013).

Table 2.1 provides a summary of the metrological characteristics during the 2009-2010 study period.

Table 2.1. Summary of metrological parameters at Auchencorth Moss. Values were sourced from 2009-2010 data.

Mean air temperature	7.1 °C (-12.0 °C to 27.5 °C) <sup>a</sup> .
Annual Precipitation (mm)	1031
Mean peat depth (m)	0.5 (<0.5 m to 5 m)
Soil pH	4.5 (±0.2)
Stream pH	5.4 (±0.9)
Mean water temperature	8.2 °C (0.0 °C to 16.7 °C) <sup>b</sup> .
Water table depth	-14.8cm (-52.4 cm to 7 cm) <sup>c</sup> .
Mean stream discharge	51.5 L s <sup>-1</sup> (1.8 L s <sup>-1</sup> to 767.5 L s <sup>-1</sup> ) <sup>d</sup> .

a. Based on measurements collected every 30 min.

b. Based on measurements collected twice a month.

c. Based on measurements collected once–twice a month.

d. Based on daily means of measurements collected twice a month.



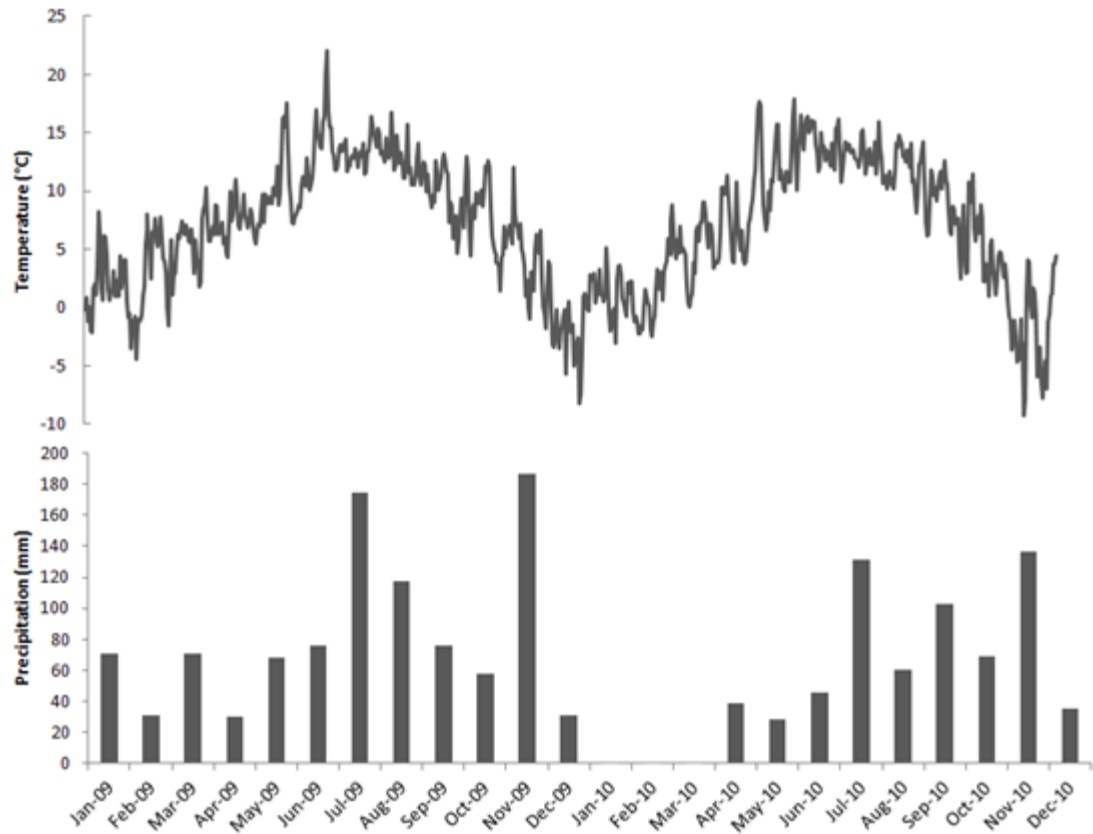


Figure 2.2. Graphs showing the mean daily air temperature (top) and monthly cumulative rainfall (bottom) for the period January 2009 – December 2010.

## 2.2 Methods

The methods used as part of this thesis are explained fully in papers I-III. Table 2.2 provides summaries of the variables studied and the methods used throughout this thesis.



Table 2.2. Summary of the variables measured and methods used as part of this thesis

Variable	Field Method	Laboratory Method	Paper		
			1	2	3
Precipitation $\text{NO}_3^-$ , $\text{NH}_4^+$ and total N	Wet only collector	Ion Chromatography (IC)/Nitrogen Specific HPLC detector (ANTEK)	x		
Stream $\text{NO}_3^-$ , $\text{NH}_4^+$ and total N	Sample from stream	IC/ANTEK	x		
Discharge/Stage height calibration	Dilution gauging	n/a	x		
Stage height	Pressure transducer/data logger	n/a	x		
Soil extractable $\text{NO}_3^-$ and $\text{NH}_4^+$	Sampling with soil auger	Extraction with KCl/analysis by IC	x		
Soil solution $\text{NO}_3^-$ and $\text{NH}_4^+$	Samples from dip wells	IC	x		
Speciation of DON	Wet only collector/sample from stream	Gas chromatography (GC×GC-NCD)	x		
Water table depth	Dip well	n/a: online analysis (flux modelled)	x		
$\text{NH}_3$ concentration and flux	AMANDA/MARGA	n/a: online analysis (flux modelled)		x	
$\text{NH}_3$ concentration	DELTA	Flow injection analysis ( $\text{NH}_3$ )/IC ( $\text{NO}_2^-$ , $\text{NO}_3^-$ , $\text{SO}_4^{2-}$ and $\text{Cl}^-$ ).		x	
$\text{NH}_3$ concentration	TAG	Flow injection analysis ( $\text{NH}_3$ )			
$\text{HNO}_3$ and HONO concentration and flux	MARGA	n/a: online analysis (flux modelled)		x	
Aerosols $\text{NO}_3^-$ and $\text{NH}_4^+$ concentration and flux	MARGA	n/a: online analysis (flux modelled)		x	



Table 2.2 continued. Summary of the variables measured and methods used as part of this thesis, continued

Variable	Field Method	Laboratory Method	Paper		
			1	2	3
Wind speed and direction	Ultrasonic anemometer	n/a		x	
Temperature and relative humidity	Humitter probe	n/a		x	
Net radiation	NRLite net radiometer	n/a		x	
Solar radiation	Pyranometer	n/a		x	
N <sub>2</sub> O flux	Static chambers	Gas chromatography			x
NO and NO <sub>2</sub> flux	Gradient tower				x



### 3. Aims and objectives

This study focuses on the N-cycle in a relatively unpolluted remote-rural peatland setting, called Auchencorth Moss. As an established long term field site, Auchencorth Moss has a variety of equipment already in place, measuring many of the components of the N-cycle. By looking at these past measurements, it was possible to identify gaps in N data collection and to identify the most important components of the overall export/import balance. The main aims and objectives of this study are outlined below:

1. The primary objective was to construct an updated, more comprehensive N-budget at Auchencorth Moss, and to assess whether the site is a net source or sink of N.
2. Since  $N_{\text{org}}$  is rarely measured at Auchencorth Moss, a special focus on dissolved organic nitrogen (DON) was made. As well as establishing the concentration and fluxes of DON, this study attempted to identify individual compounds of  $N_{\text{org}}$  in precipitation and stream water.
3. In order to establish fluxes of various nitrogen based inorganic aerosol and acidifying gases, inferential modelling was used to calculate fluxes from hourly concentrations of these compounds. Exchange parameterisations for  $\text{HNO}_3$ , HONO and the aerosol compounds were taken from the literature and earlier studies at the site, whilst a dynamic canopy compensation point model was used to estimate the  $\text{NH}_3$  fluxes, and the parameters updated using data derived from fluxes measured by the AMANDA gradient technique.
4. In order to establish if the rates of N deposition have changed over the last 14/15 years, fluxes of wet and dry deposition from the 1995 LIFE project (Fowler et al. 1996) were compared to the equivalent fluxes presented in this study.



#### **4. Paper 1: The import and export of organic nitrogen species at a Scottish moorland**

R.M. McKenzie, J.N. Cape, E. Nemitz, J. Drewer, M.Z. Özel, J.F. Hamilton, M.A. Sutton, M.W. Gallagher, U. Skiba.



# The import and export of organic nitrogen species at a Scottish moorland

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## Abstract

Precipitation, stream and soil water samples were collected from a moorland catchment and analysed for organic and inorganic nitrogen over a two year period. The results indicate dissolved organic nitrogen (DON) contributes up to 10.0% of the total dissolved nitrogen (TDN) in wet only deposition, 99.3% in soil water, and 74.6% in stream water. The stream DON results were consistent with results obtained elsewhere but the precipitation DON contributions were lower. No correlations were observed between precipitation and stream for dissolved inorganic nitrogen (DIN) or DON. In the precipitation samples, weak-moderate correlations were observed between ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ); but no correlation was found between DIN and DON. In the stream samples, no correlations were observed between  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  or DON.

Precipitation DIN showed a loose seasonal pattern, with peak concentrations occurring between January and June, with DON concentrations tending to be lower in the winter months. Stream water DON and  $\text{NH}_4^+$  showed no obvious seasonal pattern but  $\text{NO}_3^-$  showed larger concentrations in cooler months and the smallest during warmer months, with the exception of June and July 2010, where concentrations were high.

Precipitation and stream DON was analysed using GC×GC-NCD to try and identify individual compounds. 10 unique compounds were detected, of which 5 only could be identified: pyrrole, benzonitrile, dodecylamine, N-nitrosodipropylamine and decylamine. 5 compounds were present in both precipitation and stream samples: pyrrole, benzonitrile and unknown compounds B, E and F.

*Keywords: organic nitrogen, ammonium, nitrate, precipitation, stream, GC×GC-NCD*



## 4.1 Introduction

Atmospheric deposition of nitrogen (N) has increased dramatically over the last century as a result of industrial and agricultural activities (Galloway et al. 2004). In the last 150 years, the amount of global anthropogenic reactive nitrogen has increased by a factor of 12.5; from  $\sim 15 \text{ Tg N y}^{-1}$  in 1860 to  $\sim 187 \text{ Tg N y}^{-1}$  in 2005 (Galloway et al. 2008). The total deposition of N in the UK was estimated to be approximately 330 Gg (in 2004) with wet and cloud deposition accounting for approximately 211 Gg, (63.9%) with the rest consisting of dry deposition (Fowler et al. 2009, Hertel et al. 2011).

Altering the chemistry of precipitation inputs to ecosystems which are dependent on atmospheric deposition for nutrients, such as N, can disturb the way in which N is utilised. Problems such as N-saturation may result in N being leached from the soil and into nearby water bodies (Adamson et al. 1998). Eutrophication and acidification may occur in both terrestrial and aquatic ecosystems.

The wet deposition of the dissolved inorganic nitrogen (DIN) compounds ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) have been studied at length (Violaki et al. 2010, Cape et al. 2011, Zhang et al. 2012). The former is largely produced by the dissolution of  $\text{NH}_3$  and the scavenging of the  $\text{NH}_4^+$  aerosol and the latter by the dissolution of  $\text{HNO}_3$  in the troposphere (Russell et al. 1998, Cornell et al. 2003, Tian et al. 2011). The dissolved organic nitrogen (DON) fraction is less well documented due to difficulties in measuring it, but it can be an important fraction of the total dissolved nitrogen (TDN) deposited, and can potentially be biologically available as a source of N (Russell et al. 1998, Neff et al. 2002, Cornell et al. 2003, Cape et al. 2004). The sources of DON are not well understood, but it is known to be ubiquitous in the environment; present in particulate, gaseous and aqueous phases (Cornell et al. 2003, Cape et al. 2004, Özel et al. 2011). Studies have shown that it can contribute on average 30%, and up to 50%, of the wet deposition of water soluble N (Neff et al. 2002, Cape et al. 2004, Zhang et al. 2008, Cape et al. 2011, Cornell 2011, Zhang et al. 2012). Several atmospheric species of DON are considered hazardous to human health, and appear on the Environment Protection Agency (EPA) hazardous air pollutant list (Özel et al. 2011). Sources of DON are believed to include: pollen; sea spray; soil dust; deposits from fauna and flora; the scavenging of aerosols; and reactions in the atmosphere between inorganic gaseous nitrogen species and organic compounds (Prospero et al. 1996, Russell et al. 1998, Cornell et al. 2003, Calderon et al. 2007, Zhang et al. 2008, Violaki et al. 2010). Some work has been done to identify organic N compounds, so that their sources can be



traced. Amino acids, urea, aliphatic amines and peptides have all been found in the atmosphere and are from naturally occurring sources (Calderon et al. 2007, Violaki et al. 2010). The main anthropogenic organic compounds are believed to be N-heterocyclic compounds, nitro-phenols and nitro-polycyclic aromatic hydrocarbons (Violaki et al. 2010). Alky amides have also been identified and are believed to result from reactions between  $\text{NH}_3$  and fatty acids at high temperatures (Cheng et al. 2006) with photochemical reactions believed to be responsible for the presence of alky nitrates and peroxyacyl nitrates (Violaki et al. 2010).

As with wet deposition, N is present in streams as both DIN and DON, with most focus usually being on the DIN fraction. DIN, in particular  $\text{NO}_3^-$ , is often used as an indication of N saturation, with higher stream concentrations and changes in seasonal patterns usually indicating an increase in the leaching of DIN from the catchment (Cundill et al. 2007, Daniels et al. 2012). DON, on the other hand is not often measured in spite of being the most dominant fraction in waters draining peatland. DON is known to contribute 60-90% of TDN in peatland streams (Yesmin et al. 1995).

Various techniques have been developed to identify individual organic nitrogen compounds, but many are not sensitive enough to detect these compounds in low concentrations (Özel et al. 2010). Gas chromatography (GC) is one such technique. By using a multi-dimensional GC-technique and comprehensive two-dimensional GC, GC×GC, and coupling it with a nitrogen chemiluminescence detector (NCD), better separation and improved limits of detection can be achieved than by conventional one-dimensional GC (Özel et al. 2006, Adam et al. 2007, Adahchour et al. 2008, Özel et al. 2010). GC×GC-NCD has recently been used to investigate the presence of organic nitrogen compounds in diesel fuel, atmospheric aerosol, nitrosamines in meat and vegetables and nicotine and N-nitrosamines in house dust (Adam et al. 2007, Özel et al. 2010, Özel et al. 2011, Kocak et al. 2012, Ramirez et al. 2012).

The aim of this study was to investigate the contribution of DON to TDN of wet deposition and TDN export via a stream at a typical NW European acid moorland over a two year period. In addition to this, an attempt was made to identify individual DON compounds present in a selection of precipitation and stream samples.



## 4.2 Site and methods

### 4.2.1 Study area

Auchencorth Moss (Fig. 4.1) is an ombrotrophic peat bog located in south Scotland, approximately 18 km southwest of Edinburgh (National Grid Reference NT221562; lat. 55°47'34 N; long. 03°14'35 W). The site is used primarily for low intensity sheep grazing (less than one livestock unit km<sup>-2</sup>) and in 2009 a small herd of cows (15-20) also grazed on the site.

The volume of peat in the catchment is estimated to be ~50 million m<sup>3</sup>, with depths up to 5 m, and an average depth of 50 cm. The total peat coverage is ~1214 ha, of which approximately 170 ha is extracted (located 1.75 - 3.4 km W-SW of the monitoring station) (Mitchell and Mykura 1962, Dinsmore 2008).

The Black Burn runs SW to NE of the CEH atmospheric monitoring station at Auchencorth, and drains into the North Esk river. It has a catchment area of approximately 335 ha, which is fed by numerous tributaries, including one which originates in the area of peat extraction. There are a number of overgrown ditches laid out in parallel which is evidence of past drainage activities. The elevation of the catchment is approximately 250-300 m and the main soil type is Histosols (85% coverage); with Gleysol (9%), Humic Gleysol (3%) and Cambisols (3%) present mostly at the margins of the catchment (Billett et al. 2004).

The vegetation consists of numerous hummocks and hollows; the hollows are depressions up to 30 cm deep and are dominated by blankets of *Sphagnum* mosses, with various sedges, monocotyledons and other bryophytes also present; the hummocks can be up to 30 cm high, although *Sphagnum* mosses are present, there is a larger density of vascular plants, with the dominant species being *Deschampsia flexuosa*, *Eriophorum vaginatum* and *Juncus effusus*. Flechard and Fowler (1998) and Dinsmore (2008) have presented more detailed vegetation information for Auchencorth Moss.

The mean water table depth was determined from nine dip wells located close to the monitoring station (Fig. 4.1) and was -14.8 cm, ranging from -52.4 to 7 cm above the peat surface during the study period (January 2009 - December 2010).



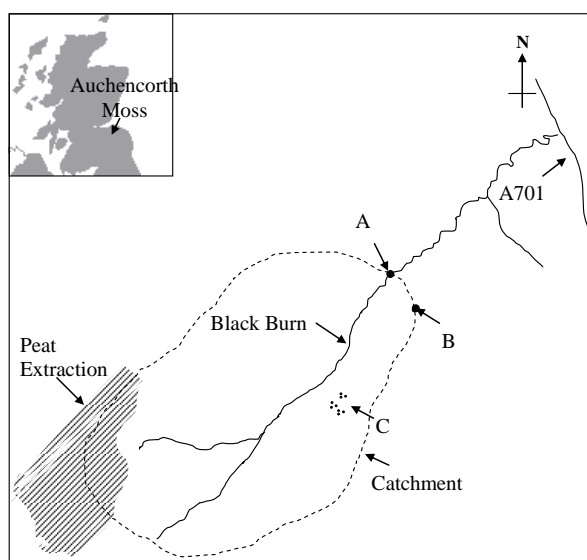


Figure 4.1: Schematic map of catchment and sampling sites at Auchencorth Moss. Key: (A) study catchment outlet and stream sampling site; (B) monitoring station (wet only analyser); (C) dip wells. Adapted from Dinsmore et al. (2010).

#### 4.2.2 Wet Only

Auchencorth Moss is an EMEP supersite contributing to the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe, [http://www.emep.int/index\\_facts.html](http://www.emep.int/index_facts.html)). Precipitation was collected daily using an automated wet-only collector (Eigenbrodt NSA 181/KS, Frankfurt, Germany). A sensor detected when rain fell, opening the lid and allowing rain to be collected in a PTFE-coated funnel draining to refrigerated polyethylene bottles. When rainfall ceased, the sensor closed the lid, protecting the samples from contamination from dry deposition and animal inputs. The collector was kept at 4°C by an internal cooling system and samples were manually emptied once a week, where they were stored in a cool room also at 4°C. Samples were analysed by Ion Chromatography (IC) for  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , following EMEP protocols (<http://www.nilu.no/projects/ccc/manual/index.html>).

A Metrohm 761 Compact Ion Chromatograph (IC) connected in parallel with a Metrohm 733 IC Separation Centre to a Metrohm 766 IC sample processor (Metrohm Ltd., Herisau, Switzerland) measured  $\text{NO}_3^-$  and  $\text{NH}_4^+$  respectively.  $\text{NO}_3^-$  was determined by pumping an eluent solution of 3.2 mM sodium carbonate and 1.0 mM sodium bicarbonate through a Metrosep A Supp 5 column. For  $\text{NH}_4^+$  determination, an eluent solution of 24 mM boric acid, 5 mM tartaric acid and 0.7 mM dipicolinic acid, was



pumped through a Metrosep C1 column. Typical detection limits were  $1 \mu\text{mol N l}^{-1}$  for both  $\text{NO}_3^-$  and  $\text{NH}_4^+$ .

For analysis of TDN ( $\text{TDN} = \text{DIN} + \text{DON}$ ) subsamples were obtained (a minimum of 5 ml) where possible, and filtered using Millipore Hydrophilic PTFE ( $0.45 \mu\text{m}$  pore size) syringe filters prior to freezing and later analysed for TDN by high-temperature catalytic oxidation using an ANTEK 8060-M Nitrogen Specific HPLC Detector (ANTEK Instruments Inc., Houston, TX, USA). The analysis was conducted in flow-injection mode, in which  $20 \mu\text{l}$  samples were introduced into an eluent stream of 10% methanol in deionised water at a flow rate of  $250 \mu\text{l min}^{-1}$ . It was then combusted in oxygen at  $1050^\circ\text{C}$ , producing nitric oxide (NO) which was detected by chemiluminescence. The detection limit for TDN was  $\sim 1 \mu\text{mol N l}^{-1}$ . DON was determined by subtracting DIN from TDN.

The subsamples were also analysed for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  at the same time DON was analysed and compared to the EMEP samples. The samples compared well with an average standard error of  $\pm 0.22 \mu\text{mol N l}^{-1}$  between  $\text{NO}_3^-$  samples and  $\pm 1.45 \mu\text{mol N l}^{-1}$  between  $\text{NH}_4^+$  samples. The analysis was carried out according to the IC description above.

DON is generally underestimated as a result of errors associated with measuring TDN and DIN compounding and thus reducing the accuracy of the DON calculation (Cornell et al. 2003). A negative bias may result from these combined uncertainties, from DON not being fully converted during the total N analysis, and from losses due to the collection and storage procedure (Russell et al. 1998, Cornell et al. 2003). Small negative values of DON were included in the data analyses in order to prevent this source of bias. The limit of detection of DON was determined by the summation of the detection limits of the 3 independent measured concentrations ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and TDN) and was  $3 \mu\text{mol N l}^{-1}$ .

#### 4.2.3 Soil water

Soil water was collected once or twice per month from nine dip wells, from which the water table was also measured. They were filtered within 24 hours of collection, using Millipore Hydrophilic PTFE ( $0.45 \mu\text{m}$  pore size) syringe filters and stored frozen until analysis. The dip wells consisted of high-density polyethylene perforated pipes ( $0.04 \text{ m}$  diameter) buried in the ground, with rubber bungs to prevent contamination. Samples



were analysed for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and TDN by the IC and ANTEK methods described previously. DON was determined by subtracting DIN from TDN.

#### 4.2.4 KCl-extractable mineral N

Soil cores were collected at a depth of 0-10 cm at three locations (next to the dip wells), in spring and autumn in 2009 and in spring, summer and winter in 2010.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were extracted from soil samples using KCl; 15 g of soil were shaken for 1 hour with 50 ml of 1M KCl solution at a rate of 100 rpm. Samples were then filtered using Whatman 42 filter papers and frozen prior to analysis by IC. TDN was not measured, so DON could not be determined.

#### 4.2.5 Stream water

Stream water was collected using a 300 ml glass bottle once a week from the Black Burn, to the north of the field station. The samples were filtered within 24 hours of collection, using Millipore Hydrophilic PTFE (0.45 $\mu\text{m}$  pore size) syringe filters and frozen until ready for analysis. Samples collected from January 2009 – October 2009 were analysed for TDN,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  using a San<sup>++</sup> Automated Wet Chemistry Analyzer/Continuous Flow Analyzer (SKALAR, The Netherlands). Samples from November 2009-November 2010 were analysed for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and TDN using the IC and ANTEK methods described above. In both cases, DON was determined by subtracting DIN from TDN.

Discharge was determined from water height using manually calibrated rating curves ( $R^2 > 0.90$ ) based on measurements of dilution gauging (Dinsmore, per. com.). Pressure transducers were used to measure water height at 10 minute intervals. Until April 2009, a Druck PDCR 1830 series pressure transducer was used at the sample site (Fig. 4.1). After April 2009, an In Situ Inc. Level Troll® pressure transducer located ~2 km downstream was used.

#### 4.2.6 GC×GC-NCD

Comprehensive two-dimensional gas chromatography coupled to a nitrogen chemiluminescence detector (GC×GC-NCD) was used to separate DON into different peaks and identify individual components where possible. The samples were cleaned by solid phase extraction (SPE) in order to trap the DON using Superclean ENVI-18 SPE tube 20  $\mu\text{m}$  polymeric  $\text{C}_{18}$ -reverse phase 500 mg-3 ml SPE cartridges (SUPELCO, Bellefonte, PA, USA). Cartridges were conditioned with 5 ml methanol followed by 5



ml of water at a rate of 2-5 ml min<sup>-1</sup>. The sample was then passed through the cartridge at a rate of 2-5 ml min<sup>-1</sup>. The cartridge was thoroughly dried under vacuum for ~30 minutes. Following drying, the cartridge was eluted with 5 ml dichloromethane (DCM), and then concentrated in a stream of nitrogen to a volume of ~ 0.1 ml. The GC×GC-NCD was an Agilent 7890 GC coupled with an Agilent 255 NCD (Agilent Technologies, Palo Alto, CA, USA). 1 µl extracts were injected in pulsed splitless mode at a temperature of 280 °C and a pressure of 30 psi for 2 min, using a Gerstel automated liquid injector (Gerstel, Mulheim an der Ruhr, Germany). The first dimension column was a non-polar BPX5 (30 m x 0.32 mm i.d. x 0.25 µm film thicknesses), set to an initial temperature of 55°C for 1 min. The temperature was then increased at a rate of 5°C min<sup>-1</sup> until 305°C where it was isothermally held for 1 min. The second column was a BPX50 (1.5 m x 0.10 mm i.d. x 0.10 µm film thickness) set to an initial temperature of 70°C for 1 min, the temperature was then increased at a rate of 5 °C min<sup>-1</sup> until 320°C where it was isothermally held for 1 min. Both columns were from SGE Analytical Science (VIC, Australia). Helium was used as a carrier gas at a constant flow of 1 mL min<sup>-1</sup> and the data was collected at 50 Hz. Pyrolysis was carried out at 900°C under hydrogen flow rate of 4 ml min<sup>-1</sup> and oxygen flow rate of 10 ml min<sup>-1</sup>.

The detector shows an equimolar response regardless of the chemical state of the organic nitrogen (except azo compounds), allowing nitrogen-containing compounds to be quantified without the need for a separate calibration standard for each compound (Yan 2002, Özel et al. 2011). Details of the optimization of the NCD response and the analytical performance with respect to equimolar response using standards was evaluated by Özel et al. (2011).

### **4.3 Results**

#### **4.3.1 Meteorology**

Total rainfall was determined from the volume of rain collected in the wet only analyser. In 2009 the total rainfall was 902 mm with monthly totals varying from 16 mm in February to 180 mm in November. The mean monthly temperature varied from 0.5 °C in December to 13.7 °C in July, with a yearly mean of 7.6 °C. In 2010 the total rainfall was 732 mm with monthly totals varying from 21 mm in May to 128 mm in November. However, in 2010 a significant amount of snow fell, interfering with the wet-only collector and resulting in less precipitation collection during January-March. It is estimated that 423 mm of precipitation fell during these months (an additional 291



mm), making the total precipitation collected for 2010 approximately 1023 mm. This additional precipitation was estimated from the ratio of discharge and precipitation, measured at the stream sampling site by the Black Burn (Fig 4.2.) (Skiba et al. 2013). The mean monthly temperature varied from -2.0 °C in December to 13.6 °C in July, with a yearly mean of 6.6 °C

No correlation was observed between rainfall or temperature and DIN or DON in the stream, precipitation or dip wells. Correlations were tested using Pearson's correlation coefficient.

#### 4.3.2 Wet-only N deposition

Figure 4.2 shows the volume-weighted monthly mean concentrations of N in precipitation. The temporal variation of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  follow a similar pattern, with DON differing. In both 2009 and 2010 (Table 4.1),  $\text{NH}_4^+$  was the dominant component of wet only deposition with an annual mean deposition of 27.2  $\mu\text{mol N l}^{-1}$  (58%) and 30.7  $\mu\text{mol N l}^{-1}$  (53%) respectively. The contribution of  $\text{NO}_3^-$  was greater in 2010 than in 2009, with mean concentrations of 15.0  $\mu\text{mol N l}^{-1}$  (32%) in 2009 and 22.7  $\mu\text{mol N l}^{-1}$  (39%) in 2010. Although DON contributed the least to annual concentrations in both years, on a monthly timescale, there were a few occasions when DON exceeded  $\text{NO}_3^-$  (March-09, June-09, Aug 09 and Oct 10). A loose seasonal pattern can be observed for  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , with peak concentrations occurring between January and June. This is more obvious in 2010. DON has no clear seasonal pattern, although the lowest concentrations seem to occur in the winter months (Nov- Jan). A weak, but significant correlation was found between  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in 2009 ( $R^2 = 0.45$ ,  $p = 0.000$ ). In 2010, a stronger correlation between  $\text{NH}_4^+$  and  $\text{NO}_3^-$  was also observed ( $R^2 = 0.62$ ,  $p = 0.000$ ). No correlations were observed between  $\text{NH}_4^+$ , DON, temperature or precipitation;  $\text{NO}_3^-$ , DON, temperature or precipitation or DON, temperature or precipitation. Correlations were tested using Pearson's correlation coefficient.



Table 4.1. Statistics of annual concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , DON and TDN for 2009 and 2010 in wet only precipitation. Values are based on individual samples collected over the two year period. N\* indicates the number of samples collected.

	$\text{NO}_3^-$ $\mu\text{mol N l}^{-1}$	$\text{NH}_4^+$ $\mu\text{mol N l}^{-1}$	DON $\mu\text{mol N l}^{-1}$	TDN $\mu\text{mol N l}^{-1}$
<u>2009</u>				
Mean	15.0	27.2	4.7	46.9
Min	0.8	0.7	-1.6	5.7
Max	148.4	273.4	49.8	426.2
Standard deviation	20.5	34.5	3.6	49.6
N*	227	227	63	63
% TDN	31.9	58.1	10.0	100
<u>2010</u>				
Mean	22.7	30.7	4.8	58.3
Min	2.2	2.4	-2.5	8.7
Max	259.9	218.0	45.4	482.6
Standard deviation	29.9	32.8	4.6	59.0
N*	169	169	63	63
% TDN	38.9	52.8	8.3	100

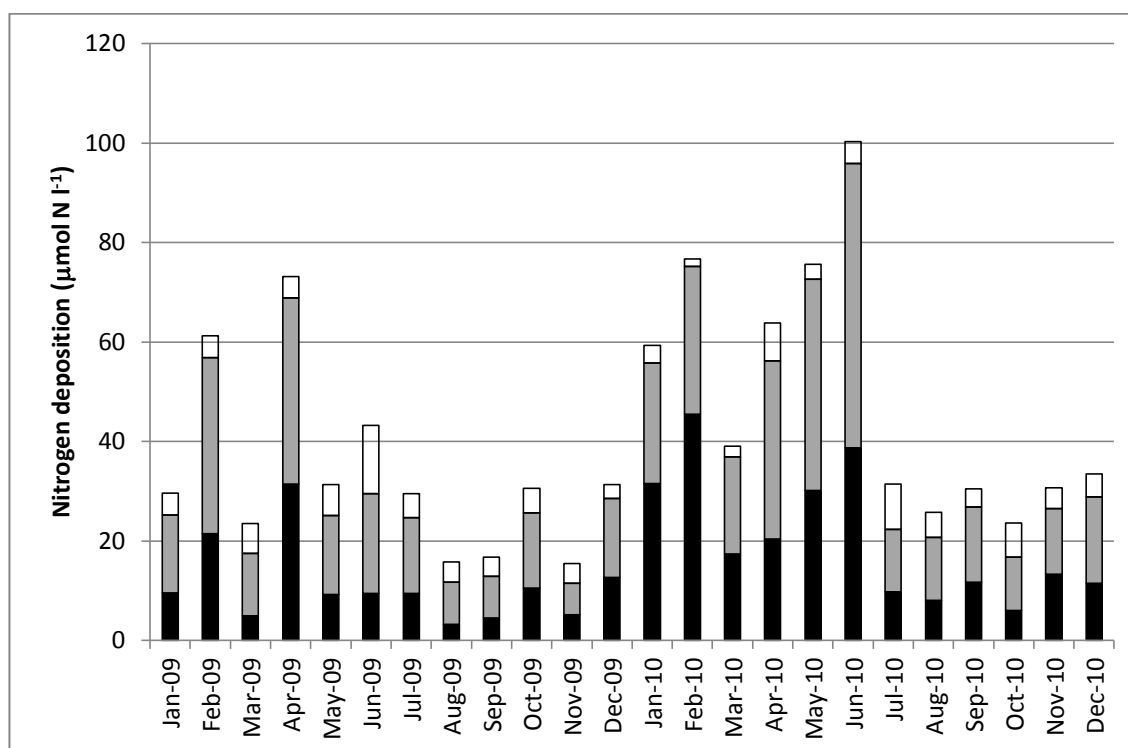


Figure 4.2. Volume-weighted monthly average concentrations of  $\text{NH}_4^+$  (grey),  $\text{NO}_3^-$  (black) and DON (white) in wet only precipitation.



#### 4.3.3 Soil water and KCl-extractable N

Due to gaps in the data, caused by the dip wells being dry and thus no sample to be collected, it is difficult to assess seasonal patterns. From the data available, it appears that DON concentrations were larger in the warmer months compared to cooler months (November to March) and that peak concentration for DON occurred in September in both years (Fig. 4.3). The contribution of DON to TDN was higher in 2010 at 99.3% compared to 85.4% in 2009 (Table 4.3).  $\text{NH}_4^+$  and  $\text{NO}_3^-$  followed similar patterns, with concentrations in 2009 appearing to increase in the spring, peaking in August. In 2010, both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations generally remained low, with much smaller peak occurring in July.  $\text{NO}_3^-$  mean annual concentrations were  $1.2 \mu\text{mol N l}^{-1}$  (1.8% of TDN) in 2009 and  $0.2 \mu\text{mol N l}^{-1}$  (0.3% of TDN) in 2010.  $\text{NH}_4^+$  mean annual concentrations were also larger in 2009, than 2010;  $8.6 \mu\text{mol N l}^{-1}$  compared to  $0.2 \mu\text{mol N l}^{-1}$ . The contribution of  $\text{NH}_4^+$  to TDN was thus much larger in 2009 at 12.8% and just 0.4% in 2010.

Soil extractions from 2 samples in 2009 and 3 samples in 2010 found no detectable  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  concentrations of  $28.8 \pm 11.9 \mu\text{mol N l}^{-1}$  and  $38.5 \pm 20.0 \mu\text{mol N l}^{-1}$  for 2009 and 2010, respectively.



Table 4.2. Statistics of annual concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , DON and TDN for 2009 and 2010 in soil water. Values are based on individual samples collected over the two year period.  $N^*$  indicates the number of samples collected.

	$\text{NO}_3^-$ $\mu\text{mol N l}^{-1}$	$\text{NH}_4^+$ $\mu\text{mol N l}^{-1}$	DON $\mu\text{mol N l}^{-1}$	TDN $\mu\text{mol N l}^{-1}$
<u>2009</u>				
Mean	1.2	8.6	57.3	67.1
Min	0.0	0.0	10.7	10.7
Max	5.8	91.2	318.7	388.8
Median	0.0	0.6	47.6	53.6
Standard deviation	1.9	14.9	44.1	54.4
$N^*$	72	72	72	72
% of TDN	1.8	12.8	85.4	100
<u>2010</u>				
Mean	0.2	0.2	59.2	59.6
Min	0.0	0.0	22.5	22.5
Max	8.3	7.1	284.5	284.5
Median	0.0	0.0	43.8	43.8
Standard deviation	1.1	1.2	43.1	43.2
$N^*$	54	54	45	45
% of TDN	0.3	0.4	99.3	100

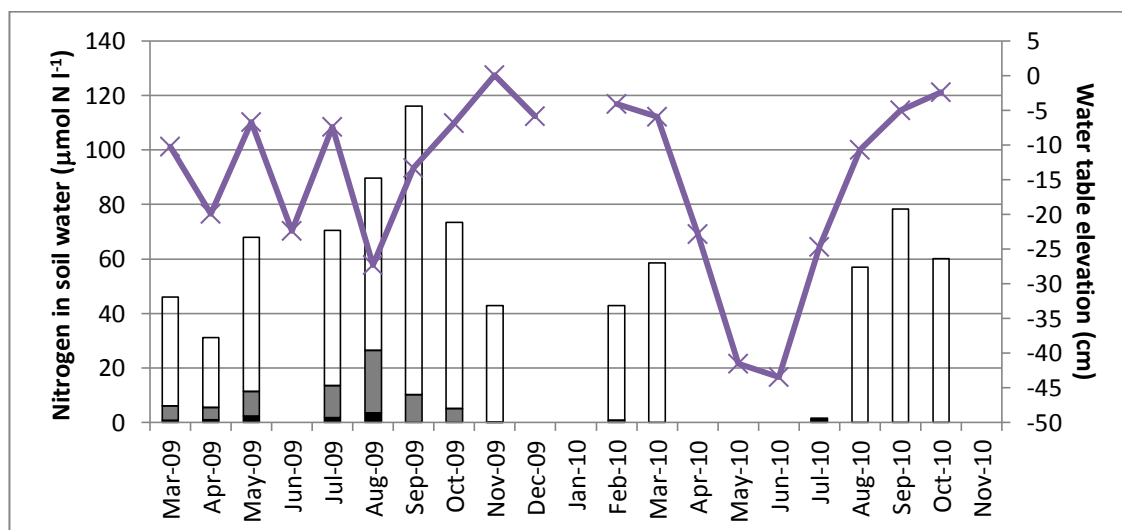


Figure 4.3. Monthly concentrations of  $\text{NH}_4^+$  (grey),  $\text{NO}_3^-$  (black) and DON (white) in soil water. The line represents monthly water table elevation. A blank space indicates the dip wells were dry (Dec 2009 was frozen) on the day of collection.

#### 4.3.4 Concentration and forms of N in stream water

Monthly mean discharge-weighted concentrations of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and DON are presented in Figure 4.4, and a basic statistical analysis of annual stream water chemistry is presented in Table 4.3. DON is the dominant N species found in the stream water,



with the highest concentrations tending to appear in the summer/autumn months, but in general there was no clear seasonal pattern. Monthly mean DON concentrations ranged from 9.8 to 96.4  $\mu\text{mol N l}^{-1}$  in 2009 and 15.5 to 104.2  $\mu\text{mol N l}^{-1}$  in 2010. Annual mean concentrations were 48.1  $\mu\text{mol N l}^{-1}$  in 2009 and 50.0  $\mu\text{mol N l}^{-1}$  in 2010, contributing, on average, 74.6% and 74.3% of TDN.

Monthly mean concentrations of  $\text{NO}_3^-$  ranged from 0.0 to 13.7  $\mu\text{mol N l}^{-1}$  in 2009 and 0.0 to 15.2  $\mu\text{mol N l}^{-1}$  in 2010. Annual mean concentrations were 2.3  $\mu\text{mol N l}^{-1}$  in 2009 and 4.5  $\mu\text{mol N l}^{-1}$  in 2010. In 2009, concentrations varied seasonally; largest  $\text{NO}_3^-$  concentrations were measured during the cooler months and the smallest during the warmer months. In summer 2009 there was no detectable  $\text{NO}_3^-$ . In 2010 stream water  $\text{NO}_3^-$  concentrations initially followed a similar pattern as in 2009, with concentrations increasing during the winter months and decreasing as temperature increased and summer approached. However, there was a large increase in  $\text{NO}_3^-$  concentrations in June and July 2010. Consequently average annual  $\text{NO}_3^-$  concentrations in 2010 were nearly double of those in 2009, contributing 6.6% of TDN compared to 3.6% of TDN (Table 4.3). Monthly median concentrations for  $\text{NO}_3^-$  for the whole period showed a similar pattern to monthly discharge-weighted mean concentrations, with the exception of June 2010, which is reduced to a summer low of 0  $\mu\text{mol N l}^{-1}$ , suggesting the monthly mean value was skewed by an unusually large value. Median concentrations made little difference to the July 2010 maximum. July 2010 also showed a maximum in the mean concentrations of DON and  $\text{NH}_4^+$ .

Monthly mean concentrations of  $\text{NH}_4^+$  ranged from 5.4 to 21.9  $\mu\text{mol N l}^{-1}$  with an annual mean of 14.1  $\mu\text{mol N l}^{-1}$  in 2009, and 0.0 to 52.3  $\mu\text{mol N l}^{-1}$  with an annual mean of 12.9  $\mu\text{mol N l}^{-1}$  in 2010. Concentrations of  $\text{NH}_4^+$  are consistently higher than  $\text{NO}_3^-$  and there is no clear seasonal pattern. No correlation was observed between  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , DON, discharge, temperature (both air and stream) or precipitation. Correlations were tested using Pearson's correlation coefficient.



Table 4.3. Statistics of annual concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , DON and TDN for 2009 and 2010 in stream water. Values are based on individual samples collected over the two year period. N\* indicates the number of samples collected.

	$\text{NO}_3^-$ $\mu\text{mol N l}^{-1}$	$\text{NH}_4^+$ $\mu\text{mol N l}^{-1}$	DON $\mu\text{mol N l}^{-1}$	TDN $\mu\text{mol N l}^{-1}$
<u>2009</u>				
Mean	2.3	14.1	48.1	64.5
Min	0.0	5.4	9.8	24.8
Max	13.7	21.9	96.4	118.2
Median	0.0	14.3	46.7	64.4
Standard deviation	3.6	2.8	20.5	21.3
N*	43	43	43	43
% of TDN	3.6	21.9	74.6	100
<u>2010</u>				
Mean	4.5	12.9	50.0	67.4
Min	0.0	0.0	15.5	15.5
Max	15.2	52.3	104.2	144.8
Median	4.1	7.9	46.0	58.6
Standard deviation	3.6	13.8	20.4	30.9
N*	48	48	48	48
% of TDN	6.6	19.1	74.3	100

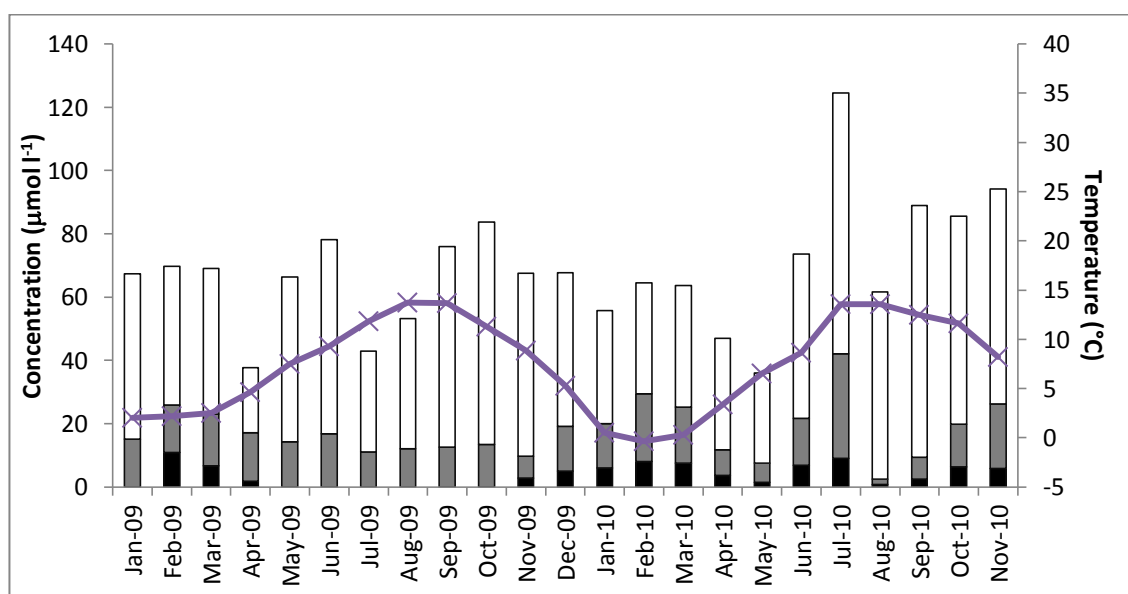


Figure 4.4. Discharge weighted monthly mean concentrations of  $\text{NH}_4^+$  (grey),  $\text{NO}_3^-$  (black) and DON (white) in stream water. The line represents mean monthly air temperature.



#### 4.3.5 DON speciation by GC×GC-NCD

Tables 4.4 and 4.5 display breakdowns of the individual DON compounds detected by the GC×GC-NCD and their concentrations for precipitation and stream water, respectively. The plasticiser N-butyl-benzenesulphonamide (not included in tables) was a prominent compound in all samples, with extremely high concentrations, sometimes higher than TDN detected in the precipitation by ANTEK. We assumed that the N-butyl-benzenesulphonamide detected was most likely to be a contaminant. The source of this contamination is currently being investigated and the compound was thus excluded from the results.

In 13 of the 31 precipitation samples, and 2 of the 21 stream samples no compounds were detected or the peaks were too small to be distinguishable from background noise. The limit of detection (LOD) using the optimized method has been determined between 0.16-0.27 pgN using GC×GC-NCD (Özel et al. 2011).

Peak identification was carried out by comparing the two retention times (rt1 and rt2) of the peaks observed in the samples, with the retention times of known standards. This resulted in an unavoidable margin of error for identification, although co-elution is greatly reduced using GC×GC. There were several peaks, consistently present in some samples, that could not be identified as they did not match any of the retention times of standards already run, so have been labelled “Unknown” A-F. In total 10 unique compounds were found to be present in the stream and precipitation, of which only 5 could be identified. Tables 4.4 and 4.5 present a summary of the compounds identified in precipitation and stream water DON, respectively. Both the precipitation and the stream water contained 8 distinct compounds, 5 of which were in common.

The most common compound identified in the precipitation samples was Unknown E, present in 10 samples, followed by Unknown D in 6 samples and Unknown B in 5 samples, with mean concentrations of  $0.3 \mu\text{mol N l}^{-1}$ ,  $0.14 \mu\text{mol N l}^{-1}$  and  $0.2 \mu\text{mol N l}^{-1}$ , respectively assuming an equimolar response and 100 % recovery during SPE. Two precipitation samples contained pyrrole, with a mean concentration of  $0.03 \mu\text{mol N l}^{-1}$ . Unknown F was in 3 samples (mean concentrations of  $0.1 \mu\text{mol N l}^{-1}$ ), dodecylamine was in 2 samples (mean concentration of  $0.02 \mu\text{mol N l}^{-1}$ ), and Unknown C was in one sample (concentration of  $0.02 \mu\text{mol N l}^{-1}$ ). The precipitation samples did not contain any Unknown A, N-nitrosodipropylamine or decylamine, which were found in the stream samples.



The most common compound identified in the stream samples was Unknown A, the mean concentration was  $2.0 \mu\text{mol N l}^{-1}$  (Table 4.5). Pyrrole was the next most common compound, found in 18 of the stream samples, with a mean concentration of  $1.2 \mu\text{mol N l}^{-1}$ . Unknown E and F both appeared in 9 stream samples, with mean concentrations of  $0.5 \mu\text{mol N l}^{-1}$  and  $0.4 \mu\text{mol N l}^{-1}$ . N-nitrosodipropylamine (NDPA) is present in 4 stream samples, followed by Unknown B and Decylamine in 3 stream samples. Mean concentrations were  $0.2 \mu\text{mol N l}^{-1}$  for all three compounds. Unknown D, Unknown C and dodecylamine, which were found in the precipitation samples, were not present in the stream samples.

In both the stream and precipitation samples, only 1 sample contained benzonitrile, with means of  $0.01 \mu\text{mol N l}^{-1}$  (precipitation) and  $0.1 \mu\text{mol N l}^{-1}$  (stream).

Figures 4.5a and 4.6a display breakdowns of the monthly means of individual DON compounds detected by the GC×GC-NCD and the remaining DON detected by ANTEK for precipitation and stream water, respectively. Figures 4.5b and 4.6b show the monthly means of individual DON compounds detected by the GC×GC-NCD only, to make this fraction more visible. In both cases, the majority of DON was “other”, contributing a mean of 85.8% and 92.3% of total DON detected in precipitation and stream water, respectively. This represents the DON not detected by the GC×GC-NCD, but was measured by ANTEK. This indicates that the GC×GC-NCD was only able to speciate a small fraction of the DON present. This is likely to be in part a result of losses of highly polar DON compounds during the SPE step and large molecular weight species that are not volatile enough to be analysed by GC. In the precipitation samples, Unknown E is the only compound present in all 5 sampling months, and is the only compound identified in September. October had the most number of the identified compounds present, with 6 of the 8 compounds measured (Fig. 4.5b). In the stream samples, pyrrole and Unknown A are present in all 4 sampling months. October also had the most number of the identified compounds present, with 7 of the 8 compounds present (Fig. 4.4).



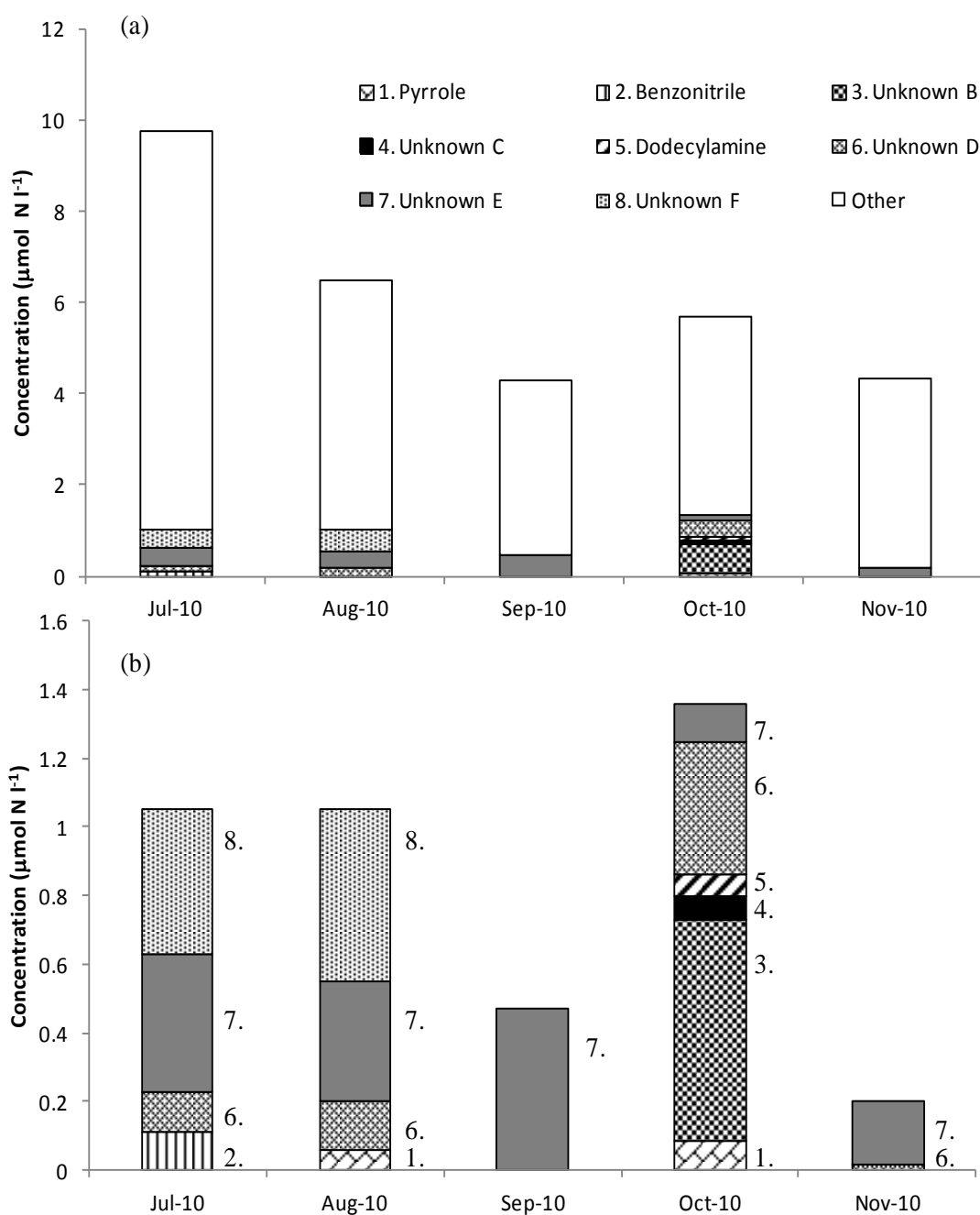


Figure 4.5. Mean monthly concentrations of the individual compounds found in precipitation water. (a) includes the fraction identified by ANTEK but not GCxGC-NCD (white bar). (b) Excludes the fraction identified by ANTEK so the speciation achieved by GCxGC-NCD is more clearly seen.



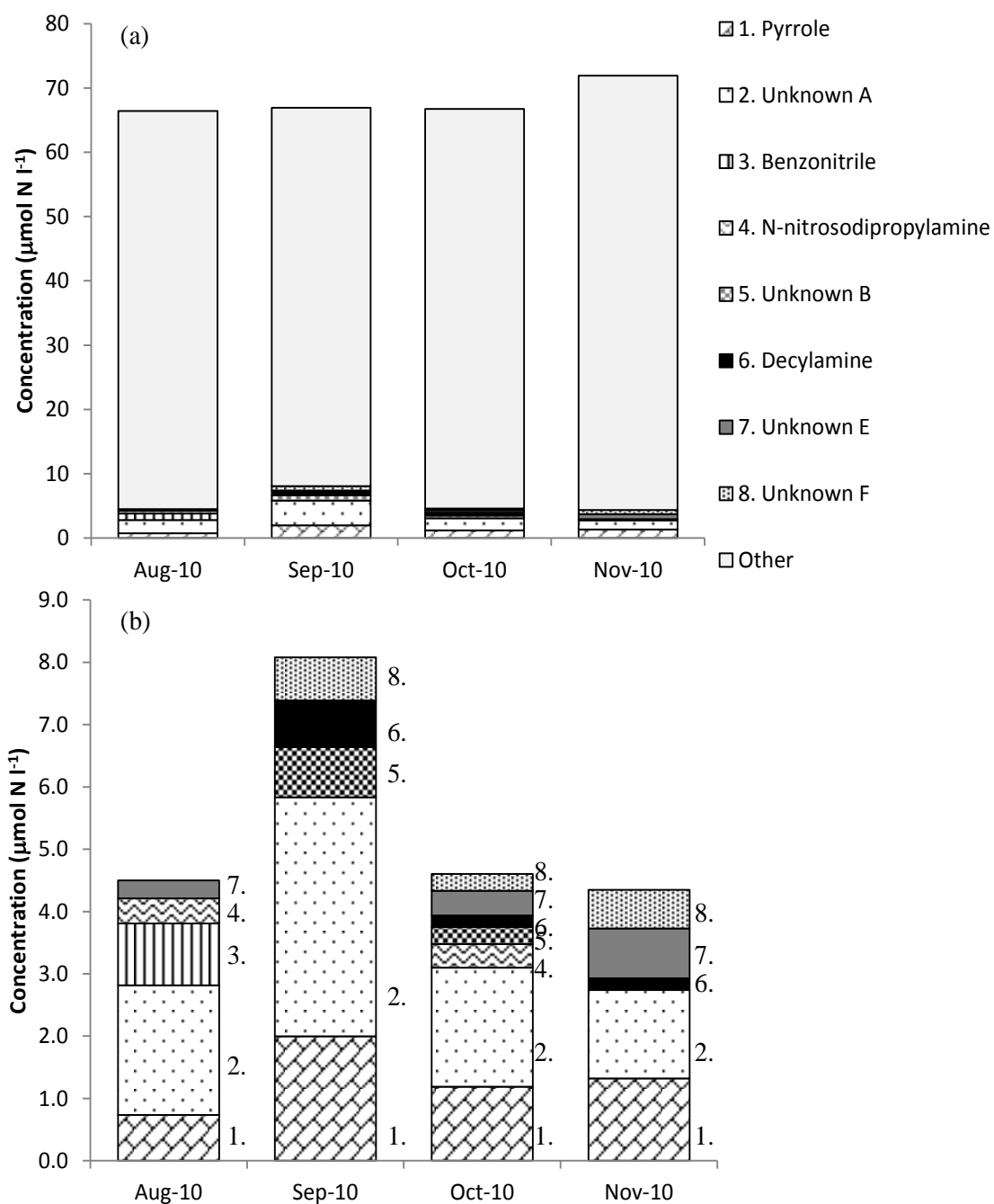


Figure 4.6. Mean monthly concentrations of the individual compounds found in stream water. (a) includes the fraction identified by ANTEK but not GCxGC-NCD. (b) Excludes the fraction identified by ANTEK so the fraction detected by GCxGC-NCD is more clearly seen.



Table 4.4. Summary of compounds and their concentrations ( $\mu\text{mol N l}^{-1}$ ) detected by the GC $\times$ GC-NCD, and DON concentrations ( $\mu\text{mol N l}^{-1}$ ) detected by ANTEK in precipitation samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the GC $\times$ GC-NCD. Blank spaces indicate a measured value below the detection limit.

Sample rt1/rt2	DON (ANTEK)	Pyrrole 375/1.24	Benzonitrile 825/1.8	Unknown B 11.45/1.52	Unknown C 1218/1.48	Dodecylamine 1590/1.5	Unknown D 1615/1.7	Unknown E 1910/1.7	Unknown F 2200/2.09
09/07/2010	9.2							1.6	1.7
13/07/2010	13.8		0.4				0.5		
14/07/2010	6.5								
15/07/2010	5.5								
09/08/2010	9.4						0.6		1.8
12/08/2010	6.5							0.3	0.3
20/08/2010	3.5	0.2						0.6	
23/08/2010	2.4							0.5	
06/09/2010	3.1							1.9	
13/09/2010	3.2								
14/09/2010	5.8								
18/09/2010	3.3								
01/10/2010	0.5								
05/10/2010	1.0	0.7		2.0					
06/10/2010	-2.4								
18/10/2010	2.1			0.7			0.7		
21/10/2010	19.8			1.3		0.5	2.4		
24/10/2010	7.1			1.2					
25/10/2010	1.2			0.5		0.7	1.8		



Table 4.4. continued. Summary of compounds and their concentrations ( $\mu\text{mol N l}^{-1}$ ) detected by the GC $\times$ GC-NCD, and DON concentrations ( $\mu\text{mol N l}^{-1}$ ) detected by ANTEK in precipitation samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the GC $\times$ GC-NCD. Blank spaces indicate a measured value below the detection limit.

Sample rt1/rt2	DON (ANTEK)	Pyrrole 375/1.24	Benzonitrile 825/1.8	Unknown B 11.45/1.52	Unknown C 1218/1.48	Dodecylamine 1590/1.5	Unknown D 1615/1.7	Unknown E 1910/1.7	Unknown F 2200/2.09
26/10/2010	5.8				0.5			0.9	
01/11/2010	3.9								
02/11/2010	7.0						0.1		
03/11/2010	5.1							0.4	
04/11/2010	2.9								
05/11/2010	3.9								
06/11/2010	4.6								
08/11/2010	9.9							0.4	
09/11/2010	-2.4								
10/11/2010	-0.2								
11/11/2010	5.0							0.7	
13/11/2010	6.1							0.6	



Table 4.5. Summary of compounds and their concentrations ( $\mu\text{mol N l}^{-1}$ ) detected by the GC×GC-NCD, and DON concentrations ( $\mu\text{mol N l}^{-1}$ ) detected by ANTEK in stream water samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the GC×GC-NCD. Blank spaces indicate a measured value of below the detection limit.

Sample rt1/rt2	DON (ANTEK)	Pyrrole 375/1.24	Unknown A 415/1.24	Benzonitrile 825/1.8	N-nitrosodipropylamine 970/1.4	Unknown B 11.45/1.52	Decylamine 1295/1.64	Unknown E 1910/1.7	Unknown F 2200/2.09
11/08/2010	45.9	1.3	3.2					0.9	
19/08/2010	54.8	0.2	0.3		1.2				
26/08/2010	85.2	0.7	2.7	3.0					
10/09/2010	30.5	0.2	0.8			1.6			1.4
30/09/2010	87.2	3.8	6.9				1.5		
06/10/2010	57.8	5.0	3.9				1.8		
12/10/2010	69.4	0.8	2.1			1.4			
14/10/2010	60.1		0.7			1.3			
15/10/2010	49.1								
18/10/2010	46.1	1.8	3.4						
19/10/2010	75.0		1.4		1.3			1.0	0.8
21/10/2010	58.2	2.3	4.0						
23/10/2010	65.9	0.3	1.9		0.7			1.2	0.5
26/10/2010	56.5	1.0							0.9
28/10/2010	57.6	0.7	1.8		1.7			1.8	0.6
02/11/2010	61.5	0.6	2.3					1.9	1.0
03/11/2010	69.5	2.5	3.4					0.4	
04/11/2010	79.4	0.6	0.6					0.4	0.7
05/11/2010	58.9								
10/11/2010	70.7		0.5					0.5	0.4
11/11/2010	65.6	4.3	1.8				1.1	1.6	1.7



## 4.4 Discussion

### 4.4.1 The composition of N in precipitation

Cape et al. (2004) studied several sites in the UK on a range of land uses and noted an annual cycle for DIN and DON, with peak concentrations for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  occurring in the late spring (April-June 2000-2002) and a DON peak occurring in late summer (June-August 2000-2002). Both DIN and DON showed minima in winter. The data presented here is similar, but with earlier DIN maxima in early spring (Feb-April in 2009 and Feb-June 2010) followed by lower values in the autumn and beginning of winter. DON also peaked earlier than reported by Cape et al. (2004) but roughly a month after DIN peaks in both 2009 and 2010. Generally, sources of  $\text{NH}_4^+$  in precipitation tend to be agricultural in origin and sources of  $\text{NO}_3^-$  in precipitation from combustion activities (Cape et al. 2011). Although Auchencorth Moss is located in a rural setting and with minimal agricultural activity on the peatland itself; there are several chicken farms in the area. Chickens farms emit ammonia ( $\text{NH}_3$ ), which when dissolved in rainwater, produces  $\text{NH}_4^+$  (Schlesinger 1997).  $\text{NH}_4^+$  also makes up a large fraction of atmospheric aerosols and is often transported further downwind of its source (Nieder and Benbi 2008), where it can then be washed out and deposited by precipitation.

Sources of  $\text{NO}_3^-$  include motor vehicles and stationary combustion sources (power stations, domestic heating) following atmospheric oxidation of the emitted nitrogen oxides. As a secondary pollutant, nitric acid and nitrates are less easily traced back to sources. The sources of DON are more difficult to generalise, but a spring maxima may be due to the release of pollen, plant debris and spores during the spring, which have been suggested as sources of DON (Violaki et al. 2010), or to seasonal patterns in spreading manure. Conversely, an autumn maximum may be linked to decomposition of vegetation (Cape et al. 2004). The contribution of DON to TDN is low at Auchencorth – 10.0% and 8.3% in 2009 and 2010, respectively – when compared to the literature average of 30% (Cornell et al. 2003, Cape et al. 2004, Zhang et al. 2008, Cape et al. 2011, Zhang et al. 2012) which is likely to be the result of differing sources and varying contributions of anthropogenic inputs. The proportion is markedly less than found at Easter Bush, a site 10km north of Auchencorth Moss, but closer to agricultural sources (arable fields, animal grazing) (Gonzalez Benitez et al. 2009). In areas of intensive agricultural activity DON in precipitation increases, and is thought to be due to the



addition of N fertilisers, especially urea (Neff et al. 2002, Zhang et al. 2012). Auchencorth Moss does not receive fertilisers and the number of sheep/cattle on site was low. Also, many of these studies used bulk precipitation collectors instead of wet-only collectors, and these are likely to have additional  $N_{org}$  deposited via dry deposition, and thus larger  $N_{org}$  concentrations (Gonzalez Benitez et al. 2010).

Previous studies of precipitation DIN and DON have found varying degrees of correlation between DON,  $NH_4^+$  and  $NO_3^-$ . Violaki et al. (2010) found no correlation between DON,  $NH_4^+$  and  $NO_3^-$  in wet deposition in the Eastern Mediterranean. Zhang et al. (2008) also found no correlation between DON,  $NH_4^+$  and  $NO_3^-$  in precipitation at 15 sites in China, but when an additional 37 sites from across the globe were added to the study, positive relationships were found, suggesting a common or similar source of DON and DIN on a global, but not regional, scale. In a number of studies, DON and  $NH_4^+$  have been correlated, or more closely correlated than to  $NO_3^-$ , suggesting DON is more closely associated with agricultural sources than from combustion processes (Cape et al. 2004, Chen et al. 2008, Cape et al. 2011, Zhang et al. 2012). The study conducted here observed weak to moderate correlations between  $NH_4^+$  and  $NO_3^-$  but no correlation between DIN and DON. This suggests that whilst the DIN compounds might share a common source, DON does not. This is further supported by the later seasonal maxima of DON compared to those of the DIN compounds (Cape et al. 2011).

#### 4.4.2 N in the Soil

August 2009 had the highest DIN concentrations and was the driest month that still produced enough sample for analysis. Samples collected in drier periods or from dipwells situated in drier parts of the moss were more viscous and contained lots of particulate matter, making filtering difficult. In contrast, DIN concentrations in dipwells during wetter periods or in wetter parts of the moss were more dilute and samples contained much less particulate matter. Adamson et al. (2001) found higher  $NH_4^+$  concentrations, but lower DON concentrations, during periods of low water table in a blanket bog in England. They suggested that the microbial community responsible for ammonification benefited from the fluctuating water table to a higher degree than nitrifying organisms, resulting in enhanced  $NH_4^+$  concentrations, which then accumulated if the fluctuation continues (Adamson et al. 2001, Daniels et al. 2012). This may be due to nitrifiers being unable to cope with the stress as well as ammonifiers



(Voroney 2007). Although the mean water table was lower in 2010, 2009 saw a greater degree of water table fluctuation (Fig. 4.4).

Interestingly, the TDN and DIN deposited as precipitation in 2010 was larger than in 2009, but the soil chemistry showed larger concentrations of TDN and DIN in 2009 than in 2010. The larger DIN concentrations in 2009 may be due to the activities of sheep which grazed on this moorland at very low livestock density of less than 10 ewes per ha. In 2009, sheep and sheep droppings were observed in and around the vicinity of the dip wells and where the soil cores were collected; the small cattle herd (15-20) also had access to this area. However, in 2010, there were no cattle on site and the sheep frequented an alternative area of the peatland.

The type of vegetation present in an ecosystem is known to have an effect on the availability of N. Bog vegetation and the associated litters, such as the *Sphagnum* mosses found at Auchencorth, can strip N, particularly  $\text{NO}_3^-$ , from precipitation, depending on rainfall and vegetation N requirements (Adamson et al. 1998). This would likely result in less N detected in the soil and associated waters. The vegetation cover at Auchencorth does not change significantly year on year, but the location, type and density of livestock does vary unpredictably.

#### 4.4.3 The composition of N in stream water

Numerous studies into stream water N concentrations have found DON to be the most dominant form with contribution varying from 54% to 82% annually (Chapman et al. 2001, Cundill et al. 2007, Helliwell et al. 2007a). Similarly,  $\text{NO}_3^-$  was commonly the second most dominant species, with  $\text{NH}_4^+$  being present in much lower concentrations. For example, Cundill et al. (2007) conducted a study at several points along a blanket peat-dominated catchment in the North Pennine uplands and found the annual mean concentrations of DON,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  to be  $32.5 \mu\text{mol N l}^{-1}$  (82.1%),  $6.2 \mu\text{mol N l}^{-1}$  (15.7%), and  $0.9 \mu\text{mol N l}^{-1}$  (2.2%), respectively. At Auchencorth Moss, the Black Burn DON concentrations were also the dominant form of N, at 74.6% ( $48.1 \mu\text{mol N l}^{-1}$ ) and 74.3% ( $50.0 \mu\text{mol N l}^{-1}$ ) for 2009 and 2010, respectively. These high TDN contributions of DON are typical of waters that drain peatlands due to their high organic matter content, often steep slopes promoting surface runoff and high rainfall. In addition, anaerobic and acid conditions reduce mineralisation of DON and nitrification to  $\text{NO}_3^-$  (Yesmin et al. 1995, Adamson et al. 1998, Chapman et al. 2001). However, in contrast to the studies highlighted above, at Auchencorth higher annual  $\text{NH}_4^+$  concentrations



were observed than  $\text{NO}_3^-$  concentrations in both 2009 and 2010, with means of  $14.1 \mu\text{mol N l}^{-1}$  (21.9%) in 2009 and  $12.9 \mu\text{mol N l}^{-1}$  (19.1%) in 2010 for  $\text{NH}_4^+$ , and  $2.3 \mu\text{mol N l}^{-1}$  (3.6%) in 2009 and  $4.5 \mu\text{mol N l}^{-1}$  (6.6%) in 2010 for  $\text{NO}_3^-$ . Helliwell et al. (2007a) compared four upland regions in the UK and found  $\text{NO}_3^-$  concentrations were lower when waters drained peaty soils than those which drained more mineral soils. Usually, the leaching of inorganic N is dominated by  $\text{NO}_3^-$ , whereas  $\text{NH}_4^+$  remains in the soil in weak association with organic matter and incorporation into clay lattices (Scherer 1993, Chapman and Edwards 1999, Davies et al. 2005, Helliwell et al. 2007a). The anaerobic conditions resulting from waterlogged soils may inhibit the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ , resulting in a higher incidence of  $\text{NH}_4^+$  leaching into nearby water bodies (Helliwell et al. 2007a). Fluctuating water tables have also been linked to higher  $\text{NH}_4^+$  concentrations from the mineralisation of organic nitrogen (Daniels et al. 2012, Paul and Clark 1996). Vegetation can also influence river water N-chemistry; peatlands with extensive blanket bog vegetation often exhibit lower  $\text{NO}_3^-$  concentrations than those that drain mineral soils (Chapman et al. 2001, Cundill et al. 2007).

A previous study carried out at the Black Burn in 2008, approximately 2.5 km downstream from the sampling site reported here, also found DON to be the dominant species (mean concentration of  $47.9 \mu\text{mol N l}^{-1}$ ) contributing 71.3 % of the TDN, followed by  $\text{NH}_4^+$  (mean concentration  $10.7 \mu\text{mol N l}^{-1}$ ), contributing 16.0% of TDN, and  $\text{NO}_3^-$  (mean concentration  $8.6 \mu\text{mol N l}^{-1}$ ), contributing 12.8% of TDN (Vogt 2011). The DON values are comparable to the study reported here, but the Vogt study found lower  $\text{NH}_4^+$  and higher  $\text{NO}_3^-$  values. These differences may be due to the location of the Vogt study site, which was further downstream, next to a busy road, and was frequented by sheep more regularly than the upstream site from this study. This may have resulted in additional N inputs from the sheep and road traffic, increasing the amount of N leached/deposited into the stream as  $\text{NO}_3^-$ . Also, some  $\text{NH}_4^+$  may have been nitrified to  $\text{NO}_3^-$  as it was transported downstream towards the Vogt sampling site (Helliwell et al. 2007a). No correlation was found between the wet deposition of N and the stream output.

#### 4.4.4 Seasonal Patterns of N in stream water

Although no clear seasonal pattern was identified for DON, the general trend was higher concentrations in warmer months. Chapman et al. (2001) studied 28 Scottish upland streams and found DON to be larger in the summer than winter months. It was



suggested that this was due to an increase of in-stream DON production, rather than increased leaching from the soil, as a result of algae/microorganisms in stream. Winter months would have cooler temperatures, less sunlight and a higher frequency of storm events, resulting in less primary production and DON being washed away more frequently.

The seasonal pattern of  $\text{NO}_3^-$ , where concentrations were higher in cooler months and lower in warmer months has been observed in numerous upland studies (Black et al. 1993, Chapman et al. 2001, Daniels et al. 2012). In warmer months, the biological uptake of  $\text{NO}_3^-$  by plants and microbes is at its highest, immobilising  $\text{NO}_3^-$ . In winter, productivity declines, increasing the amount of  $\text{NO}_3^-$  available to be leached into the stream (Black et al. 1993, Chapman et al. 2001, Helliwell et al. 2007b). The summer peaks in June and July 2010 are unusual and different to the summer lows observed in 2009. The high June value appears to be due to one high concentration, skewing the mean monthly concentration: the median value for June was  $0 \mu\text{mol N l}^{-1}$ . The high July 2010 peak is also evident in the mean concentrations of DON, and  $\text{NH}_4^+$ , and is still reflected in median values. The reason for these high values are unclear, however the differences in discharge and precipitation between the two sampled years may be a contributing factor. The monthly discharge was 59% higher in June 2009 and 11% higher in July in 2009 than in the corresponding months in 2010. Likewise, precipitation was 39% higher in June 2009 and 24% higher in July 2009 than in the corresponding months in 2010. Stream temperatures were similar but overall cooler in 2009.

#### 4.4.5 DON speciation by GC×GC-NCD

Most of the DON in both the precipitation and stream samples remained unresolved. Whilst some of the compounds detected by the GC×GC-NCD appear in both sets of data, the main two compounds identified in the stream water, were either present in small amounts or not present at all. This suggested that at least some sources of DON in precipitation and stream waters are different.

Schulten and Schnizer (1998) investigated the chemistry of organic matter of humic substances and soils. Amongst other compounds they identified pyrrole and benzonitrile, along with derivatives of pyrrole. They concluded that heterocyclic N compound, of which pyrrole is one, were an important constituent of soil organic matter, contributing up to 35% of total N. Pyrrole and pyrrolic compounds are a major N source in coal and are often found in peats; they can result from the aerobic



breakdown of the tetrapyrrole ring found in chlorophyll or from the breakdown of extensin, which is a type of hydroxyproline-rich polymer found in the cell walls of plants (van Smeerdijk and Boon 1987, Schulten and Schnizer 1998). It is therefore likely that the source of pyrrole in the streams was the peat in the surrounding catchment. Pyrrole has also been identified in fog waters where it was found to be quickly degraded during transport by photochemistry (Anastasio and McGregor 2000). It is thought to be present in the atmosphere originating from soil dust rich in humic/fluvic material (Schulten and Schnizer 1998, Anastasio and McGregor 2000). This may explain the presence of a small amount of pyrrole found in the precipitation samples.

The three other compounds identified were all amines: Dodecylamine (found only in the precipitation), NDPA and Decylamine (both only found in the stream).

#### 4.4.6 GC×GC-NCD limitations

Although the application of GC×GC-NCD to precipitation and stream water samples was largely successful, there were a number of issues. The main issue was the presence of what appeared to be a contamination peak. Blank water samples were included before sample analysis and N-butyl-benzenesulphonamide was not detected. N-butyl-benzenesulphonamide is a plasticiser, and may have leached into the samples from the storage bottles when stored in the freezer prior to analysis, or from SPE extraction tubes by reaction with the DCM. This warrants further investigation, but is outwith the scope of this paper.

Another issue was that in samples with low DON concentrations, such as the precipitation samples, the individual compounds detected by GC×GC-NCD were higher than expected. This may be due to peak areas being difficult to quantify in the presence of baseline noise, with difficulties in estimating accurately the quantities close to the limit of detection. It was not possible to determine a base level in order to correct for this issue during this study.

In order to remove the DIN and water prior to analysis, solid phase extraction was used. The most polar, water-soluble compounds, such as amino acids and urea, will be lost during this step. Further work is needed to improve the extraction procedure to maximise the applicability of the technique. Alternative approaches include liquid-liquid extractions or stir bar sorptive extraction. Another issue is the small sample size of precipitation samples, which combined with low concentrations, means that many of



the compounds are below the detection limit. In the stream samples, part of the DON may be in less volatile forms, that although they can be measured by the ANTEK, are not amenable to a GC analysis.

Identification of the peaks may be improved by running more standards of known compounds, where possible.

#### 4.5 Conclusions

DON is an important constituent in streams and precipitation and needs to be measured routinely. The volume-weighted concentration of DON found in the precipitation in this study varied between  $-1.6 \mu\text{mol N l}^{-1}$  and  $49.8 \mu\text{mol N l}^{-1}$ , with a mean contribution to TDN of 10.8% in 2009. In 2010, the volume-weighted concentration of DON varied between  $-2.5 \mu\text{mol N l}^{-1}$  and  $45.4 \mu\text{mol N l}^{-1}$ , with a mean contribution to TDN of 8.3%.

At Auchencorth Moss the DON in precipitation was below the average concentrations in the literature, but often these studies used bulk precipitation collectors instead of wet-only collectors, and these are likely to have additional  $\text{N}_{\text{org}}$  deposited via dry deposition, and thus larger  $\text{N}_{\text{org}}$  concentrations (Gonzalez Benitez et al. 2010). Differences may also be due to land use and pollution inputs, as many of the sites in the literature were in urban areas, or rural areas with high agricultural activity

DON in stream water showed no clear seasonal pattern, with little variation in monthly discharge-weighted means. It was a major contributor to TDN in both 2009 (74.6%) and 2010 (74.3%), which is consistent with other literature where streams are located within a peatland catchment. Concentrations of  $\text{NH}_4^+$  were higher than  $\text{NO}_3^-$ , which was unusual for a stream but consistent with previous observations further downstream of this study. There were no correlations between precipitation N and stream N but this study only considered wet deposition, and dry deposition is likely to have contributed at least 40% of the deposited N to the catchment (Hertel et al. 2011, Vogt 2011), which may alter this relationship. The fact that N export in the stream exceeded wet only N deposition (McKenzie et al. 2013, Chapter 6, this volume) suggest N deposited by precipitation is retained within the peatland, and that the peat is a source of N for streams. This is also suggested by the presence of pyrrole, the large DON concentrations and the high  $\text{NH}_4^+$  in stream water, the latter of which may be as a result of the mineralisation of organic N stored in peat.

In soil water, DON contributed 85.4% and 99.3% of TDN in 2009 and 2010 respectively. The mean concentrations of DON did not vary greatly between the years



(57.3  $\mu\text{mol N l}^{-1}$  in 2009 and 59.2  $\mu\text{mol N l}^{-1}$  in 2010) but the concentration of  $\text{NH}_4^+$  did (8.6  $\mu\text{mol N l}^{-1}$  in 2009 and 0.2  $\mu\text{mol N l}^{-1}$  in 2010). These results suggest the localised impact of animal waste and importance of water table variation on the availability of N to plants and on immobilisation.

GC $\times$ GC-NCD shows promise as a technique to identify compounds in stream water/precipitation. The number of unknown compounds detected may be reduced by running more standards for comparison. The contamination issue needs to be investigated to determine when/how a plasticiser was leached into the samples. The base-line issue needs addressing and may be resolved by alternative SPE to improve the resolution of DON and remove the background noise.

#### 4.6 Acknowledgements

This work was funded by the UK Natural Environment Research Council (NERC) through PhD studentship grant number NE/H526351/1. The authors would like to gratefully acknowledge the assistance of Kerry Dinsmore, Iain Leith, Ivan Simmons and Netty van Dijk, with sample collection, and Harwell laboratory for some sample analysis.

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**5. Paper 2: Dry deposition of inorganic nitrogen compounds to a Scottish moorland**

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# Dry deposition of inorganic nitrogen compounds to a Scottish moorland

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## Abstract

Fluxes of  $\text{NH}_3$ ,  $\text{HNO}_3$ , HONO and the aerosols  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were estimated at a semi-natural moorland in SE Scotland by applying inferential deposition models to hourly measured concentrations. Exchange parameterisations for  $\text{HNO}_3$ , HONO and the aerosol compounds were taken from the literature and earlier studies at the site. The  $\text{NH}_3$  flux was measured over a 7-month period in 2009 using the aerodynamic gradient method, and the results were used to refine a bi-directional dynamic exchange model.

The dynamic model builds on the bi-directional stomatal and cuticular flux estimated by the static model by considering also the desorption of  $\text{NH}_3$  from the leaf surface, which is treated in analogy to an electrical capacitor. This enables the dynamic model to reproduce morning emissions, which are underestimated by the static model. Several parameters were updated, including a doubling of the stomatal compensation point, a reduction of minimum resistance for leaf adsorption from 20 to 15  $\text{s m}^{-1}$  and a ten-fold increase in the removal flux ( $K_r$ ) from the leaf surface to  $-0.1 \text{ s}^{-1}$ . A comparison between several  $\text{NH}_3$  measuring techniques deployed at the site showed varying degrees of agreement, indicating that the absolute concentration measurement still contributes to the uncertainty in estimating  $\text{NH}_3$  deposition, but overall temporal variation was agreeable.

A comparison between the modelled compounds of 2009 and 2010 were compared to an equivalent 1995 dataset. Results showed dry deposition increased by  $0.42 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  when 1995 and 2009 were compared, but only by  $0.03 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  when 1995 and 2010 were compared. The largest difference between 1995 and 2009/2010 was attributed to an increase in  $\text{NH}_3$  flux. Changes in the theory of HONO behaviour resulted in HONO having been estimated to be deposited in 1995 but emitted in both 2009 and 2010, but in the absence of direct measurements this flux remains uncertain.



Aerosol  $\text{NO}_3^-$  also noticeably increased between 1995 and 2009/2010, but this may reflect improved measurement techniques.

*Keywords: Ammonia, AMANDA, MARGA, dry deposition*

## 5.1 Introduction

Nitrogen (N) is the limiting nutrient in many terrestrial ecosystems, and in areas where N-inputs are scarce, this can result in the presence of vegetation species which have specifically adapted to live in N-poor conditions. Whilst the majority of N in the atmosphere is in the non-reactive form of  $\text{N}_2$  and only available to N fixing plants, concentrations of reactive N compounds ( $\text{N}_r$ ) have been on the increase for decades as a result of human activities such as food and energy production (Galloway et al. 2004, Nieder and Benbi 2008).

An increase in the deposition of reactive nitrogen in sensitive settings may result in significant changes to the ecosystem by allowing more vigorous nitrophilic species to flourish with increasing sources of N, thus causing a change in the species composition of vegetation (Pitcairn et al. 1995). Some studies have suggested that as an indirect effect of increased N deposition, microbial decomposition of litter may be sped up (Bragazza et al. 2007), thus reducing the accumulation rate of peat.

At high N deposition loadings, “N saturation” is another threat and can result in significant export of N (as well as other soil nutrients such as potassium and magnesium) out of the soil and into nearby water bodies (Adamson et al. 1998, Trebs et al. 2006). This in turn may result in algal blooms (eutrophication) which is damaging to existing water life and biodiversity. Excessive nitrate ( $\text{NO}_3^-$ ) in our water supplies has been associated with methemoglobinemia in newborns (blue baby syndrome) and may thus pose a danger to human health. Some  $\text{N}_r$  compounds are present as aerosols, dominated by ammonium ( $\text{NH}_4^+$ ) and  $\text{NO}_3^-$ . Aerosols can also cause health problems as well as affect radiative forcing, cloud formation and reduced visibility (Adams et al. 2001, Thomas et al. 2009, Massad et al. 2010, Ramanathan et al. 2007). The deposition of nitrates ( $\text{HNO}_3$  and  $\text{NO}_3^-$ ), or even of the bases  $\text{NH}_3$  and  $\text{NH}_4^+$  (depending on their chemical fates after deposition) can contribute to the acidification of soils and water bodies by releasing  $\text{H}^+$  into the soil (Binkley and Richter 1987, Flechard and Fowler 1998a, Nemitz et al. 2004). HONO is an important source of the hydroxyl radical (OH); an oxidising species which produces pollutants such as ozone ( $\text{O}_3$ ) in the troposphere



(Acker and Moller 2007). In polluted areas, HONO has been found to produce up to 34% of the total OH formed during the day (Alicke et al. 2002).

Atmospheric N deposition occurs via wet deposition (through precipitation) and dry deposition. Dry deposition is the direct deposition of gases or aerosols to the Earth's surface and depends on the properties and concentration of the compounds being deposited, the biological, absorption and physico-chemical properties of the receiving surface and the turbulent transport properties of the boundary layer (Seinfeld and Pandis 2006, Trebs et al. 2006, Fowler et al. 2009, Hertel et al. 2011). In the UK, the total deposition of  $N_r$  in 2004 was estimated to be approximately 330 Gg yr<sup>-1</sup> with the dry deposition of ammonia (NH<sub>3</sub>), nitric acid (HNO<sub>3</sub>) and aerosol deposition (sum of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) accounting for approximately 48 (14.5%), 57 (17.3%) and 16 Gg yr<sup>-1</sup> (0.05%) of the deposition (Fowler et al. 2009, Hertel et al. 2011). These compounds, along with HONO, are important contributors to the dry deposition of  $N_r$ .

The dry deposition mechanisms differ between these compounds: HNO<sub>3</sub> is highly adsorptive or “sticky” and is quickly deposited to surfaces (Huebert and Robert 1985, Wesely and Hicks 2000, Seinfeld and Pandis 2006). The exchange of both NH<sub>3</sub> and HONO is bi-directional, meaning they can be both deposited and emitted between the atmosphere and the surface. The direction of exchange largely depends on their ambient concentration in comparison to their concentration within the soil/vegetation and the rate at which these species are consumed/produced (Trebs et al. 2006). The NH<sub>3</sub> flux is also affected by the wetness and the acid ratio of the water film on the surface of vegetation, which neutralises the NH<sub>3</sub> present and can enhance its uptake via the cuticle (Massad et al. 2010). The efficiency of aerosol dry deposition depends on the size of the particles (Seinfeld and Pandis 2006) in which NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> is contained as well as the aerodynamic roughness of the receptor surface.

The aim of this paper is to estimate the fluxes of NH<sub>3</sub>, HNO<sub>3</sub>, HONO and the aerosols NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> at Auchencorth Moss, an ombrotrophic moorland in central Scotland, where the inputs of N are dominated by atmospheric deposition, making it particularly vulnerable to changes in the concentrations of atmospheric N compounds. This is achieved by applying an inferential deposition model to hourly concentration time-series of the five  $N_r$  compounds, measured with a wet chemistry denuder/steam jet aerosol collector analyser. While exchange parameterisations for HNO<sub>3</sub>, HONO and the aerosol compounds were taken from the literature and earlier studies at this site, the NH<sub>3</sub> flux was measured over a 7 month period in 2009 using the aerodynamic gradient



method, and the results are used to refine a bi-directional dynamic exchange model. The new  $\text{NH}_3$  flux results are compared to an earlier, more extensive dataset from 1995 to assess any changes in the deposition rates induced by changes in the chemical climate at this site, which experienced a decrease of mean concentrations of  $\text{NH}_3$  and the interacting  $\text{SO}_2$ , at the same time as new chicken houses in the vicinity now lead to larger  $\text{NH}_3$  peak concentrations. In addition, differences in the mean monthly concentrations of  $\text{NH}_3$  measured by four different instruments are discussed.

## 5.2 Site and methods

### 5.2.1 Study area

Auchencorth Moss is an ombrotrophic peat bog located in south Scotland, approximately 18 km southwest of Edinburgh (National Grid Reference NT221562; lat.  $55^\circ 47' 30\text{N}$ ; long.  $03^\circ 14' 20\text{W}$ ). The volume of peat is estimated to be  $\sim 50$  million  $\text{m}^3$ , with peat depths of up to 5 m, but an average depth of 50 cm, and a total peat coverage of  $\sim 1214$  ha (Mitchell and Mykura 1962, Dinsmore 2008). Approximately 170 ha of peat, 1.75 – 3.4 km W-SW of the study site, are used for extraction. There are a number of farms in the surrounding area, with the site itself used for low intensity sheep grazing (less than one livestock unit  $\text{km}^{-2}$ ). In 2009 a small herd of cows (15-20) were also grazed on the site.

The vegetation consists of numerous hummocks and hollows typically associated with a peatland setting. The hollows are depressions up to 30 cm deep and are dominated by blankets of *Sphagnum* mosses, with various sedges, monocotyledons and other bryophytes also present. The hummocks can be up to 30 cm high, although *Sphagnum* mosses are present, there is a larger density of vascular plants, with the dominant species being *Deschampsia flexuosa*, *Eriophorum vaginatum* and *Juncus effuses*. Further information with regards to vegetation at Auchencorth Moss has been presented by Flechard and Fowler (1998a) and Dinsmore (2008). The leaf area index (*LAI*) was not measured directly during the study period; instead it was estimated from the relationship between *LAI* and canopy height  $h_c$  derived during an earlier study and varied from  $1.01 \text{ m}^2 \text{ m}^{-2}$  to  $2.09 \text{ m}^2 \text{ m}^{-2}$ .



### 5.2.2 NH<sub>3</sub> flux measurements and micrometeorological theory

The flux of NH<sub>3</sub> was determined by a hybrid method that combines the aerodynamic gradient method for NH<sub>3</sub> with the eddy-covariance approach for momentum, as described by Flechard and Folwer (1998b), and implemented as:

$$F_t = -u_* k \frac{d\chi}{d[\ln(z-d) - \psi_H(z-d)/L]}, \quad (1)$$

where  $F_t$  is the total flux,  $k$  is the von Karman constant (0.41),  $z$  is the height above the ground,  $d$  is the displacement height (the displacement of the ground level due to vegetation),  $\chi$  is the vertical profile concentration of NH<sub>3</sub>,  $\psi_H$  is the atmospheric stability correction for heat and  $L$  is the Obukhov stability length. The friction velocity ( $u_*$ ) was derived from eddy-covariance measurements of momentum transfer using an ultrasonic anemometer (Windmaster Pro; Gill Instruments; Lymington, UK), together with wind speed and wind direction.

The NH<sub>3</sub> concentration profile was determined using an AMANDA (Ammonia Measurement by ANnular Denuder sampling with online Analysis), a continuous-flow wet denuder gradient system with a detection limit of 0.02  $\mu\text{m}^{-3}$ . This provided continuous measurements of NH<sub>3</sub> from June to December 2009 and consisted of 3 continuously rotating denuders, placed at 3 heights: 0.75 m, 2.3 m and 6.4 m. Each denuder has two concentric glass tubes with a space of approximately 1.5 mm which are partially filled with a weakly acidic absorption or ‘stripping’ solution (NaHSO<sub>4</sub>). The continuous rotation of the denuders results in this solution continuously coating the denuder surface. The solution level within the denuder is controlled through a conductivity measurement which steers a peristaltic fill pump. At the same time, ambient air is sucked through at 20-25 l min<sup>-1</sup> and any NH<sub>3</sub> present is absorbed into the liquid phase, where it dissociates to NH<sub>4</sub><sup>+</sup>. The solution is then pumped through a debubbler before it is mixed with a solution of NaOH containing 100 ppm NH<sub>4</sub><sup>+</sup>. This converts the NH<sub>4</sub><sup>+</sup> back into NH<sub>3</sub> gas. The NH<sub>3</sub> is then passed through a membrane and mixed with double-deionised (DD) water, converting it back into NH<sub>4</sub><sup>+</sup>, the concentration of which is determined by conductivity and allows the concentration of NH<sub>3</sub> to be determined. The particular AMANDA instrument used in this study had been of the original design of Wyers et al. (1993), but upgraded to a newer conductivity detector, which always monitored the quality of the DD water, and to a PC based data



acquisition and control system. Flux measurements were discarded for wind directions between 90° to 200° due to location of other instrumentation and monitoring cabins which would have caused disturbance to the flow of air.

Temperature and relative humidity were measured using a humitter probe (Humitter 50YC, Vaisala Inst., USA). Rainfall was measured using a precipitation tipping bucket (Campbell instruments, UK). Net radiation was measured using a NRLite net radiometer (Kipp and Zonen, Delft, The Netherlands) and solar radiation was measured using a pyranometer (Skye Instruments, Llandrindod Wells, UK).

### 5.2.3 Concentration measurements

#### 5.2.3.1 MARGA

The MARGA (Measuring AeRosol and GAses; Applikon, NL) compiles average hourly concentrations of a range of inorganic aerosol and acidifying gases. Ambient air is drawn through the sampling box at rate of 1 m<sup>3</sup> hr<sup>-1</sup>. The sampling box consists of a wetted rotating denuder which absorbs any water soluble gases present. This was similar to the denuder used in the AMANDA system, except that Milli-Q grade deionised water with hydrogen peroxide as biocide was used as an absorption solution to capture both NH<sub>3</sub> and acidic gases. Aerosols pass through the denuder and into a steam-jet-aerosol-collector where the water-soluble aerosol components are condensed in a supersaturated environment. The aerosols are then separated from the airstream by condensational growth in a cyclone. The solutions are collected over an hour period, degassed and mixed with an internal standard. They are then analysed by online anion and cation chromatographs. Detection limits were 0.08 µg m<sup>-3</sup> for NH<sub>3</sub>, HONO and NH<sub>4</sub><sup>+</sup>; and 0.05 µg m<sup>-3</sup> for HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup>. The MARGA operated at Auchencorth Moss was a two-channel MARGA-2s, one of which was operated with a 10 µm and the other with a 2.5 µm aerosol size-cut. A more detailed description of the system and analysis of the results has been presented elsewhere (Twigg et al. 2012)

#### 5.2.3.2 Bulk denuder measurements by DELTA and TAG

The DELTA (Denuder for Long-Term Atmospheric sampling) measures monthly average ambient concentrations of a number of trace gases and aerosols, which has been used in a UK network since 1998 and in a European network 2008-2010 (Flecharde et al. 2011). The DELTA consists of four denuders (duplicate denuders coated with CaCO<sub>3</sub> for capture of acidic gases, followed by duplicate denuders coated with citric acid for



capture of  $\text{NH}_3$ ), through which air is sampled at  $0.3 \text{ l min}^{-1}$  for one month, after which time the denuders are extracted and analysed by flow injection analysis (similar to the AMANDA detector) for  $\text{NH}_3$  and anion IC for  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ . It thus derives concentrations of  $\text{NH}_3$  and the acidic gases  $\text{HNO}_3$ ,  $\text{SO}_2$ ,  $\text{HCl}$  and  $\text{HONO}$ , from which the acid ratio,  $a_r$ , may be calculated as (Massad et al. 2010, Flechard et al. 2011):

$$a_r = \frac{[\text{HNO}_3] + [\text{HCl}] + [\text{SO}_2] * 2}{[\text{NH}_3]}, \quad (2)$$

where the concentrations are in mixing ratios (ppb).

The TAG (Time Averaged Gradient) system uses DELTA-type samplers in gradient configuration to obtain monthly averaged gradients, from which a monthly average flux of  $\text{NH}_3$  and  $\text{HNO}_3$  is calculated. The sampling pump is switched off whenever conditions are unsuitable for average flux calculations (too non-neutral stratification; low wind speed; obstructed wind sector). Thus, unlike the DELTA, the concentrations provided by the TAG do not cover all conditions. A detailed description of the TAG system has been presented by Famulari et al. (2010).

#### 5.2.4 Inferential dry deposition models

##### 5.2.4.1 Ammonia

Surface/atmosphere exchange can be described through a series of resistances, in analogy to electrical resistances as defined by Ohm's law. Figure 5.1a shows a basic deposition-only model where the total flux ( $F_t$ ) is determined by three resistances: the aerodynamic resistance ( $R_a$ ), the laminar boundary resistance ( $R_b$ ) and the canopy resistance ( $R_c$ ), with the total resistance ( $R_t$ ) being the sum of all three.



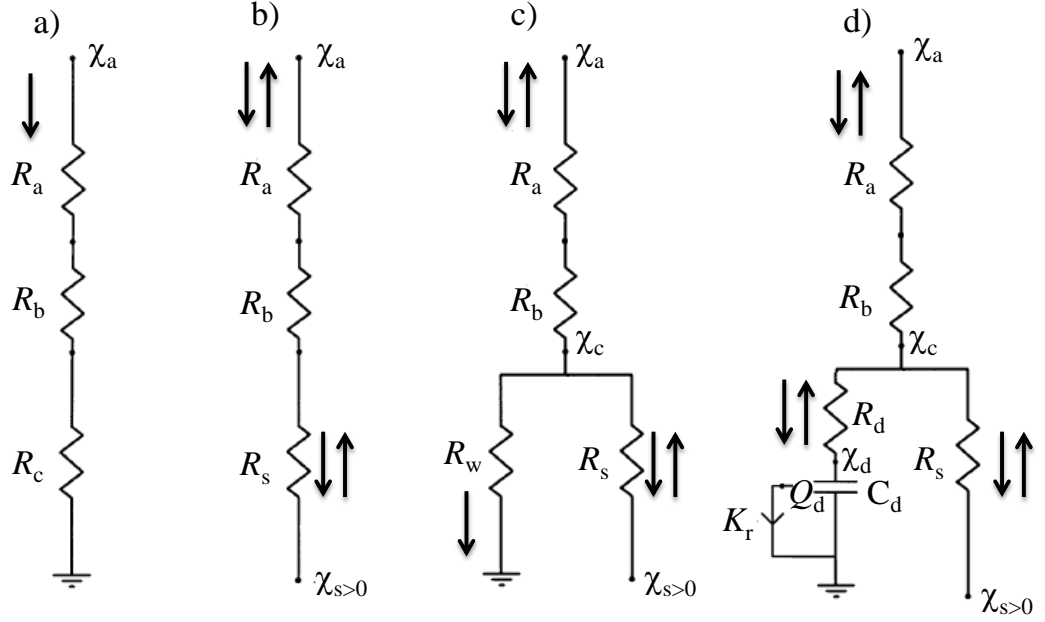


Figure 5.1. Resistance frameworks used to describe the surface exchange with ammonia, showing (a) the deposition-only  $R_c$  model, (b) the stomatal exchange model, (c) the single-layer canopy compensation point model and (d) the single layer capacitance model.

If the concentration is available, the flux can be determined from parameterisations of these resistances by:

$$F_t = \frac{-\chi_a(z_{ref})}{(R_a(z_{ref}) + R_b + R_c)}, \quad (3)$$

where  $\chi_a$  the air concentration at height  $z$ .  $R_a$  and  $R_b$  can be calculated from meteorological parameters which can be directly measured using a sonic anemometer:

$$R_a(z) = \frac{u(z-d)}{u_*^2} - \frac{\psi_H\left(\frac{z-d}{L}\right) - \psi_M\left(\frac{z-d}{L}\right)}{ku_*}, \quad (4)$$

where  $\Psi_M$  is the integrated stability function for momentum and

$$R_b = u_*^{-1} \left[ \left( \frac{z_0 u_*}{v_a} \right)^{0.24} \left( \frac{v_a}{D_x} \right)^{0.8} \right], \quad (5)$$



where  $\nu_a$  is the kinematic viscosity of air ( $1.42 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ ) and  $D_x$  is the molecular diffusivity of the depositing compound.

This model assumes a zero concentration of the compound being deposited at the surface, and thus the flux is only one directional (deposition). In the case of  $\text{NH}_3$  the flux can be bi-directional. This is due to the gas phase  $\text{NH}_3$  in the stomatal cavities – the stomatal compensation point ( $\chi_s$ ) - which forms in equilibrium with the  $\text{NH}_4^+$  concentration in the apoplastic fluid  $[\text{NH}_4^+]$  (Farquhar et al. 1980). When  $\chi_s > \chi_a$   $\text{NH}_3$  is emitted, and when  $\chi_s < \chi_a$ ,  $\text{NH}_3$  is deposited.  $\chi_s$  is linked to  $[\text{NH}_4^+]$  through the Henry and solubility equilibria of  $\text{NH}_3$  and  $\text{NH}_4^+$  which are function of the pH of the apoplastic fluid and temperature (Nemitz et al. 2000):

$$\chi_s = \frac{161500}{T} e^{-10378T^{-1}} \frac{[\text{NH}_4^+]}{[\text{H}^+]}, \quad (6)$$

where  $T$  is the temperature in Kelvin and all concentrations are in  $\text{mol l}^{-1}$  at 1 atm. The apoplastic concentration ratio  $\Gamma = \left( \frac{[\text{NH}_4^+]}{[\text{H}^+]} \right)$  describes a dimensionless, temperature independent emission potential of the vegetation.

Figure 5.1b considers the role of the stomata in the exchange of gases, for a simplified case where other exchange pathways (e.g. with the leaf cuticle, see below) is negligible as it might be in controlled environment experiments at a low relative humidity ( $RH$ ).  $R_c$  is replaced by the stomatal resistance ( $R_s$ ), thus:

$$F_t = - \frac{\chi_a(z_{ref}) - \chi_s}{(R_a(z_{ref}) + R_b + R_s)}. \quad (7)$$

#### *Static canopy compensation point model- cuticular resistance*

A further improvement to the previous resistance models is the canopy compensation point model, which describes the bi-directional exchange of ammonia via the stomata, but also considers uptake by the cuticle (Fig. 5.1c) (Sutton and Fowler 1993). An additional resistance, known as the cuticular resistance,  $R_w$ , is required.  $R_w$  is mainly affected by the thickness of the leaf surface water film and its pH (van Hove and Adema 1996, Massad et al. 2010). The chemical composition of this water film will be affected by the concentration of atmospheric acids, which will also affect the pH.  $RH$  controls the thickness of these water films which can provide an efficient sink for  $\text{NH}_3$  (van



Hove and Adema 1996, Flechard et al. 1999). Because  $R_w$ , cannot be directly measured, it is often estimated by only considering the night time fluxes from which it can be derived by plotting the canopy resistance of an inverted Eq. (3) against  $RH$ . Since the stomata are closed at night, it is assumed that exchange will occur only via the cuticle in a fashion similar to Figure 5.1a. Thus, by only considering period of high  $R_s$  and excluding period with a high  $R_a + R_b$ ,  $R_w$  can be approximated by  $R_c$ .

The net flux of  $NH_3$  is dependent on the difference between the concentration of  $NH_3$  at the canopy compensation point ( $\chi_c$ ) (which unlike  $\chi_s$  reflects both the stomatal and cuticular exchange pathway), and the atmosphere ( $\chi_a$ ), with net emissions occurring when  $\chi_c > \chi_a$ , and net deposition occurring when  $\chi_c < \chi_a$ . Whilst net emission can only occur when  $\chi_s > \chi_c$ , even in these conditions  $NH_3$  emitted by the stomata can sometimes be taken up by the cuticles (through  $R_w$ ) and may therefore not necessarily escape the canopy.

The canopy compensation point is defined as:

$$\chi_c = \frac{\frac{\chi(z-d)}{R_a(z-d)+R_b} + \frac{\chi_s}{R_s}}{(R_a(z-d)+R_b)^{-1} + R_s^{-1} + R_w^{-1}}. \quad (8)$$

#### *Dynamic canopy compensation point model – cuticular capacitance*

Measured fluxes have sometimes shown transient morning emissions which the cuticular resistance model is unable to replicate. This may be due to the oversimplification of the role the cuticle plays for  $NH_3$  exchange. The cuticular resistance model describes the absorption of  $NH_3$  by the cuticle as depending only on a resistance, but studies suggest the cuticle can re-release some or all of the deposited  $NH_3$ , which may be represented in the resistance analogue as a capacitor. Leaf wetness associated with leaf cuticles acts as a sink for  $NH_3$  deposition, with  $NH_3$  being stored in the water film layer, which is linked to relative humidity. As morning dew or invisible water microlayers on the leaf surfaces evaporate,  $NH_3$  is released resulting in morning emissions (Sutton et al. 1995, Asman et al. 1998, Flechard et al. 1999, Massad et al. 2010). An improved cuticular capacitance model developed by Sutton et al. (1995) is shown in Figure 5.1d. As a result of the link between this water film layer and  $RH$ , it is



expected that, for a given pH, and according to Henry's Law, the leaf surface would have a capacitance and the flux of the capacitor ( $F_d$ ) becomes:

$$F_d = -\frac{(\chi_d - \chi_c)}{R_d}, \quad (9)$$

where  $\chi_d$  is the adsorption concentration ( $\mu\text{g m}^{-3}$ ) and  $R_d$  is the charging resistance of the capacitor. The capacitance ( $C_d$ ) can be defined as:

$$C_d = \frac{Q_d}{\chi_d}, \quad (10)$$

where  $Q_d$  is the adsorption charge ( $\mu\text{g m}^{-2}$ ) of the capacitor.  $C_d$  can be derived using the solubility equilibria determined by Sutton and Fowler (1993), and by considering the Henry equilibrium constant and an equivalent water-film thickness ( $M_{H_2O}$ ):

$$C_d = M_{H_2O} \frac{[\text{NH}_4^+] + [\text{NH}_3 \cdot \text{H}_2\text{O}]}{[\text{NH}_3]_{(g)}} = M_{H_2O} \left[ \frac{[\text{H}^+]}{10^{(1.6035 - 4707.6/T)} + 10^{((1477.7/T) - 1.6937)}} \right], \quad (11)$$

where both  $C_d$  and  $M_{H_2O}$  are in metres and  $T$  is in Kelvin.  $M_{H_2O}$  can be estimated using a similar humidity response as  $R_w$ :

$$M_{H_2O} = LAI * 20^{([RH - 60]/10)}, \quad (12)$$

where LAI is the leaf area index of the canopy.

By treating the cuticle as a capacitor, the flux becomes dependent on a previous flux.

This requires a time set, so an initial value of  $Q_d$  or  $\chi_d$  is required, thus:

$$\chi_{d\{i\}} = \frac{Q_{d\{i\}}}{C_d}, \quad (13)$$

and the flux becomes:

$$F_d = -\frac{(\chi_{d\{i\}} - \chi_{c\{i\}})}{R_d}. \quad (14)$$

$\chi_c$  is modified to include the capacitor so:



$$\chi_c = \frac{\frac{\chi(z-d)}{R_a(z-d)+R_b} + \frac{\chi_s}{R_s} + \frac{\chi_d}{R_d}}{(R_a(z-d)+R_b)^{-1} + R_s^{-1} + R_d^{-1}}. \quad (15)$$

The new charge after  $t$  seconds becomes:

$$Q_{d\{i+t\}} = Q_{d\{i\}} - (F_d \cdot t). \quad (16)$$

In order to account for any net removal of  $\text{NH}_3$  from the air by leaf surfaces, a reaction rate constant,  $K_r$ , ( $\text{s}^{-1}$ ) is added to Eq. (16) so that:

$$Q_{d\{i+t\}} = Q_{d\{i\}} - (F_d \cdot t) + Q_{d\{i\}} K_r. \quad (17)$$

$T$  and  $RH$  are important in determining the resistances and compensation points. They can be directly measured at a reference height, but the difference between the values at the reference height and the actual surface layer where exchange takes place may be significant. The  $T$  and  $RH$  at the surface layer ( $z_0'$ ) can be determined using the following calculations:

$$T(z_0') = T(\text{air}) + \frac{H}{(\rho_a \cdot c_p)} (R_a(\text{ref}) - R_b(\text{H}_2\text{O})), \quad (18)$$

where  $\rho_a$  is the density of air ( $1.01 \text{ g m}^{-3}$ ) and  $C_p$  is the specific heat capacity of air ( $1236 \text{ J kg}^{-1} \text{ K}^{-1}$ ) and

$$RH(z_0') = \frac{e(z_0')}{e_{\text{sat}}(T(z_0'))} \quad (19)$$

Where  $e(z_0')$  is the water vapour pressure at the surface layer, and  $e_{\text{sat}}(T(z_0'))$  is the saturated water vapour at temperature,  $T$ , at the surface layer.

$$e(z_0') = e(\text{ref}) + \frac{\lambda E}{\lambda} (R_a(\text{ref}) - R_b(\text{H}_2\text{O})), \quad (20)$$

where  $\lambda E$  is the latent heat flux ( $\text{W m}^{-2}$ ) and  $\lambda$  is the latent heat of evaporation ( $\text{J s}^{-1}$ )



#### 5.2.4.2 HONO

The sources of HONO are not well understood, presenting a challenge when attempting to model its behaviour. It is generally believed that HONO is formed during the night, and is then rapidly broken down during the day by photolysis, resulting in lower concentrations of HONO during the day. HONO is a secondary pollutant and although it is capable of bi-directional exchange, it is not known to be directly emitted by plants (Schimang et al. 2006, Trebs et al. 2006). However, it is believed to be emitted as a result of NO<sub>2</sub> reacting with water on surfaces such as plant cuticles, soil surfaces or aerosols (Acker et al. 2004, Schimang et al. 2006). For this reason, the compensation point is believed to be a function of the NO<sub>2</sub> mixing ratio (Stutz et al. 2002, Trebs et al. 2006) where:

$$\chi_c(HONO) = 0.03 \cdot \chi_c(NO_2, z_{ref}). \quad (21)$$

#### 5.2.4.3 HNO<sub>3</sub>

HNO<sub>3</sub> is highly soluble and reactive. Its “sticky” nature ensures it is quickly and irreversibly absorbed on to surfaces (Huebert and Robert 1985, Wesely and Hicks 2000, Seinfeld and Pandis 2006). Thus the flux is one-directional (deposition) and can be calculated using the principles of the model in Figure 5.1a and Eq. 3. Since it has long been accepted that the  $R_c$  in relation to HNO<sub>3</sub> is zero (Huebert and Robert 1985, Wesely and Hicks 2000) Eq 3 can be modified to:

$$F_t = \frac{-\chi_a(z_{ref})}{(R_a(z_{ref}) + R_b)}. \quad (22)$$

#### 5.2.4.4 Aerosol deposition

The deposition of the aerosols NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were calculated as the product of the air concentration multiplied by the depositional velocity,  $V_d$ :

$$F_t = -\chi_a(z_{ref}) * V_d(z_{ref}), \quad (23)$$

$V_d$  is estimated through parameterisation of the gravitational settling velocity,  $V_g$  (which is a function of particle size),  $R_a$  and surface depositional velocity,  $V_{ds}$ , allowing atmospheric transport characteristics to be determined (Slinn 1982):



$$V_d = \frac{V_{g+1}}{\left(\frac{R_{d+1}}{V_{ds}}\right)}, \quad (24)$$

where

$$V_{ds} = \alpha u_*. \quad (25)$$

Alpha was derived by multiplying the size-dependent deposition velocity ( $V_d(D_p)$ ) measured by Nemitz et al. (2002) at Auchencorth with typical size distributions of the accumulation mode in which  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (fine) are found.

### 5.3 Results

#### 5.3.1 Measured concentration

##### 5.3.1.1 Comparison of ammonia concentration measurement approaches

In addition to the AMANDA measurements presented here,  $\text{NH}_3$  is measured on a long term bases at Auchencorth using the MARGA, DELTA and TAG. Each method measures  $\text{NH}_3$  on different time scales and, when compared, the results showed a variation in the monthly averages of  $\text{NH}_3$  concentration. A summary of the monthly means for each methods can be found in Table 5.1.

##### 5.3.1.2 AMANDA and MARGA

When comparing the AMANDA with the MARGA, in order to compare like data with like, the AMANDA data were extrapolated to 3.55m (the height of the MARGA) averaged over an hourly period, and only overlapping (paired) data points were used.

The regression analysis revealed a moderate correlation of  $R^2 = 0.62$  ( $N = 7$ ;  $P < 0.05$ ), with a slope of 1.06 and an intercept of  $0.11 \mu\text{g m}^{-3}$ . When forced through zero, the slope was 1.16, which implies a positive bias of 16% ( $R^2 = 0.73$ .  $N = 7$ ;  $P < 0.02$ ).

The mean monthly MARGA concentrations were somewhat higher than those reported by the AMANDA, with the exception of June 2009. A similar temporal pattern was observed (Fig. 5.2), with a maximum occurring in July and a minimum in August.



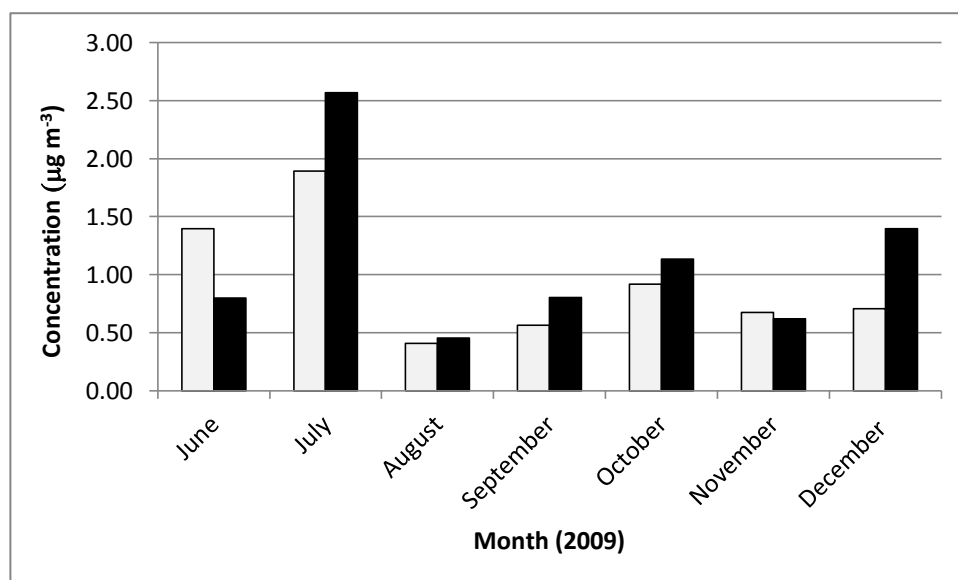


Figure 5.2. The mean monthly concentration of  $\text{NH}_3$  as measured by the AMANDA (white) and MARGA (black), using paired concentrations only at a height of 3.55m.

#### 5.3.1.3 AMANDA, MARGA and DELTA

The DELTA measured monthly  $\text{NH}_3$  concentrations, but due to the logistics of collecting the samples, the “month” reported was not always aligned with the calendar month. Monthly AMANDA and MARGA mean concentrations were calculated to match the DELTA months, whereby all available data points were used. Both the DELTA and AMANDA data at a height of one metre were used. However, it was not possible to extrapolate the single height MARGA data to this height; therefore data from 3.55 m height was used. Figure 5.3 shows the differences in the monthly mean concentrations between these measurement techniques.

The regression of AMANDA and DELTA showed no significant correlation at  $R^2 = 0.42$  ( $N = 7$ ;  $P > 0.1$ ), with a slope of 1.09 and an intercept of  $-0.08 \mu\text{g m}^{-3}$ ; and the regression of MARGA and DELTA gave a weak correlation of  $R^2 = 0.38$  ( $N = 12$ ;  $P < 0.05$ ), with a slope of 1.69 and an intercept of  $-0.24 \mu\text{g m}^{-3}$ . When forced through zero, AMANDA and DELTA still showed no significant correlation at  $R^2 = 0.35$  ( $N = 7$ ;  $P > 0.1$ ), with a slope of 0.99 (bias of -1%); and the regression of MARGA and DELTA also showed no significant correlation at  $R^2 = 0.26$  ( $N = 12$ ;  $P > 0.05$ ), with a slope of 1.46 (bias of +46%).

Once again the results showed similar temporal patterns with the MARGA tending to have the highest monthly concentrations. The DELTA and AMANDA monthly means compared more favourably than the DELTA and MARGA, which is reflected in the  $R^2$ .



This may be related to the 2.55 m height difference between the MARGA and the DELTA and the prevalence of deposition gradients at this site (see below).

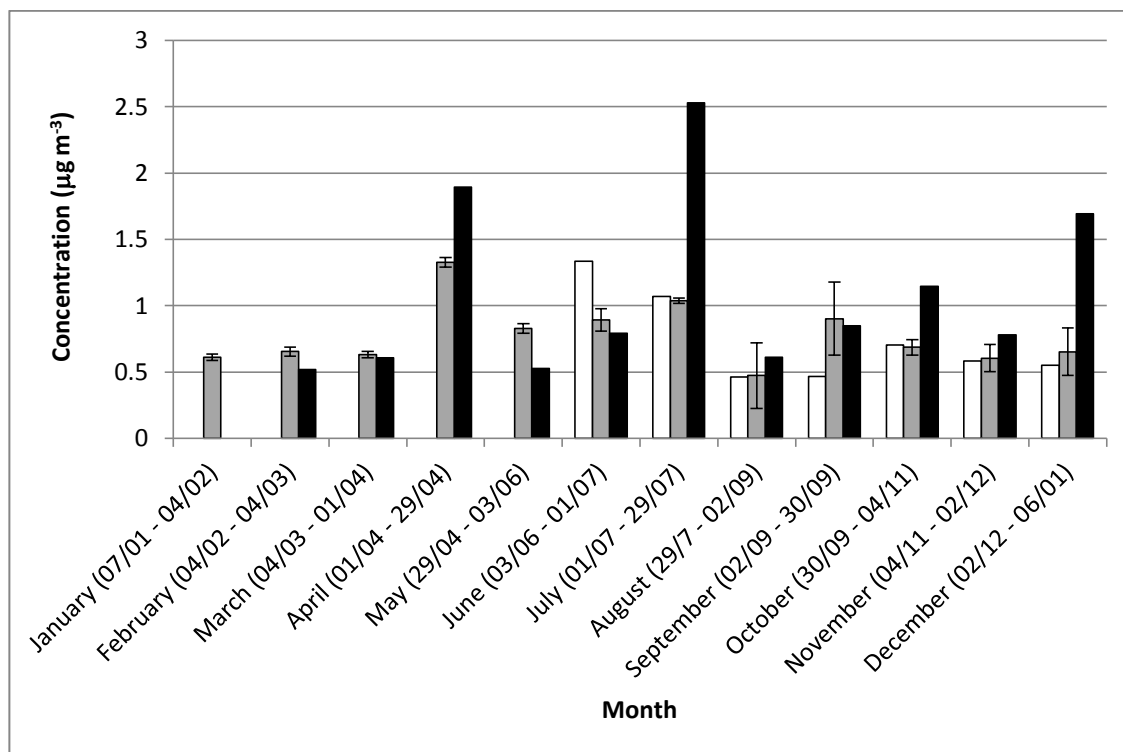


Figure 5.3. The mean monthly concentration of  $\text{NH}_3$  as measured by the DELTA (Grey), AMANDA (white) and MARGA (Black). Both the AMANDA and the DELTA are concentrations at 1 m, whereas the MARGA concentrations are from 3.55 m.

#### 5.3.1.4 AMANDA, MARGA and TAG

The TAG was also measured on a monthly basis, and again due to the logistics of collecting the samples, the month was not a true calendar month. The AMANDA and MARGA monthly concentrations were adjusted to match the DELTA months and only data points measured when the TAG was switched on were used to calculate the monthly mean concentrations. The TAG data was extrapolated to 1 m for comparison with the AMANDA and to 3.55 m to compare with the MARGA. Figure 5.4 shows the differences in the monthly mean concentrations between these measurement techniques. The regression of AMANDA and TAG gave a highly significant correlation of  $R^2 = 0.82$  ( $N = 7$ ;  $P < 0.01$ ), with a slope of 2.10 and an intercept of  $-0.12 \mu\text{g m}^{-3}$ , but the regression of MARGA and TAG gave no correlation, with  $R^2 = 0.04$  ( $N = 12$ ;  $P > 0.1$ ), with a negative slope of  $-0.12$  and an intercept of  $0.71 \mu\text{g m}^{-3}$ . When forced through



zero, AMANDA and TAG still showed a significant correlation of  $R^2 = 0.57$  ( $N = 7$ ;  $P < 0.05$ ), but with a slope of 1.74 (bias of +74%).

The mean monthly MARGA concentrations were higher than the TAG, with the exception of June 2009. Although the temporal pattern was similar, this is not reflected in the poor correlation. The opposite is true when comparing the TAG with the AMANDA; AMANDA consistently measured lower concentrations than the TAG, with a slightly more variable temporal pattern.

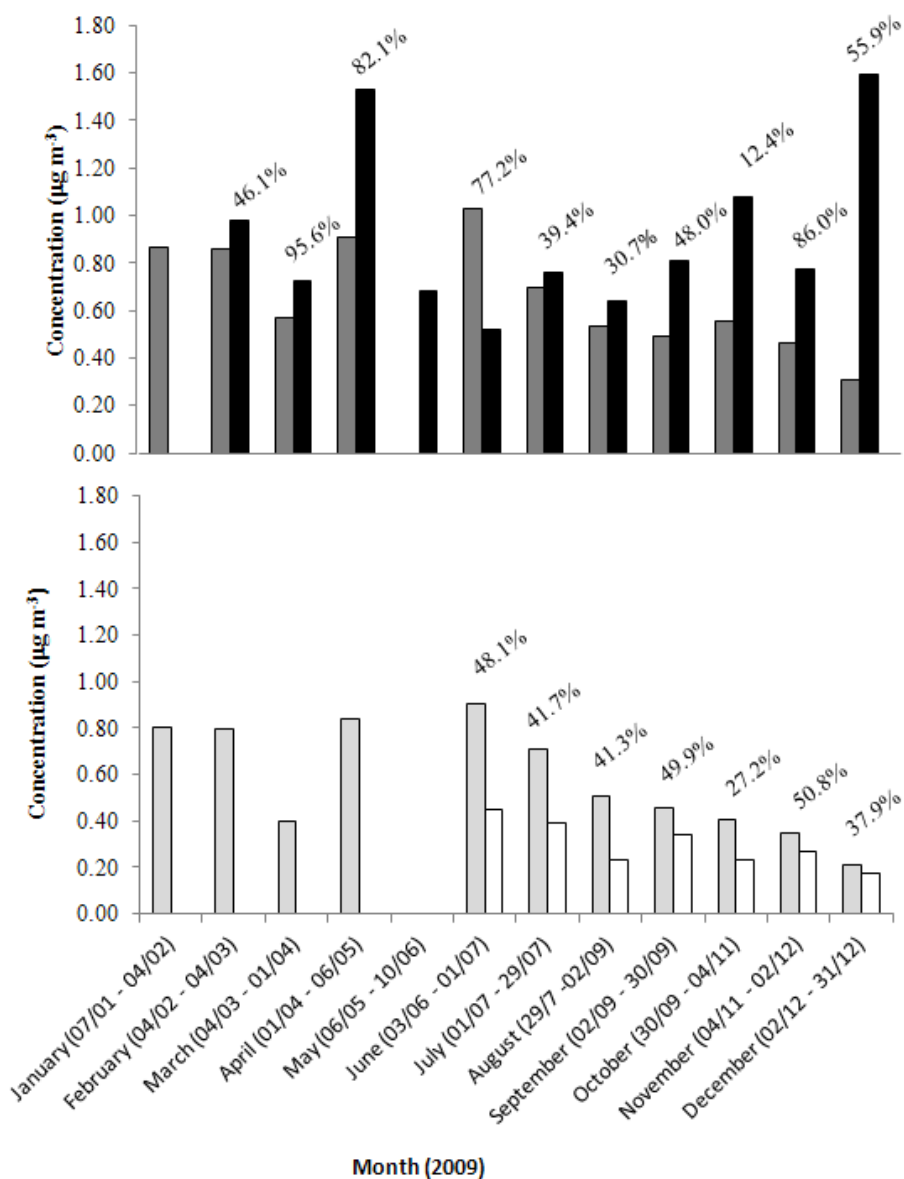


Figure 5.4. The mean monthly concentration of  $\text{NH}_3$  as measured by the TAG {3.55m} (dark grey), MARGA (black), TAG {1m} (light grey) and AMANDA (white). The percent coverage of the AMANDA/MARGA for when the TAG was on is shown above the bars.



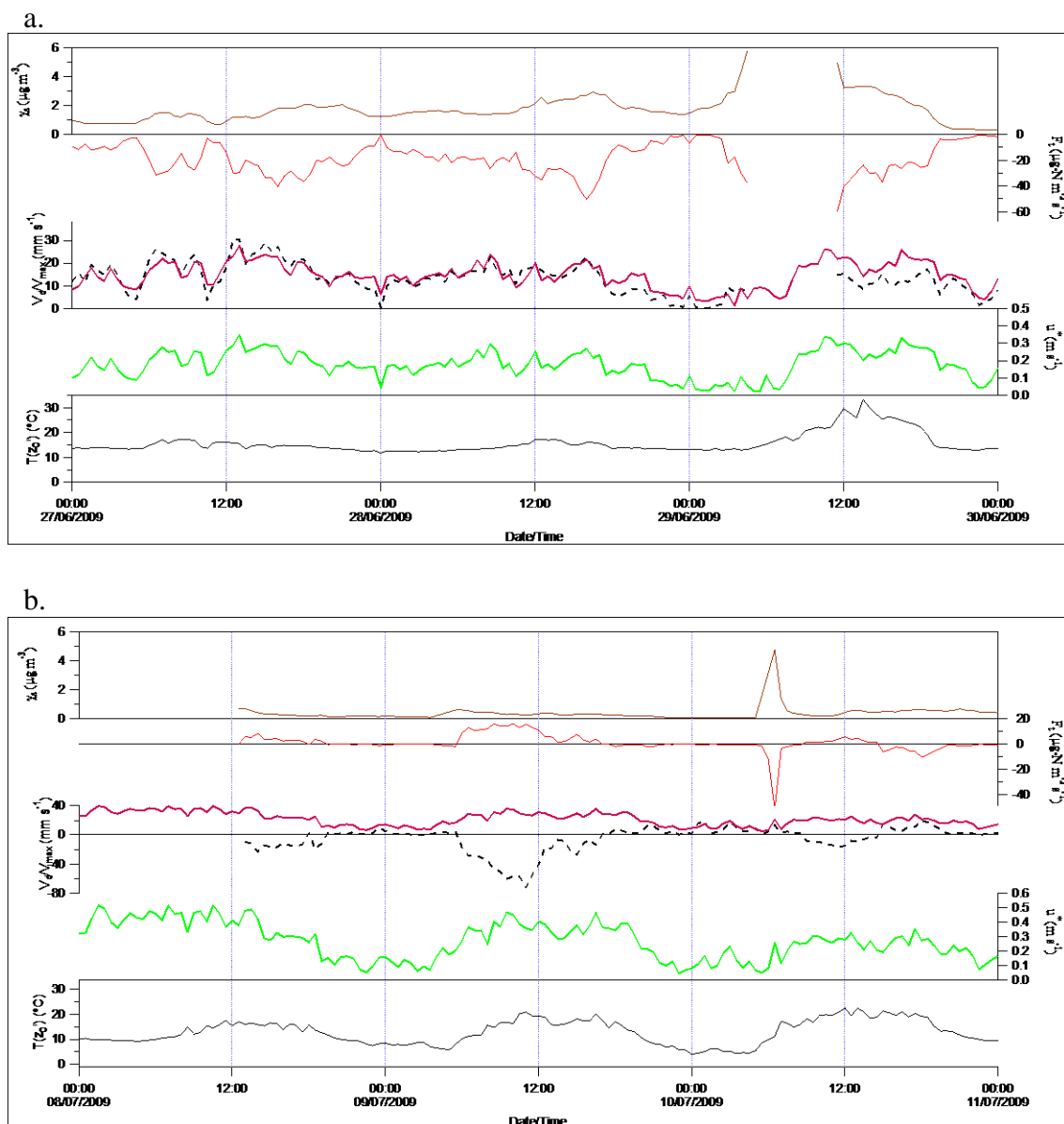
Table 5.1. Summary of statistics for monthly  $\text{NH}_3$  concentrations of the AMANDA, MARGA, DELTA and TAG. All data points available were used to calculate the statistics in the table. Minimum and maximum values for the AMANDA and MARGA relate to 30 minute and 1-hour values, respectively. Concentrations are in  $\mu\text{g m}^{-3}$ .

Month	AMANDA			MARGA			DELTA (1 m)	TAG (1 m)
	Min	Max	Mean	Min	Max	Mean	Mean	Mean
Jan-09							0.61	0.80
Feb-09				0.23	2.84	0.64	0.65	0.79
Mar-09				0.01	9.38	0.61	0.63	0.40
Apr-09				0.04	12.34	1.97	1.33	0.84
May-09				0.07	6.77	0.67	0.83	
Jun-09	0.02	7.92	1.30	0.09	11.69	0.72	0.89	0.90
Jul-09	0.02	14.33	1.03	0.07	27.69	2.49	1.04	0.71
Aug-09	0.01	24.66	0.47	0.19	6.46	0.57	0.47	0.51
Sep-09	0.02	6.44	0.47	0.01	14.19	0.88	0.90	0.46
Oct-09	0.02	13.14	0.83	0.10	7.99	1.47	0.69	0.41
Nov-09	0.01	6.06	0.50	0.06	15.49	0.75	0.60	0.35
Dec-09	0.00	27.27	0.55	0.20	16.10	1.73	0.65	0.21

### 5.3.2 Ammonia exchange

Figures 5.5a and b show examples of the ammonia flux measured with the  $\text{NH}_3$  gradient system for two 72-hour periods, in relation to the air concentration and selected meteorological parameters. Also shown is the deposition velocity ( $V_d = -F/\chi$ ) in comparison to the maximum deposition velocity possible if the deposition were constrained by turbulence only ( $V_{\text{max}} = 1/(R_a + R_b)$ ). The time series shows that, during this period, the deposition velocity initially approached  $V_{\text{max}}$  within the uncertainty of the measurement (zero canopy resistance). Under these conditions, the deposition flux increases with increasing concentration ( $\chi$ ) and/or increasing turbulence ( $u_*$ ). On 29<sup>th</sup> June and during periods of emission observed in Figure 5.5b,  $V_d$  increasingly changed to smaller values when the canopy warmed up. These warmer conditions may have dried out the canopy (decreasing the capacity of the leaf surface to take up  $\text{NH}_3$ ) or may have increased the temperature dependent stomatal compensation point.





Figures 5.5 a and b. Example time-series of the measured  $\text{NH}_3$  concentration and flux in relation to the meteorological variables  $u^*$  and  $T(z_0')$  for periods of (a.) deposition and (b.) emission. Also shown is the deposition velocity ( $V_d$ ) in comparison with the maximum deposition velocity allowed by turbulence ( $V_{\text{max}}$ ); see text.

The summary statistics of the  $\text{NH}_3$  exchange fluxes as measured using the AMANDA is presented in Table 5.2, which also compares the data with the equivalent 7 months from earlier measurements during 1995 as part of the LIFE project (Fowler et al. 1996).

Valid AMANDA flux measurements were obtained for approximately 42% of the time during June and December 2009. Fluxes ranged from  $-73.16 \text{ ng-N m}^{-2} \text{s}^{-1}$  (deposition) to  $43.20 \text{ ng-N m}^{-2} \text{s}^{-1}$  (emission) with a mean deposition flux of  $-3.10 \text{ ng-N m}^{-2} \text{s}^{-1}$ . The coverage during June and December 1995 was approximately 53%, with fluxes ranging



from  $-125.83 \text{ ng-N m}^{-2} \text{ s}^{-1}$  (deposition) to  $12.07 \text{ ng-N m}^{-2} \text{ s}^{-1}$  (emission), with a mean deposition flux of  $-4.71 \text{ ng-N m}^{-2} \text{ s}^{-1}$ .

For both the 1995 and 2009 datasets, the monthly mean fluxes were all deposition.

The months with the largest deposition occurred in June 2009 and November 1995, with the smallest deposition occurring in August 2009, compared to September 1995. The only two months where deposition in 2009 exceeded deposition in 1995 were June and September. The 2009 data had less variation in the autumn and winter months, than in 1995. Overall, the annual deposition flux in 2009 is approximately 34% less than the equivalent period in 1995.

Table 5.2. Comparison between fluxes from the 1995 LIFE project (Fowler et al. 1996) and the campaign presented in this paper. Fluxes are measured in  $\text{ng-N m}^{-2} \text{ s}^{-1}$  and statistics relate to 30-minute values.

	2009					1995
Month	Min	max	median	st dev	mean	mean
June	-73.16	20.52	-2.60	9.17	-9.56	-3.31
July	-59.85	43.20	-3.07	12.08	-2.05	-3.76
August	-53.64	11.81	-0.49	6.16	-1.51	-5.60
September	-57.43	8.22	-1.29	6.28	-3.04	-2.69
October	-31.08	25.15	-1.37	6.53	-2.17	-4.54
November	-36.08	21.23	-0.70	5.73	-2.12	-10.13
December	-25.43	3.45	-1.43	5.21	-3.04	-4.44
Average Flux	-73.16	43.20	-1.21	7.88	-3.10	-4.71

The frequency distribution (Fig. 5.6) of the fluxes for both the 2009 and the equivalent 7 month period of the 1995 LIFE campaign show that negative fluxes dominate at Auchencorth Moss, which is consistent with the results in Table 5.2. The 1995 dataset consists of 5421 30-minute averaged data points collected over a continuous 7 month period, with negative fluxes contributing 91.0% of the measurements. The 2009 data consists of 4278 30-minute averaged data points collected over a 7 month period (June – December), with negative fluxes contributing 75.6%: an increase in emissions of 15.4% in 2009 compared to 1995. This is demonstrated in Figure 5.6, which shows a higher frequency of emission fluxes in 2009 and a higher frequency of depositional fluxes in 1995.



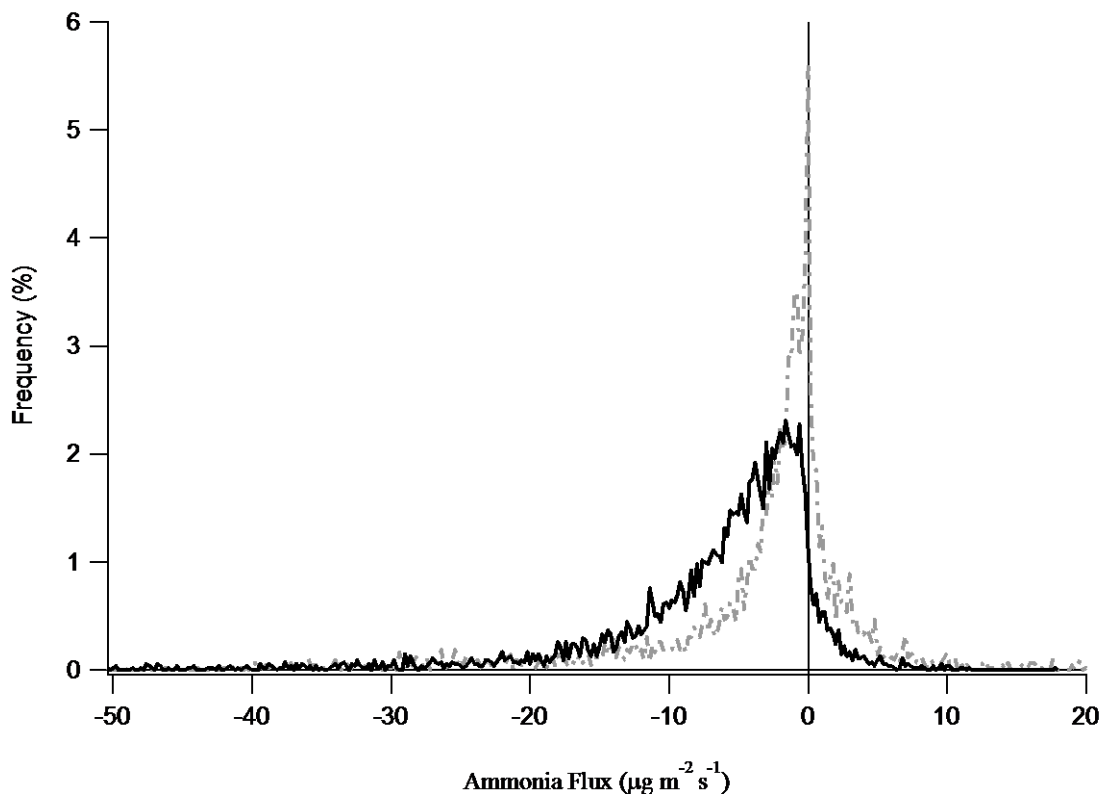


Figure 5.6. Frequency distribution of 30 minute average  $\text{NH}_3$  fluxes measured between June to December in 1995 (black, solid) and 2009 (grey, dotted).

### 5.3.3 Updated ammonia model parameterisation

The measured flux was used to assess and refine the model parameterisation of Flechard et al. (1999) with the aims (i) to investigate potential changes in the efficiency of the different exchange processes with time and (ii) to develop the most appropriate parameterisation to predict annual deposition from the MARGA long-term concentration measurement. To achieve the best fit between the model and the measured data, several parameters required assessing/updating. The 1995 AMANDA flux measurements were reproduced with a canopy compensation model (describing cuticular exchange as deposition only) and a full leaf chemistry model (Flechard et al. 1999). In the 2009 data, transient emission peaks were clearly observed on several mornings, suggesting that drying leaf surfaces accounted for temporary emission fluxes. Since a full leaf chemistry model is not appropriate to simulate the long-term MARGA data, however, here we decided to parameterise the capacitance model of Sutton et al. (1998):



**The stomatal resistance ( $R_s$ )** was based on the parameterisation suggested by Wesley (1989), but with the addition of a linear dependence on  $LAI$ , so that:

$$R_s = \min(R_{\max}, R_i(1 + 200 * (S_t + 0.1)^{-1})^2(400 + (T(40 - T))^{-1}LAI_{ref}/LAI)), \quad (26)$$

where  $S_t$  is the global radiation in  $W\ m^{-2}$ ,  $T$  is the temperature in  $^{\circ}C$  and  $R_{\max}$  is the maximum resistance ( $= 5000\ s\ m^{-1}$ ).  $R_i$  is the minimum bulk canopy stomatal resistance for water vapour at optimum light conditions; it is dependent on land use and vegetation type and here set as  $60\ s\ m^{-1}$ .  $LAI_{ref}$  is the value of  $LAI$  to which the  $R_i$  relates.

Flechar et al. (1999) used the bulk stomatal resistance to water vapour transfer,  $R_{seb}$  adapted from Hicks et al. (1987):

$$R_{seb} = \frac{R_{st}' \left(1 + \frac{b'}{S_t}\right)}{f_e f_T f_w}, \quad (27)$$

where,  $R_{st}'$  and  $b'$  are empirical parameters which vary with plant species and were fitted to measured data, and  $f_e$ ,  $f_T$  and  $f_w$  are the physiological stress factors of vapour pressure deficit, temperature and water potential, respectively. However, on this occasion a better fit was achieved using the simpler Wesley parameterisation with the  $LAI$  dependence providing an improved representation of the changing canopy.

**The stomatal emission potential ( $\Gamma_s$ )** was derived by fitting temperature response curves of the combined Henry and dissociation equilibrium (Eq. 6) to the concentrations at which the flux changed sign (from emission to deposition or vice versa) following the methodology of Nemitz et al. (2004) (Fig. 5.7). Prior to this exercise, data were selected for dry conditions, during which the cuticular pathway can be neglected, and for reasonably turbulent conditions. The time series of  $\Gamma_s$  used in the model fit is shown in Table 5.3, compared with the earlier values used by Flechar and Folwer (1998b).



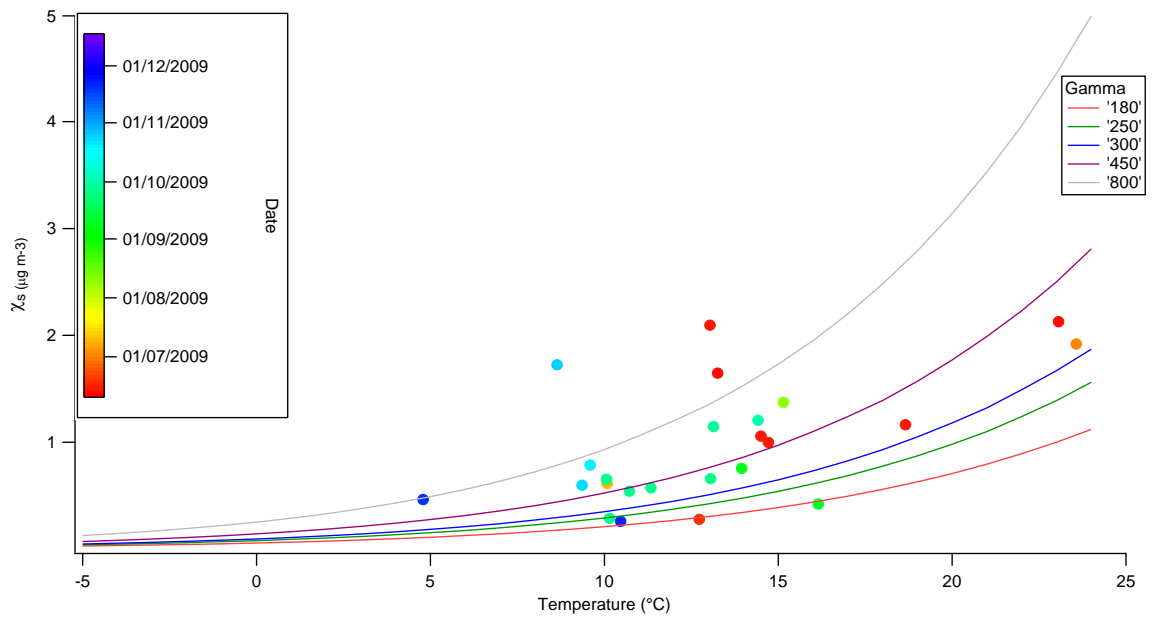


Figure 5.7.  $\Gamma_s$  was determined from the best fit curves to  $\chi_a$  for conditions where the flux changed from emission to deposition (and vice versa) against temperature, using Eq. (6).

Table 5.3. The mean monthly  $\Gamma_s$  used in the models based on data collected as part of the 1995 LIFE campaign and 2009. Flechard et al. (1999) modelled selected dates in 1995, hence the gaps for November and December 1995 where the model was not run. Best fit annual  $\Gamma_s$  for 1995 = 180 (based on 12 months data), 2009 = 350 (based on 7 months data) (Fig. 5.7).

Month	$\Gamma_s$	
	2009	1995
June	167	180
July	388	367
August	283	350
September	445	167
October	221	50
November	200	
December	180	

**I Cuticular resistance.** Due to the very limited range of  $RH$  and vapour pressure deficit ( $vpd$ ) observed during the measurement period, it was not possible to derive a robust new relationship of  $R_w$  as a function of  $RH$  or  $vpd$ . Thus, for the purpose of this study,  $R_w$  was parameterised according to Flechard et al. (1999), with the addition of an  $LAI$  dependence:



$$R_w = R_{w \min} + 100 * (1 - e^{-2*vpd})LAI_{ref}/LAI, \quad (28)$$

where  $R_{w \min}$  is the minimum value of  $R_w$ ,  $vpd$  is in units of kPa, and  $R_w$  is in units of  $s \, m^{-1}$ . A somewhat better model fit to night-time measurement data under wet conditions was found for  $R_{w \min} = 15 \, s \, m^{-1}$  than for Flechard's original value of  $20 \, s \, m^{-1}$ , which was therefore adapted here. Both values lie within the scatter of the measurements (Fig. 5.8).

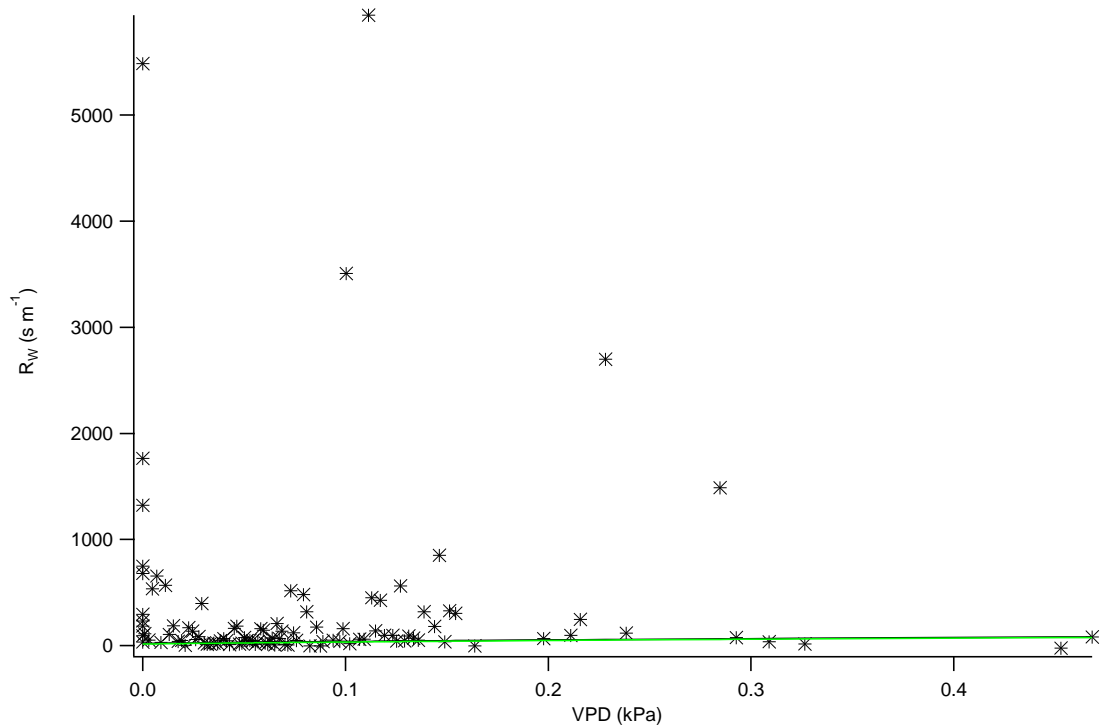


Figure 5.8. Relationship between night-time  $R_w$  (for  $R_a + R_b < 250 \, s \, m^{-1}$  and  $R_s > 5000 \, s \, m^{-1}$ ), together with the relationship used by Flechard et al. (1999) (black line) and the relationship used here for  $LAI = LAI_{ref} = 1.83 \, m^2 \, m^{-2}$  (green line).

**(d) Adsorption / desorption resistance.** In the capacitance model the cuticular exchange is parameterised by  $R_d$ , which in the original parameterisation by Sutton et al. (1998) is linked to the capacitance ( $C_d$ ) (represented by the amount of leaf water stored on the leaves) through

$$R_d = 5000 / C_d \quad (29)$$



In this approach  $C_d$  is thought to be a more mechanistic predictor of the leaf water surface area, which is what the *vpd* parameterisation of  $R_w$  is attempting to simulate. However, to maximise comparability between the new parameterisation and the old parameterisation and also between the static single-layer and the dynamic capacitance model, we here use  $R_d = R_w$ .

**(e) Leaching flux.** Another parameter required in the dynamic capacitance model is the leaching flux ( $K_r$ ), which describes a continuous loss from the plant surface pool, either by liquid film transfer into the stomata, through trans-cuticular uptake or by wash-off to the ground. We found that the data could better be simulated with a 10-fold larger leaching flux than used by Sutton et al. (1995), i.e.  $K_r = -0.1$ , because otherwise the morning desorption peaks were overestimated. The moorland vegetation has a significant contribution from nonvascular plants, which may provide additional pathways of  $\text{NH}_3$  uptake.

In addition,  $\text{NH}_3$  can be removed from the water surface/film layer of the leaf surface by precipitation, effectively re-setting the build-up of ammonia in the capacitor (cuticle). For this reason, when it rained the capacitor is reset to a zero charge ( $Q_d = 0$ ).

Figure 5.9 shows the flux modelled with the static and dynamic modelling approach for an example period in relation to meteorological parameters. Also shown are the component fluxes  $F_w$  (cuticular flux),  $F_s$  (stomatal flux) and  $F_d$ .

The morning and night-time deposition is likely to be the result of the presence of dew or microscopic water layers on the leaf surface, resulting in a small surface resistance. Since the stoma closes in the absence of daylight, stomatal exchange is inhibited and ammonia can only be deposited, to the wet leaf surface. As the day progresses the dew evaporates and the stoma open, allowing ammonia to be emitted. This is reflected in the behaviour of  $F_s$ , which shows little to no flux during the dark hours, followed by a period of emission during the morning/afternoon. It also contributes the most to the total emission. During the same period, deposition to the cuticle increases, suggesting that some of the  $\text{NH}_3$  emitted is re-deposited to the leaf cuticle.  $F_d$  emission coincides with the additional emission seen in the capacitance model, as would be expected. Both models generally capture this morning emission, with the dynamic model better capturing the initial emission but somewhat over-estimating the peak emission period.



Both models overestimate the morning deposition, although in general the dynamic model overestimates less than the static model over the whole 7 month period.

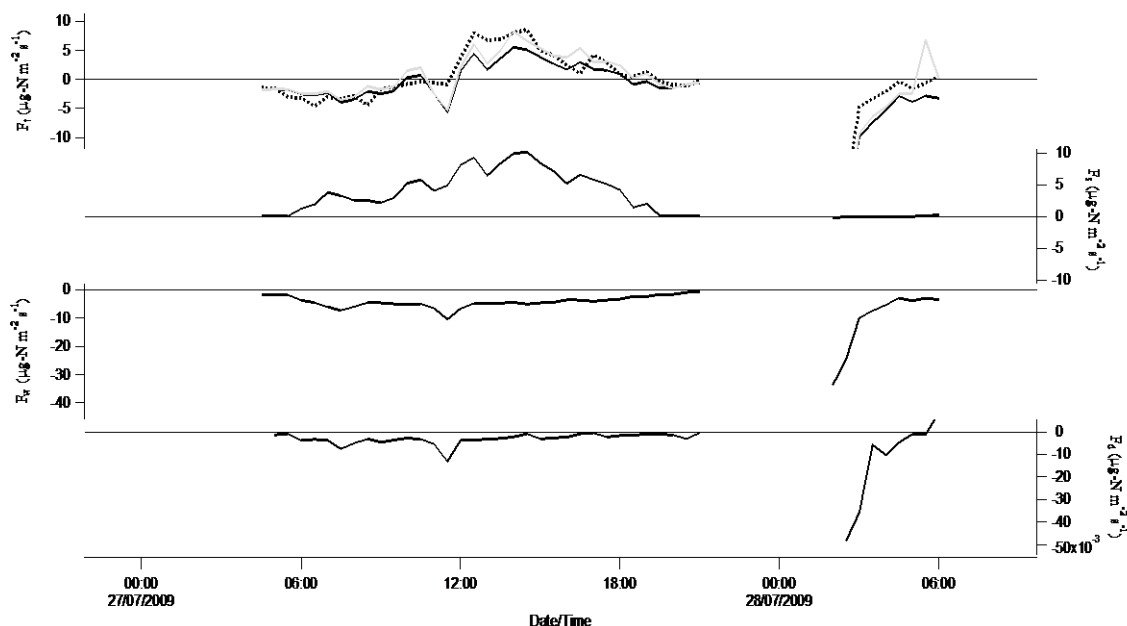


Figure 5.9. An example of morning emission peaks showing the measured (dotted line), compared to the static model (solid black line) and dynamic model (solid grey line).

#### 5.3.4 Inferred annual dry deposition of reactive N compounds

The dynamic model parameterised above was applied to hourly concentrations of  $\text{NH}_3$  measured by the MARGA in 2009 and 2010. The gases  $\text{HNO}_3$ , HONO and the aerosols  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were also measured by the MARGA, and were modelled via the appropriate inferential models outlined in the Methods Section. For this exercise gaps up to a length of 3 hours in the  $\text{NH}_3$  concentration or meteorological data were gap-filled by linear interpolation. This resulted in 3531 hourly data values, covering 40% of the time. Because the remaining gaps were not equally distributed over the different months and day/night conditions, the calculation of the annual flux by simply averaging the available data may lead to a bias.

Instead, monthly average diurnal cycles (Fig. 5.10) were calculated based on the available data and these were averaged to derive the best estimate of the annual total deposition. Effectively, this results in a gap filling by mean diurnal variation (MDV), as has been used to gap fill longer gaps in measured  $\text{CO}_2$  fluxes (Moffat et al. 2007).



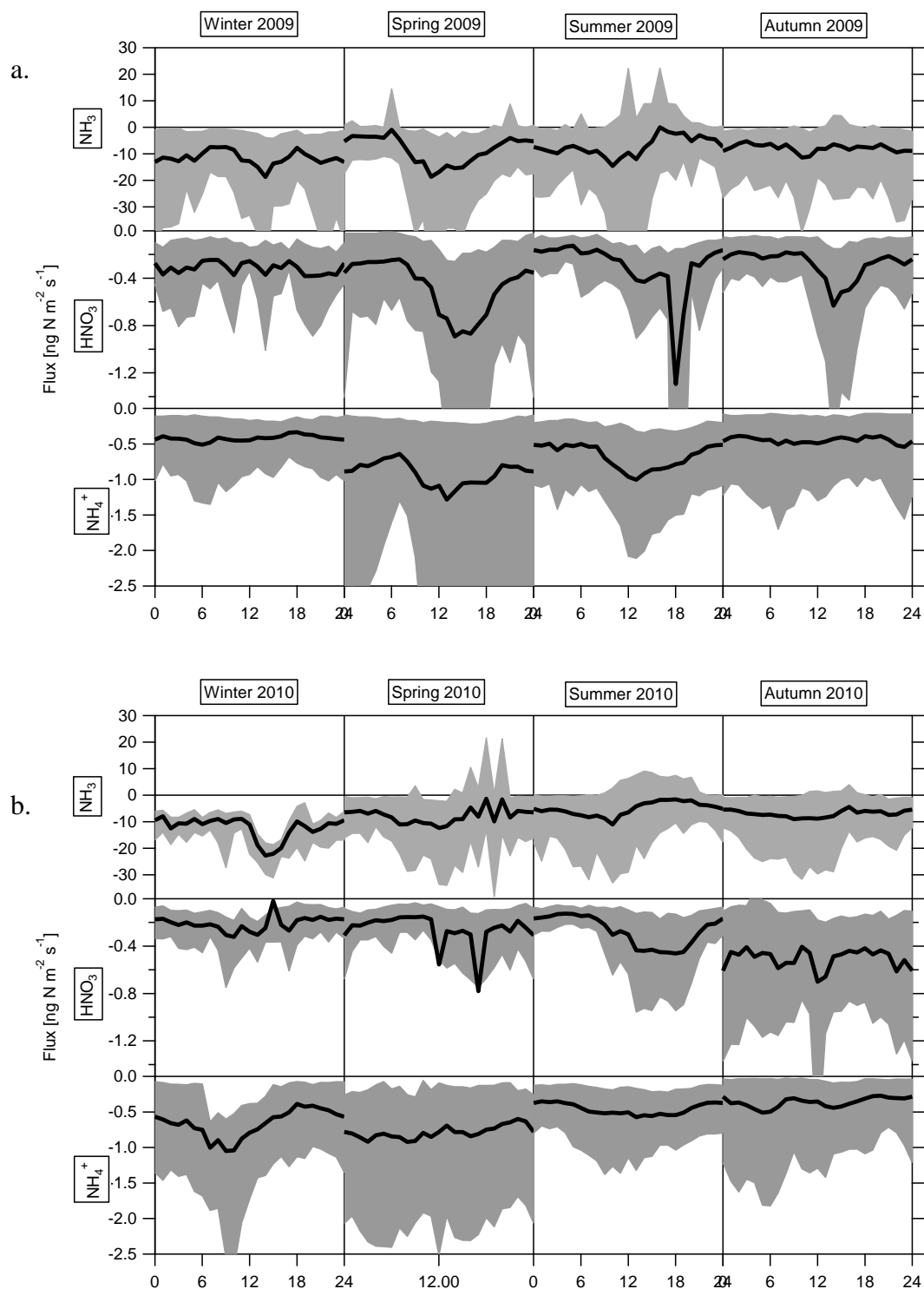


Figure 5.10. Diurnal cycles of selected compounds, according to season in a. 2009 and b. 2010. Winter = Dec/Jan/Feb; spring = Mar/Apr/May; summer = Jun/Jul/Aug; autumn = Sep/Oct/Nov. Grey shaded areas are the 5<sup>th</sup> and 95<sup>th</sup> percentile values which represents the data range without the most extreme values.



Figure 5.10 shows the diurnal cycles of selected compounds in 2009 and 2010. In general, both years show similar temporal and seasonal daily cycles for all of the compounds.

### $NH_3$

The lowest deposition occurred in the summer; depositional fluxes were more prominent in the early mornings, with less deposition, and more emission, occurring as the day progressed. By the evening, deposition had increased again. The autumn showed less variation in  $NH_3$  than in the other seasons, with less deposition in the morning than in the summer, and more deposition (and/or less emission) in the afternoon. The winter overall had the most deposition, with more deposition in the afternoon and little to no emission. The afternoon deposition is more pronounced in the 2010 data than 2009. Spring also has an increase in deposition in the afternoon; this time it is more pronounced in 2009 than 2010. In both 2009 and 2010, some emission is predicted to have occurred in the afternoon.

### $HNO_3$

In both spring and summer, deposition increased in the afternoon, before decreasing as the evening progressed, reflecting the diurnal cycle in the concentration, linked to photochemical production. Autumn 2009 showed a similar pattern to the spring and summer but autumn 2010 did not. There was little variation in the winter in both years, although in 2010 there is a slight drop in deposition in the late afternoon.

### $NH_4^+$

Ammonium ( $NH_4^+$ ) is here depicted as one of the aerosol species. Spring and summer 2009 showed an increase in deposition during the middle of the day. Both autumn and winter 2009 showed little variation in deposition. In 2010, winter shows the most variation; deposition increased in the morning, then decreased to a deposition minimum in the early evening. Deposition increased again slightly as the evening progressed. In summer 2010 there was a slight increase in deposition in the morning to afternoon, but it is much less pronounced than in 2009. There was little variation in spring and autumn 2010. At Auchencorth aerosol concentrations are mainly driven by mesoscale transport pattern, which does not follow a clear diurnal pattern, rather than by local meteorological parameters, such as the temperature effect on the  $NH_4NO_3$  equilibrium.



In addition, turbulence, the governing parameter of the deposition, shows little diurnal variability with generally windy nights at this exposed Scottish moorland site.

Figure 5.11 depicts the annual flux of the reactive N compounds modelled from the MARGA, while Tables 5.4 and 5.5 display the monthly flux breakdown for 2009 and 2010, respectively.  $\text{NH}_3$  is predicted to have contributed the most to the total dry deposition of inorganic N to Auchencorth. In 2009,  $\text{NH}_3$  deposition was greater than in 2010, and this change accounted for most of the difference in N deposition between the two years. In both years, the largest deposition occurred in December and the least in August.

Annual mean fluxes of  $\text{HNO}_3$  were similar for both years, but they showed different seasonal patterns. In 2009, the highest deposition occurred in April, but in 2010 it was in November. The lowest deposition occurred in October 2009 but in 2010 it was May.

HONO was the only compound predicted to have given a net emission, based on the uncertain parameterisation used here, with more emissions predicted to have occurred in 2010. December 2009 was the only month in which the mean flux of HONO was deposition.

Aerosol deposition was also larger in 2009 compared with 2010. Again there were some seasonal differences with the largest deposition of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  (fine), and  $\text{NO}_3^-$  (coarse) occurring in April 2009, but in 2010 occurring in May, December and March, respectively.

Overall, there was more deposition of all the compounds in 2009 compared with 2010, and less overall HONO emission.



Table 5.4. Mean monthly deposition fluxes of reactive N compounds measured by MARGA in 2009. Fluxes are in  $\text{ng-N m}^{-2} \text{s}^{-1}$ . Negative fluxes indicate net deposition and positive fluxes indicate net emission.

Month	NH <sub>3</sub>	HNO <sub>3</sub>	HONO	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup> (fine)	NO <sub>3</sub> <sup>-</sup> (coarse)	Total
Jan-09							
Feb-09	-6.60			-0.43			-7.03
Mar-09	-5.79	-0.51		-0.79	-0.50	-2.57	-10.16
Apr-09	-13.53	-0.54	1.04	-1.47	-0.83	-4.50	-19.83
May-09	-6.15	-0.37	0.37	-0.50	-0.14	-0.92	-7.72
Jun-09	-5.00	-0.27	0.13	-0.87	-0.11	-0.68	-6.79
Jul-09	-11.70	-0.33	0.63	-0.73	-0.14	-0.97	-13.24
Aug-09	-4.65	-0.33	1.32	-0.45	-0.09	-0.50	-4.71
Sep-09	-4.78	-0.51	0.19	-0.36	-0.15	-1.08	-6.69
Oct-09	-10.17	-0.16	0.07	-0.68	-1.05	-2.22	-14.21
Nov-09	-8.37	-0.18	0.30	-0.31	-0.12	-0.85	-9.52
Dec-09	-16.44	-0.32	-0.77	-0.41	-0.23	-1.34	-19.50
Total Flux (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	-2.67	-0.11	0.12	-0.20	-0.11	-0.49	-3.47

Table 5.5. Mean monthly deposition fluxes of reactive N compounds measured by MARGA in 2010. Fluxes are in  $\text{ng-N m}^{-2} \text{s}^{-1}$ . Negative fluxes indicate net deposition and positive fluxes indicate net emission.

Month	NH <sub>3</sub>	HNO <sub>3</sub>	HONO	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup> (fine)	NO <sub>3</sub> <sup>-</sup> (coarse)	Total
Jan-10							
Feb-10	-6.01	-0.28	0.13	-0.77	-0.42	-2.84	-10.20
Mar-10	-7.33	-0.32	0.24	-0.68	-0.45	-3.03	-11.57
Apr-10	-9.07	-0.36	0.38	-0.55	-0.23	-1.29	-11.12
May-10	-7.08	-0.07	0.10	-1.13		-1.30	-9.48
Jun-10	-8.39	-0.39	0.11	-0.80	-0.25	-1.65	-11.38
Jul-10	-4.56	-0.25	0.73	-0.34	-0.05	-0.54	-5.02
Aug-10	-2.41	-0.18	0.52	-0.24	-0.05	-0.44	-2.81
Sep-10	-4.94	-0.25	0.69	-0.44	-0.10	-0.59	-5.64
Oct-10	-6.54	-0.30	0.70	-0.40	-0.18	-1.17	-7.89
Nov-10	-9.53	-0.95		-0.26	-0.10	-0.61	-11.44
Dec-10	-18.66	-0.14	0.86	-0.56	-0.47	-2.02	-20.99
Total Flux (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	-2.42	-0.10	0.14	-0.18	-0.07	-0.44	-3.08



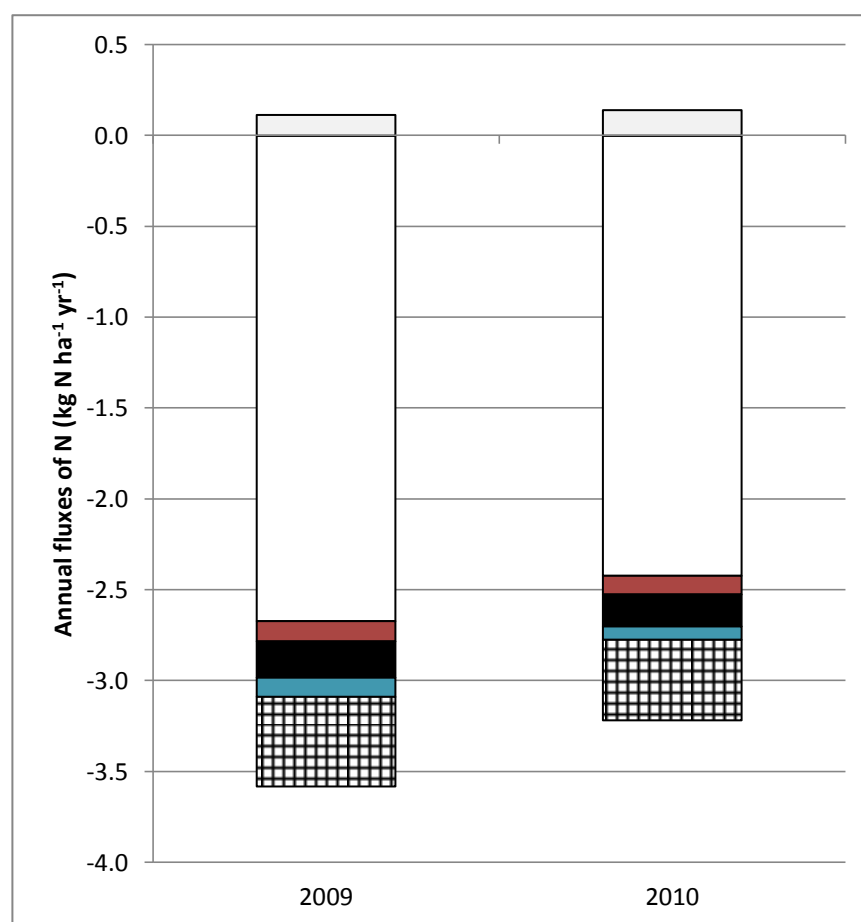


Figure 5.11. Chart depicting the annual flux of MARGA gases and aerosols in 2009 and 2010. A negative value indicates a net deposition and a positive value indicates net emission. HONO (grey), NH<sub>3</sub> (white), HNO<sub>3</sub> (red), NH<sub>4</sub><sup>+</sup> (black), NO<sub>3</sub><sup>-</sup> {fine} (blue), NO<sub>3</sub><sup>-</sup> {coarse} (squared).

Table 5.6 compares the annual dry deposition of N to Auchencorth Moss estimated for 1995, 2009 and 2010. Here the measurement methodology differed between the earlier measurements and the measurements reported here. While hourly MARGA concentration values were available for 2009 and 2010, batch sampling methods with offline chemical analysis were used in 1995. In 1995, HNO<sub>3</sub> was sampled with batch denuder technique (Keuken et al. 1988) hourly for one day every week and the samples were analysed offline by liquid anion chromatography. The aerosol components (NH<sub>4</sub><sup>+</sup>) and (NO<sub>3</sub><sup>-</sup>) were sampled weekly by low-volume fine and coarse filter samplers, each sampling for 15 minutes within every hour (Erisman et al. 2001). These filter samplers may suffer artefacts due to evaporation, especially for long sampling periods and warm temperatures (> 20 °C), which are however rare at this site.



Total dry deposition of the inorganic N components reported here was largest in 2009 at  $-3.47 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . Total deposition in 1995 and 2010 were very similar at  $-3.05 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  and  $-3.08 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , respectively. As with the MARGA data, in 1995 the largest contributor to dry deposition was  $\text{NH}_3$ , although it was less than in 2009/2010.  $\text{HNO}_3$  deposition was 3 times larger in 1995 than in 2009/2010. It must be noted, however, that many of the analyses of the 1995 batch denuder samples were below the detection limit, which was much higher for the offline technique than for the MARGA online technique. Data below this limit were replaced with a value corresponding to half the detection limit, which may have resulted in a biased high estimate.

HONO showed deposition in 1995, as opposed to the net emission observed in 2009 and 2010, but this is due to the application of a different inferential model for the HONO exchange for the earlier study, which, in the absence of the recent studies showing bi-directional behaviour, assumed HONO to deposit similar to  $\text{HNO}_3$ .

Deposition of  $\text{NO}_3^-$  (fine) aerosol in 1995 was similar to 2010 and thus smaller than in 2009. Deposition of  $\text{NO}_3^-$  (coarse) and  $\text{NH}_4^+$  aerosols was less in 1995;  $\text{NO}_3^-$  (coarse) showed the biggest change when compared to 2009/2010. Here again a different formulation of the deposition velocity was used in the earlier study, in addition to the potential of the earlier measurements having suffered evaporation artefacts.

Table 5.6. Comparison of annual dry deposition fluxes from 1995, 2009 and 2010. 1995 data are taken from Fowler et al. (1996).

Dry deposition of N	1995 $\text{kg N ha}^{-1} \text{ yr}^{-1}$	2009 $\text{kg N ha}^{-1} \text{ yr}^{-1}$	2010 $\text{kg N ha}^{-1} \text{ yr}^{-1}$
$\text{NH}_3\text{-N}$	-2.34	-2.68	-2.42
$\text{HNO}_3\text{-N}$	-0.36	-0.11	-0.10
HONO – N	-0.07	0.12	0.14
Aerosol $\text{NH}_4^+\text{-N}$	-0.09	-0.20	-0.18
Aerosol $\text{NO}_3\text{-N}$ (fine)	-0.08	-0.11	-0.07
Aerosol $\text{NO}_3\text{-N}$ (coarse)	-0.11	-0.49	-0.44
Total	-3.05	-3.47	-3.08

Flechard et al. (2011) estimated fluxes of gaseous  $\text{NH}_3$ ,  $\text{HNO}_3$  and  $\text{NO}_2$  as well as aerosol  $\text{NH}_4^+$  and  $\text{NO}_3^-$  at various European sites, including Auchencorth, using 4 different inferential models. The models estimated the following range of results for Auchencorth:  $\text{NH}_3$ , -1.5 to  $-3.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ;  $\text{HNO}_3$ , -0.4 to  $-0.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  and -0.1



to  $-0.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  each for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  aerosol. The fluxes of  $\text{NH}_3$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (fine) estimated during this study fall within the range estimated by the four models investigated by Flechard et al. (2011). However, the estimates of  $\text{HNO}_3$  and  $\text{NO}_3^-$  (coarse) present here, are higher and lower estimates respectively, in comparison to the four inferential models. The models used by Flechard et al. (2011), used monthly mean gas/aerosol concentrations from data collect in 2007-2008 and measured using a DELTA system, while the present study uses hourly data and also a different inferential modelling approach. The use of monthly mean concentrations for inferential modelling cannot accurately reproduce the co-variance between the deposition rate and the concentration. For example,  $\text{HNO}_3$  is photochemically produced and therefore shows a strong diurnal cycle with the peak during the day. This coincides with the time of day when turbulence and deposition rates are also highest. Combining elevated concentrations with elevated deposition rates leads to a higher overall deposition flux than would be derived from average concentrations; the larger deposition flux calculated from the hourly data is consistent with this effect and should represent the more accurate estimate.

## 5.4 Discussion

### 5.4.1 Accuracy of $\text{NH}_3$ concentration measurement

There have been several inter-comparisons of a variety of  $\text{NH}_3$  measurement instrumentation over the years, with varying results, demonstrating the difficulties of accurately measuring atmospheric  $\text{NH}_3$  (Milford et al. 2000, Sutton et al. 2001, Whitehead et al. 2008, Norman et al. 2009, von Bobrutzki et al. 2010).

A recently comparison of eleven atmospheric ammonia measurement techniques by von Bobrutzki et al. (2010), found most measurement approaches agreeing within 84% for concentrations above  $10 \mu\text{g m}^{-3}$ . However, the accurate measurement of small  $\text{NH}_3$  concentrations remains a challenge. As part of their study, von Bobrutzki et al. (2010) showed good agreement between the AMANDA and other wet chemical methods even at concentrations in the region 1 to  $10 \mu\text{g m}^{-3}$ . The DELTA denuder has been extensively verified against other measurement approaches and usually shows the most consistent performance for  $\text{NH}_3$  (Sutton et al. 2001). As such, the comparison between the two online wet chemistry systems (MARGA, AMANDA), the DELTA dry denuder and the TAG denuders (virtually identical to the DELTA but operated for selected periods and at several heights) is somewhat disappointing. Much of the inconsistencies



can be explained by the fact that concentrations were very variable and the online systems do not provide 100% cover of the periods over which the DELTA and TAG denuders operated. Moreover, these measurements were not targeted at an instrument intercomparison, and although an attempt was made to interpolate concentration gradients to a common height, where possible, DELTA and MARGA each provide a single-height measurement, at different heights. Perhaps better results would have been achieved during a shorter study specifically designed for this purpose, where instruments were able to be more reliably run together and at the same location on site; the AMANDA and TAG systems were located closest together and further north of the site than the MARGA and DELTA, which were spread out further south.

The temporal resolutions of the instruments were different, with DELTA and TAG measuring on a monthly timescale, the MARGA hourly, and the AMANDA every 30 minutes. The coverage of the MARGA and AMANDA varied, with AMANDA measuring 42% of the time and the MARGA measuring 50% and 51% (7 month and 12 month periods respectively). From the most robust comparison, using only paired samples, it appears however, that the MARGA reported systematically somewhat larger concentrations than the AMANDA (by 16%). There is also a difference in the statistical distribution between the AMANDA and MARGA measurements as visible in the log-probability plot (Fig. 5.12), although this compares the full year's MARGA data with 7 months of AMANDA data. Nevertheless, the MARGA concentrations start to drop off at concentrations below  $0.2 \mu\text{g m}^{-3}$ , while the AMANDA measurements continue to be close to log-normally distributed down to concentrations of  $0.01 \mu\text{g m}^{-3}$ . These values may be interpreted as approximate effective limits of detection, indicating that the MARGA instrument has the higher detection limit and larger uncertainty when measuring small concentrations.



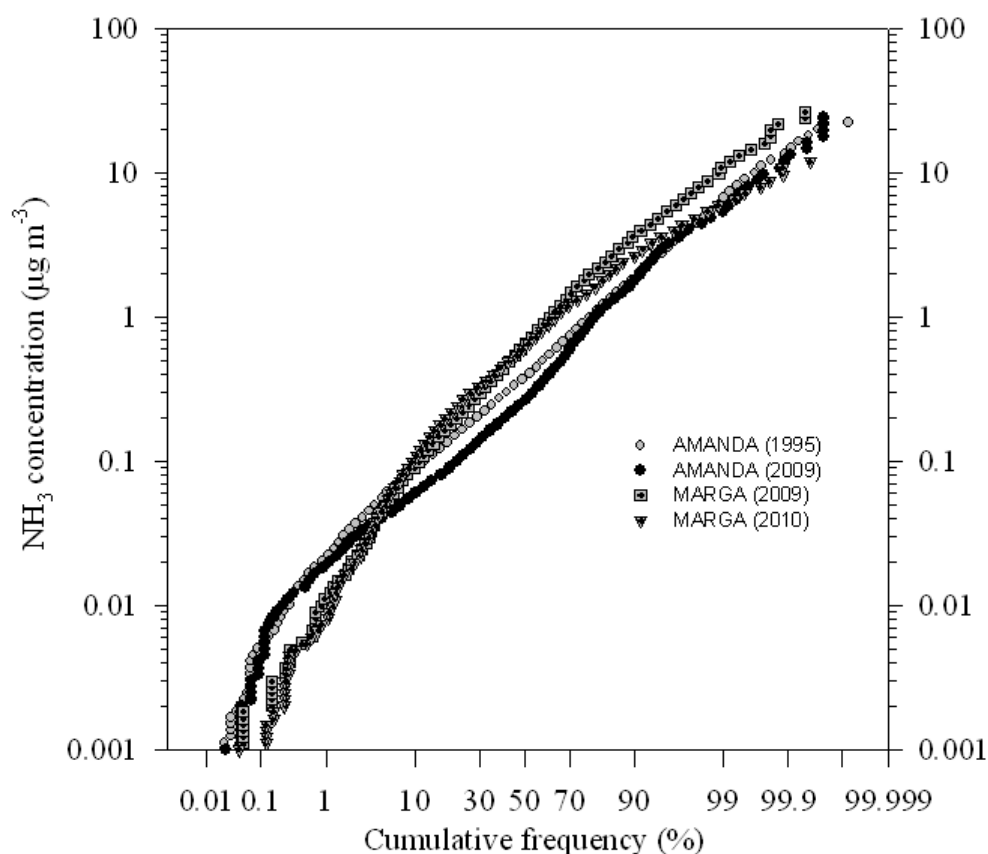


Figure 5.12. Log-probability plot of ammonia concentrations. The grey dots represent 30 minute averages collected by the AMANDA between Feb 1995 and Feb 1996 at a height of 0.43 m. The Black dots represent 30 minute averages collected by the AMANDA between June 2009 and December 2009 at a height of 1m. The grey squares represent hour averaged collected by the MARGA between January 2009 and December 2009 at a height of 3.55 m. The grey triangles represent hour averaged collected by the MARGA between January 2010 and December 2010 at a height of 3.55 m. All available data were used.

#### 5.4.2 Changes in the behaviour of ammonia between 1995 and 2009 and new dry deposition parameterisation

Changes in the behaviour in ammonia over the 14 years between the measurement years (1995 and 2009) may reflect changes in air concentrations (following changes in local sources), changes in meteorology, changes in the ecosystem status or changes in the overall pollution climate.

Since 1995, there has been an increase in the number and size of the chicken farms in the area, situated to the SE of the measurement site. Despite this, continuous long-term



measurements with the DELTA denuder indicate that the average concentrations of  $\text{NH}_3$  have decreased somewhat at Auchencorth (Fig. 5.13). In the highly time-resolved measurements by MARGA and AMANDA, however, the additional local sources of  $\text{NH}_3$  are reflected in the higher peak concentration and a second mode in the log-normal distribution (Fig. 5.12), presumably associated with the SW wind directions. Both AMANDA datasets show non-linearity below  $0.01 \mu\text{g m}^{-3}$  which is due to being below the detection limit ( $0.02 \mu\text{g m}^{-3}$ ) of the AMANDA. As mentioned previously, the MARGA data deviated from a straight line, but the 2010 data were more aligned than 2009.

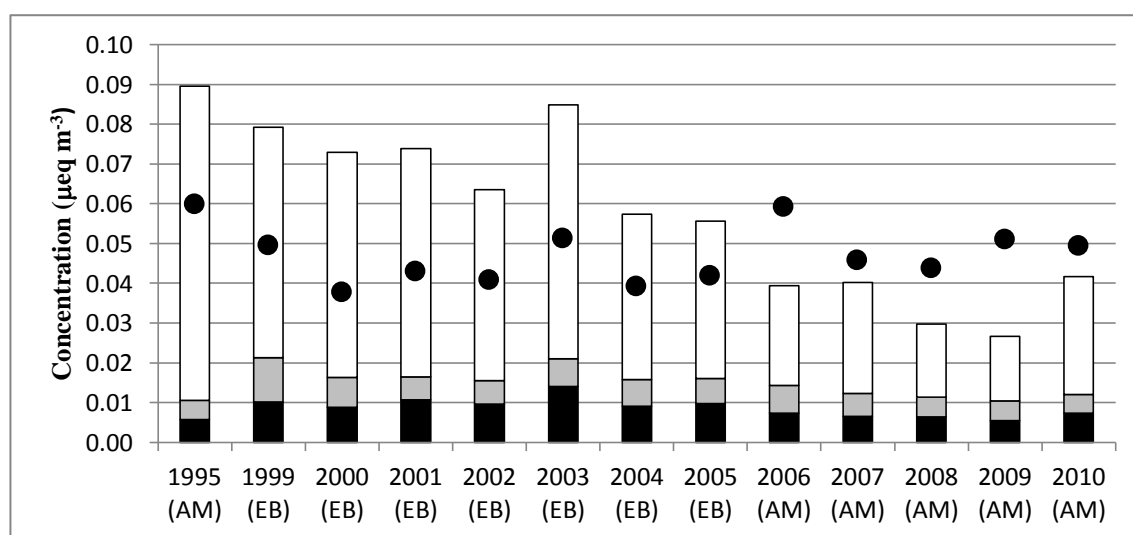


Figure 5.13. Concentration changes of  $\text{SO}_2$  (white),  $\text{HCl}$  (grey),  $\text{HNO}_3$  (black) and  $\text{NH}_3$  (black dot). Data for the acid concentrations at Auchencorth Moss (AM) was only available for 1995 and 2006-2010. The concentrations for the years 1999-2005 were taken from Easter Bush (EB), a site 2 km NE of Auchencorth Moss, which has comparable data for  $\text{SO}_2$ ,  $\text{HCl}$  and  $\text{HNO}_3$ .  $\text{NH}_3$  for all years was collected at Auchencorth Moss. Data was not available for 1996-1998.

The measured fluxes decreased by 34% if comparing the 7 months of measurements with the equivalent period in 1995 (Table 5.2). However, the monthly modelled fluxes (Tables 5.4 & 5.5) suggest that much variability is to be expected in how the fluxes are distributed over the year and thus this difference may not be reflected in the annual values. Indeed, despite the decrease in mean concentrations, the estimated annual  $\text{NH}_3$  deposition is estimated not to have changed significantly between 1995 and 2009, based on the parameterisations used here.



The annual net flux depends not only on the mean air concentration, but also its seasonal and diurnal variability, the meteorology and the state of the vegetation. The frequency distribution of the measured fluxes has changed markedly (Fig. 5.6), dominated by smaller deposition fluxes, showing more emission events, but also more extreme deposition events. Changes in the parameterisations that best fit the measurement data can help elucidate changes in the process. The deposition to leaf surfaces is governed by surface wetness and the interactions with acidic compounds that co-deposit and keep the pH of the leaf layers low. The review of Massad et al. (2010) revealed large variability in the  $R_w$  parameterisations between studies and, while it is still a challenge to provide a generalised equation, there generally does appear a dependence on acidity. The effect of  $\text{NH}_3$ - $\text{SO}_2$  co-deposition is included, for example, in the EMEP chemical transport model, where it is parameterised on the basis of the molar ratio of  $\text{SO}_2/\text{NH}_3$  concentration in air. Fowler et al. (2009) pointed out that as  $\text{SO}_2$  concentrations have declined significantly,  $\text{HNO}_3$  and  $\text{HCl}$  now contribute significantly to the total deposition of acidity and should therefore be taken into account. Thus, a more comprehensive acidity ratio ( $a_r$ ) may be defined according to Eq. (2). Figure 5.13 shows that acid gas concentrations fell between 1995 and 1999-2010, and this is also reflected in a decrease in  $a_r$  (Figure 5.14). In terms of concentrations, gases other than  $\text{SO}_2$  now contribute typically 1/4 to total acidity and this contribution is larger for deposition because  $\text{HNO}_3$  and  $\text{HCl}$  deposit more efficiently than  $\text{SO}_2$ . Figure 5.13 shows the changes in concentrations of  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{NH}_3$ , which are used to calculate the  $a_r$ . From 1995, the biggest change in concentration was a decrease in  $\text{SO}_2$ .  $\text{HCl}$  changed very little with  $\text{HNO}_3$  varying slightly: 2009 had less  $\text{HNO}_3$  deposition than 1995, but 2010 had more. Overall, it would be expected that  $R_w$  declined between 1995 and 2009/10. While the scatter in the derived values of  $R_w$  was too large to confirm this with the measurement data, the fact that night-time deposition fluxes could be modelled more successfully with a reduced  $R_{w,\text{min}}$  of  $15 \text{ s m}^{-1}$ , compared with the 2009 value of  $20 \text{ s m}^{-1}$ , may be taken as a confirmation for this change. In the absence of a robust empirical relationship between  $R_w$  and  $a_r$  for this site, the co-deposition was only accounted for in the inferential model by choosing this smaller value of  $R_{w,\text{min}}$ .



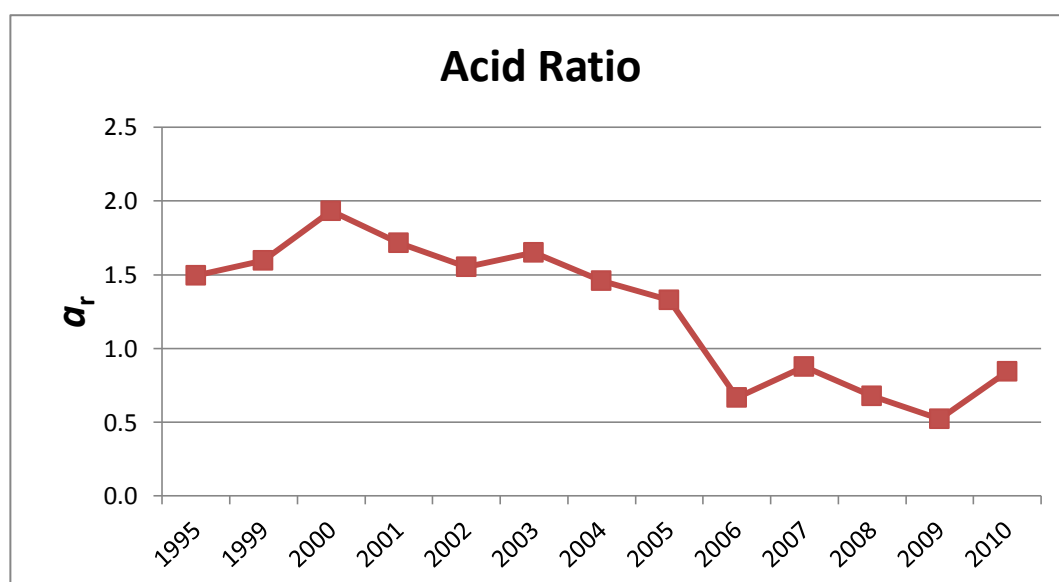


Figure 5.14. Changes in acid ratio at Auchencorth Moss between 1995 and 1999-2010

Flechar et al. (1999) developed a dynamic model which included estimates of the chemistry of the leaf surface (estimated from both wet and dry deposition), which included the compounds considered in the calculation of  $a_r$ . This is outwith the scope of this paper, but the inclusion of dynamic response presented here is designed to be an approximation of the leaf chemistry.

$\Gamma_s$  is dependent on the vegetation, ecosystem type and amount of N deposition. The results presented here show a best fit annual  $\Gamma_s$  for 1995 was 180 and increased to ~350 in 2009. Both these values are within the range expected for semi-natural vegetation, and less than the mean derived from a meta-analysis of published data, but larger than would be expected for the N input at this site. Massad et al. (2010) summarised the  $\Gamma_s$  derived from 60 studies of non-managed ecosystems (forest and semi-natural) and 96 studies of managed ecosystems (arable and grassland). They found mean  $\Gamma_s$  values of 502 and 782, respectively. When split into the four ecosystem subgroups, mean  $\Gamma_s$  results were 378 for semi-natural ( $n=51$ ;  $\Gamma_s$  range = 3-2930); 1194 for forest ( $n=9$ ;  $\Gamma_s$  range = 27-5604); 774 for arable ( $n=69$ ;  $\Gamma_s$  range = 43-5233) and 802 for grasslands ( $n=27$ ;  $\Gamma_s$  range = 16-4751). These studies were a mixture of fertilised and non-fertilised, and had a range of annual N deposition; with the managed ecosystems generally having more fertilisation. Typically,  $\Gamma_s$  is low for non-fertilised ecosystems (20-100) and larger for fertilised ecosystems (300-3000) (Loubet et al. 2009). Higher values of  $\Gamma_s$  were found to be associated with larger N inputs, both from atmospheric deposition and fertiliser application Massad et al. (2010).



Nemitz et al. (2004) derived a large  $\Gamma_s$  of 1200 for an unfertilised Dutch heathland, which is more than treble the mean derived from the Massad summary. It does, however, fall within the range of  $\Gamma_s$  (3-2930) and this high value was attributed to higher levels of N deposition in the region. Other studies have shown increases in  $\Gamma_s$  for up to two weeks after fertilisation applications (Milford et al. 2001, Loubet et al. 2002, Mattsson et al. 2009). The effect of livestock on  $\Gamma_s$  is largely unknown, as there is not enough data to draw any conclusions (Massad et al. 2010). Livestock graze and excrete nitrogen, allowing the mobilisation of nitrogen, and potentially adding/removing nitrogen from the system; this may have an effect on  $\Gamma_s$  and warrants further investigation. Based on their meta-analysis Massad et al. (2010) proposed a relationship between  $\Gamma_s$  and atmospheric (inorganic) N deposition. The total atmospheric N input at Auchencorth has been estimated to be 8.01 kg N ha<sup>-1</sup> yr<sup>-1</sup> (McKenzie et al. 2013, Chapter 6, this volume), which reduces to 7.36 kg N ha<sup>-1</sup> yr<sup>-1</sup> without inputs from organic nitrogen in wet deposition and without net N<sub>2</sub>O uptake, both of which were not considered in deriving the relationship of Massad et al. (2010). At this N deposition a  $\Gamma_s$  of 251 is predicted, which is consistent with the range used in reproducing the measured fluxes at Auchencorth, although it is clear from that meta-analysis that there is considerable variability in the low N input range.

## 5.5 Conclusions

The reactive nitrogen gases ammonia (NH<sub>3</sub>), nitric acid (HNO<sub>3</sub>) and nitrous acid (HONO) as well as the aerosol compounds ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) in PM<sub>2.5</sub> and PM<sub>10</sub> are continuously monitored at hourly resolution at the Auchencorth Moss monitoring site. Here the data are used for the inferential modelling of dry deposition for 2009 and 2010, using the micrometeorological parameters measured at this site. Whilst the parameterisations for the modelling of most compounds are taken from the literature, for NH<sub>3</sub>, an existing inferential model was refined using 7 months of flux measurements made with a three-point gradient monitor. These new flux data were also compared to comparable measurements made in 1995 to assess whether the parameters that control NH<sub>3</sub> deposition have changed over the past 15 years, e.g. in response to changes in chemical composition.

The ratio of acid concentrations to NH<sub>3</sub> has more than halved over the time period, making it more likely that NH<sub>3</sub> can be released from drying leaf surfaces in the morning



and a dynamic model that accounts for the effect was chosen to simulate this process. Contrary to this decrease in acid ratio, the new dataset could be better reproduced using a smaller minimum cuticular resistance ( $R_{w,min}$ ) than was used in the static model to simulate the 1995 data, but because the role of the resistance is somewhat different in the two frameworks, direct comparison is problematic.

More clearly, the values of the emission potential ( $\Gamma_s$ ) appear to have almost doubled between 1995 and 2009/10 and this may be due to an increase in peak  $\text{NH}_3$  concentrations due to the construction of new chicken farms SSE of the site and the somewhat increased total atmospheric N input (McKenzie et al. 2013, Chapter 6, this volume), which is known to control  $\Gamma_s$  (Massad et al. 2010).

In 2009 the dry deposition of the reactive nitrogen compounds considered in this study was similar to the 1995 value, while for 2010 it was 13.7% larger, with most of this increase attributable to  $\text{NH}_3$ . Some significant uncertainties remain in the atmospheric N deposition budget: first,  $\text{NH}_3$  deposition estimates are still limited by the ability to measure small ambient  $\text{NH}_3$  concentrations accurately as demonstrated by the variability found between the four  $\text{NH}_3$  measurement techniques deployed at this site. Second, the understanding of HONO exchange and its production at surfaces is very limited: while the 1995 parameterisation treated HONO as depositing rapidly like  $\text{HNO}_3$ , the 2009/10 parameterisation is bi-directional and predicts net emission.

Compared with a recent inferential modelling exercise at this site (Flechar et al. 2011), which applied four different inferential models to monthly concentration data, the use of hourly data results in significantly larger deposition fluxes for  $\text{HNO}_3$ , probably because the diurnal cycles in  $\text{HNO}_3$  concentration and turbulence are correlated. This demonstrates the advantage of highly time-resolved measurements for the calculation of accurate deposition budgets.

## 5.6 Acknowledgements

This work was funded through the EU projects NitroEurope (FP6) and ÉCLAIRE (FP7) and by the UK Natural Environment Research Council (NERC) through PhD studentship grant number NE/H526351/1. The authors would like to gratefully acknowledge the assistance of Ivan Simmons, Iain Leith and Mhairi Coyle with the measurements.



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### **6. Paper 3: The nitrogen-budget at Auchencorth Moss**

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# The nitrogen budget of a Scottish semi-natural moorland.

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## Abstract

Nitrogen (N) is known to be a limiting nutrient in peatlands and as such, the vegetation present has adapted to living in low N conditions. This makes such ecosystems particularly vulnerable to increases in N deposition. The N-budget of Auchencorth Moss, a Scottish moorland, was estimated in order to assess its N status and to compare the inputs with a study from 15 years before. The main contributor to the total N deposition of  $-9.01 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  was found to be ammonia ( $\text{NH}_3$ ), followed by the wet deposition of ammonium ( $\text{NH}_4^+$ ). Dissolved organic nitrogen (DON), which is not routinely included in N budgets, contributed 6.5% of total deposition. The largest loss of N was by far DON via the draining stream with N losses of  $-5.31 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  or 71.8% of total export. Deposition decreased by  $0.79 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , or 10.0%, between 1995 and 2009/2010, but it is unclear whether this reflects a trend or inter-year variability. The largest decrease was the wet deposition of DIN which decreased by 25.0%. Dry deposition was found to have increased by 14.3%. DON,  $\text{N}_2\text{O}$  and N-fixation were not included in the comparison as they were not previously considered but contributed a total of 18.4% to the total deposition in 2009/2010. Overall, Auchencorth was found to be accumulating N in 2009/10, with deposition exceeding export by  $-1.61 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , consistent with the accumulation of carbon.

*Keywords: reactive nitrogen, wet deposition, dry deposition, DON, stream export*

## 6.1 Introduction

Peatlands cover approximately 2-3% of the Earth's surface and although carbon rich, tend to be nutrient poor (Bragazza et al. 2007). They are characterised by acidic soil, high water tables, poor oxygenation, and it is these conditions, along with low temperatures, which slow down the decomposition of litter, resulting in an accumulation



of organic matter (Adamson et al. 1998, Bragazza et al. 2007). Nitrogen (N) is often a limiting nutrient in peatlands, so the vegetation present is adapted to low N conditions. Increases in the deposition of reactive nitrogen ( $N_r$ ) can encourage more nitrophilic vegetation species to flourish at the expense of existing vegetation (Pitcairn et al. 1995). These changes may result in the decomposition rate of the vegetation increasing and thus to a loss of peat (Bragazza et al. 2007). Since peatlands are believed to store around a third of the world's carbon, a loss of this ecosystem would result in more carbon being released into the atmosphere (Bragazza et al. 2007). Other consequences of increased  $N_r$  deposition include a loss of biodiversity as a result of eutrophication and acidification; an increase in the production of the greenhouse gas  $N_2O$  as a result of increased microbial activity and N-saturation resulting in increased leaching of N out of the soil and into waterways (Vitousek et al. 1997, Adamson et al. 1998, Wamelink et al. 2009). Since the industrial revolution the amount of anthropogenic  $N_r$  deposited has increased globally by a factor of ~12.5 (Galloway et al. 2008), with food production being attributed to 70% of total  $N_r$  emissions (Nieder and Benbi 2008) and the burning of fossil fuels another major source.

Despite measures being taken to reduce the deposition of  $N_r$ , globally anthropogenic  $N_r$  deposition is estimated to reach ~267 Tg N  $yr^{-1}$  by 2050 as a result of an increasing population and demands for meat and fossil fuels (Galloway et al. 2004).

It is important to monitor fluxes of N in order to assess its impact on ecosystems, particularly N sensitive ones, as the damage done may cause them to disappear.

The aim of this study was to construct an N budget at Auchencorth Moss, a semi-natural moorland in south-east Scotland, by examining the annual fluxes and to discuss changes in N deposition from an earlier study in 1995, taking into account the inputs of N fixation as well as inorganic and organic N compounds from the atmosphere and animals, and also the export through the stream.

## **6.2 Site and methods**

### **6.2.1 Study area**

Auchencorth Moss is an ombrotrophic peat bog located in south Scotland, approximately 18 km southwest of Edinburgh (National Grid Reference NT221562; lat. 55°47'30N; long. 03°14'20W). The volume of peat is estimated to be ~50 million  $m^3$ , with peat depths of up to 5 m, an average depth of 50 cm, and a total peat coverage of ~1214 ha (Mitchell and Mykura 1962, Dinsmore 2008). Approximately 170 ha of peat,



1.75 - 3.4 km W-SW of the study site, are used for extraction. There are a number of farms in the surrounding area, with the site itself used for low intensity sheep grazing (less than one livestock unit km<sup>-2</sup>). In 2009 a small herd of cows (15-20) also grazed the site.

The vegetation consists of numerous hummocks and hollows typically associated with a peatland setting. The hollows are depressions up to 30 cm deep and are dominated by blankets of *Sphagnum* mosses, with various sedges, monocotyledons and other bryophytes also present. The hummocks can be up to 30 cm high, although *Sphagnum* mosses are present, there is a larger density of vascular plants, with the dominant species being *Deschampsia flexuosa*, *Eriophorum vaginatum* and *Juncus effuses*. Further information with regards to vegetation at Auchencorth Moss has been presented by Flechard and Fowler (1998) and Dinsmore (2008).

The Black Burn runs SW to NE of the CEH atmospheric monitoring station at Auchencorth Moss, and drains into the North Esk river. It has a catchment area of approximately 335 ha, which is fed by numerous tributaries, including one which originates in the area of peat extraction. There are a number of overgrown ditches laid out in parallel which is evidence of the drainage activities of the 1900s and 1960s. The elevation of the catchment is approximately 250-300 m and the main soil type is Histosols (85% coverage); with Gleysol (9%), Humic Gleysol (3%) and Cambisols (3%) present mostly at the margins of the catchment (Billett et al. 2004).

Figure 6.1 indicates the locations of the sampling sites at Auchencorth Moss and Table 6.1 provides a summary of the metrological characteristics during the study period.



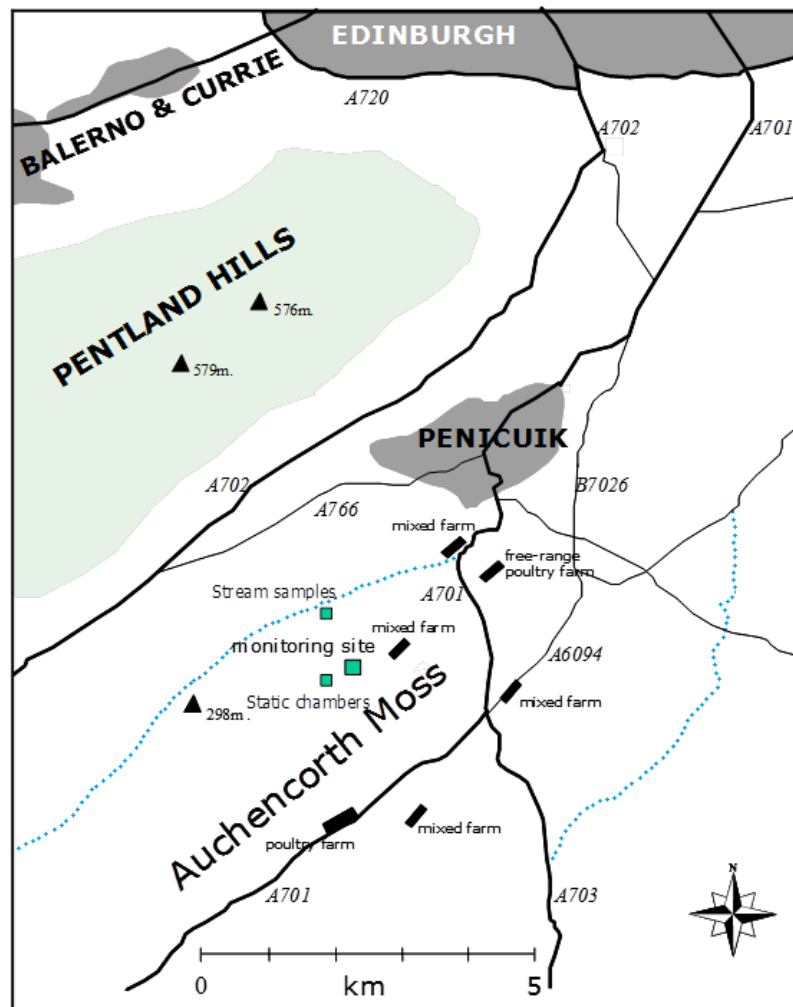


Figure 6.1. Schematic map of the sampling sites at Auchencorth Moss. The green squares indicate the location of the stream site, static chamber site and monitoring station. The black boxes indicate the location of surrounding farms and the blue dotted line indicates a stream.



Table 6.1. Summary of metrological parameters at Auchencorth Moss. Values were sourced from 2009-2010 data.

Mean air temperature	7.1 °C (-12.0 °C to 27.5 °C)
Annual Precipitation (mm)	1031
Mean peat depth (m)	0.5 (<0.5 m to 5 m)
Soil pH	4.5 ( $\pm 0.2$ )
Stream pH	5.4 ( $\pm 0.9$ )
Mean water temperature	8.2 °C (0.0 °C to 16.7 °C)
Water table depth	-14.8 cm (-52.4 cm to 7 cm)
Mean stream discharge	51.5 L s <sup>-1</sup> (1.8 L s <sup>-1</sup> to 767.5 L s <sup>-1</sup> ) <sup>d</sup> .

a. Based on measurements collected every 30 min.

b. Based on measurements collected twice a month.

c. Based on measurements collected once–twice a month.

d. Based on daily means of measurements collected twice a month.

### 6.2.2 Wet deposition of N

Auchencorth Moss is an EMEP supersite contributing to the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe ([http://www.emep.int/index\\_facts.html](http://www.emep.int/index_facts.html)). Precipitation was collected daily using an automated wet-only collector (Eigenbrodt NSA 181/KS, Frankfurt, Germany). Samples were analysed for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> using Ion Chromatography (IC) and, where sample volume allowed, for total dissolved nitrogen (TDN) by high-temperature catalytic oxidation (ANTEK). Dissolved organic nitrogen (DON) was determined by subtracting dissolved inorganic nitrogen (DIN = NO<sub>3</sub><sup>-</sup> + NH<sub>4</sub><sup>+</sup>) from TDN. Precipitation measurements and machine specifications are outlined in detail by McKenzie et al. (2013, Chapter 4, this volume).

### 6.2.3 Dry deposition of N – inferred

The MARGA (Monitoring instruments for AeRosol and GAses; Applikon, NL) compiles average hourly concentrations of a range of inorganic aerosol and acidifying gases, including NH<sub>3</sub>, HNO<sub>3</sub> and HONO as well as the aerosol compounds NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. Briefly, the MARGA consists of a wetted rotating denuder which strips any water-soluble gases present. Aerosols pass through the denuder and into a steam-jet-aerosol-collector where the water-soluble aerosol components are condensed, then separated from the airstream by a cyclone. The solutions are degassed and mixed with



an internal standard, then analysed by online anion and cation chromatographs. A more detailed description of the system and analysis of the results has been presented elsewhere (Twigg et al. 2012).

Fluxes of  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{HONO}$  and aerosol  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were estimated by applying inferential deposition models to the hourly MARGA concentration time-series, details of which are provided by McKenzie et al. (2013, Chapter 5, this volume).

#### 6.2.4 Dry deposition of N – gradient flux

Fluxes of  $\text{NO}$  and  $\text{NO}_2$  were measured continuously using a Thermo 42CTL trace level  $\text{NO}_x$  analyser (Thermo Environmental Instruments Inc., Franklin, MA, USA). Concentration measurements were cycled through 3 different heights, with 3 minutes at each measurement height. Fluxes were then calculated according to the micrometeorological aerodynamic gradient theory (Coyle, pers. com.).

#### 6.2.5 Soil water

Soil water was collected once or twice per month from nine dip wells located next to static chambers. Samples were analysed for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and TDN by the IC and ANTEK methods described previously by McKenzie et al. (2013, Chapter 4, this volume). DON was determined by difference between DIN and TDN.

#### 6.2.6 KCl extractable mineral N

Soil cores were collected at a depth of 0-10 cm at three locations (close to the static chambers), in spring and autumn in 2009 and in spring, summer and winter in 2010.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were extracted from soil samples using KCl and analysed by IC. Methodology details are outlined by McKenzie et al. (2013, Chapter 4, this volume). TDN was not measured, so DON could not be determined.

#### 6.2.7 Stream export

Stream water was collected once a week from the Black Burn, to the north of the field station. Samples collected from January 2009 – October 2009 were analysed for TDN,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  using a San<sup>++</sup> Automated Wet Chemistry Analyzer/Continuous Flow Analyzer (SKALAR, The Netherlands). Samples from November 2009-November 2010 were analysed for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and TDN by IC and ANTEK. In both cases, DON was determined by subtracting DIN from TDN.



Discharge was determined from water height using manually calibrated rating curves based on measurements of dilution gauging (Dinsmore, pers. com.). More details on stream water methodology and analysis can be found in McKenzie et al. (2013, Chapter 4, this volume)

Downstream export of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and DON was calculated according to “method 5” of Walling and Webb (1985):

$$\text{Flux} = K \times Q_r \times \frac{\sum_{i=1}^n [C_i \times Q_i]}{\sum_{i=1}^n Q_i}, \quad (1)$$

where K is the conversion factor for scaling up to annual catchment values,  $Q_r$  is the mean discharge for the study period in  $\text{L s}^{-1}$ , n is the total number of samples,  $C_i$  is the instantaneous concentration in  $\text{mg L}^{-1}$  and  $Q_i$  the instantaneous discharge in  $\text{L s}^{-1}$ . The standard error (SE) of the mean load was calculated according to Hope et al. (1997):

$$SE = F \times \sqrt{\text{var}(C_F)} \quad (2)$$

where F is the total annual discharge in  $\text{L yr}^{-1}$  and  $\text{var}(C_F)$  is the variance of the flow-weighted mean concentration ( $C_F$ ) in  $\text{mg L}^{-1}$ , calculated according to:

$$\text{var}(C_F) = \left[ \sum (C_i - C_F)^2 \times \frac{Q_i}{Q_n} \right] \times \sum \frac{Q_i^2}{Q_n^2} \quad (3)$$

where  $Q_n$  is the sum of all the  $Q_i$  values. Both the flux and SE are expressed as  $\text{mg yr}^{-1}$  and converted to  $\text{kg N ha}^{-1} \text{ yr}^{-1}$  for the purposes of this paper.

#### 6.2.8 Nitrous oxide flux measurements by Static Chambers

Nitrous oxide ( $\text{N}_2\text{O}$ ) fluxes were measured using an adaption of the static chambers method as described by Livingston and Hutchinson (1995), which allows the flux of a gas to be calculated by measuring its accumulation over a period of time within a chamber of known volume.

Nine chambers were installed all within approximately 25 m radius of each other, and approximately 0.4 km from the monitoring enclosure. The chambers were positioned in groups of three and covered the main vegetation types. Each group of chambers contained a chamber which covered one of the following groups of vegetation: hollows



dominated by mosses; hummocks dominated by sedges; and hummocks containing *Juncus*.

Chambers consisted of opaque bases made from polypropylene (diameter of 40 cm), with a 4.5 cm polypropylene flange, and were permanently fixed *in situ* in the peat, to a depth of ~5 cm (Clayton et al. 1994, Dinsmore et al. 2009). The chamber lids were dome shaped and made of flexible, transparent polyethylene, also attached to a 4.5 cm polypropylene flange; allowing the lids to be securely fixed to the chamber base (Clayton et al. 1994, Macdonald et al. 1996).

The determination of the volume of the chambers required a method which took into account the varying presence of hummocks, hollow and vegetation. In this case the tracer gas SF<sub>6</sub> was used. A known concentration (4.75 ppb) and volume (500 ml) of SF<sub>6</sub> was introduced to each closed chamber, in which a fan had been placed to circulate the gas introduced. After ~5 minutes a sample was taken and stored in the Tedlar® bags (SKC Ltd, Dorset, UK) until analysis. The concentration (C) of SF<sub>6</sub> was determined and from this the chamber volume (V) was calculated using the follow equation:

$$V_{Chamber} = \frac{V_{injected} \times C_{injected}}{C_{Chamber}} \quad (4)$$

Volumes were approximately 30 litres for chambers containing *J. effuses* and approximately 17 litres for all other chambers.

Samples were collected via a three way tap attached to the base of the chamber at time intervals of 0 min (ambient), ~30 min and ~ 60 min, using a 100 ml air-tight syringe and placed in Tedlar® bags until analysis (no more than one week after sampling). Samples were transferred into glass vials and analysed using a HP5890 Series II gas chromatograph (GC) (Agilent Technologies, Stockport, UK) equipped with an electron capture detector (ECD) (detection limit: N<sub>2</sub>O < 0.2 ppmv). Fluxes presented here are the mean of all nine chambers, and were collected once a month.

### 6.3 Results

Nitrogen can be deposited to an ecosystem via atmospheric deposition, N-fixation and agricultural activities such as N fertilisation and deposits from livestock. It is removed as a result of gaseous emissions from vegetation and the soil, leaching/runoff into streams where it is the exported out and from agricultural activities such as grazing and the subsequent removal of livestock. Table 6.2 shows the annual budget of N at



Auchencorth Moss, for the period January 2009 to December 2010. Negative fluxes indicate net deposition (input) of N and positive fluxes indicate net emission (loss) of N.

Table 6.2. Average annual fluxes of nitrogen to Auchencorth Moss (2009 – 2010).

Compound	Emission/Deposition (kg N ha <sup>-1</sup> yr <sup>-1</sup> )
<b>Wet deposition</b>	
NH <sub>4</sub> <sup>+</sup> -N	-1.84
NO <sub>3</sub> <sup>-</sup> -N	-1.37
DON	-0.58
Total wet deposition	<b>-3.79</b>
<b>Dry deposition</b>	
NH <sub>3</sub> -N	-2.55
HNO <sub>3</sub> -N	-0.11
Aerosol NH <sub>4</sub> <sup>+</sup> -N	-0.19
Aerosol NO <sub>3</sub> <sup>-</sup> -N (fine)	-0.09
Aerosol NO <sub>3</sub> <sup>-</sup> -N (coarse)	-0.47
NO <sub>2</sub> -N	-0.74
N <sub>2</sub> O-N	-0.07
Total dry deposition	<b>-4.22</b>
Total atmospheric deposition	<b>-8.01</b>
<b>Other deposition</b>	
N-fixation	-1.00
<b>Total deposition</b>	<b>-9.01</b>
<b>Emission</b>	
HONO -N	0.13
NO-N	0.11
Total emission	<b>0.24</b>
<b>Stream Export</b>	
Downstream NH <sub>4</sub> <sup>+</sup> -N	1.29
Downstream NO <sub>3</sub> <sup>-</sup> -N	0.40
Downstream DON	5.31
Total stream export	<b>7.00</b>
<b>Other export</b>	
Livestock	0.16
<b>Total export</b>	<b>7.40</b>
<b>Net flux</b>	<b>-1.61</b>

### 6.3.1 Wet deposition of N

The total flux of N deposited by wet deposition was -3.79 kg N ha<sup>-1</sup> yr<sup>-1</sup>. The main N compound deposited was NH<sub>4</sub><sup>+</sup> (-1.84 kg N ha<sup>-1</sup> yr<sup>-1</sup>), followed by NO<sub>3</sub><sup>-</sup> (-1.37 kg N ha<sup>-1</sup>



yr<sup>-1</sup>) with DON contributing the least, but still a significant fraction, to deposition (-0.58 kg N ha<sup>-1</sup> yr<sup>-1</sup>). Seasonal variations of wet only NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and DON were discussed in McKenzie et al. (2013, Chapter 4, this volume). Briefly, a weak seasonal pattern was observed for both NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, with peak concentrations occurring between January and June. DON had no clear seasonal pattern, although in the winter months (Nov- Jan), concentrations appeared to be lower. Monthly mean fluxes ranged from -0.04 to -0.27 kg N ha<sup>-1</sup> month<sup>-1</sup> for NO<sub>3</sub><sup>-</sup>; -0.07 to -0.36 kg N ha<sup>-1</sup> month<sup>-1</sup> for NH<sub>4</sub><sup>+</sup> and -0.01 to -0.16 kg N ha<sup>-1</sup> month<sup>-1</sup> for DON.

### 6.3.2 Dry deposition of N

The total flux of reactive N deposited by dry deposition was -4.22 kg N ha<sup>-1</sup> yr<sup>-1</sup>. The main N compound deposited was NH<sub>3</sub> (-2.55 kg N ha<sup>-1</sup> yr<sup>-1</sup>) contributing 60.4% of dry deposition.

Total aerosol deposition was -0.75 kg N ha<sup>-1</sup> yr<sup>-1</sup> (dominated by coarse NO<sub>3</sub><sup>-</sup> coarse, -0.47 kg N ha<sup>-1</sup> yr<sup>-1</sup>) and contributed 17.8% to total dry deposition.

Seasonal variation of NH<sub>3</sub>, HNO<sub>3</sub> and aerosols were discussed in McKenzie et al. (2013, Chapter 5, this volume). NH<sub>3</sub> deposition was highest in December, and lowest in the summer/autumn months, monthly mean deposition ranged from -0.06 to -0.48 kg N ha<sup>-1</sup> month<sup>-1</sup>. Seasonal variation in HNO<sub>3</sub> flux was difficult to assess due to stark differences in variation between 2009 and 2010. In 2009, the highest deposition occurred in the spring, and the lowest in the autumn, but in 2010, the highest deposition was in the autumn and the lowest deposition occurred in the spring. Monthly mean deposition ranged from -0.002 to -0.025 kg N ha<sup>-1</sup> month<sup>-1</sup>.

Both NO<sub>3</sub><sup>-</sup> aerosols generally deposited more in the spring and least in the summer. NH<sub>4</sub><sup>+</sup> was deposited more in late spring/early summer, but deposited less in the autumn. Monthly mean fluxes ranged from -0.006 to -0.04 kg N ha<sup>-1</sup> month<sup>-1</sup> for NH<sub>4</sub><sup>+</sup>; -0.001 to -0.03 kg N ha<sup>-1</sup> month<sup>-1</sup> for NO<sub>3</sub><sup>-</sup> (fine) and -0.01 to -0.12 kg N ha<sup>-1</sup> month<sup>-1</sup> for NO<sub>3</sub><sup>-</sup> (coarse).

The annual flux of N<sub>2</sub>O at Auchencorth Moss was a small net uptake of -0.07 kg N ha<sup>-1</sup> yr<sup>-1</sup> with the yearly means ranging from 0.00 kg N ha<sup>-1</sup> yr<sup>-1</sup> in 2009 to -0.15 kg N ha<sup>-1</sup> yr<sup>-1</sup> in 2010. Figure 6.2 shows the monthly mean flux of N<sub>2</sub>O over the study period. Monthly mean fluxes ranged from -0.08 to +0.02 kg N ha<sup>-1</sup> month<sup>-1</sup>, with emissions generally occurring in the summer and autumn months, and deposition in the spring. The winter months of December 09 and February 10 both showed deposition; however,



winter in early 2009 showed mean emission. Overall, 2009 had more emission and less deposition than 2010, which is reflected in the difference in the annual mean flux.

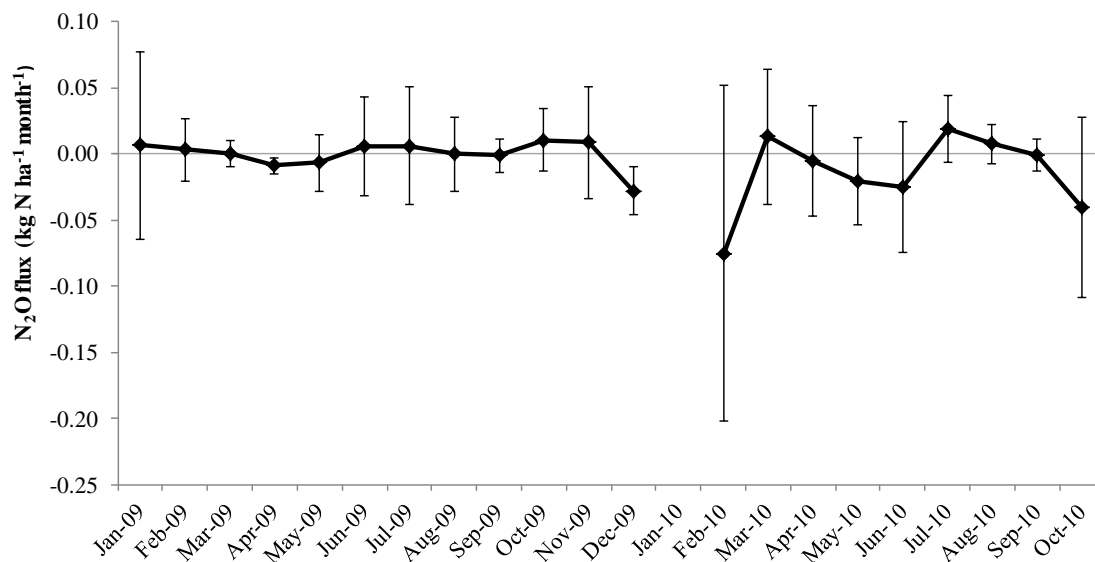


Figure 6.2. Variation in N<sub>2</sub>O fluxes. Data are monthly averages of 9 chambers collected either, monthly or bimonthly. The errors bars represent the standard deviation of all the samples collected for that month. No data is available for Jan, Nov and Dec 2010 due to snow.

The measured annual NO<sub>2</sub> flux was -0.74 kg N ha<sup>-1</sup> yr<sup>-1</sup>, and was the second largest N compound dry deposited. Generally, most deposition occurred in the spring and autumn months, with the least occurring in summer. The only month when the mean NO<sub>2</sub> flux showed emission was December 2009 (Fig. 6.3). Fluxes ranged from -0.12 to 0.03 kg N ha<sup>-1</sup> month<sup>-1</sup>. By contrast, the measured NO flux was clearly bi-directional and overall showed a small net emission from Auchencorth Moss of 0.11 kg N ha<sup>-1</sup> yr<sup>-1</sup>. Figure 6.4 shows the monthly mean flux of NO. Mean deposition of NO occurred in Jan, Aug and Nov 2009, and in Jan, Oct, Nov and Dec 2010. Generally, more emission occurred in the spring and summer months, and the least in the winter. Monthly mean fluxes ranged from -0.009 to 0.031 kg N ha<sup>-1</sup> month<sup>-1</sup>. Soil emission of NO can be converted into NO<sub>2</sub> by reaction with O<sub>3</sub>, before it reaches the measurement height, and this is likely to have been the reason for the apparent NO<sub>2</sub> net emission flux observed in Dec 2009. Because of the chemical interactions between NO, NO<sub>2</sub> and O<sub>3</sub>, the measured fluxes may not represent the actual exchange of the two compounds with the vegetation. However, the



two fluxes are added for the calculation of the budget and the total  $\text{NO}_x$  flux remains conserved during the chemical conversion.

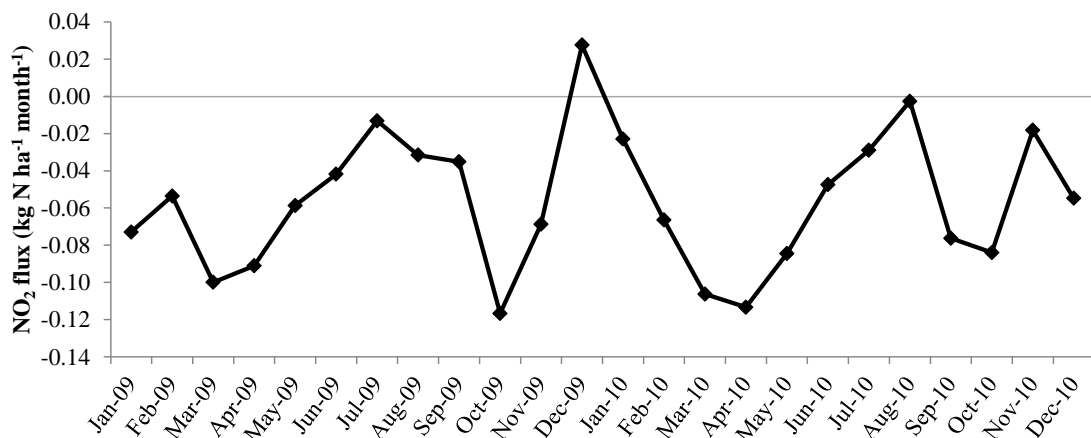


Figure 6.3. Variation in  $\text{NO}_2$  fluxes between Jan 2009 and Dec 2010. The flux is measured in  $\text{kg N ha}^{-1} \text{ month}^{-1}$ .

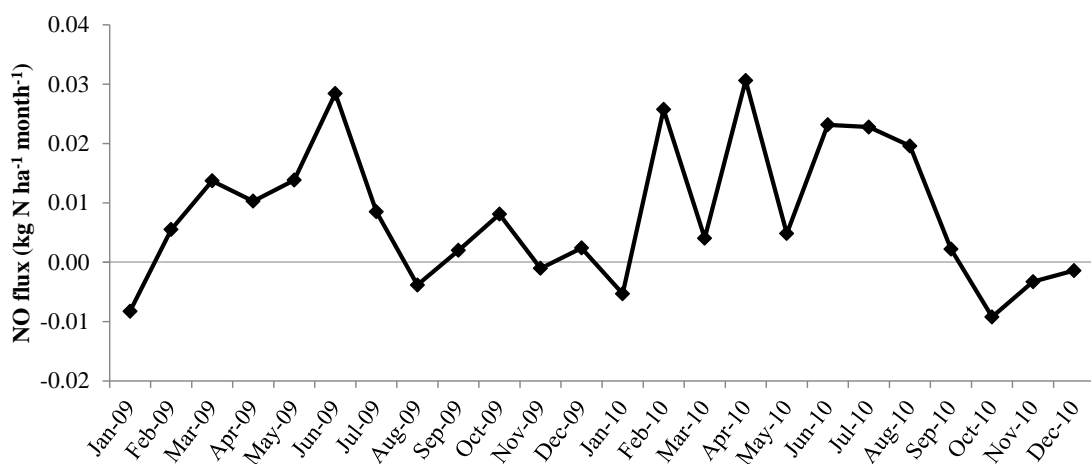


Figure 6.4. The monthly mean flux of NO from January 2009 to December 2010. The flux is measured in  $\text{kg N ha}^{-1} \text{ month}^{-1}$ .

The flux of nitrous acid ( $\text{HONO}$ ) was inferred from the MARGA concentration measurements using a compensation point approach as detailed by McKenzie et al. (2013, Chapter 5, this volume). The only month in which  $\text{HONO}$  was predicted to be deposited was December 2009. Overall, more  $\text{HONO}$  is thought to have been emitted in the summer months, and the least in the winter months, with monthly mean fluxes ranging from  $-0.02$  to  $0.03 \text{ kg N ha}^{-1} \text{ month}^{-1}$ .



### 6.3.3 N-fixation

N-fixation was not measured, and is generally low in soils with a low pH, and where there are few legumes (Vitousek et al. 2002). Non-symbiotic N-fixation may occur and estimates of N-fixation of  $<1\text{--}2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  were suggested for semi-natural ecosystems including Auchencorth Moss by Skiba et al. (2009), based on estimates by Vitousek et al. (2002) of  $1\text{--}1.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . For the purpose of this study, a flux of  $1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  was assumed.

### 6.3.4 N pools

$N_r$  can be found in the peatland water in which the peat sits (soil water) and dissolved in the soil itself. The soil water showed a mean concentration of  $0.90 \text{ mg l}^{-1}$  of nitrogen, comprising of  $0.81 \text{ mg l}^{-1}$  DON,  $0.07 \text{ mg l}^{-1}$  of  $\text{NH}_4^+$  and  $0.01 \text{ mg l}^{-1}$  of  $\text{NO}_3^-$ . Seasonal variations of soil water  $N_r$  was discussed in McKenzie et al. (2013, Chapter 4, this volume). Briefly, gaps in the time series due to dry dip wells made seasonal variations in  $N_r$  difficult to describe, but the available data showed DON concentrations were larger in the warmer months compared to cooler months (November to March) and that peak concentration for DON occurred in September.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  followed similar patterns, with concentrations in 2009 appearing to increase in the spring, peaking in August. In 2010, both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations remained low, with small peaks occurring in July.

Soil extractions from 5 samples (2 from 2009 and 3 from 2010) found no detectable  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  concentrations of  $0.47 \pm 0.27 \text{ mg l}^{-1}$ .

### 6.3.5 Livestock

Livestock can affect the N-budget of a site by removing N via grazing and adding N via excretion. N is also removed when an animal is removed from the land, due to the N which has been assimilated into its body for biological processes such as growth and wool production. Emissions caused by housing and additional animals feed, can also impact on N, but these are not relevant to the livestock at Auchencorth Moss which continuously lives outdoors. Based on a calculation of the contribution of grazing livestock to the on-field N budget of an intensively managed grassland less than 20 km away from Auchencorth Moss (Jones et al. pers. comm.), the total flux attributed to livestock at Auchencorth Moss was estimated to be  $-0.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  by Skiba et al.



(2013) which was derived from a livestock unit (LSU) density of  $< 0.2 \text{ LSU ha}^{-1}$ , where 1 LSU = 1 cow, 10 sheep or 25 lambs.

Misselbrook et al. (2000) derived an emission factor for livestock of  $4.7 \text{ g N animal}^{-1} \text{ day}^{-1}$  for beef cattle and  $0.6 \text{ g N animal}^{-1} \text{ day}^{-1}$  for sheep grazed on uplands, from which they estimated the N excretion for (non-dairy) cattle to be  $51 \text{ kg N animal}^{-1} \text{ yr}^{-1}$  and  $12 \text{ kg N animal}^{-1} \text{ yr}^{-1}$  for sheep. From this, the livestock flux at Auchencorth Moss was determined to be  $-1.22 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in 2009 and  $-0.59 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in 2010. However, since the animals were fed solely on the vegetation at Auchencorth, this excretion is considered to be a recycling of N, rather than a true addition of N, and is thus excluded from the budget. As a result, the overall annual livestock flux consists of the amount of N removed as a result of meat production; estimated to be  $0.27 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in 2009 and  $0.04 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in 2010, with an overall mean flux of  $0.16 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . This is at odds with the earlier livestock flux estimate of  $-0.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  of Skiba et al. (2013).

#### 6.3.6 Denitrification

Complete denitrification results in the emission of molecular  $\text{N}_2$  and is an anaerobic process. In the presence of low levels of oxygen, partial denitrification occurs and can result in the release of NO or  $\text{N}_2\text{O}$  instead of  $\text{N}_2$ .

Šimek and Cooper (2002) reviewed numerous studies conducted over a 50 year period on the relationship between soil pH and denitrification. They concluded that as the acidity of a soil increases, the amount of N released as  $\text{N}_2\text{O}$  increases and thus the denitrification ratio of  $\text{N}_2\text{O}/\text{N}_2$  increases. Wrage et al. (2001) also noted this relationship and suggested that at low pH the nitrous oxide reductase which facilitates the reaction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  is inhibited, resulting in  $\text{N}_2\text{O}$  to be released instead of  $\text{N}_2$ . The peat at Auchencorth Moss is acidic (pH= 4.5, Table 6.1.) and  $\text{N}_2\text{O}$  emission is small and often  $\text{N}_2\text{O}$  is deposited (Fig. 6.2). Therefore, it is unlikely that there will be measurable fluxes of  $\text{N}_2$  into the atmosphere and thus  $\text{N}_2$  emissions are considered to be negligible.

#### 6.3.7 Stream export

Total export by the stream was  $7.00 \pm 0.50 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . By far the largest contributor was DON with  $5.31 \pm 0.36 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (75.9%), followed by  $\text{NH}_4^+$   $1.29 \pm 0.23 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (18.4%) and  $\text{NO}_3^-$  with  $0.40 \pm 0.07 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (5.7%).

Monthly mean fluxes ranged from 0.01 to  $0.67 \text{ kg N ha}^{-1} \text{ s}^{-1}$  for DON, 0.00 to  $0.08 \text{ kg N ha}^{-1} \text{ s}^{-1}$  for  $\text{NH}_4^+$  and 0.00 to  $0.03 \text{ kg N ha}^{-1} \text{ s}^{-1}$  for  $\text{NO}_3^-$ . Seasonal variations of wet only



$\text{NH}_4^+$ ,  $\text{NO}_3^-$  and DON were discussed in McKenzie et al. (2013, Chapter 4, this volume). Briefly, in 2009, concentrations varied seasonally, with the largest  $\text{NO}_3^-$  concentrations occurring during cooler months and the smallest during warmer months. In 2010 stream water  $\text{NO}_3^-$  concentrations initially followed a similar pattern as in 2009, with concentrations increasing during the winter months and decreasing as temperature increased and summer approached. However,  $\text{NO}_3^-$  concentrations were large in June and July 2010, when in 2009  $\text{NO}_3^-$  was below the detection limit. Concentrations of  $\text{NH}_4^+$  were consistently higher than  $\text{NO}_3^-$  and there was no clear seasonal pattern. DON also showed no clear seasonal pattern, although highest concentrations tended to occur in the summer/autumn months.

## 6.4 Discussion

In areas with no human intervention, deposition of N is low at  $\leq -0.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Galloway et al. 2008). Average European background levels of N deposition are slightly higher at  $\sim -3 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  with some areas as high as  $-18 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (Wamelink et al. 2009). It is estimated that by 2050, deposition of N may reach  $-50 \text{ kg ha}^{-1} \text{ yr}^{-1}$  in the worst polluted regions of the world (Galloway et al. 2008). In order to assess the damage increased N inputs will have, “critical loads” have been estimated for a number of vulnerable ecosystems as the amount of N deposition below which significant ecosystem effects do not occur. Critical loads have been used for a number of years as a risk assessment tool to provide a quantitative estimate of the damage that may be done to an ecosystem if the critical load limits are exceeded (Dise et al. 2011). For peatlands, the critical load for N deposition is estimated to be  $-5$  to  $-10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  with observations at sites that have exceeded critical loads showing a loss and/or reduction of characteristic bog species, such as *sphagnum*, and an increase in vascular plant cover (Bobbink and Hettelingh 2011). Auchencorth Moss is within range of this estimate, but at the upper limits at  $-9.01 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . Auchencorth Moss has so far not shown obvious signs of N damage, but an increase in N deposition of only a few percent may start to have an impact, making it important to monitor changes in deposition.

### 6.4.1 N deposition

Globally, measures have been taken to reduce the amount of N deposition by reducing the amount of N emitted to the atmosphere, and although progress has been made, deposition is still high. Between 1990 and 2010, UK emissions of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) fell by 62% and emissions of  $\text{NH}_3$  fell by 21%, but there has been little change in overall N



deposition to the UK (RoTAP 2012). It is not clear why the decrease in emissions has not been reflected by a decrease in deposition. Parallel changes in the oxidation capacity of the atmosphere may have changed the gas/aerosol partitioning, atmospheric lifetime and transport distance of reactive nitrogen and shipping emissions have changed little.

Figures 6.5 and 6.6 show the percentage breakdown of the contribution of N compounds to total deposition and total export of N from Auchencorth Moss.

Of the  $-9.01 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  deposited to Auchencorth Moss, 88.9% was deposited from the atmosphere and the remaining 11.1% from N-fixation. Atmospheric deposition totalled  $-8.01 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , with wet deposition contributing 47.3 % ( $-3.79 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) and dry deposition 52.7% ( $-4.22 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ).

Reduced N ( $\text{NH}_x = \text{NH}_3$ , wet  $\text{NH}_4^+$  and aerosol  $\text{NH}_4^+$ ) contributed  $-4.58 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (57.2% of atmospheric deposition) compared to oxidised N ( $\text{NO}_y = \text{HNO}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ , wet  $\text{NO}_3^-$  and aerosol  $\text{NO}_3^-$ ) which deposited  $-2.85 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (35.6% of atmospheric deposition). Some  $\text{NO}_y$  compounds were also emitted on average (HONO and NO) with a total loss of  $0.24 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  or 3.2% of total export. It is estimated that ~60% of the total atmospheric N deposited to the UK is in the form of  $\text{NH}_x$  (Pitcairn et al. 1998) and ~33% as  $\text{NO}_y$ , (Galloway et al. 2004), so the figures presented here are close to what would be expected in the UK.

Although organic N ( $\text{N}_{\text{org}}$ ) is known to be ubiquitous in the environment (present in particulate, gaseous and aqueous phases), the sources of  $\text{N}_{\text{org}}$  are not well understood (Cornell et al. 2003, Cape et al. 2004, Özel et al. 2011). This, coupled with difficulties in measuring  $\text{N}_{\text{org}}$ , result in it often being left out of N budgets. The results presented here suggest around 6.5% of total deposition to Auchencorth Moss was in the form of DON in precipitation (Fig. 6.5). In terms of wet deposition, DON contributed 15.3%, which is lower than the mean of 30% found in precipitation elsewhere (Cornell et al. 2003, Cape et al. 2011, Zhang et al. 2012). Dry deposition of  $\text{N}_{\text{org}}$  was not measured for the same reasons mentioned above. A study by Gonzalez Benitez et al. (2010) measured water soluble organic N (WSO<sub>N</sub>) in gas and aerosol phases and found them to be present in significant quantities, suggesting that dry deposition of  $\text{N}_{\text{org}}$  may also be an important contributor to N deposition.



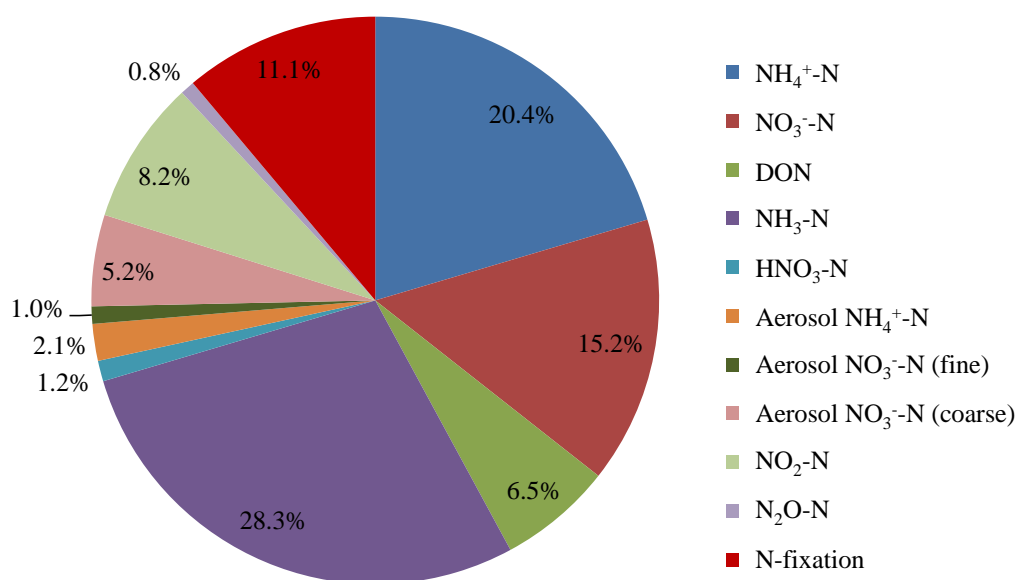


Figure 6.5. Pie chart depicting the different fractions and percentage contribution to the total N deposition at Auchencorth Moss over the period January 2009 to December 2010.

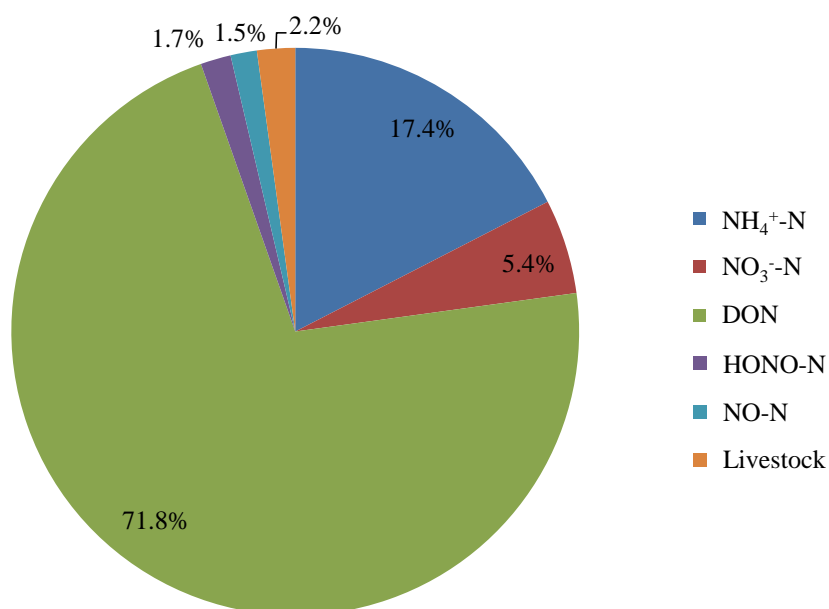


Figure 6.6. Pie chart depicting the different fractions and percentage contribution to the total N loss at Auchencorth Moss over the period January 2009 to December 2010.



#### 6.4.2 Losses of N

Total loss of N was  $7.24 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , with the majority (94.6%) exported by the stream. DON proved to make the biggest contribution to export, contributing 71.8% of N loss (Fig. 6.6). This is not unusual for a peatland stream, as numerous studies have shown DON makes up a significant concentration (54% to 82%) of N in this type of ecosystem (Chapman et al. 2001, Cundill et al. 2007, Helliwell et al. 2007). What is more unusual is the large  $\text{NH}_4^+$  stream flux and the much lower  $\text{NO}_3^-$  flux in comparison. Helliwell et al. (2007) concluded that in acidic, waterlogged catchments less  $\text{NH}_4^+$  is oxidised to  $\text{NO}_3^-$  and thus more is available to be leached into the stream. The reason is that nitrification rates are either very slow or inhibited in acidic soils and the waterlogged peatlands do not provide optimal conditions for aerobic processes such as nitrification. Water table fluctuations have also been linked to higher concentrations of  $\text{NH}_4^+$  which can result in increased mineralisation of  $\text{N}_{\text{org}}$  (Paul and Clark 1996, Daniels et al. 2012).

The stream at Auchencorth Moss is fed by atmospheric deposition, leaching from the surrounding peatland and numerous tributaries, one of which originates above a peat extraction site. It is possible that the disturbance caused by peat extraction may result in increased mineralisation rates, releasing otherwise immobile  $\text{NH}_4^+$ , and to a lesser extent  $\text{NO}_3^-$ , into the stream.

NO is known to be a short-lived molecule in the atmosphere and deposition is not considered to be significant (RoTAP 2012). Even at the measurement height, some NO may already have been converted to  $\text{NO}_2$  by reaction with  $\text{O}_3$ . At Auchencorth Moss, a small net emission was measured, which is surprising in an ecosystem where acid, wet conditions and relatively small concentrations of mineral N prevail. NO is usually emitted from soil as a result of nitrification when soils are reasonably dry and not too acid (Skiba et al. 1997). Usually, any NO formed via denitrification is consumed by denitrifiers rather than emitted to the atmosphere (Davidson et al. 1993). The low concentration of N found in the soil water and soil extracts support suggestions that there is little free N in the soils and that this is washed out rather than utilised via nitrification or denitrification. The very low flux rates of  $\text{N}_2\text{O}$  support this argument. A detailed investigation into NO fluxes from Auchencorth Moss is underway as part of the EU project ECLARE and will monitor NO emissions, using automated dynamic chambers over a one year period, which are more sensitive than the gradient system.



#### 6.4.3 Comparison of past and present atmospheric N budgets

The flux of various N compounds at Auchencorth Moss was measured/modelled as part of the 1995 LIFE project (Fowler et al. 1996). The results are presented in Table 6.3, along with fluxes of the same N compounds measured as part of this study, 14-15 years later. The estimated decrease in deposition of  $0.79 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  since 1995 would represent a reduction of N input of 10.0%, although it is unclear to what extent this difference reflects an actual trend or inter-annual variability. The largest reduction in deposition was via wet deposition where the input of DIN fell by  $1.07 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (25.0%), with the  $\text{NH}_4^+$  flux falling by  $0.58 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (24.0%) and the  $\text{NO}_3^-$  flux falling by  $0.49 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (26.3%). This loss of N input is in contrast to the behaviour of dry deposition, which increased by  $0.52 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (14.3%). In 1995, the flux of HONO and NO were depositional and contributed a total of  $-0.19 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  but in this study, both were net emitted and contributed to a  $0.24 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  loss of N. The difference in HONO was explained by McKenzie et al (2013, Chapter 5, this volume): since HONO was not known to be bi-directional, the 1995 model estimate assumed HONO to be deposited much like  $\text{HNO}_3$ . It is therefore likely that the depositional flux of HONO was overestimated in 1995. As mentioned in Section 5.1, the NO emission flux is large for an oligotrophic ecosystem such as Auchencorth Moss and represents a large change from 1995. In 1995 a net NO deposition was measured. It is possible that the emission measured during 2009/2010 was an over estimation and is currently being investigated further as part of the EU project ECLAIRE. Comparisons of the fluxes of  $\text{HNO}_3$  and the aerosols were discussed in by McKenzie et al (2013, Chapter 5, this volume) with the conclusion that some of the stark changes were a result of improved measuring techniques and improved model parameterisation. The LIFE estimate did not include deposition from  $\text{N}_{\text{org}}$ ,  $\text{N}_2\text{O}$ , or N-fixation, which this study estimated to have contributed  $-1.66 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , or 18.6%, to N deposition.

The total reduced N ( $\text{NH}_x$ ) was  $-4.85 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in 1995 and  $-4.58 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in this study, a fall of 5.6%. Total oxidised N deposition was  $-3.06 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in 1995 and  $-2.78 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , a fall of 9.2%. Note that the deposition of  $\text{NO}_y$  in 1995 included the deposition of NO and HONO, both of which are excluded from the deposition flux of  $\text{NO}_y$  presented by this study as they are now estimated to be emitted. The decrease in  $\text{NO}_y$  is less than the findings of the RoTAP report (2012), which found a reduction in  $\text{NO}_y$  deposition of 23% across the UK over a 30 year period (1990-2010).



The small decrease in wet deposited  $\text{NH}_x$  is more encouraging than the RoTAP report (2012), which found little change in  $\text{NH}_x$  deposition, over the same 30 year period.

Table 6.3. Summary of the main fluxes of N measured as part of the 1995 LIFE project (Fowler et al. 1996) and from this study. Note that  $\text{N}_{\text{org}}$ ,  $\text{N}_2\text{O}$  and N-fixation are missing from this table, as they were not measured in the 1995 study.

Compound	N-flux 1995	N-flux 2009/2010
$\text{NH}_4^+\text{-N}$	-2.42	-1.84
$\text{NO}_3^-\text{-N}$	-1.86	-1.37
<b>Total wet deposition</b>	<b>-4.28</b>	<b>-3.21</b>
$\text{NH}_3\text{-N}$	-2.34	-2.55
$\text{HNO}_3\text{-N}$	-0.36	-0.11
HONO-N	-0.07	0.13
Aerosol $\text{NH}_4^+\text{-N}$	-0.09	-0.19
Aerosol $\text{NO}_3^-\text{-N}$ (fine)	-0.08	-0.09
Aerosol $\text{NO}_3^-\text{-N}$ (coarse)	-0.11	-0.47
$\text{NO}_2$	-0.46	-0.74
NO-N	-0.12	0.11
<b>Total dry deposition</b>	<b>-3.63</b>	<b>-4.15</b>
<b>Total atmospheric deposition</b>	<b>-7.91</b>	<b>-7.36</b>
<b>Total atmospheric flux</b>	<b>-7.91</b>	<b>-7.12</b>

Overall, the N balance for Auchencorth Moss showed a net input of N, with a deposition flux of  $-1.61 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . This is in contrast to Drewer et al. (2010), who previously estimated an N budget at Auchencorth Moss, with a net loss of  $2.40 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . Although the total atmospheric input of N was reported to be higher by Drewer et al. (2010), estimates did not include DON or  $\text{NO}_2$  and the additional input of N-fixation.  $\text{N}_2\text{O}$  was also considered to be emitted rather than deposited. These additional inputs accounted for 26.6% of total deposition reported here. Export of DON via the stream was not measured but estimated as 79% of the total N, compared to the 73% reported here, leading to an over estimation of DON export. However, HONO, livestock flux and NO were not considered and would have increased the loss of N. Had the additional sources of N deposition been included, the total balance would have resulted in a net input of N, even with the additional N loss and overestimated DON export. This demonstrates the importance of ensuring all pathways of N inputs and exports are considered when estimating N budgets, as to exclude one may result in the N-status of an ecosystem to be incorrectly identified.



#### 6.4.4 Uncertainties

One issue yet to be addressed are the uncertainties associated with the data presented here. Vogt et al. (2013) attempted to quantify the uncertainties associated with their N-budgets. They found the overall uncertainties to be large, and whilst the mean flux of their moorland site indicated a net loss of N, the range of uncertainties meant the budget could also have been in balance, or potentially gaining N. Estimates for uncertainties for wet deposition were  $\pm 20\%$ , for dry deposition  $\pm 20\%$  -  $\pm 50\%$ , for  $\text{N}_2$ -fixation up to 200% and for stream export  $\pm 20\%$ . When applied to the data presented here, the overall uncertainty was calculated to be  $\pm 2.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (calculated as the square root of the sum of the squares of the individual errors). This gave a total N flux range of  $1.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  N to  $-4.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . This means that whilst the mean N flux suggests a net input of N of  $-1.61 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , the large range of the uncertainty estimates indicate Auchencorth could potentially be losing N.

#### 6.5 Conclusions

Auchencorth Moss was found to be a net sink for nitrogen (N), with deposition exceeding export by  $-1.61 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ : total deposition was  $-9.01 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  compared to total export of  $7.40 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . Although atmospheric deposition contributed the most to the total input of N, the additional input of N via N-fixation counted for 11.1% of total N inputs, and so should not be considered insignificant. Dissolved organic nitrogen (DON) was important to both the input and export of N, with deposition exceeding those of the individual aerosol components (coarse nitrate 5%, ammonium 2% and fine nitrate 1%),  $\text{HNO}_3$  (1%) and  $\text{N}_2\text{O}$  (1%). 71.8% of total export was in the form of DON, which was exported by the stream. This demonstrates the importance of including DON in N-budget estimates as it represents a significant source and export of N.

The comparison to the 1995 LIFE project (Fowler et al. 1996) showed that N deposition of the equivalent N compounds has decreased by  $\sim 10.0\%$ : since 1995 wet deposition has fallen but dry deposition has increased, probably due to the construction of additional poultry farms in the vicinity of this moorland.

The importance of including all aspects of N inputs was highlighted via a comparison with an estimate of N fluxes at Auchencorth Moss by Drewer et al (2010). That study did not include DON,  $\text{NO}_2$  and N-fixation depositional fluxes, which could have increased deposition estimates by over a quarter. The inclusion of these additional



inputs of N, would have changed the estimate that this moorland is losing N to the conclusion that it is accumulating nitrogen. The N accumulation is consistent with the fact that this peatland was found to also accumulate C, even if aqueous losses are taken into consideration (Dinsmore et al., 2010).

## 6.6 Acknowledgements:

We wish to thank the UK Natural Environment Research Council (studentship number NE/H526351/1), the EU projects 'NitroEurope' (FP6) and ECLAIRE (FP7), and the University of Manchester for supporting this study. The landowner at Auchencorth Moss for access to the fieldsite and CEH staff, especially Ian Leith, Sarah Leeson and Ivan Simmons for managing the site measurements.

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## 7. Summary and Conclusions

The nitrogen (N) budget of Auchencorth Moss, a semi-natural moorland in SE Scotland, was estimated in order to assess its N-status, and to compare deposition with a study from 14/15 years ago. Annual fluxes of N deposition were estimated from measurements of wet only deposition, estimates of N-fixation and livestock deposition and from atmospheric deposition modelled from hourly concentration measurements. Exports were estimated from stream measurements and from atmospheric emissions modelled from hourly concentration measurements.

Paper 1 was primarily concerned with dissolved organic N (DON) and its contribution to the import and export of N. DON concentrations were calculated in precipitation, soil water and stream water by subtracting measured concentrations of dissolved inorganic N (DIN) from total N. An attempt to identify individual DON compounds was made using GC×GC-NCD; two-dimensional GC (GC×GC) coupled with a nitrogen chemiluminescence detector (NCD).

Paper 2 was primarily concerned with the dry deposition of selected N containing compounds, inferred from two years of semi-continuous hourly concentration measurements, and reassessing the parameters of a static and dynamic inferential model used to estimate  $\text{NH}_3$  fluxes. A comparison between  $\text{NH}_3$  concentrations measured by four different instruments was made, with varying degrees of agreement. A brief comparison between the modelled fluxes estimated for 2009 and 2010 was made to a 1995 data set also measured at Auchencorth Moss.

Paper 3 established the overall N-budget of Auchencorth Moss using annual flux estimates established in Paper 2 and by calculating annual fluxes from the concentrations of wet deposition and stream export established in Paper 1. Additional fluxes of  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ , livestock and N-fixation were also included in the budget. A more comprehensive comparison between the mean 2009/2010 data set and 1995 data set was made.

The main findings of this study are outline below:



## 7.1 Organic Nitrogen

Paper 1 examined the volume/discharge weighted monthly mean concentrations of dissolved inorganic nitrogen ( $\text{DIN} = \text{NH}_4^+ + \text{NO}_3^-$ ) and DON in precipitation and stream water. Whilst at 9.2%, the mean contribution of DON to the total dissolved N in precipitation was well below the mean of 30% reported in the literature, this may have been partly due to the differences in sample collection. The use of bulk collectors in many of these studies is likely to have resulted in additional  $\text{N}_{\text{org}}$  deposited via dry deposition, and thus larger  $\text{N}_{\text{org}}$  concentrations. The stream DON concentrations were consistent with what would be expected in a peatland environment.

High concentrations of DON were also found in the soil water, contributing up to 99.3% of the total dissolved N (TDN). The mean concentration of DON did not change significantly between years, but the concentration of DIN was more variable, resulting in lower contribution of TDN in 2009 (85.4% compared to 99.3% in 2010).

Paper 3 examined the overall yearly flux of DON in precipitation and stream water. The contribution of the annual flux of DON in precipitation was higher than the contribution of monthly mean concentrations (15.3%), but was still roughly half of what was reported in the literature. The annual flux of DON in stream water was the dominating loss of N from the peatland, with a total contribution to the export of 71.8%. In terms of the overall deposition of N to Auchencorth, DON precipitation counted for 6.5% of N inputs.

These results demonstrate the importance of DON to both the deposition and export of N and that by not measuring it, a significant source and loss of N is being overlooked.

### 7.1.1 Speciation of dissolved organic nitrogen

An attempt to identify individual compounds of DON was made using GC×GC-NCD. As far as this author is aware, this technique has not previously been applied to water samples. Unfortunately, a contamination issue was identified and whilst the source was not determined during this study, it is likely to be as result of either leaching from the frozen storage bottle or leached from the SFE tubes used. Despite this, GC×GC-NCD has proven to be a useful tool in identifying DON compounds, with eight distinct compounds observed in precipitation and same number in stream samples. In total ten unique compounds were detected: pyrrole, benzonitrile, N-nitrosodipropylamine, decylamine and dodecylamine, and six unknowns, with five of these found in both the precipitation and stream samples: pyrrole, benzonitrile and three of the unknowns.



An obvious drawback to this technique is the reliance on having the retention times of previously run standards for identification. Of the ten unique compounds, only half were matched to known standards and the remaining five will remain unknown until a match is found when more standards are run. It is difficult to assess where the DON compounds came from as they are ubiquitous in the environment and sources, both natural and anthropogenic, remain largely unknown. It is also unclear whether they are emitted directly or formed as secondary pollutants in the gas phase, aerosol or cloud droplets. This makes anticipating which standards are required to create a set of reference retention times difficult.

Another limitation is that the compounds detected by this method cannot consistently account for all the DON present in a sample; between 84 and 100% of DON in stream water could not be speciated. For example, the technique cannot measure very polar species such as urea which nevertheless contribute to DON.

## 7.2 Atmospheric modelling

Paper 2 estimated the fluxes of  $\text{NH}_3$ ,  $\text{HNO}_3$ , HONO and the aerosols  $\text{NH}_4^+$  and  $\text{NO}_3^-$  using hourly concentrations measured by the MARGA, a wet chemistry denuder/steam jet aerosol collector analyser.

A dynamic canopy compensation point model was used to estimate the  $\text{NH}_3$  fluxes, and the parameters updated using data derived from fluxes measured by the AMANDA; a wet-chemistry gradient system with online analysis, from which fluxes were calculated using the aerodynamic gradient method. This dynamic model builds on the bi-directional stomatal and cuticular flux estimated by a static model, but it additionally simulates the desorption of  $\text{NH}_3$  from the leaf surface by treating it analogously to an electric capacitor. This enables the dynamic model to reproduce emission peaks detected in the morning, which the static model does not capture. The stomatal emission potential ( $\Gamma_s$ ) is dependent on the ecosystem type and amount of N deposition and was found to have increased from an annual mean of 180 (in 1995) to an annual mean of 350 (in 2009), possibly in response to additional  $\text{NH}_3$  input from an increased number of chicken farms. The cuticular resistance  $R_w$  was updated by reducing  $R_{w,\text{min}}$  from  $20 \text{ s m}^{-1}$  to  $15 \text{ s m}^{-1}$ .  $R_w$  is believed to have a dependence on leaf acidity, which is affected by the interactions of surface wetness with depositing acidic atmospheric compounds. This keeps the pH of the leaf layers low. Although the acid ratio decreased considerably between 1995 and 2010 and an increase of  $R_w$  would therefore be expected,  $R_w$  has a



somewhat different role in the static and dynamic modelling which might explain the lower value required in the present modelling exercise.

The leaching flux ( $K_r$ ), was increased from the standard value of  $-0.01 \text{ s}^{-1}$  to  $-0.1 \text{ s}^{-1}$  as the former value substantially exaggerated emission peaks. The moorland vegetation has a significant contribution from nonvascular plants, which may provide additional pathways of  $\text{NH}_3$  uptake, and thus a larger  $K_r$  was required.

Overall there was not much difference between the two models, but the dynamic model tended to capture the initial morning emissions better. The static model tended to overestimate  $\text{NH}_3$  deposition compared with the AMANDA flux measurements and thus the dynamic model was used to model the annual fluxes based on the MARGA  $\text{NH}_3$  concentration data.

In order to estimate the  $\text{HNO}_3$  flux, a basic resistance framework in which deposition is one directional was used. Aerosol fluxes were estimated as a product of the air concentrations multiplied by the depositional velocity. As HONO is considered bi-directional, and the flux is thought to be a function of  $\text{NO}_2$  mixing ratios, a canopy compensation point based on this mixing ratio was used to estimate the flux.

The results of the models used for this study were generally consistent with previous inferential modelling efforts made at Auchencorth using data from 2007-2008. Then four different models were used and the fluxes of  $\text{NH}_3$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (fine) estimated during this study fell within the range estimated by these models. Additionally, estimates of  $\text{NO}_2$  reported in paper 3, also fall between the ranges of 0 to  $-1.1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  estimated by these four models. However, the estimates of  $\text{HNO}_3$  and  $\text{NO}_3^-$  (coarse) presented in paper 2, are over and under estimated respectively, in comparison to the four models. The discrepancy for  $\text{HNO}_3$  in particular can be attributed to the effect of the diurnal correlation between concentration and turbulence which cannot be captured by the monthly model, which is therefore expected to underestimate deposition.

### 7.3 Ammonia comparison

Paper 2 compared concentrations of ammonia between several instruments located within the main monitoring station at Auchencorth Moss. The varying degree of agreement highlights the difficulty in accurately measuring  $\text{NH}_3$ . With the measurements not specifically designed for an intercomparison, there were several issues which contributed to the poor correlation between some of the measurement techniques and these are discussed in paper 2.



## 7.4 Overall N budget

Paper 3 looked at the overall N-budget at Auchencorth, by comparing estimates of annual deposition of N to the annual export of N. The result showed Auchencorth Moss to be a net sink of N of  $-1.61 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ .

### 7.4.1 Deposition

Flux estimates of  $\text{NH}_3$ ,  $\text{HNO}_3$ , and the aerosols  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were taken from the results of the models in paper 2, and fluxes of wet only (both DIN and DON) from fluxes derived from concentration measurements outlined in paper 1.

The additional fluxes of NO and  $\text{NO}_2$  were derived from measurements from a gradient tower at Auchencorth, to which gradient theory was applied.

The flux of N-fixation was estimated based on lower limits expressed in the literature.

Total deposition to Auchencorth was  $-9.01 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , with  $-8.01 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  deposited from the atmosphere. 57.2% of total atmospheric N deposited as reduced N, ( $\text{NH}_x = \text{NH}_3 + \text{wet NH}_4^+ + \text{aerosol NH}_4^+$ ) and 35.6% of total atmospheric N deposited as oxidised N, ( $\text{NO}_y = \text{HNO}_3 + \text{N}_2\text{O} + \text{NO}_2 + \text{wet NO}_3^- + \text{aerosol NO}_3^-$ ). The remaining 7.2% of atmospheric deposition was in the form of DON. The ratio of  $\text{NH}_x$  to  $\text{NO}_y$  at Auchencorth Moss of 57.2% / 35.6% was similar to the 60% / 33% ratio estimated for the UK. DON and N-fixation were not included in deposition estimates made by the RoTAP report from which the UK figures were obtained. In terms of overall deposition to Auchencorth Moss,  $\text{NH}_x$  contributed 50.8%,  $\text{NO}_y$  contributed 31.6%, DON contributed 6.5% and N-fixation contributed the remaining 11.1%.

### 7.4.2 Export

Annual downstream fluxes of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and DON were calculated using data derived from the concentration and discharge data established in paper 1. Flux estimates of HONO were taken from the results of the models in paper 2, and fluxes of NO were derived from measurements from a gradient tower at Auchencorth, to which gradient theory was applied.

Livestock fluxes were derived from estimates of N loss as a result of animal removal; N deposited as a result of livestock excretion was considered to be a recycling of N, rather than a true addition of N, and is thus excluded from the flux estimate. Previously, the influence of small numbers of livestock at this site has been considered insignificant, as had the impact of N loss via removal of animals.



Total export of N at Auchencorth Moss was  $7.40 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . As discussed previously DON was by far the largest exporter of N, responsible for 71.8% of total N loss. Unusually the  $\text{NH}_4^+$  flux is larger than the  $\text{NO}_3^-$  flux and whilst the reasons for this discrepancy remain unclear, it is possibly that it was due to enhanced mineralisation caused by disturbance of the peat at the upstream peat extraction site, releasing otherwise immobile  $\text{NH}_4^+$ , and to a lesser extent  $\text{NO}_3^-$ , into the stream.

The small net emission of NO was surprising in an ecosystem where acid, wet conditions and relatively small concentrations of mineral N prevail. Further investigation using a more sensitive technique is under way to provide more accurate estimates of NO fluxes.

#### 7.4.3 Comparison of past and present atmospheric N budgets

Both papers 2 and 3 make comparisons between this study and a budget established for 1995 as part of an EU LIFE project. Whilst paper 2 compares only the dry deposition/emission of  $\text{NH}_3$ ,  $\text{HNO}_3$ , HONO, and the aerosols  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , paper 3 also includes the wet deposition of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and the dry deposition/emission of NO and  $\text{NO}_2$ .

The comparison by paper 3 suggests that since 1995, the deposition of the equivalent N compounds measured in 2009/2010 has decreased by  $\sim 10.0\%$ .  $\text{NH}_x$  decreased by 5.6% and  $\text{NO}_y$  decreased by 9.2%. These decreases were due to a 25% reduction in the wet deposition of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . In contrast dry deposition increased by 14.3%, despite the fact in 1995 both NO and HONO were considered depositional, whereas in 2009/2010 they were estimated to be emitted and thus excluded from the  $\text{NO}_y$  deposition flux estimated in 2009/2010. NO emissions have previously been mentioned in this summary (Section 7.4.2). Improvements in knowledge of HONO behaviour resulted in the use of a bidirectional model to estimate fluxes for the 2009/2010 study, whereas in 1995 flux estimates were based on the assumption that HONO behaved like  $\text{HNO}_3$  and therefore would only be deposited. The LIFE report on the 1995 measurements did not include the deposition of N via DON in precipitation, N-fixation or  $\text{N}_2\text{O}$  and these missing elements contributed an additional 18.4% source of deposited N in 2009/2010. It also did not measure N export. It remains unclear to what extent the changes between 1995 and 2009/2010 represent a long-term trend or inter-annual variability.

The importance of including all aspects of N deposition and export was highlighted via a comparison of an N budget previously estimated at Auchencorth by Drewer et al.



(2010). The Drewer et al. (2010) study estimated deposition using the 1995 LIFE wet deposition data and estimated DON export as it was not measured. It also did not include DON in precipitation,  $\text{NO}_2$ , or N-fixation, which could have increased deposition estimates by over a quarter. The inclusion of these additional inputs of N, would have changed the estimate from the Drewer et al. (2010) study that this moorland is losing N to the conclusion that it is in fact accumulating nitrogen.



## 8. Recommendations and Future work

(a.) This study has demonstrated that DON is important to both the deposition and export of N. It is advisable that measurement of DON should be routinely established when measuring nitrogen compounds in both atmospheric deposition and stream waters.

(b.) An investigation into the dry deposition of organic N compounds would benefit overall N-budgeting, as would more investigation into the sources of  $N_{org}$ , knowledge of which remains patchy. Currently the origin of the DON compounds found in precipitation remains unknown.

(c.) Further development of the GC×GC-NCD, including comparison with a wider range of standard compounds in order to identify all detected  $N_{org}$  compounds. It is necessary to investigate the contamination issue so that the source can be identified and eliminated.

(d.) Whilst denitrification is estimated to be low in this peatland setting, it is the main pathway by which N is re-emitted to the atmosphere, and certainly important in N fertilised ecosystems. Experimentation is limited in the literature, and is largely laboratory based, due the difficulties in measuring this flux. Further work is required to improve measurement techniques to ensure that this potentially important loss of N is considered in future N-budget estimates.

(e.) The N-fixation values were taken from the literature. More experimentation to determine a range of values for differing ecosystems is needed.

(f.) Although there have been numerous comparisons between  $NH_3$  instruments, a more targeted comparison of  $NH_3$  techniques to find out why there was such variability at this site is needed. The measurements used here integrated over different time-periods and where operated at different heights and the results of the intercomparison should therefore not be over-interpreted.

(g.) Because only three years of data were available for the analysis (1995, 2009 and 2010), it is unclear to what extent the change between 1995 and 2009/10 reflects a real



long-term trend or year-to-year variability. Typically 12 years of continuous measurements would be needed to make a robust statement on the trends in deposition.

(h.) Differences were found between the dry deposition inferred from the hourly concentration data in this study and an earlier estimate using monthly mean concentrations, especially for  $\text{HNO}_3$ . This highlights that the monthly results cannot account for the correlation between concentration and deposition rate over the diurnal cycle. The hourly concentration data could be used to quantify the error for the monthly estimates and derive empirical correction procedures.

(g.) Whilst the inferential model predicts net emission of HONO at this site, in agreement with recent measurements of HONO fluxes above vegetation, the modelling framework applied to the 1995 data had assumed HONO to be deposited. Measurements of HONO gradients at Auchencorth Moss would be required to confirm the direction of the flux and, more widely, a mechanistic understanding of the behaviour of HONO needs to be developed in order to predict its exchange.



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