

# **Nitrogen isotopes in atmospheric deposition in Northern Germany – consequences of emission changes**

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## Zusammenfassung

Der Eintrag von reaktivem Stickstoff über atmosphärische Deposition ist ein Schlüsselprozess im Stickstoffkreislauf, der überall auf der Welt zu einem Nährstoffeintrag führt. Aufgrund der Emissionen von Stickoxiden ( $\text{NO}_x$ ) und Ammoniak ( $\text{NH}_3$ ) von anthropogenen Quellen hat die Deposition von reaktivem Stickstoff im Vergleich zu vorindustriellen Zeiten deutlich zugenommen. Dies führte zu Eutrophierung von Ökosystemen und Versauerung von Böden. Um diese Phänomene zu mindern, wurden in Europa und anderen hochentwickelten Regionen die Emissionen reduziert; folglich kam es zu einer Verringerung der atmosphärischen Stickstoffdeposition und zu einer Veränderung der quellenspezifischen Zusammensetzung.

In dieser Arbeit wurde mit Hilfe von Isotopenverhältnissen des Stickstoffs in atmosphärischer Deposition gezeigt, dass zeitliche und räumliche Unterschiede in der N-Isotopie auf Veränderungen der Emissionen von N-Quellen und der unterschiedliche räumliche Wirkung dieser Quellen zurückzuführen sind. Zusätzlich konnte mit Isotopenuntersuchungen geklärt werden, inwieweit der atmosphärische N-Eintrag verantwortlich für das Biomassenwachstum in einem Hochmoor ist.

In Kapitel 2 wurde ein Vergleich von Depositionsdaten (Gehalte und Isotope) aus den 1980er Jahren mit der heutigen Situation vor dem Hintergrund der generellen Reduzierung der  $\text{NO}_x$ - und  $\text{NH}_3$ -Emissionen durchgeführt. Hierzu wurden Nass- und Trockendeposition auf  $\text{NO}_3^-$ - und  $\text{NH}_4^+$ -Gehalte und N-Isotope von  $\text{NO}_3^-$  an dem durchschnittlich belasteten Standort Geesthacht in Norddeutschland gemessen. Die Ergebnisse ergaben im Vergleich zu den historischen Werten einen deutlich geringeren Nitratgehalt und höhere N-Isotope im deponierten Nitrat. Da  $\text{NO}_x$ -Quellen N-isotopenspezifisch emittieren, war heutzutage aufgrund des Emissionsrückgangs ein geringerer Isotopenwert zu erwarten. Die überraschend höheren Isotopenwerte können auf eine positive Verschiebung des Isotopenbereichs von Kraftwerken und Verkehr hindeuten, welcher durch den Einsatz von Katalysatoren zustande gekommen ist.

In Kapitel 3 wurde der Einfluss der Schadstoffbelastung von reaktivem Stickstoff in der Atmosphäre an unterschiedlich beeinflussten Orten auf die N-Deposition und N-Isotope in deponiertem Nitrat betrachtet. Hierzu wurden die Messwerte von zwei Standorten miteinander verglichen, die am geringer belasteten Küstenstandort List auf Sylt und die am höher belasteten Standort Geesthacht. Es wurde wie in Kapitel 2 Nass- und Trockendeposition gemessen. Wie erwartet wurde insgesamt eine höhere N-Deposition mit höheren

NH<sub>4</sub><sup>+</sup>-Gehalten am Standort Geesthacht festgestellt, was aus höheren Aktivitäten aus der Landwirtschaft resultiert. Im Gegensatz dazu wurden höhere Nitrat-Gehalte und höhere N-Isotope in Nass- und Trockendeposition am Küstenstandort List ermittelt. Diese Ergebnisse können durch den höheren Einfluss von Seesalz-Aerosolen und Schiffsemissionen am Küstenstandort erklärt werden.

Die Beeinflussung des Biomassenwachstums von *Sphagnum* Moosen in einem Hochmoor durch den Nährstoffeintrag aus der Atmosphäre wurde in Kapitel 4 diskutiert. Dazu wurden N-Gehalte und N-Isotope von deponiertem Nitrat und Ammonium von den zwei dominierenden *Sphagnum* Moosen und vom Porenwasser der Moose untersucht. Die Ergebnisse ergaben insgesamt höhere N-Isotopenwerte in atmosphärischer Deposition als in der Biomasse der *Sphagnum* Pflanzen und deren Porenwasser. Für das Wachstum der Moose wird also nicht der Stickstoff aus der Deposition genutzt, sondern recycelter Stickstoff innerhalb des Ökosystems stellt den Nährstoffbedarf der Moose sicher. Der Prozess der Remineralisierung stellt hierbei die Hauptquelle des genutzten Stickstoffs dar.

## Abstract

The input of reactive nitrogen by atmospheric deposition is a key process of the nitrogen cycle which leads to a nutrient input worldwide. Based on the emission of ammonia ( $\text{NH}_3$ ) and nitrogen oxide ( $\text{NO}_x$ ) by anthropogenic sources, the N deposition loads increased considerably on a global level compared to preindustrial times causing eutrophication and acidification phenomena in ecosystem. To mitigate these effects emissions of air pollutants were reduced in Central Europe and other developed regions leading to a decrease of N deposition load and its composition with respect to sources of nitrogen.

In this thesis N isotopic ratios in atmospheric deposition clarify that differences in N isotopes on a temporal and spatial dimension are caused by emission changes of N sources and the different spatial impact of those sources. Furthermore the impact of atmospheric N inputs on the growth of *Sphagnum* biomass in a raised peat bog was identified by analysing N isotopes

In the context of the overall decrease of  $\text{NO}_x$  and  $\text{NH}_3$  emissions in Central Europe, a comparative study was conducted comparing historical N deposition loads and N isotopes from the 1980s with present-day situation (chapter 2). Dry and wet deposition of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and N isotopes of  $\text{NO}_3^-$  were sampled at the medium polluted study site Geesthacht in Northern Germany. Results indicated lower  $\text{NO}_3^-$  loads and higher N isotopes compared to historical values in deposited  $\text{NO}_3^-$ . Since  $\text{NO}_x$  sources emit N isotopes specifically, it was expected that isotope values decreased due to the change of  $\text{NO}_x$  emissions. The cause for higher values was the implementation of catalytic converters in traffic engines and in power plants, which led to a positive shift of emitting isotope ranges of these  $\text{NO}_x$  sources.

The main objective of chapter 3 was to explore the influence of reactive nitrogen pollution level in the air on the N deposition fluxes.  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition loads and the N isotopes of  $\text{NO}_3^-$  were investigated at differently affected sites. The study was conducted by using the same sampling procedure as in chapter 2 at the less polluted coastal site in List on the island Sylt and at the more polluted site in Geesthacht. As expected a higher N deposition load was observed at the site in Geesthacht, which can be attributed to a higher influence of agricultural activity resulting in higher  $\text{NH}_4^+$  deposition loads. In contrast, higher  $\text{NO}_3^-$  loads and higher N isotopes were observed in wet and dry deposition at the coastal site. These results reveal that the impact of sea-salt aerosols and  $\text{NO}_x$  emissions by ships is higher at the coastal site.

The influence of nutrient input by atmospheric deposition on the biomass growth of *Sphagnum* species in an ombrotrophic peat bog were investigated in chapter 4. In order to look into the nutrient requirements of *Sphagnum* mosses, N concentrations and N isotopes of three compartments were sampled: atmospherically deposited  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , the biomass of dominating *Sphagnum* species and the pore water of those plants. Overall higher N isotope values were observed in atmospheric deposition than in the biomass of *Sphagnum* mosses and their pore water. The main finding was that directly atmospheric N inputs are not responsible for the biomass growth. In fact, recycled N which mainly originates of remineralization processes ensures the nutrient supply for mosses.

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## List of publications

The thesis is based on three scientific publications. One is published in a peer-reviewed journal; the second is in the review process and the last one is in preparation for submission:

- Beyn, F., Matthias, V., Dähnke, K.: Changes of atmospheric nitrate deposition in Germany – an isotopic perspective. *Environmental Pollution* (2014), **194**, 1-10
- Beyn, F., Matthias, V., Aulinger, A., Dähnke, K.: Do N-isotopes in atmospheric nitrate deposition reflect air pollution levels? Submitted to *Atmospheric Environment* (2014)
- Jung, F., Schmidt, S., Jensen, K., Dähnke, K.: From atmospheric nitrogen deposition to *Sphagnum* growth – an in-situ isotopic approach to N cycling in an ombrotrophic peat bog in Northern Germany. In preparation

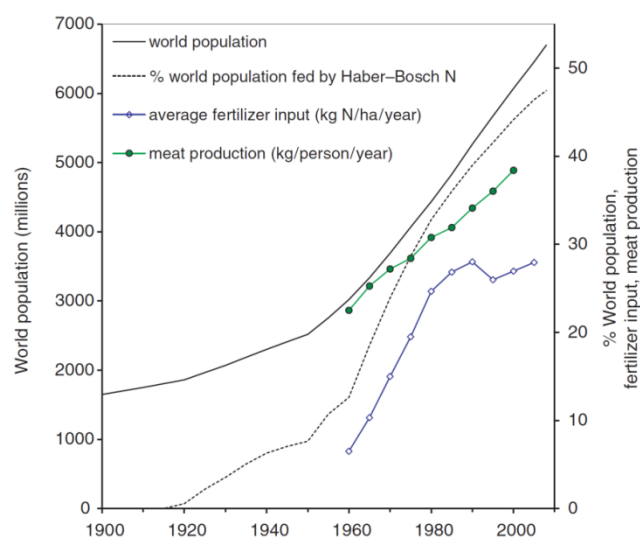


# 1. Introduction

## 1.1. The perturbation of the nitrogen cycle

The origin of current world population is irrevocably coupled with the usage of energy sources and the production of synthetic fertilizer. Compared to high abundance of inert  $N_2$  in the air, the availability of reactive nitrogen ( $N_R$ ), which includes transformable nitrogen compounds, is usually limited in natural environments by sources like biological nitrogen fixation, biomass burning and lightning. Thus, at natural conditions without additional  $N_R$  sources, the production of food is limited.

Since the onset of industrialization during the middle of the 19<sup>th</sup> century anthropogenic activities have perturbed the natural nitrogen cycle. During that time, the combustion of fossil fuels for energy and heat production initiated the acceleration of the nitrogen cycle and led to non-reversible mobilization of  $N_R$ . To sustain a larger food production for a growing world population, Haber and Bosch developed the industrial production of synthetic fertilizer at the beginning of the 20<sup>th</sup> century (Erisman et al., 2008) resulting in a progressively increase of used  $N_R$  (Fig. 1.1). Nowadays, fossil fuel combustion and the Haber-Bosch procedure in agriculture and industry have led to an excess of  $N_R$  in ecosystems reaching globally so far a maximum. In consequence, the  $N_R$  creation from anthropogenic sources overwhelms those of natural ones (Fowler et al., 2013).



**Figure 1.1:** Trends in Human population and fertilizer use in the 20<sup>th</sup> century (edited after Erisman et al., 2008).

The previously mentioned processes of  $N_R$  mobilization implicate the emission of  $NO/NO_2$  ( $NO_X$ ) by fossil fuel combustion and ammonia ( $NH_3$ ) by agricultural activities into the atmosphere.

The two main sources of atmospheric  $NO_X$  are the energy production, which is mainly derived from generating electricity by coal-fired power plants, and the sector of transportation (Erisman et al., 2011), which implicates the traffic of any vehicle on the road, in the air and on water. Also  $NO_X$  emissions from soils as a by-product of nitrification and denitrification are an important source (Stohl et al., 1996). Atmospheric  $NH_3$  is mainly derived from processes in the agriculture sector. Synthetic fertilizer production (Haber-Bosch) and livestock management, which produce manure, are one of the most important sources. During production as well as during application of fertilizer and manure huge amounts of  $NH_3$  are emitted.

The main sink for atmospheric  $NO_X$  and  $NH_3$  is the process of deposition, which is in principle the nutrient supply for ecosystems via the atmosphere. Nowadays the transportation of emitted  $N_R$  and subsequent deposition of oxidized ( $NO_Y$ ) and reduced ( $NH_X$ ) atmospheric species have become the major distribution processes regarding the global N cycle (Galloway et al., 2008).

The formation of  $N_R$  in the atmosphere and its deposition have severe consequences for human health and ecosystems. The occurrence of atmospheric  $NO_X$  and  $NH_3$  affect the air quality negatively such as increasing tropospheric ozone (Galloway et al., 2003) and formation of additional aerosols (Ansari and Pandis, 1998; Erisman et al., 2007; Ferm, 1998). Harmful effects of increased N deposition are eutrophication phenomena to marine and terrestrial environments (Gruber and Galloway, 2008), acidification of soils (Hauhs and Wright, 1986) and a loss of biodiversity (Dise and Stevens, 2005). However, the surplus of  $N_R$  can also result in higher  $CO_2$  uptake ability in N-limited ecosystems (Townsend et al., 1996).

The amount of atmospheric  $N_R$  inputs to marine environments indicate that a significant fraction of all  $N_R$  inputs to marine ecosystems have an atmospheric origin. Comparing N deposition loads with the riverine inputs in the North Sea, overall atmospheric  $N_R$  fluxes contain one third of the riverine inputs (Rendell et al., 1993); other studies confirmed a significant amount (up to 50%) of atmospheric N deposition to coastal water bodies

compared to other external  $N_R$  supply (Paerl, 1997; Spokes and Jickells, 2005; Whittall et al., 2003). Nevertheless, coastal environments have basically a lower N pollution level than terrestrial ecosystems, because major  $N_R$  sources are land-based and affect terrestrial sites more severely than coastal ones. Deposition studies in Europe (Bencs et al., 2009; Yeatman et al., 2001), North-America (Gao et al., 2007; Russell et al., 1998) and in Asia (Fang et al., 2011; Ham et al., 2010) confirm that continental air-masses have higher N loads than air-masses of marine origin. The studies also show that these observations are detached from the overall amount of N deposition at the site.

The overall consequences of N deposition to ecosystems can be illustrated by the exceedance of critical loads for eutrophication by atmospheric N deposition. In Germany almost 50% of terrestrial ecosystems are threatened to eutrophication by atmospheric  $N_R$  inputs (Schaap et al., 2014).

### **1.1.1. Ombrotrophic ecosystems**

As atmospheric N deposition is for all ecosystems of importance, ombrotrophic ecosystems are particularly sensitive to atmospheric  $N_R$  inputs, because the  $N_R$  balance of these kinds of ecosystems is totally dependent of the  $N_R$  inputs by atmospheric wet and dry deposition due to the absence of other external  $N_R$  sources (Bobbink et al., 1998). Ombrotrophic ecosystems are morphological excluded from  $N_R$  inputs from groundwater and discharge from surrounded areas. In consequence, other important  $N_R$  sources like fertilizer washout or indirect  $N_R$  deposition by transport of originally atmospheric-derived  $N_R$  to regions do not have an impact on these ecosystems.

Ombrotrophic ecosystems in Europe are raised peat bogs, which have typically nutrient-poor conditions to which plant species are adapted. Further, acidic conditions (pH~4) are prevailing, which lead to a basically low bacterial activity (Urban and Eisenreich, 1988). Thus, in regards to the N cycling, biological driven processes, like nitrification or denitrification, are at natural conditions inhibited or very low. In addition, this low pH leads to incomplete decomposition of biomass resulting in peat production in deeper layers.

In a natural state, *Sphagnum* plants are adapted to these conditions and are widely spread in peat bogs. *Sphagnum* retains completely atmospheric  $N_R$  inputs (Aldous, 2002b; Williams

et al., 1999a); thus, the availability of  $N_R$  for other species is low. But, due to high mobilization of  $N_R$  since industrialization times, nowadays the N deposition flux has severe consequences for the biodiversity, especially in peat bogs.

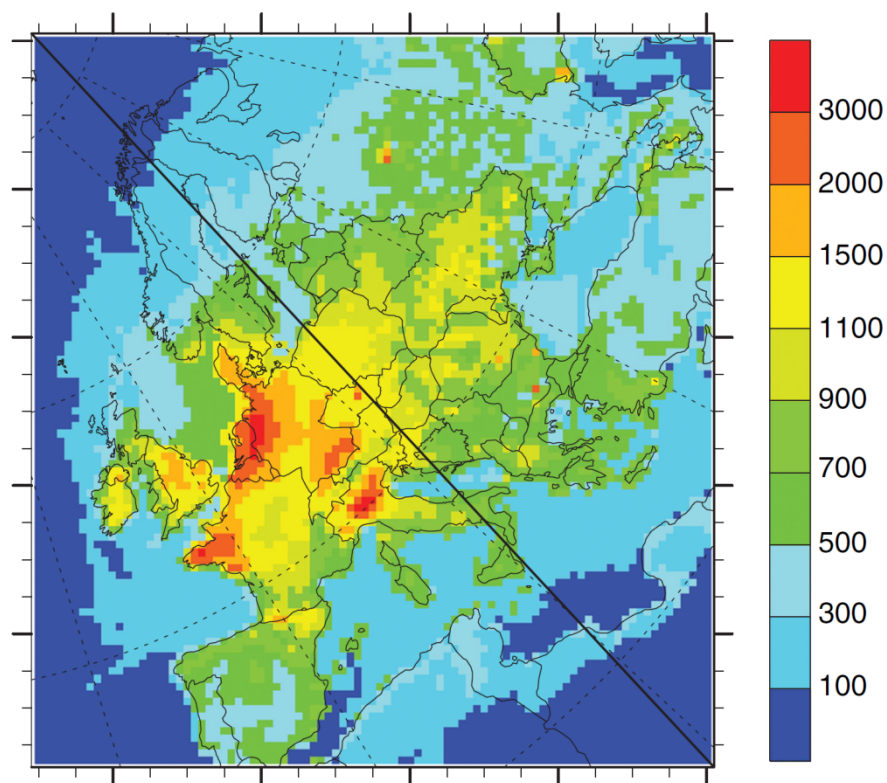
*Sphagnum* mosses are supposed to adapt to changing conditions such as higher N tissue content (Jauhiainen et al., 1998a). This adapting strategy has been used in many studies to estimate past N deposition levels. Hence, the N deposition load at a peat bog reflects N content in mosses (Harmens et al., 2011; Schroder et al., 2010), because  $NO_3^-$  and  $NH_4^+$  are incorporated in biomass at a same level even then the N deposition exceeds natural loads (Jauhiainen et al., 1998b).

## 1.2. Deposition of $N_R$ in Europe

In Europe,  $NH_X$  and  $NO_Y$  deposition are both relevant (Simpson et al., 2011), even though modelled (Simpson et al., 2006) and measured (e.g. Dammgen, 2007; Fowler et al., 2005b) deposition loads of  $N_R$  show in general a greater part of reduced than oxidized N in total deposited  $N_R$ . However, also the organic parts are important (Cornell, 2011). About 10% of the total N deposition composes organic N in Europe (Cape et al., 2012). Since the majority of N deposition is inorganic, only this part is investigated in the thesis.

Continuous measurements for wet N deposition ( $NO_3^-$  and  $NH_4^+$ ) are carried out in the European Monitoring and Evaluation Programme (EMEP), but only modelled data exists regarding dry N deposition. The EMEP wet deposition monitoring network was established for quality assurance in the dry and wet N deposition modelling of the programme. EMEP sites are distributed over Europe and were chosen in regions, which are not interfered by point sources, because they should represent a relative low pollution level of  $N_R$  compounds to reproduce background concentrations of pollutants (Yttri, 2012).

In Germany N deposition loads are generally estimated in the range of 10-25 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Fig. 1.2). Regions of higher N loads are located in Western Germany, lower pollution levels are in areas with less agricultural activity like in forest ecosystems and coastal regions (Simpson et al., 2006).

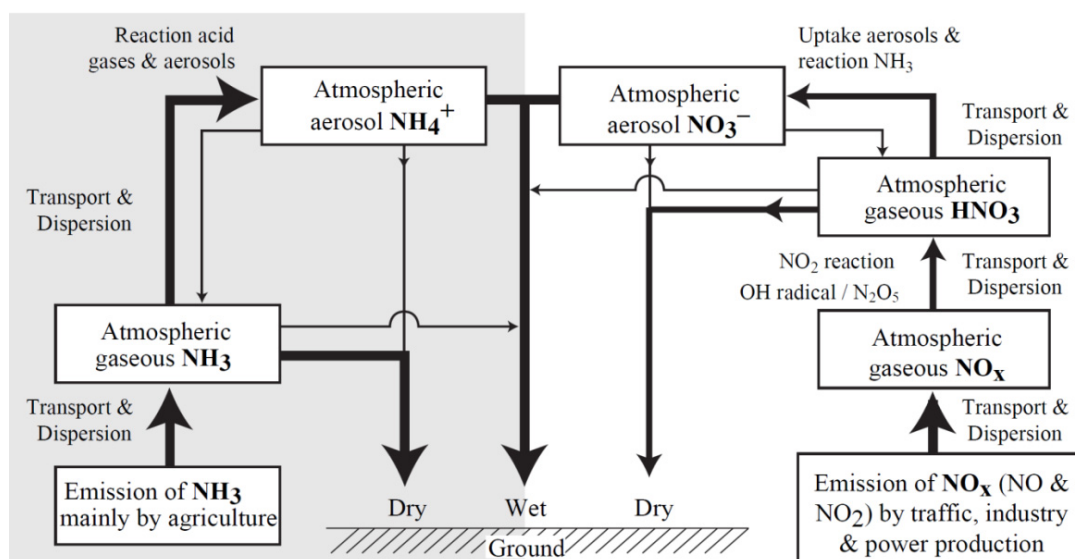


**Figure 1.2:** Calculated N-Deposition flux ( $\text{mg N m}^{-2}$ ) to semi-natural ecosystems in Europe for the year 2000 (Simpson et al., 2011).

Considering European deposition loads, the total N deposition load in countries is strongly coupled with  $\text{NH}_x$  deposition flux and concurrent  $\text{NH}_3$  emission budget of the country. For instance, the region around the Netherlands is an area of high N loads (Fig. 1.2) with concurrent high  $\text{NH}_3$  emissions (Buijsman and Erisman, 1988). This is one example why a detailed view on transport, transportation and deposition processes of  $\text{N}_R$  can help to understand N deposition fluxes.

### 1.2.1. Transport, transformation and deposition processes of $\text{N}_R$

Once released to the atmosphere, emitted  $\text{NH}_3$  and  $\text{NO}_x$  pass through different transformation and transportation pathways until they are deposited on the surface (Fig. 1.3). Gaseous ( $\text{NH}_3$ ,  $\text{HNO}_3$ ) or particulate ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ) deposition are considered as dry deposition and the scavenging of gaseous and particulate  $\text{N}_R$  compounds via precipitation is known as wet deposition.



**Figure 1.3:** Illustration of inorganic  $N_R$  species pathways in the atmosphere (edited after Hertel et al., 2006).

With increased transport and dispersion,  $NH_3$  can either be transformed to particulate  $NH_4^+$  in reaction with gases and aerosols or it is retained in gaseous form. Despite a very short residence time and concurrent low transportation range of gaseous  $NH_3$  in the atmosphere, particulate  $NH_4^+$  can have a lifetime of days and thus can be transported over a long range (>1000 km) (Ferm, 1998).

In comparison to different behaviour of reduced  $N_R$  compounds, all oxidized products are usually transported over a long range, because the lifetime of  $NO_x$  is estimated to be 1-2 days in the atmosphere (Liang et al., 1998). Atmospheric  $NO_x$  is converted to  $NO_3^-$  species by several chemical reactions in the atmosphere (Fig. 1.3). The pathway of emitted NO is the oxidation to  $NO_2$  by reacting with  $O_3$ . Afterwards  $NO_2$  is oxidized to gaseous  $HNO_3$ . In summer this oxidation is driven by the reaction with OH radicals, in winter it occurs via the reaction with  $N_2O_5$  (Finlayson-Pitts and Pitts Jr, 2000; Seinfeld and Pandis, 1998). Gaseous  $HNO_3$  sticks immediately on any surface (ground and particles) and hence can have a very short lifetime, if it is dry deposited. It also can generate particulate  $NO_3^-$  by the incorporation of new aerosols or the reaction with  $NH_3$ . The lifetime of gaseous  $HNO_3$  and particulate  $NO_3^-$  in the atmosphere is similar to  $NO_x$  (Liang et al., 1998) and thus can be transported over a long range.

Summing up the overall transportation characteristics of  $N_R$  compounds in the atmosphere until deposition,  $NO_Y$  products are more frequently transported over a longer range than  $NH_X$  products (Ferm, 1998; Fowler et al., 2007).

As a consequence of the chemical behaviour and residence time, the majority of main gaseous atmospheric  $N_R$  species ( $NH_3$ ,  $HNO_3$ ) are dry deposited, while particulate  $NO_Y$  and  $NH_X$  compounds are mainly removed from the atmosphere by wet deposition processes (Hertel et al., 2011) (Fig. 1.3).

The quantitative estimation of both dry and wet deposition to total N deposition shows on average approximately an equal distribution in continental Europe (Simpson et al., 2011). Due to the absence of an established method measuring dry deposition, a more precise statement is not possible. However, concerning the deposition fluxes to marine ecosystems, it is known that dry deposition of oxidized and reduced  $N_R$  are lower compared to terrestrial sites, which is caused by higher surface roughness (Bartnicki and Fagerli, 2008). Thus, wet deposition is much more important in marine areas.

### **1.2.2. Trend of $N_R$ deposition in Europe**

Knowing that the pollution of atmospheric  $N_R$  compounds and N deposition is not only a local problem for ecosystems, a political aim was to reduce the  $N_R$  emissions. Thus, since the end of the 20<sup>th</sup> century N deposition have changed.

To reduce the impact of high  $NO_X$  and  $NH_3$  air concentrations in Europe and other highly developed regions, management practices were developed to reduce the air emissions. As the source of  $NH_3$  in the atmosphere is almost exclusive derived from agricultural activities, the reduction efforts are focused on this sector. A more efficient use of manure/fertilizer application on the field (Skjøth et al., 2008) led to a  $NH_3$  emission decrease of almost 20% in Germany between 1990 and 2010 (UBA, 2012).

Since fossil fuel combustion processes are the main source of atmospheric  $NO_X$  in Germany, efforts to reduce  $NO_X$  emissions are introduced in these combustion processes. The most important technologies are oil/water emulsification in vehicle engines, staged combustion in industry processes and selective reduction with or without catalytic converters (Joynt and Wu, 2000). The result of such technologies is a substantial change of  $NO_X$  emission in Europe. In Germany, the  $NO_X$  emissions were reduced by 50% since

1990 (UBA, 2012). Also, in other highly developed countries, such as Great Britain or the Benelux countries,  $N_R$  emissions decreased similarly (Fowler et al., 2007).

In consequence, the recent changes in  $N_R$  emissions have impacted the N deposition loads in Europe. It was observed that the loads of  $NO_3^-$  have decreased more strongly than those of  $NH_4^+$  deposition, which resulted in higher molar ratios of  $NH_4^+/NO_3^-$  (Fowler et al., 2005b; Francaviglia et al., 1995). In Central Europe the decrease of  $NO_3^-$  deposition is rather low in comparison to the reduction of  $NO_X$  emission. This can be ascribed to large parts of  $NO_X$  being exported to Eastern Europe due to prevailing westerly wind conditions (Fowler et al., 2007).

Nevertheless, despite an overall decrease of the two major  $NO_X$  emission sources, ship emissions have the opposite trend: In 2010 the emission of ships increased by almost 20% in comparison to 1990 in Germany (UBA, 2012). The increasing influence of ship emissions to the  $NO_X$  level in the North Sea region has already been observed (Matthias et al., 2010). The increase is mainly caused by non-regulation of  $NO_X$  outputs from ships in European seas, as restrictions are mostly intended to mitigate  $SO_X$  air concentration by limiting sulphur content in shipping fuels (IMO, 2009).

To conclude about N deposition loads, which are known to have a high scatter within a year or between years at one site, because wind direction or local N sources can vary strongly at a site (Gyldenkerne et al., 2005), it is necessary to look at meteorological parameters, the backward calculation of air-masses (backward trajectories) and the isotopic composition of  $N_R$  compounds in atmospheric deposition.

### 1.3. N isotopes of emission and deposition

The abundance of stable isotopes of nitrogen,  $^{15}N$  and  $^{14}N$ , varies in earth spheres due to isotope fractionation in biological, physical and chemical processes. The ratio of both isotopes in natural abundance samples is denoted in comparison to the ratio of a standard.

The deviation to the standard is expressed as the  $\delta^{15}N$  value:

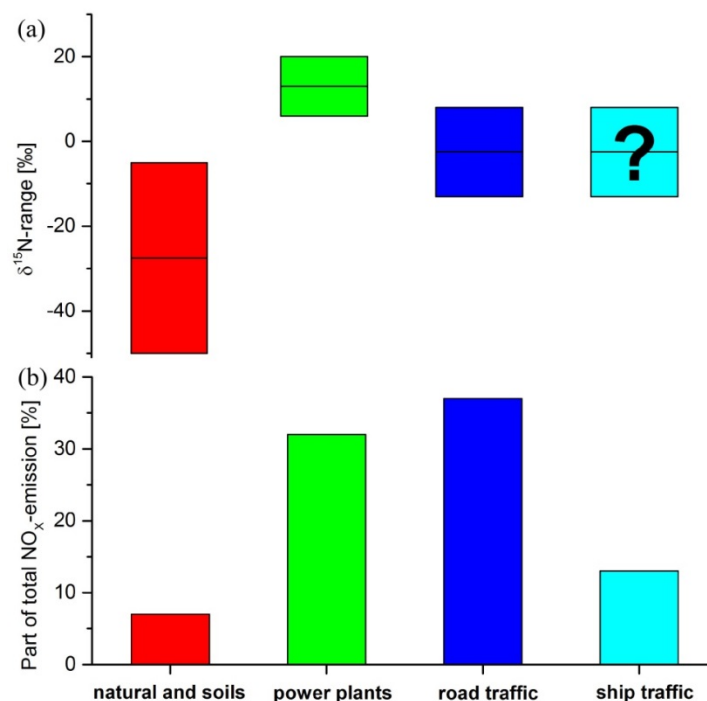
$$\delta^{15}N [‰] = \left( \frac{^{15}N / ^{14}N_{sample}}{^{15}N / ^{14}N_{standard}} - 1 \right) * 1000$$



The standard for all kind of  $\delta^{15}\text{N}$  measurements is atmospheric  $\text{N}_2$ , which has by definition a  $\delta^{15}\text{N}$  value of 0‰.

There are two kinds of isotope effects. The equilibrium isotope effect means that one substance incorporates more  $^{14}\text{N}$  than the other, if both substances are in equilibrium. The other more frequently occurring isotopic effect is the uni-directional kinetic isotope effect, which is described by the easier metabolic transformation of the lighter  $^{14}\text{N}$  isotope than the heavier  $^{15}\text{N}$ . An example for both types of isotope effects is the process of  $\text{NH}_3$  volatilization. During volatilization an equilibrium effect occurs between gaseous and dissolved  $\text{NH}_3$ , which causes less incorporation of  $^{15}\text{N}$  into the gaseous form. Kinetic fractionation takes place during diffusion processes of  $\text{NH}_3$ , which enriches the residual part of the substrate (Heaton, 1986).

Fundamentally, atmospheric  $\text{N}_\text{R}$  species have different sources as each of the sources generates a certain N isotope range. With regards to  $\text{NO}_3^-$  deposition, the range of  $\delta^{15}\text{N}$  of the most important  $\text{NO}_\text{X}$  sources are known: In general, natural and agricultural sources emit isotopically depleted  $\delta^{15}\text{N}\text{-NO}_\text{X}$  compared to industrial derived  $\text{NO}_\text{X}$ , which represents the majority of Germany's  $\text{NO}_\text{X}$  emissions (Fig. 1.4b).



**Figure 1.4:** Proportion of main sources to Germany's  $\text{NO}_\text{X}$  inventory in 2010 and their  $\delta^{15}\text{N}\text{-NO}_\text{X}$  ranges.

Stationary sources like coal-fired power plants emit  $\text{NO}_x$  usually in the range of +6 to +13‰ (Heaton, 1990; Kiga, 2000). Isotope investigations of road traffic  $\text{NO}_x$  resulted in values of -13 to +8‰ (Ammann et al., 1999; Heaton, 1990; Pearson et al., 2000). The isotope value of  $\text{NO}_x$  emitted by ships has not been investigated yet, but it is probably in the range of road traffic  $\text{NO}_x$  (Fig. 1.4a)

In contrast to direct anthropogenic sources, biogenic  $\text{NO}_x$  emissions from soil are strongly depleted in  $^{15}\text{N}$  and range between -49 and -20‰ (Li and Wang, 2008). This emission is derived from bacterial activity, which emits  $\text{NO}_x$  as a by-product of nitrification and denitrification. Natural derived  $\text{NO}_2$  is usually depleted in  $^{15}\text{N}$  (Ammann et al., 1999; Heaton, 1986). Consequently, remote areas have lower  $\delta^{15}\text{N}\text{-NO}_x$  values than those that include industrial sources (Kendall et al., 2008).

Worldwide, there are many studies, which investigate N isotopes of bulk, wet or dry N deposition (Tab. 1.1). The observations resulted usually in high winter and low summer values, which was mainly caused by seasonality of  $\text{NO}_x$  sources and oxidation pathways of  $\text{NO}_2$  (Freyer, 1991). Further, particulate isotope values are higher than those of gaseous  $\text{HNO}_3$  and wet deposited  $\text{NO}_3^-$ ; this was explained by a partitioning effect between gaseous and particulate  $\text{NO}_3^-$ . The equilibrium fractionation between both species led to higher fraction of depleted  $^{15}\text{N}$  in the gaseous form (Freyer et al., 1993).

**Table 1.1:** Collection of worldwide measured isotopic ranges of atmospheric  $\text{NO}_3^-$  species.

Deposition type <sup>1</sup>	Region	Isotope range	Reference
Bulk	Pretoria, S-Africa	-7.1 to +4.1‰	(Heaton, 1987)
Bulk	Tennessee, N-America	-2 to +6‰	(Garten, 1992)
Bulk	4 sites across Germany	-10 to +4‰	(Freyer, 1991)
Wet	Chesapeake Bay, N-America	-4 to +5‰	(Russell et al., 1998)
Wet	North Eastern, N-America	-8.1 to +3.2‰	(Elliott et al., 2007)
Wet	Guangzhou, China	-4.9 to +10.1‰	(Fang et al., 2011)
Wet	Xi'an city, China	-2 to +9‰	(Xing and Liu, 2012)
Wet	Niigata, Japan	-8 to +2‰	(Fukuzaki and Hayasaka, 2009)

Table 1.1: continued.

Deposition type <sup>1</sup>	Region	Isotope range	Reference
Wet	Chonnam, South-Korea	-5.2 to +4.4‰	(Lee et al., 2012)
Wet	Crete, Greece	-5.7 to -3.4‰	(Mara et al., 2009)
Particulate	Pretoria, South-Africa	-2.1 to +12.1‰	(Heaton, 1987)
Particulate	Jülich, Germany	-3 to +14‰	(Freyer, 1991)
Particulate	North-Eastern, N-America	-9.5 to +14.1‰	(Elliott et al., 2009)
Dry	Crete, Greece	-4.2 to -1.7‰	(Mara et al., 2009)
Aerosol	Gulf of Aqaba, Israel	-6.9 to +1.9‰	(Wankel et al., 2010)
Aerosol	2 sites in Great Britain	-7 to +6‰	(Yeatman et al., 2001)
Gaseous	Jülich, Germany	-2 to +2‰	(Freyer, 1991)
Gaseous	North Eastern, N-America	-4.9 to +10.8‰	(Elliott et al., 2009)

<sup>1</sup>Deposition types are separated in bulk deposition (wet + dry deposited compounds), dry deposition (all dry deposited compounds), wet deposition (all wet deposited compounds), particulate (all particulate compounds), aerosol (only aerosol (particle size: <10 µm) compounds) and gaseous (only gaseous compounds) parts.

The N isotopic values of emitted NH<sub>3</sub> are mainly caused by agricultural activity and are basically <sup>15</sup>N-depleted. Because N isotopes of emitted NH<sub>3</sub> are more <sup>15</sup>N-depleted than NO<sub>x</sub> sources, the δ<sup>15</sup>N of dry and wet deposited NH<sub>x</sub> is lower as those of NO<sub>y</sub> species (Freyer, 1978; Garten, 1992; Heaton, 1987; Jia and Chen, 2010; Yeatman et al., 2001).

## 1.4. Focus and thesis outline

### 1.4.1. Focus and motivation

The main motivation of the thesis was to investigate N isotopes of atmospheric  $\text{NO}_3^-$  in regards to changes of  $\text{NO}_x$  source pattern and overall decrease of  $\text{NO}_x$  emissions in Central Europe since the 1980s. The lack of investigations with the focus on the emission changes creates the fundament to the thesis.

In Germany the last N isotopic study was reported by Freyer in 1991. In the 1980s he collected and investigated samples at few sites in Germany (Tab. 1.1). These data can be attributed to a status quo before reduction technologies were implemented. Thus, present-day measurements are suitable for investigating the influence of emission changes on N isotopes in  $\text{NO}_3^-$  deposition. Due to the emission decrease of  $^{15}\text{N}$ -enriched industry sources a decline of N isotopes was expected in comparison to the values from the 1980s.

Current N isotopic studies investigating N isotopes in atmospheric  $\text{NO}_3^-$  species with respect to N pollution level and changing  $\text{NO}_x$  emission pattern were missing. To look at the spatial influences of the change, a marine affected and a terrestrial affected site are a proper choice, because the influence of marine sources (ship emissions) are getting much more important compared to 20 years ago. An upcoming question in regards to overall changing  $\text{NO}_x$  emissions was: Is the air pollution level at a site still reflected in N isotopes in deposited  $\text{NO}_3^-$ ?

In order to investigate the consequences of changing N deposition (loads and isotopes) to ecosystems, it was reasonable to analyse peat bogs (see chapter 1.1.1). In-situ investigations of N deposition load and N isotopes in relation to the N content and N isotopes of dominating *Sphagnum* mosses were conducted for supplementing missing data of that ecosystem. It was expected that *Sphagnum* plants retained atmospheric  $\text{N}_R$  inputs completely. Thus, the assumption was that N isotopes in the biomass reflect those of deposited  $\text{N}_R$  ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ).

## 1.4.2. Thesis Outline

The thesis consists of three chapters and publications, respectively (chapter 2, 3, 4).

### Chapter 2

#### **Changes in atmospheric nitrate deposition in Germany – An isotopic perspective**

Fabian Beyn, Volker Matthias and Kirstin Dähnke

*Environmental Pollution* (2014), 194, 1-10

The motivation of this study was the existing lack of recent  $\delta^{15}\text{N}$  data of atmospheric deposited  $\text{NO}_3^-$  in continental Central Europe. The latest isotope deposition data were investigated across Germany in 1980s (Freyer, 1991). The publication deals with the investigation whether the decline in  $\text{NO}_x$  emissions of 50% in Germany (UBA, 2012) are reflected in a historical comparison of N isotopes in atmospheric deposition. This approach can be used, because changes in emissions of  $\text{N}_R$  are affecting the N deposition load (Fowler et al., 2007) rather than changes in atmospheric chemistry or transportation processes (Dentener et al., 2006).

Based on known isotope ranges of main  $\text{NO}_x$  sources, a decline in isotope values in comparison to the results of Freyer, 1991 in Germany was hypothesized, because the contribution to the total  $\text{NO}_x$  budget of relative enriched  $\delta^{15}\text{N}\text{-NO}_x$  by power plants and traffic has decreased, while the contribution of highly depleted  $\delta^{15}\text{N}\text{-NO}_x$  by soil emissions has increased.

A typical seasonal  $\delta^{15}\text{N}$  variation of dry and wet deposited  $\text{NO}_3^-$  was explored having the highest values in winter and the lowest ones in summer. However, in comparison to the values in the 1980s significant higher values from autumn till spring were observed. Backward trajectories indicate that land-based sources have the highest influence on the results. These observations were attributed to a change in combustion patterns through implementation of catalytic converters in coal-fired power plants and traffic engines to more positive  $\delta^{15}\text{N}$  values in emitted  $\text{NO}_x$ . The influence of this change was mitigated in summer, because the influence of  $^{15}\text{N}$ -depleted soil emissions is high and  $^{15}\text{N}$ -enriched power plants emissions are low.

The contribution of co-authors was

Co-work of manuscript structure and proofreading (Volker Matthias)

Co-work of manuscript concept, structuring and proofreading (Kirstin Dähnke)

### Chapter 3

#### **Do N-isotopes in atmospheric nitrate deposition reflect air pollution levels?**

Fabian Beyn, Armin Aulinger, Volker Matthias and Kirstin Dähnke

Submitted to *Atmospheric Environment* (2014)

In this publication the approach was to investigate the impact of the overall pollution level on N deposition and isotopes at a coastal (List on Sylt) and terrestrial (Geesthacht) site.

Usually the anthropogenic imprint is higher at the terrestrial site Geesthacht, which is caused by higher influence of land-based NO<sub>x</sub> sources. Further, agricultural sources are much closer to Geesthacht, which lead to an overall higher pollution level of NH<sub>3</sub> at this site. Regarding isotopic values, polluted areas have basically a higher  $\delta^{15}\text{N}$  values in deposited NO<sub>3</sub><sup>-</sup> than areas with a lower pollution level (Kendall et al., 2008). Because of that, in total a higher N deposition flux and on average higher  $\delta^{15}\text{N}$ -NO<sub>3</sub><sup>-</sup> values in wet and dry deposition were hypothesized in Geesthacht than in List.

Concerning the total N deposition at both sites, a higher load at Geesthacht than in List was observed, which can be attributed to higher NH<sub>4</sub><sup>+</sup> loads at the site in Geesthacht. However, bulk average NO<sub>3</sub><sup>-</sup> fluxes are higher in List. Regarding  $\delta^{15}\text{N}$  values of deposited NO<sub>3</sub><sup>-</sup>, in both wet (-0.1 vs. -1.0‰) and dry deposition (+3.1 vs +1.9‰) significantly higher  $\delta^{15}\text{N}$  values were observed in List.

The surprisingly higher NO<sub>3</sub><sup>-</sup> loads in List can most likely be attributed to higher impact of sea-salt aerosols and the emerging source ship emissions. The differences in  $\delta^{15}\text{N}$  values also are explained by the higher influence of ship emissions and the implementation of NO<sub>x</sub> reduction technologies in ship engines, but due to missing political regulations, the use of those technologies is optional and thus plays most likely only a minor role in the North Sea region.

The contribution of co-authors was

- Conducting model calculations (Armin Aulinger)
- Supplements to manuscript in atmospheric chemistry content, proofreading (Volker Matthias)
- Co-work of manuscript concept, structuring and proofreading (Kirstin Dähnke)

## Chapter 4

### **From atmospheric nitrogen deposition to *Sphagnum* growth – an in-situ isotopic approach to N cycling in an ombrotrophic peat bog in Northern Germany**

Fabian Jung, Sebastian Schmidt, Kai Jensen, Kirstin Dähnke, in preparation for submission

This chapter is based on the comparison of frequently measured N isotope values in  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition and N isotopes in the biomass of dominant *Sphagnum* species during 2012 in the raised bog Hartshoper Moor.

The nutrient cycling in an ombrotrophic peat bog is usually coupled with atmospheric deposition, which is the only external  $\text{N}_R$  source (Bobbink et al., 1998). Although the N deposition load is far from original conditions and the function of peat bogs has changed, in usual cases the biomass of *Sphagnum* mosses in European peat bogs reflect N deposition, which suggests that deposited N is retained in mosses (Harmens et al., 2011; Schroder et al., 2010). Many studies documented a relationship between N content in mosses and N deposition load as well as the positive correlation between N isotopes in mosses and the molar ratio of  $\text{NH}_4^+/\text{NO}_3^-$  in deposition. Based on these observations we suggest that  $\delta^{15}\text{N}$  values of deposited  $\text{NO}_3^-$  and  $\text{NH}_4^+$  reflect  $\delta^{15}\text{N}$  values of dominant *Sphagnum* species.

Overall averaged  $\delta^{15}\text{N}$  value in N deposition was  $+0.3 \pm 4.9\text{‰}$  ( $\delta^{15}\text{N-NH}_4^+$ :  $-1.7 \pm 6.4\text{‰}$ ;  $\delta^{15}\text{N-NO}_3^-$ :  $+2.3 \pm 2.9\text{‰}$ ), while hollows dominated *Sphagnum cuspidatum* and hummocks dominated *Sphagnum papillosum* show significantly lower values of  $-5.9 \pm 1.1\text{‰}$  and  $-6.9 \pm 0.8\text{‰}$ , respectively.

As the distinct differences in isotope values suggest, recent atmospheric  $N_R$  inputs are not the main N source for the growth of *Sphagnum* species in the peat bog, which is no longer N-limited. The main  $N_R$  requirements for *Sphagnum* growth stem rather from internal cycling process than from current atmospheric N loads. Most likely the biological driven process of N remineralization is the main  $N_R$  source for *Sphagnum* mosses. The fate of deposited  $N_R$  cannot ultimately be explained, possible sinks are the transport downwards to the peat layer or the utilization by vascular plants.

The contribution of co-authors was

- Co-work of manuscript concept, sampling of *Sphagnum* mosses and pore water, analysing *Sphagnum* samples, proofreading of the manuscript (Sebastian Schmidt)
- Co-work of manuscript concept and proofreading of the manuscript (Kai Jensen)
- Co-work of manuscript concept, structuring and proofreading (Kirstin Dähnke)



## 2. Changes in atmospheric nitrate deposition in Germany – an isotopic perspective

Fabian Beyn, Volker Matthias and Kirstin Dähnke

*Environmental Pollution* (2014), **194**, 1-10

### Abstract

We investigated the isotopic composition of atmospheric  $\text{NO}_3^-$  deposition at a moderately polluted site in Western Europe over an annual cycle from December 2011 to November 2012. On average, we measured load-weighted  $\delta^{15}\text{N}$  values of +0.1 and +3.0‰ in wet and dry deposition, respectively. A comparison to source-specific N emission trends and to isotope data from the 1980s reveals distinct changes in  $\delta^{15}\text{N}\text{-NO}_3^-$  values: In contrast to the increasing relative importance of isotopically depleted natural  $\text{NO}_x$  sources, we find an increase of isotope values in comparison to historical data. We explore the role of land-based N sources, because backward trajectories reveal a correlation of higher  $\delta^{15}\text{N}$  to air mass origin from industrialized areas. Nowadays isotopically enriched  $\text{NO}_x$  of coal-fired power plants using selective catalytic converters and land-based vehicle emissions, which use same technology, are apparently the main driver of rising  $\delta^{15}\text{N}$  values in nitrate deposition.

### 2.1. Introduction

The increasing production of food and energy worldwide has enhanced today's anthropogenic emissions of reactive nitrogen ( $\text{N}_R$ ) compounds to the world's ecosystems, with manifold consequences such as acceleration of the natural nitrogen cycle (Erisman et al., 2007; Galloway et al., 2004), eutrophication of both terrestrial and marine ecosystems (Bouwman et al., 2002; Kendall et al., 2008; Smith et al., 1999), and elevated concentrations of nitrogenous compounds in the atmosphere. These atmospheric nitrogen

loads have a relatively short residence time in the atmosphere in the range of hours to days (Galloway et al., 2003) and are swiftly transferred back to both marine and terrestrial ecosystems, where they contribute to eutrophication phenomena (Gruber and Galloway, 2008).

Furthermore, NO<sub>x</sub> and ammonia contribute to aerosol formation (Ansari and Pandis, 1998; Erisman et al., 2007; Ferm, 1998), and NO<sub>x</sub> leads to increased atmospheric ozone concentrations (Galloway et al., 2003). Moreover, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, major compounds of atmospheric nitrogen deposition, are a source of acid deposition with potentially harmful consequences for soils and forest ecosystems (Hauhs and Wright, 1986).

Major anthropogenic NO<sub>x</sub> sources are fossil fuel combustion by industry and power plants and traffic, whereas natural sources like lightning or soil volatilization of NO<sub>x</sub> play a minor role in the NO<sub>x</sub> emission budget both in Germany (Tab. 2.1) (UBA, 2012) and globally (Bouwman et al., 2002). The main source of ammonia, the precursor of NH<sub>4</sub><sup>+</sup> deposition, is agriculture, with synthetic fertilizer and animal husbandry being the most important sources (Bouwman et al., 1997).

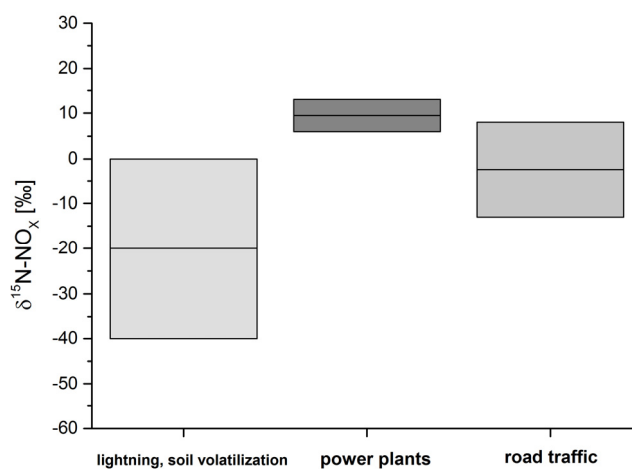
**Table 2.1:** NO<sub>x</sub> absolute and relative emission inventory of Germany in 1990 and 2010 and source specific changes - including the major sources road traffic, industry/power plants, soil volatilization and ship traffic (after UBA, 2012).

Source	Absolute Emissions [Gg]			Relative Emissions		
	1990	2010	Change	1990	2010	Change
Road traffic	1500	600	-60%	48%	37%	-23%
Industry / power plants	1150	515	-55%	37%	32%	-14%
Soil volatilization	135	102	-26%	3%	7%	+130%
Ship traffic	180	210	+17%	6%	13%	+117%
<b>Overall</b>	<b>3130</b>	<b>1620</b>	<b>-48%</b>	<b>94%</b>	<b>89%</b>	

To curb man-made eutrophication and reduce the health risks associated with high atmospheric NO<sub>x</sub> and ammonia concentration, management practices aim to reduce atmospheric N<sub>R</sub> loads. Important reduction measures for NO<sub>x</sub> include staged combustion

in industry processes and selective reduction with or without catalytic converters (Joynt and Wu, 2000). Jointly, these reduction efforts have led to a nearly 50% decrease of  $\text{NO}_x$  emissions in Germany since 1990 (Tab. 2.1). The emission inventory of ammonia indicate only a decrease of less than 20% since 1990 (UBA, 2012). Total nitrogen deposition in Europe is monitored within the EMEP (European Monitoring and Evaluation Programme) network, but a direct attribution of nitrogen deposition to its respective natural or anthropogenic sources remains difficult.

For such source assessment of  $\text{NO}_x$  emissions, stable isotope ratios of nitrogen are useful, because isotope values of industrial  $\text{NO}_x$  generally are significantly elevated over those of agricultural or natural sources (Fig. 2.1) (Kendall et al., 2008). For instance,  $\delta^{15}\text{N}\text{-NO}_x$  values of coal-fired power plants range from +6 to +13‰ (Heaton, 1990; Kiga, 2000), and while vehicle emissions have a wider range (-13 to +6‰), most studies have found positive values in tailpipe exhaust, roadside denuders and roadside vegetation (+3.7, +5.7, and +3.8‰, respectively) (Ammann et al., 1999; Moore, 1977; Pearson et al., 2000).



**Figure 2.1:** Known  $\delta^{15}\text{N}$  values in  $\text{NO}_x$  emissions from natural and anthropogenic sources. Data are compiled from Ammann et al., 1999; Heaton, 1990; Li and Wang, 2008; Moore, 1977; Pearson et al., 2000.

In contrast to industrial pollution, biogenic emissions from soil volatilization are isotopically depleted, with values as low as -49‰ found after fertilization (Li and Wang, 2008). As a consequence,  $\delta^{15}\text{N}$  of  $\text{NO}_x$  emissions in polluted areas is considerably higher than in pristine regions (Kendall et al., 2008 and references therein), and relative changes

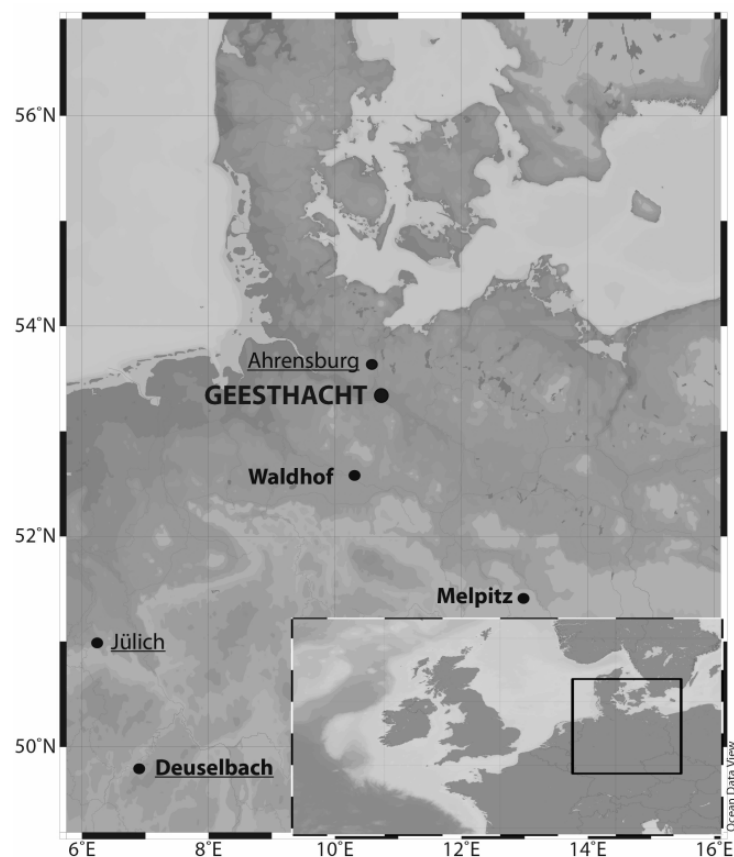
between natural and industrial sources can be detected based on these source specific isotope signatures (Elliott et al., 2007; Freyer, 1991).

Data of the national environmental agency (UBA, 2012) suggest that over the past 20 years, the industrial proportion of NO<sub>x</sub> to the total NO<sub>x</sub> budget has decreased in comparison to natural sources (Tab. 2.1). Consequently, sources of <sup>15</sup>N-depleted NO<sub>x</sub> gained in importance in comparison to isotopically enriched sources. Recent isotope measurements of NO<sub>3</sub><sup>-</sup> deposition in Germany are scarce, and the main objective of our study was to investigate whether this trend was reflected in decreasing isotope signatures in comparison to historical data. To test this hypothesis, we measured dry and wet N deposition and δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> at a medium polluted site in Northern Germany, Western Europe.

## **2.2. Materials and methods**

### **2.2.1. Study site**

Wet and dry deposition samples were collected near Geesthacht, southeast of Hamburg/Germany on forest surrounded grassland. The wind direction at the study site is dominated by prevailing westerlies, and it is exposed to both industrial and agricultural emissions of nitrogen: The eastern and southern surroundings are dominated by agriculture and livestock farming, and the adjacent northwestern region is dominated by shipping and road traffic and power plants close to the Hamburg metropolitan region (Fig. 2.2).



**Figure 2.2:** Location of study sites in Germany: Sampling site addressed in this study (capitals), EMEP stations considered (bold), and stations with available isotope data (underlined).

### 2.2.2. Sampling

Separate wet and dry deposition samples were taken with an atmospheric deposition sampler (WADOS, Kroneis GmbH, Austria) from December 2011 to November 2012. Separate sample collection is ensured by a heated precipitation/moisture sensor. Both collection funnels are mounted at 2.2 m to reduce the impact of local turbulence and input of soil particles into the samples.

Precipitation samples were collected daily and stored for maximum of one week at 4°C, a storage time which had no adverse effect on nutrient or isotope composition of water samples (data not shown). Integrated weekly samples were produced by mixing of daily precipitation samples. These were filtered (GF/F, 450°C, 4 hrs.) and stored frozen (-20°C) for later nutrient and isotope analysis.

Dry deposition (including gas and particulate N compounds) was sampled according to Kouvarakis et al., 2001 and Mara et al., 2009. After one week exposure to the atmosphere,

particles were eluted with MilliQ water and treated like precipitation samples. Samples showing visible signs of contamination (bird droppings, dead insects, etc.) were discarded.

### 2.2.3. Sample analyses

#### Nutrient and isotope analysis

All dry and wet deposition samples were analysed in duplicate for nitrite, nitrate and ammonium using an automated continuous flow system (AA3, Seal Analytical, Germany) and standard colorimetric techniques (Hansen and Koroleff, 2007)

Samples were analysed for isotopic composition of nitrate ( $\delta^{15}\text{N-NO}_3^-$ ) using the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001), which is based on the isotopic analysis of bacterially produced nitrous oxide ( $\text{N}_2\text{O}$ ). All isotope values are corrected for the contribution of  $^{17}\text{O}$  due to mass-dependent fractionation. To prevent the impact of mass-independent fractionation ( $\square^{17}\text{O}$ ) of atmospheric nitrate on the  $\delta^{15}\text{N}$  values, *Pseudomonas chlororaphis* were used for the production of  $\text{N}_2\text{O}$ . Unlike the commonly used strain *Pseudomonas aureofaciens*, these bacteria generate  $\text{N}_2\text{O}$ , in which oxygen derives from  $\text{H}_2\text{O}$ , not nitrate (Coplen et al., 2004).  $\text{N}_2\text{O}$  was analysed with a GasBench II, coupled to an isotope ratio mass spectrometer (Delta Plus XP, Thermo Fisher Scientific). With each batch of samples, international standards (USGS34:  $\delta^{15}\text{N} = -1.8\text{‰}$ , IAEA-NO-3:  $\delta^{15}\text{N} = +4.7\text{‰}$ ,) and an internal standard ( $\delta^{15}\text{N} = -3.0\text{‰}$ ,) were run. All isotope measurements were done in replicate, and typical reproducibility was better than 0.2‰ for  $^{15}\text{N}$  for samples and standards.

#### Backward trajectories

To evaluate the origin of deposited nitrate, backward trajectories were calculated for all days with wet deposition events using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) (Draxler and Hess, 1998) model with an altitude of 10 m above ground level at the measurement site. Choosing a low arrival height for the trajectories at this location ensures that boundary layer air masses, which carry the largest part of the deposited nitrate, are adequately considered in the trajectories, in summer as well as in winter times. Meteorological data (e.g. wind, temperature, humidity) from the National

Weather Service's National Centers for Environmental Prediction (NCEP) with the Global Data Assimilation System (GDAS) were used to compute the backward trajectories. Because the atmospheric lifetime of  $\text{NO}_x$  and  $\text{HNO}_3$  in the boundary layer is not more than 2 days and 1-2 days, respectively, a time frame of 72 hour was chosen (Liang et al., 1998).

Daily trajectories were calculated, whenever a precipitation event had occurred. Each wet deposition sample is a mixture of precipitation events over one week (see section "Sampling"), so in most cases, several (up to 7) trajectories can be attributed to each sample.

After the calculation of trajectories, a cluster analysis was conducted with all computed trajectories using standard HYSPLIT cluster analysis (Draxler, 1999) to elucidate different patterns of air mass origin and corresponding  $\delta^{15}\text{N-NO}_3^-$  values of each cluster. For each sample (which, due to pooling, can consist of different clusters), we then selected the most important cluster according to the amount of  $\text{N-NO}_3^-$  deposition, and attributed the corresponding  $\delta^{15}\text{N-NO}_3^-$  value of each sample to the respective cluster. We then calculated the according N-weighted mean  $\delta^{15}\text{N-NO}_3^-$  value of each cluster.

## **2.3. Results**

In result and discussion section significance tests were conducted with ANOVA to examine seasonal variation, differences between wet and dry deposition and, where possible, historical changes. Significance level was always 0.05.

### **2.3.1. Wet and dry N deposition**

#### **Total nitrogen deposition**

The main reactive nitrogen compounds in both dry and wet deposition samples were  $\text{NO}_3^-$  (38% of total N deposition, corresponding to an average of  $529 \mu\text{mol m}^{-2} \text{wk}^{-1}$ , Tab. 2.2) and  $\text{NH}_4^+$  (61% of total N deposition, corresponding to an average of  $819 \mu\text{mol m}^{-2} \text{wk}^{-1}$ ). Nitrite was on average less than 1% of DIN in wet and dry deposition samples (data not shown).

**Table 2.2:** Seasonally volume-weighted mean flux of nitrate and ammonium and N-weighted mean isotopes in wet (W) and dry (D) Deposition; nw: numbers of wet deposition samples, nd: numbers of dry deposition samples.

2011/12 Season	Precipitation [l m <sup>-2</sup> ]	NO <sub>3</sub> <sup>-</sup> – flux [μM m <sup>-2</sup> wk <sup>-1</sup> ]	NH <sub>4</sub> <sup>+</sup> – flux [μM m <sup>-2</sup> wk <sup>-1</sup> ]	N-Deposition [kg ha <sup>-1</sup> ]	δ <sup>15</sup> N-NO <sub>3</sub> <sup>-</sup> [‰]
Winter '11/'12 (nw = 12, nd= 9)	141	W: 398.1 D: 81.5	W: 577.9 D: 87.9	W: 1.51 D: 0.32	W: +3.5 D: +7.0
Spring '12 (nw = 7, nd = 12)	35.5	W: 499 D: 85.6	W: 844.9 D: 78.2	W: 1.52 D: 0.28	W: ±0.0 D: +3.1
Summer '12 (nw = 13, nd = 13)	231.7	W: 535.5 D: 52.8	W: 1057.8 D: 26.3	W: 2.9 D: 0.13	W: -3.0 D: -1.3
Autumn '12 (nw = 12, nd = 14)	122.7	W: 443.5 D: 32.9	W: 536.6 D: 80.5	W: 1.8 D: 0.22	W: +0.9 D: +2.5
<b>Total (Tot)</b> (nw = 44, nd = 48)	<b>549</b>	<b>W: 468.9</b> <b>D: 60.6</b> <b>Tot: 529.5</b>	<b>W: 752</b> <b>D: 66.7</b> <b>Tot: 818.7</b>	<b>W: 7.73</b> <b>D: 0.95</b> <b>Tot: 8.68</b>	<b>W: +0.1</b> <b>D: +3.0</b> <b>Tot: +0.4</b>

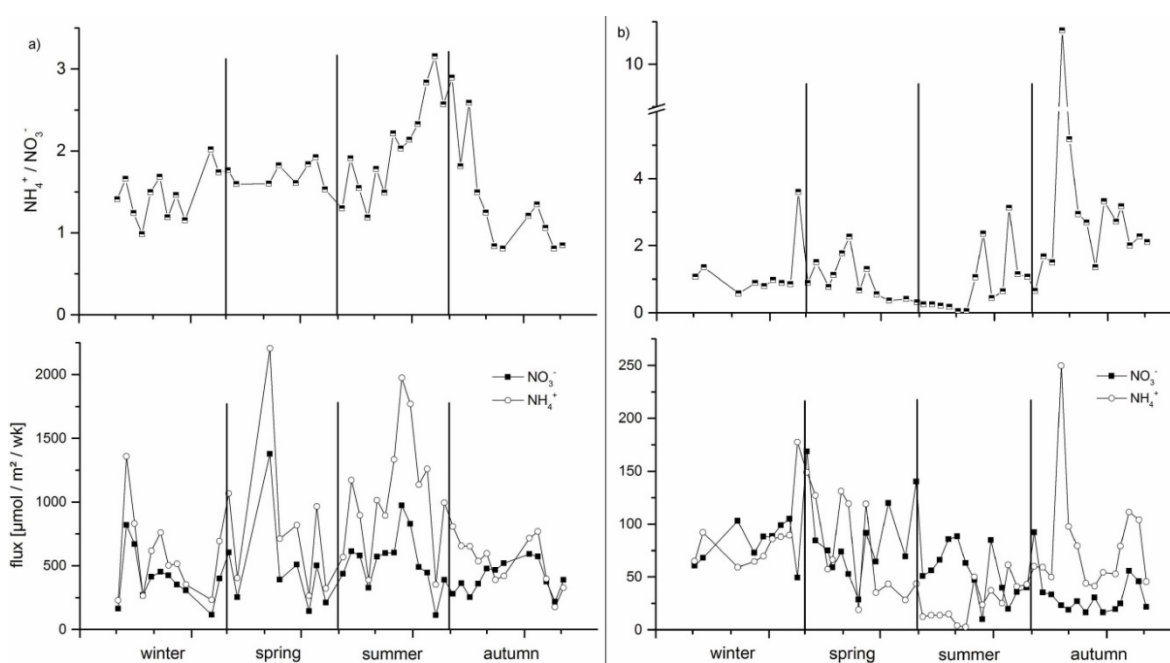
NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> concentrations are anti-correlated to the amount of precipitation, with highest concentration at times of low precipitation, decreasing with higher precipitation (data not shown). The deposition of both compounds is highest in summer, with 34% and 40% of total deposition of ammonium and nitrate, respectively, deposited during this season.

Wet deposition exceeds dry deposition by far: While the contribution of dry deposition is variable over an annual cycle and ranges from 4% in summer to 18% in winter, its average contribution amounts to 11%. Accordingly, the overall annual deposition at our study site is 7.73 and 0.95 kg N ha<sup>-1</sup> a<sup>-1</sup>, for wet and dry deposition, respectively.



### Molar ratio $\text{NH}_4^+/\text{NO}_3^-$

At our study site, the  $\text{NH}_4^+/\text{NO}_3^-$  ratio in wet deposition generally remains relatively stable throughout the year, with values mostly ranging between 1 and 3. (Fig. 2.3) Nevertheless, some seasonal trends can be discerned: In winter and spring, the  $\text{NH}_4^+/\text{NO}_3^-$  ratio is between 1 and 2, and variations are smallest ( $1.49 \pm 0.3$  and  $1.69 \pm 0.15$  in winter and spring, respectively), before they approach a maximum ratio of  $>3$  in late summer ( $1.98 \pm 0.59$ ). This maximum is followed by a swift decrease to minimal ratios of  $<1$  in autumn ( $1.44 \pm 0.7$ ). The overall volume-weighted annual mean ratio in wet deposition was 1.68.



**Figure 2.3:**  $\text{NH}_4^+/\text{NO}_3^-$  molar ratios (top) and  $\text{NH}_4^+$  and  $\text{NO}_3^-$  fluxes (bottom) of each sample in wet (a) and dry (b) deposition at our study site, wet and dry flux measurements include error bars, which are smaller than the measurement points.

In comparison to wet deposition (Standard deviation (SD): 0.58), the variation of the  $\text{NH}_4^+/\text{NO}_3^-$  ratio in dry deposition (SD: 1.77) was much higher, the ratio ranged from 0.04 to 10.8 over an annual cycle (Fig 3b). Lowest values coincide with extremely low  $\text{NH}_4^+$  fluxes in mid-summer, which are, equivalently to ratios in wet deposition, followed by an increase in late summer and early autumn. These high values coincide with high ammonium and moderate nitrate deposition. Despite the high variability, the annual mean

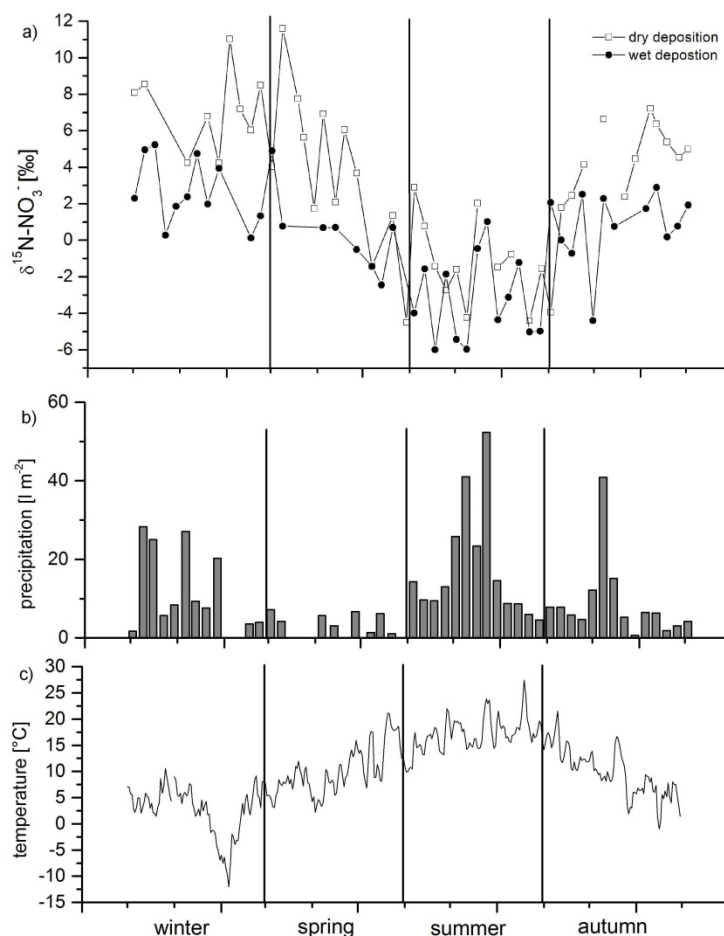
$\text{NH}_4^+/\text{NO}_3^-$  ratio was 1.59, and thus is not significantly different ( $\rho > 0.05$ ) to the molar ratio of wet deposition.

### $\delta^{15}\text{N}-\text{NO}_3^-$ of wet and dry deposition

Both in wet and dry deposition,  $\delta^{15}\text{N}-\text{NO}_3^-$  follow a similar annual pattern with significant seasonal differences between summer and winter ( $\rho < 0.001$ ): Values of wet deposition are highest in winter (mean value: +3.5‰) and gradually approach a minimum (-3.0‰) in summer, before rising again to +0.9‰ in autumn. Overall, isotope ratios in wet deposition ranged from -6.0 to +5.2‰ over the course of the year, with annual weighted mean value of +0.1‰ (Tab. 2.2).

In comparison, dry deposition values are significantly higher than wet deposition during each individual season and over the entire year ( $\rho < 0.05$ ). The range of delta values in dry deposition is higher than in wet deposition, with comparable minimum delta values in summer but much higher values in winter or spring. The seasonal spread of delta values in dry deposition is always higher than in wet deposition, but considerably more pronounced in spring (dry-SD: 4.3 vs. wet-SD: 1.29), with both extreme minimum and maximum  $\delta^{15}\text{N}-\text{NO}_3^-$  values (-4.5‰ and +11.6‰, respectively) occurring during spring. Seasonal weighted means over the course of the year are +7.0‰, +3.1‰, -1.3‰, +2.6‰ in winter, spring, summer and autumn, and the annual weighted mean is +3.0‰ (Tab. 2.2).

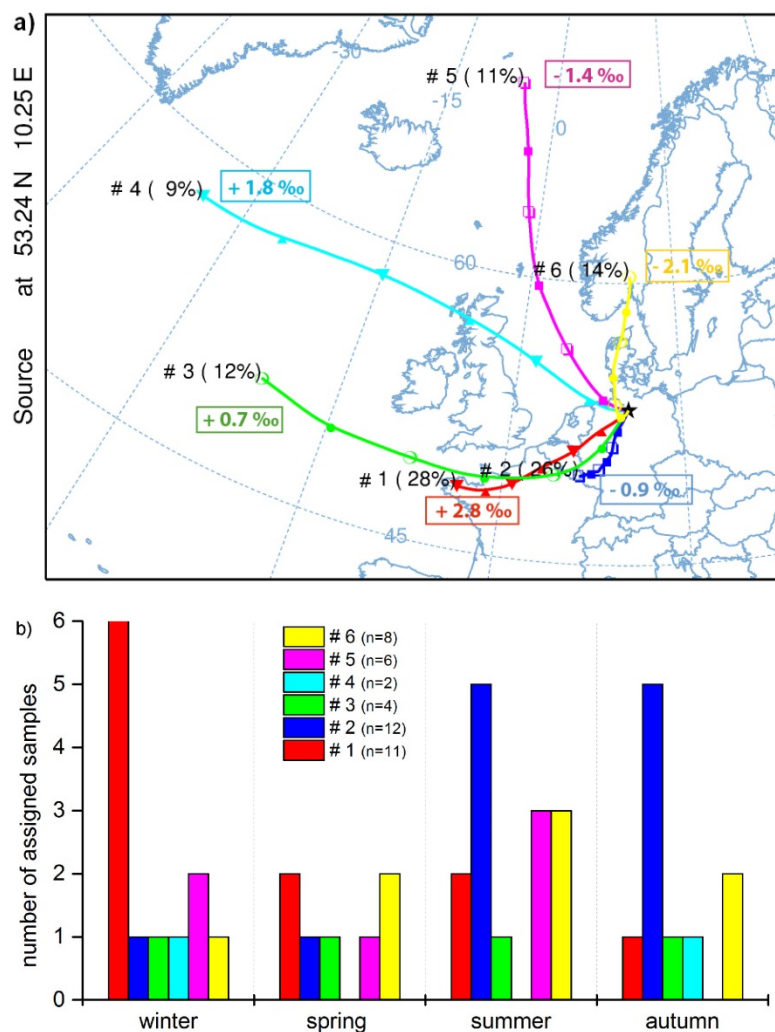
Despite considerable scatter of wet and dry deposition  $\delta^{15}\text{N}$  (Fig. 2.4a) throughout each season, we see a correlation of temperature (Fig. 2.4c) with  $\delta^{15}\text{N}$  in wet ( $r^2=0.50$ ,  $\rho < 0.001$ ) and dry deposition ( $r^2=0.63$ ,  $\rho < 0.001$ ), but not with precipitation (Fig. 2.4b) ( $\rho > 0.05$ ). The presumed correlation of  $\delta^{15}\text{N}$  with air mass origin was analysed by clustered backward trajectories.



**Figure 2.4:**  $\delta^{15}\text{N-NO}_3^-$  values of each wet and dry deposition sample (a) (error bars are smaller than symbol size), weekly precipitation amount (b) and daily mean temperature (c) and our study site.

### 2.3.2. Backward trajectories

In the analysis of backward trajectories, six clusters of distinctly different air mass origin emerged at wet deposition events: continental origin from south-west (#1), local origin (#2), west ocean origin with continental influence (#3), north-west ocean origin with continental influence (#4), north-west ocean origin (#5), and north continental influence (#6). Average N-weighted isotope values of these clusters were +2.8‰, -0.9‰, +0.7‰, +1.8‰, -1.4‰, and -2.1‰ (calculation of values is explained in chapter “methods”) for cluster #1, #2, #3, #4, #5 and #6, respectively (Fig. 2.5).



**Figure 2.5:** Mean backward trajectories of cluster analysis (#1 to #6) including all (161) backward trajectories and its N weighted mean  $\delta^{15}\text{N-NO}_3^-$  values (a) and seasonally dependent sample attribution to each cluster number (b).

## 2.4. Discussion

### 2.4.1. N deposition and its sources

Our main objective in this study was to evaluate the trend of  $\text{NO}_x$  emissions,  $\text{NO}_3^-$  deposition and N isotopes of deposited  $\text{NO}_3^-$ . To evaluate bulk N deposition and the general deposition pattern at our study site, we also briefly discuss  $\text{NH}_4^+$  deposition.

In general, inorganic N deposition is the ultimate sink for  $\text{NO}_x$  and  $\text{NH}_3$  emission, and on a global scale, changes in N emissions are reflected in total inorganic N deposition. While local deposition can depend on atmospheric conditions and regional N emission sources,

changes of  $\text{NO}_x$  emission are nicely reflected in  $\text{NO}_3^-$  deposition in Europe (Fowler et al., 2007).

N deposition at our study site is higher than at EMEP sites (data not shown), which we attribute to the fact that EMEP represent sites with a lower pollution level (Yttri, 2012), because these sample sites should not be exposed to point sources, but rather are selected to depict general trends in deposition.

Overall, deposition fluxes at our study site are typical of an industrial/agricultural impacted site in Germany (Gauger et al., 2001). Bulk N deposition is well within the range of other continental sites in Europe (Bragazza and Limpens, 2004; Thimonier et al., 2005). The deposition pattern at our study is in accordance with the expected elevated emission stemming from industry, vehicle and agriculture in the surroundings of our study site.

Sources of anthropogenic wet N deposition range from agricultural and natural biogenic emissions of ammonia to various contributors of  $\text{NO}_x$ , such as industry, road and ship traffic, and power plants (Asman et al., 1998; Delmas et al., 1997). Consequently, the molar  $\text{NH}_4^+/\text{NO}_3^-$  ratio is a reliable indicator to detect the relative local contribution of industrial versus agricultural sources to atmospheric N wet deposition (Anderson and Downing, 2006; Lee et al., 2012; Zhao et al., 2009). Ratios of less than 1.0 are typical of high industrialization and urbanization levels, whereas values above 4 indicate a high contribution of agricultural sources.

At our study site, the  $\text{NH}_4^+/\text{NO}_3^-$  ratio in wet deposition is mostly above 1, indicating that N deposition stems mainly from agricultural sources. Values in this range are relatively typical for an agricultural, yet industrialized area in which ammonium deposition only slightly exceeds elevated nitrate deposition (Fowler et al., 2005a; Freyer, 1978) (Fig. 2.3ab). In this respect, the considerable increase of molar ratios in late summer (values of  $\sim 3$ ) is interesting. It can be explained by a simultaneous increase of ammonium deposition due to application of manure to agricultural areas after harvesting and a decrease in  $\text{NO}_x$  emissions due to reduced energy consumption for heating and electricity at this warmest time of the year (AE, 2013). The decrease of the molar ratios in autumn is the flipside of this phenomenon: Now, lower temperatures and the beginning heating period lead to higher  $\text{NO}_x$  emissions and  $\text{NO}_3^-$  deposition. A concomitant ban on fertilizers from November to February reduces volatilization of ammonia around the study site (BdJ, 2012).

Dry deposition molar ratios are more difficult to explain. Values are as low as 0.04 in summer; these low ratios cannot only explained by source contribution. Besides organic matter, ammonium, nitrate, and sulphate are the most important contributors to aerosols at moderately to heavily polluted sites (Putaud et al., 2004). Particulate ammonium and nitrate mostly occur either as ammonium sulphate, ammonium bisulphate or ammonium nitrate (Robarge et al., 2002). Although we have no additional data on aerosol composition, as this was not the focus of our study, high molar  $\text{NH}_4^+/\text{NO}_3^-$  ratios can thus be taken as indicator for a preferential formation of ammonium sulphate, formed due to high atmospheric sulphate concentrations (Adams et al., 1999), whereas lower molar ratios indicate that ammonium nitrate gained in importance, which is typical in colder times (Putaud et al., 2004). In early summer, when nitrate fluxes exceed ammonium fluxes, particulate nitrate is mainly formed by the reaction of nitric acid with sea salts and mineral dust (Metzger et al., 2006).

#### **2.4.2. Trends in N deposition and emission in Germany**

A major aim of our study was to investigate whether changes in  $\text{NO}_x$  emission patterns of the past decades can be tracked down to variations in isotope values of deposited  $\text{NO}_3^-$ . To discern general trends in atmospheric N deposition during the past decades, we analysed data obtained through the European Monitoring and Evaluation Programme (EMEP) (Fig. 2.2). We will then compare these general trends to the isotope changes we see.

At the EMEP sites, wet deposition of ammonium and nitrate has been monitored since at least 1988 (Melpitz: since 1998), and we investigated the change in molar ratios  $\text{NH}_4^+/\text{NO}_3^-$  in wet deposition for the years 1988, 1998 and 2008. At Waldhof, the ratio increased from  $1.05 \pm 0.27$  in 1988 to  $1.51 \pm 0.32$  in 2008 ( $p < 0.01$ ), in Deuselbach from  $1.0 \pm 0.29$  to  $1.31 \pm 0.47$  ( $p < 0.05$ ) and at Melpitz from  $1.21 \pm 0.4$  in 1998 to  $1.57 \pm 0.47$  in 2008 ( $p < 0.05$ ). This significant increase of the  $\text{NH}_4^+/\text{NO}_3^-$  ratio at all sites is the result of decreasing nitrate deposition and mostly unchanged ammonium deposition - a trend that is at present also observed in other European countries (Fowler et al., 2005b; Francaviglia et al., 1995). However, the decrease in overall  $\text{NO}_3^-$  deposition at the EMEP sites lower than the overall decrease in  $\text{NO}_x$  emissions in Germany (Fowler et al., 2005a), because  $\text{NO}_x$  has a longer transport and retention time in the atmosphere in comparison to  $\text{NH}_4^+/\text{NH}_3$  (Asman et al., 1998): Ammonium is usually deposited locally,  $\text{NO}_3^-$  deposition is

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influenced by more distant NO<sub>x</sub> sources throughout Europe, where the decrease in NO<sub>x</sub> emissions is not as pronounced (Fowler et al., 2005a; UBA, 2012).

### 2.4.3. Isotope ratios and N-sources

To assess NO<sub>x</sub> sources contributing to atmospheric deposition in more detail, we evaluated  $\delta^{15}\text{N-NO}_3^-$  values and seasonal changes. The fluctuation and wide range of  $\delta^{15}\text{N}$  in wet and dry deposition over a seasonal cycle (Fig. 2.4a) indicate multiple sources of nitrate in deposition, such as a mix of isotopically enriched NO<sub>x</sub> emissions by coal-fired power plants, lighter NO<sub>x</sub> emissions by road traffic and very depleted natural NO<sub>x</sub> emissions (Elliott et al., 2007; Wankel et al., 2010).

$\delta^{15}\text{N-NO}_3^-$  in wet and dry deposition depends on season, with highest values in winter and lowest in summer (Fig. 2.4a). This seasonal variation can be explained by a changing emission pattern over the course of the year. Natural soil volatilization of NO<sub>x</sub> is bound to times of biological activity and relatively high temperatures (Jaegle et al., 2005; van der A et al., 2008) (Fig. 2.4c). This minor (13%, Tab. 2.1), yet important source of isotopically extremely depleted NO<sub>x</sub> is thus mainly active from spring to autumn and accordingly depletes the overall  $\delta^{15}\text{N NO}_3^-$  in wet deposition in summer times.

In winter, biogenic emissions are less important, and on top of that, the proportion of anthropogenic NO<sub>x</sub> rises, because emissions stemming from coal-fired power plants increase due to higher energy demand during the heating period. Another cause for high  $\delta^{15}\text{N}$  in wet and dry deposition in winter may be isotopic temperature-dependent exchange equilibria between NO/NO<sub>2</sub> and atmospheric NO<sub>3</sub><sup>-</sup>, which form either particulate or dissolved NO<sub>3</sub><sup>-</sup> (Freyer, 1991; Freyer et al., 1993), but the exact isotope effect of these equilibria on deposited NO<sub>3</sub><sup>-</sup> is not yet quantified.

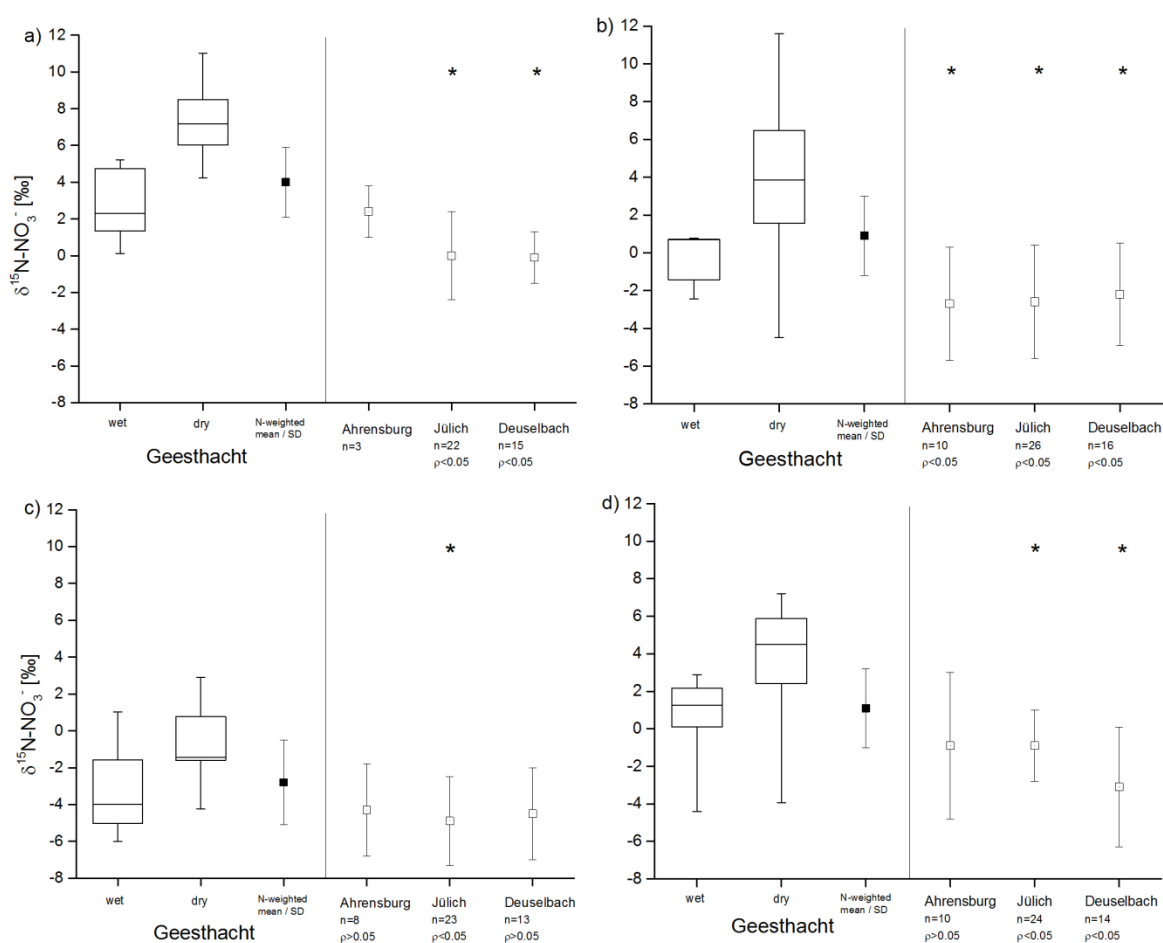
Isotope fractionation effects between particulate NO<sub>3</sub><sup>-</sup>, gaseous HNO<sub>3</sub> and dissolved nitrate (e.g. absorption of gaseous HNO<sub>3</sub> during precipitation events) lead to lower values of  $\delta^{15}\text{N-NO}_3^-$  in wet deposition (Freyer, 1991), which explains the significant differences in  $\delta^{15}\text{N}$  between wet and dry deposition.

Overall, our data are in line with comparable ranges and seasonal trends for  $\delta^{15}\text{N-NO}_3^-$  in dry deposition (Elliott et al., 2009; Mara et al., 2009; Yeatman et al., 2001) and wet deposition in North America (Elliott et al., 2007; Russell et al., 1998), and East Asia (Fang et al., 2011; Fukuzaki and Hayasaka, 2009; Lee et al., 2012).

#### 2.4.4. New sources or source signatures of NO<sub>x</sub>

An additional means to explore changes in NO<sub>x</sub> sources is the comparison of isotopic data from the past to our measurements. We considered isotope data by Freyer, 1991, who measured isotope ratios in bulk deposition at three moderately polluted German study sites in the 1980s (Fig. 2.6).

The seasonal trend of these historical isotope data aligns well with our data, but intriguingly, we see an offset towards significantly higher  $\delta^{15}\text{N-NO}_3^-$  values, which pinpoint a possible change in the relative contribution of NO<sub>x</sub> sources (Fig. 2.6).



**Figure 2.6:** Winter (a), spring (b), summer (c) and autumn (d)  $\delta^{15}\text{N-NO}_3^-$  values of own study site (left panel) in 2011-12 and historical sites in Germany (right panel). Box-whisker plots indicate: inter-quartile range (boxes), minimum and maximum values (whiskers) and median (center line) of wet and dry deposition samples; filled squares indicate N-weighted mean of all deposition samples and , SD at our site. Empty squares: N-weighted means and SD of bulk deposition samples at Ahrensburg (1980-83), Jülich (1979-84) and Deuselbach (1979-84) (Freyer, 1991). n: numbers of samples,  $\rho$ : imply the comparison of Geesthacht N-weighted mean and respective study sites. Asterisk: statistically significantly differences between historical and present isotope data. No statistical test was conducted with Ahrensburg data in winter (2.6a), because the number of samples (n=3) was too low for statistical analysis.



This is surprising, because monitoring data indicate that the relative contribution of natural/soil NO<sub>x</sub> emissions has gained in importance (Tab. 2.1), and we expected to see this change mirrored in a decrease of NO<sub>x</sub> isotope values: Soil volatilization produces NO<sub>x</sub> much more depleted in <sup>15</sup>N/<sup>14</sup>N than any anthropogenic source (Fig. 2.1), and a back-of-the-envelope calculation assuming end-member isotope values of -20‰ (Felix and Elliott, 2013), +8‰ (Felix et al., 2012; Heaton, 1990; Kiga, 2000) and +4‰ (Ammann et al., 1999; Pearson et al., 2000; Redling et al., 2013) for soil volatilization, power plants and traffic, respectively, indicates that average NO<sub>x</sub> values should have decreased by ~0.2‰ between 1990 and 2010.

Barring some uncertainty due to high scatter of seasonally averaged values, our comparison with data by Freyer, 1991 is far from showing any decrease. The positive offset varies with season, but mostly is statistically significant ( $p > 0.05$ ). Historical values are significantly lower in winter, spring and autumn (except Ahrensburg in autumn). In summer, this difference is not significant at two of three sites (Fig. 2.6). To unravel the cause of this increase, we will evaluate two different possibilities of changing in emission patterns and isotope ranges knowing it is a kind of speculation and not an unambiguous explanation.

One possibility for the  $\delta^{15}\text{N-NO}_3^-$  increase is the rising impact of a frequently overlooked NO<sub>x</sub> source, shipping emissions. Until now, there are no  $\delta^{15}\text{N}$  values available for this source, but we assume they are comparable to road traffic NO<sub>x</sub>. The overall reduction of NO<sub>x</sub> emissions can mainly be attributed to reduction efforts in industry and road traffic. In contrast, regulations for ship emissions until now mostly merely regard sulphur content in fuels. Ship NO<sub>x</sub> emissions have consequently been increasing since 1990 by 15% in Germany (Tab. 2.1), and especially in coastal areas, this source has a relatively high influence on deposition (Matthias et al., 2010). Due to the overall decrease in NO<sub>x</sub> emissions, the relative portion of ship-derived NO<sub>x</sub> in 2010 has more than doubled in comparison to 1990 (Tab. 2.1). If no measures are taken, a severe increase in ship emissions of NO<sub>x</sub> can be expected, with the accompanying negative consequences for marine and coastal regions and ecosystems (Corbett and Koehler, 2003; EEA, 2013; Matthias et al., 2012).

Another option for changing isotope values is technological developments in combustion engines and power plants. A recent study of NO<sub>x</sub> isotope values in North America (Felix et al., 2012), also finds an increase in isotope values. The authors attribute it to selective catalytic reduction (SCR) at coal-fired power plants and find average  $\delta^{15}\text{N}$  values of emitted NO<sub>x</sub> with SCR are enriched by 10‰ over those of power plants without catalytic converters. This is a plausible explanation for the positive offset we find: In contrast to the 1980s, the percentage of modern coal-fired power plants using this technology (Bradley and Jones, 2002), has increased (Felix et al., 2012).

Land-based vehicle NO<sub>x</sub> can also be a non-seasonal source of isotopically heavy NO<sub>x</sub>. (Ammann et al., 1999) found  $\delta^{15}\text{N}$  values of traffic NO<sub>2</sub> up to +10‰ in the late 1990s, and attributed these  $\delta^{15}\text{N}$  values to a change of vehicle engines, which is supported by recent studies in North-America (Redling et al., 2013). Additionally, the SCR-technology has since 2006 been used in new diesel automobile engines (Lambert, 2004), which may lead to an increase of  $\delta^{15}\text{N}$  of vehicle NO<sub>x</sub> emissions over time.

The offset in  $\delta^{15}\text{N}$  values of NO<sub>3</sub><sup>-</sup> deposition between our data and historical data depends on season, it is most pronounced from autumn to spring, but less significant in summer. This can be explained by the relative contribution of NO<sub>x</sub> sources and their respective average isotope values. NO<sub>x</sub> from new coal-fired power plants equipped with SCR-technology can explain the positive shift of  $\delta^{15}\text{N}$  between autumn and spring. Their NO<sub>x</sub> output is highest in winter and lowest in summer times due to the seasonal energy demand for heating (Stavrakou et al., 2008). In summer, soil emissions are an important NO<sub>x</sub> source with significant impact on  $\delta^{15}\text{N}$ -NO<sub>3</sub><sup>-</sup> (Felix and Elliott, 2013). This biogenic source has gained in relative importance, and in combination with reduced NO<sub>x</sub> output of power plants in warmer times, it lowers  $\delta^{15}\text{N}$ -NO<sub>3</sub><sup>-</sup> values in summer and thus to a more pronounced seasonal change.

We thus assume that the isotope change is due to a combination of SCR-emitted NO<sub>x</sub> from coal-fired power plants and traffic NO<sub>x</sub> emissions. We cannot evaluate whether ship emissions or land-based traffic are a more likely contributor based on isotope data. To unravel this, we calculated backward trajectories of air masses over the course of our sampling period.

The cluster analysis reveals that air masses from less polluted areas (cluster #5 and #6) from the north have distinctly negative  $\delta^{15}\text{N}$ -NO<sub>3</sub><sup>-</sup> values (-1.4 and -2.1‰, respectively),

whereas clusters #1, #2 and #3, which originate from more polluted south and west areas, are relatively enriched in  $\delta^{15}\text{N}$  (Fig. 2.5). Cluster #4 shows relatively enriched isotope values, but unlike other clusters, it only consists of two samples, from winter and autumn, respectively. Winter and autumn values of  $\delta^{15}\text{N-NO}_3^-$  generally are high due to the strong seasonal effects, and the positive value thus is mainly caused by seasonal enrichment. Other clusters are represented by more, and seasonally more evenly distributed, samples, so that mere seasonal effects are in part neutralized.

A more detailed look at the seasonal distribution within clusters also explains the surprising difference between clusters #1 and #2: Both clusters have their origin in polluted continental areas over the continent, but most samples in the isotopically heavy cluster #1 stem from cold seasons, whereas samples in the isotopically light cluster #2 mostly were deposited in warmer times (Fig. 2.5b). Due to this seasonal difference, the variation in  $\delta^{15}\text{N}$  values between these clusters can be explained by the typical seasonal pattern of  $\delta^{15}\text{N-NO}_3^-$  values.

Overall, the evaluation of the trajectories supports the dependence of  $\delta^{15}\text{N-NO}_3^-$  in nitrate deposition on anthropogenic  $\text{NO}_x$  emissions. Land-based sources like road traffic and power plants can be assigned to clusters #1 to #3, with most positive isotope values, whereas a more marine origin, as evidenced in clusters #5 and #6, leads to more depleted  $\delta^{15}\text{N-NO}_3^-$  values. Accordingly, the contribution of ship  $\text{NO}_x$  emissions to atmospheric deposition does not lead to a visible isotope enrichment of atmospheric deposition in our study, even though cluster 4 shows that isotope values in winter are relatively high (see discussion above). This lack of unambiguous enrichment may be due to the source signature or to the absolute amount of ship emissions, which still falls well below  $\text{NO}_x$  emissions in densely populated, industrialized areas like those contributing to clusters #1 to #3. Our backward trajectory analysis rather supports the relevance of industrial land-based emissions for the enriched isotope signatures we find.

## 2.5. Conclusions

We find a significant increase in  $\delta^{15}\text{N}$  of nitrate deposition since the 1980s in Germany between autumn and spring, while bulk nitrate deposition has decreased. Over the entire study period, we also identified a stronger seasonality of load-weighted  $\delta^{15}\text{N}$  values in wet

and dry nitrate deposition in comparison to studies from the 1980s. We attribute this change to a shift in combustion pattern due to the implementation of catalytic converters in industry and traffic. The observed offset suggests that coal-fired power plants and road traffic are the main drivers of this increase in  $\delta^{15}\text{N}$ .

Overall, our study shows that  $\delta^{15}\text{N}$  isotopes in  $\text{NO}_3^-$  deposition are a valuable tool to detect anthropogenic contribution, but that technological adaptations need to be taken into account to allow for an adequate assessment of different  $\text{NO}_x$  sources. In our case, we expected to see a shift towards more negative isotope values in nitrate deposition due to overall decreasing anthropogenic emissions, which are isotopically relatively enriched. Surprisingly, this decrease was more than made up for by changes in combustion patterns.

## **Acknowledgements**

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### 3. Do N-isotopes in atmospheric nitrate deposition reflect air pollution levels?

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#### Abstract

Dry and wet deposition of atmospheric reactive nitrogen compounds mostly originate from anthropogenic  $\text{NH}_3$  and  $\text{NO}_x$  sources. Regarding land-borne pollutants, coastal environments usually have a lower pollution level than terrestrial/urban areas, which have a greater anthropogenic imprint. To investigate this spatial characteristic, we measured  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition and N isotopes of  $\text{NO}_3^-$  ( $\delta^{15}\text{N}-\text{NO}_3^-$ ) in 94 and 88 wet and dry deposition samples, respectively, at a coastal (List on Sylt) and a terrestrial/urban site (Geesthacht) in Germany from May 2012 to May 2013. A higher total N deposition rate was observed in Geesthacht (10.4 vs. 8.9 kg N ha<sup>-1</sup> yr<sup>-1</sup>) due to higher  $\text{NH}_4^+$  deposition, which can be explained by more agricultural influence. Surprisingly, overall  $\text{NO}_3^-$  fluxes were higher at the coastal site than at the terrestrial/urban site. We assume that sea-salt aerosols and the increased influence of  $\text{NO}_x$  emissions from ships in most recent times compensate the higher terrestrial/urban pollution level and thus lead to higher  $\text{NO}_3^-$  fluxes in dry and comparable fluxes in wet deposition at the coastal site, despite a much lower impact of land-based sources. In line with this, overall mean N isotopes values of  $\text{NO}_3^-$  show higher values in List than in Geesthacht in dry (+3.1 vs. +1.9‰) as well as in wet deposition (-0.1 vs. -1.0‰). This surprising result can mainly be attributed to an emerging source of  $\text{NO}_x$ , ship emissions. We attribute this shift to new technologies in marine engines, which emit more enriched <sup>15</sup>N in comparison to older engines, and the overall increasing fraction of  $\text{NO}_x$  emissions from ships.

#### 3.1. Introduction

One of the most important sources of anthropogenic nitrogen is atmospheric inorganic N deposition, which adds surplus N in the form of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  to ecosystems. With the onset

of the Anthropocene, in which human activities have become a global geophysical force (Steffen et al., 2007), the nitrogen cycle has changed completely in ecosystems worldwide (Fowler et al., 2013). The main N-sources responsible for this rapid change are anthropogenic activities like fossil fuel combustion and the Haber-Bosch procedure, to such extent that anthropogenic emissions nowadays exceed the natural sources of reactive nitrogen on a global level. These anthropogenic processes lead to high emission amounts of  $\text{NO}_x$  ( $\text{NO}/\text{NO}_2$ ) and  $\text{NH}_3$  to the atmosphere, which in turn cause high amounts of atmospheric N deposition (Galloway et al., 2004). This high availability of reactive nitrogen leads to eutrophication in both coastal/marine and terrestrial ecosystems. Furthermore, acidification of forest and soil ecosystems, N saturation and a loss of biodiversity can be a consequences (Hauhs and Wright, 1986). But there are also beneficial effects of enhanced N deposition, such as stimulation of plant growth and  $\text{CO}_2$  uptake in N-limited ecosystems (Townsend et al., 1996).

Wet deposition is the major process scavenging N compounds from the atmosphere in Central Europe, whereas dry deposition in gaseous or particulate form is mostly a smaller fraction (Hertel et al., 2011). But during longer periods of less precipitation, dry deposition can be the dominant form of N deposition (Elliott et al., 2009). Furthermore, high sea salt aerosol concentrations can favour aerosol nitrate formation at coastal sites in the North Sea region, especially in the coarse-mode fraction (Bencs et al., 2009; van Jaarsveld and Klimov, 2011). The most abundant oxidized atmospheric N species ( $\text{NO}_y$ ) are  $\text{HNO}_3$  and particle-bound  $\text{NO}_3^-$ ; main reduced N species ( $\text{NH}_x$ ) are gaseous  $\text{NH}_3$  and particle-bound  $\text{NH}_4^+$ . Thus, considering the deposition of total inorganic N species, wet and dry N loads have to be monitored.

Both, coastal and terrestrial ecosystems are affected by N deposition, but coastal environments usually have a stronger marine influence, whereas terrestrial sites are mostly affected by land-based N sources. Many studies of wet and dry deposition indicate that air-masses of continental origin have higher N loads than marine air-masses (e.g. Bencs et al., 2009; Russell et al., 1998). The most common  $\text{NO}_x$  sources are anthropogenic ones: Coal-fired power plants, road traffic and ship emissions represent almost 90% of total  $\text{NO}_x$  emissions in Germany; biogenic soil emissions triggered by N input on soils through nitrification and denitrification of bacteria emit about 10% of total  $\text{NO}_x$  in Germany (UBA, 2012). The main  $\text{NH}_3$  sources of reduced N deposition are derived from agriculture, like animal husbandry and application of fertilizer/manure (Prospero et al., 1996). In general,

80-95% of  $\text{NO}_x$  emissions are exported compared to 40-60% of  $\text{NH}_x$  emissions. Hence,  $\text{NH}_3$  is deposited much closer to its source than  $\text{NO}_x$  (Asman et al., 1998).

To identify spatial differences of anthropogenic influences, stable isotopes of nitrogen in atmospheric nitrate deposition are a valuable tool, because anthropogenic and biogenic sources have different isotopic ranges of  $\delta^{15}\text{N}\text{-NO}_x$ : coal-fired power plants range from +6 to +20‰, while newer ones can be attributed to the end of the range (Felix et al., 2012; Heaton, 1990; Kiga, 2000). Road traffic ranges from -13 to +6‰, recent studies showing values toward the positive side of this range (Ammann et al., 1999; Pearson et al., 2000; Redling et al., 2013), while older ones reported more depleted values (Heaton, 1990).  $\delta^{15}\text{N}$  ranges of ship traffic, a  $\text{NO}_x$  source of growing importance, are not yet investigated, but are assumed to be in the same range as road traffic. In contrast, fertilized soils emit highly depleted  $\text{NO}_x$  in the range -49 to -20‰ (Li and Wang, 2008). As a consequence, polluted areas have in general considerably higher  $\delta^{15}\text{N}\text{-NO}_x$  values than remote sites (Kendall et al., 2008).

To evaluate N pollution levels and N sources along a coastal-terrestrial gradient in Central Europe, we measured wet and dry inorganic N deposition and N isotopes of deposited  $\text{NO}_3^-$  at two sites in Germany, which differ in potential N sources and their marine and land-based influences. To check the plausibility of measured N deposition data at both sites, we used a chemistry transport model (CMAQ) to get typical dry and wet modelled data of oxidized and reduced N.

Based on different pollution levels and N loads at coastal vs. urban/terrestrial sites, we expected higher wet and dry loads of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition at the polluted terrestrial site. Regarding isotope values of deposited nitrate, we hypothesize that  $\delta^{15}\text{N}$  values at the terrestrial site should be higher due to the higher influence of anthropogenic  $\text{NO}_x$  sources such as vehicle and power plant emissions.

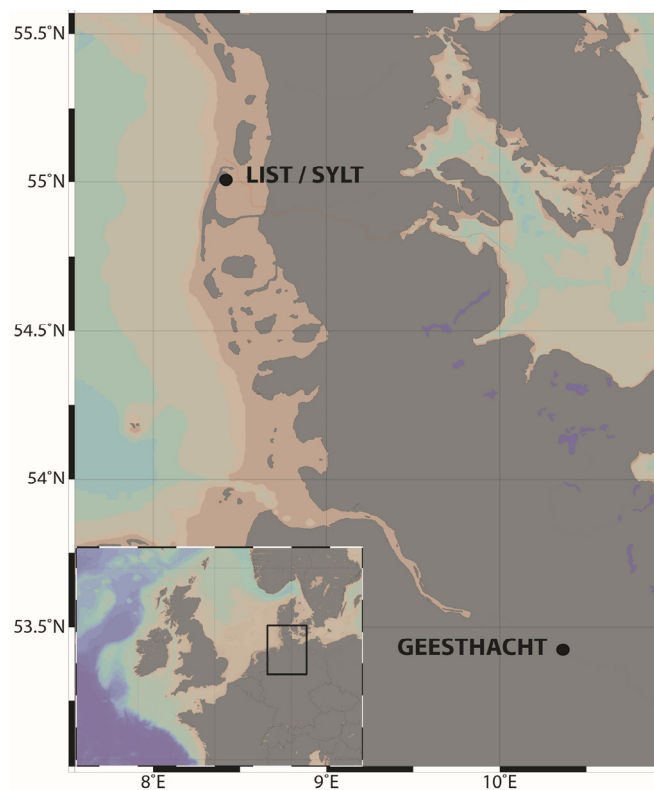
## **3.2. Materials and methods**

### **3.2.1. Study sites**

In this study we investigate two sites in northern Germany (Fig. 3.1), which differ in local N sources, geographical situation and weather conditions, but prevailing westerlies characterize dominant air masses for both sites. We chose List on the island Sylt and Geesthacht as marine

and urban/industry influenced study sites, respectively, because European Monitoring and Evaluation Programme (EMEP) data of wet deposition classified the island of Sylt as a typical coastal site with less N deposition compared to the terrestrial urban/industry influenced area of Geesthacht (Beyn et al., 2014).

The terrestrial/urban study site is located south-east of Hamburg in Geesthacht on a forest surrounded grassland. Potential local nitrogen sources mostly have an anthropogenic origin. In westerly direction, the site is affected by power plants and traffic emissions from vehicles. In all other directions, the site is surrounded by livestock farming and agriculture, i.e. regions where manure and fertilizer are applied.



**Figure 3.1:** Location of the study site Geesthacht and List on Sylt.

The study site List on the island of Sylt is located on the island of Sylt directly at the shore (which is <100 m to the east) and in distance of 225 km to Geesthacht. It represents a coastal site with typical marine affected meteorological parameters: More precipitation, less pronounced temperature amplitude (data not shown) and higher relative humidity than in Geesthacht (Tab. 3.1). The location is surrounded by dunes in northern and western direction.



Most important local anthropogenic NO<sub>x</sub> sources are traffic emissions by automobiles and ships. The economy of Sylt is strongly dependent on tourism, which varies seasonally with highest visitor counts in summer and lowest in winter (Sylt, 2013). All considerable local NH<sub>3</sub> emission sources are more than 15 km away and in south/eastern direction.

**Table 3.1:** Overview of mean meteorological parameter and mean deposition fluxes at both sites, prec. indicate: precipitation, T indicate: mean temperature, rH indicate: mean relative humidity; nw indicate: numbers of wet deposition samples, nd indicate: numbers of dry deposition samples.

Site	Meteorological parameter				Deposition data				
	prec.	no prec.	T	rH	N-NO <sub>3</sub> <sup>-</sup>		N-NH <sub>4</sub> <sup>+</sup>		Total N
	[mm]	[d]	[°C]	[%]	[mg m <sup>-2</sup> d <sup>-1</sup> ]		[mg m <sup>-2</sup> d <sup>-1</sup> ]		
				Wet	Dry	Wet	Dry	[kg ha <sup>-1</sup> ]	
List (nw: 51, nd: 44)	814	215	8.5	82.6	1.02	0.36	1.03	0.08	9.64
Geesthacht (nw: 43, nd:44)	577	219	9.2	76.6	0.93	0.13	1.62	0.15	11.23

### 3.2.2. Sample collection

At both study sites, samples were taken from May 2012 to May 2013 (401 days) using atmospheric deposition samplers with separate dry and wet deposition collection (WADOS, Kroneis GmbH, Austria). A moisture sensor ensured the separate sample collection, and both funnels were installed at 2.2 m to reduce the impact of local turbulence and soil particle inputs.

Wet depositions samples were collected daily and stored for a maximum of one week at 4°C. Integrated weekly samples were produced by mixing of daily samples. These were filtered (GF/F) and stored frozen for subsequent nutrient and isotope analysis.

Dry deposition was sampled following methods of Kouvarakis et al., 2001 and Mara et al., 2009 with glass beads placed in a funnel to prevent resuspension of deposited particles, a technique which also includes gaseous N compounds. After up to two weeks exposure to the atmosphere, particles were eluted with MilliQ water and treated like precipitation samples.

Samples showing visible signs of contamination (bird droppings, dead insects, etc.) were discarded (<1% of wet and <3% of dry deposition samples).

### 3.2.3. Analyses

#### Nutrient and isotope analysis

All deposition samples were analysed in duplicate for nitrite, nitrate and ammonium using an automated continuous flow system (AA3, Seal Analytical, Germany) and standard colorimetric techniques (Hansen and Koroleff, 2007).

All samples were analysed for isotopic composition of nitrate ( $\delta^{15}\text{N-NO}_3^-$ ) using the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001), which is based on the isotopic analysis of nitrous oxide ( $\text{N}_2\text{O}$ ). To prevent the interference of mass-independent  $^{17}\text{O}$  of atmospheric nitrate, we used *Pseudomonas chlororaphis* instead of the commonly used *Ps. aureofaciens*. *Ps. chlororaphis* generates  $\text{N}_2\text{O}$ , in which nitrogen is derived from  $\text{NO}_3^-$ , but oxygen primarily from  $\text{H}_2\text{O}$ . The sample volume was adjusted to a sample size of 10 nmol of  $\text{N}_2\text{O}$ .  $\text{N}_2\text{O}$  was extracted from the sample vials and measured with a GasBench II, coupled to an isotope ratio mass spectrometer (Delta Plus XP, Thermo Fisher Scientific). With each batch of samples, international standards (USGS34:  $\delta^{15}\text{N} = -1.8\text{‰}$ ,  $\delta^{18}\text{O} = -27.9\text{‰}$ ; IAEA-NO-3:  $\delta^{15}\text{N} = +4.7\text{‰}$ ,  $\delta^{18}\text{O} = +25.6\text{‰}$ ) and an internal standard were run. All isotope measurements were done in replicate, and typical reproducibility was better than 0.2‰.

#### Backward trajectories

To track down the origin of air masses, we calculated backward trajectories at both study sites for each day in the investigation period. We chose a travel time of 72 hours, because the lifetime of atmospheric  $\text{NO}_x$  in the boundary layer is, depending on season, not more than 2 days; atmospheric  $\text{HNO}_3$  has a similar lifetime of 1-2 days (Liang et al., 1998). We used Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) (Draxler and Hess, 1998) at 300 m above ground level to ensure that boundary layer air masses are considered in winter as well in summer times. Meteorological data were used from National Centers for Environmental Prediction (NCEP) with the Global Data Assimilation System (GDAS).

To evaluate trajectories for the air mass origin at both study sites, we conducted a cluster analysis (standard HYSPLIT cluster analysis) for all 401 computed trajectories at each study site, resulting in different air mass sectors for each cluster. We then categorized these clusters either to marine (i.e. North Sea) or continental origin (i.e. Central Europe). In cases where no clear attribution was possible, because the area of air mass origin was marine and continental (i.e. UK/Ireland/English Channel), trajectories were categorized as mixed origin. Based on this categorization, we evaluated differences in air mass origin between both sites.

### **CMAQ - chemistry transport modelling**

The CMAQ model (Byun and Ching, 1999; Byun and Schere, 2006) was used in its version 4.7.1 with the CB05 chemistry mechanism to obtain dry and wet deposition data of reduced and oxidized N compounds at both study sites. It was run for the entire year 2008 with a spinup time of 2 weeks. This year was chosen because it does not include unusual meteorological conditions in Europe and can therefore be used to represent average weather conditions in Europe and thus the model computes a typical annual N deposition pattern.

The model was set up on a 72 x 72 km<sup>2</sup> grid for entire Europe and subsequently on a nested 24 x 24 km<sup>2</sup> grid for central Europe. The vertical structure contains 30 layers up to 100 hPa in a sigma hybrid pressure coordinate system. 20 of these layers are below approximately 2 km, the lowest layer extends to approximately 36 m above ground. The model delivers hourly deposition data. It was extracted as a time series of deposition values in the grid cell containing the measurement site. The quality of the model results have been extensively tested (Matthias, 2008; Matthias et al., 2008) indicating that average ammonium and nitrate air concentrations agree to observations within approx. 30%.

### **3.2.4. Statistics**

To identify seasonal variations and possible differences of deposition data between the study sites, we performed an analysis of variance (ANOVA). We furthermore examined the relationship of deposition data and secondary parameters (temperature, humidity, radiation) by correlation analysis. The significance level was mostly 0.05, it is mentioned separately in cases when it was 0.01.

### 3.3. Results

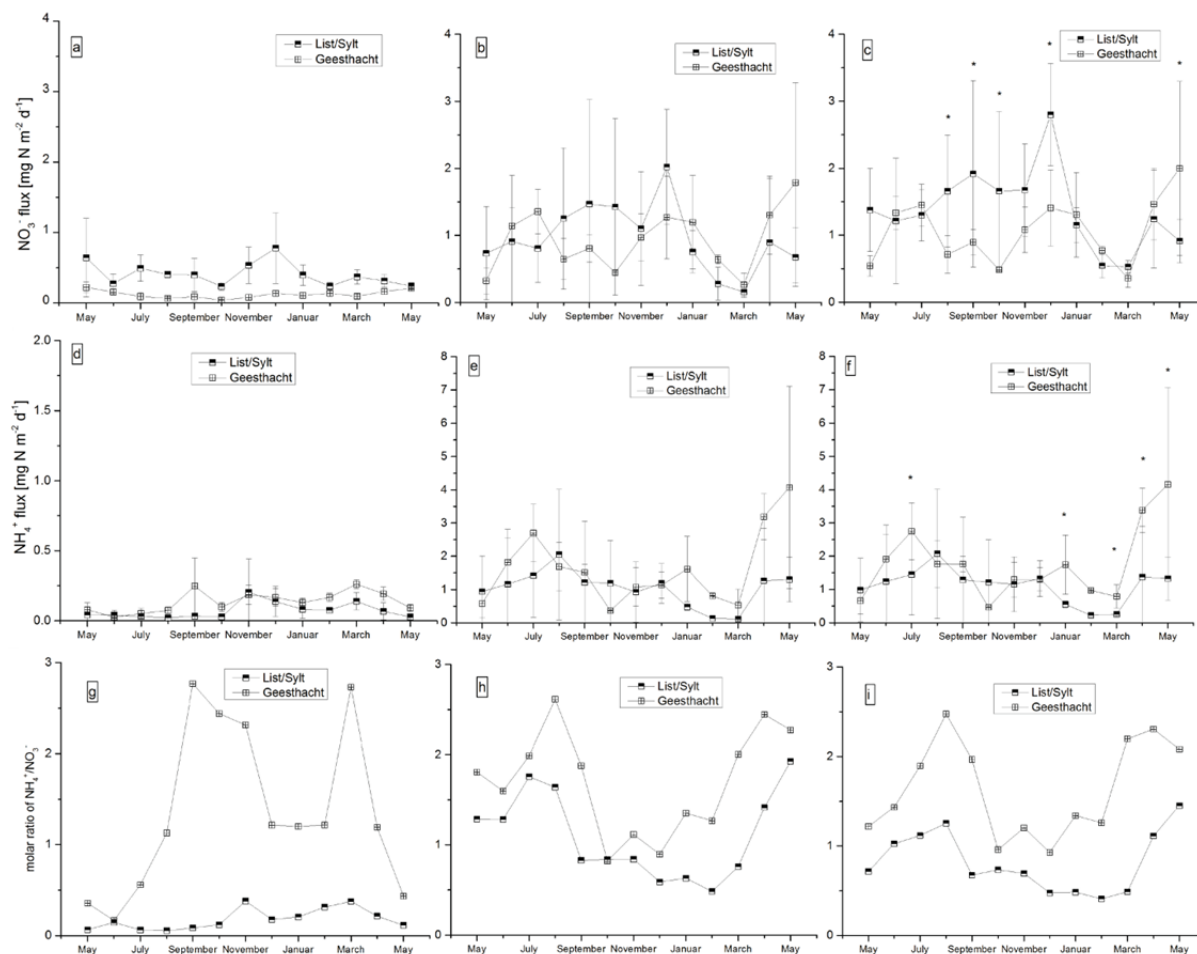
#### 3.3.1. $\text{NO}_3^-$ and $\text{NH}_4^+$ deposition fluxes

At both sites,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are the most important compounds in inorganic N deposition,  $\text{NO}_2^-$  contributes <1% of total (wet + dry) inorganic N deposition (data not shown). Over the sample period of 13 months, the total inorganic N deposition is higher in Geesthacht than in List (11.23 vs. 9.64 kg ha<sup>-1</sup>, Tab. 3.1).

#### $\text{NO}_3^-$ deposition fluxes

In contrast to total N deposition, the total nitrate deposition fluxes we observed over the course of sampling period were significantly higher in List than in Geesthacht (1.38 vs. 1.06 mg N m<sup>-2</sup> d<sup>-1</sup>,  $\rho < 0.05$ , Tab. 3.1). Higher fluxes in List were specifically evident in dry deposition (0.36 vs. 0.13 mg N m<sup>-2</sup> d<sup>-1</sup>,  $\rho < 0.05$ , Fig. 3.2a), whereas fluxes in wet deposition are similar in List and Geesthacht (1.02 vs. 0.93 mg N m<sup>-2</sup> d<sup>-1</sup>, Fig. 3.2b).

The contribution of dry to total  $\text{NO}_3^-$  deposition is by a factor of 2 higher in List than in Geesthacht (26% vs. 12%, Tab. 3.1). Altogether, total nitrate fluxes in List significantly exceed those in Geesthacht, which is most evident in autumn and winter, ( $\rho < 0.05$ , Fig. 3.2c).



**Figure 3.2:** Monthly  $\text{NO}_3^-$  (top panel) and  $\text{NH}_4^+$  (horizontal middle panel) fluxes and molar ratio of  $\text{NH}_4^+/\text{NO}_3^-$  (bottom panel) at both sites, left panel indicate (a, c, g): dry deposition, vertical middle panel (b, e, h) indicate: wet deposition, right panel indicate: total deposition (c, f, i), asterisk: statistically significant differences between study sites.

### Ammonium fluxes

Total  $\text{NH}_4^+$  deposition fluxes were significantly higher in Geesthacht over the complete sampling period (1.77 vs. 1.11  $\text{mg N m}^{-2} \text{d}^{-1}$ ,  $p < 0.05$ , Tab. 3.1). Similarly, monthly averaged total  $\text{NH}_4^+$  fluxes were usually higher in Geesthacht than in List, with significant differences in July 2012, and in January, March, April, and May 2013 (Fig. 3.2f). This higher total deposition flux in Geesthacht in comparison to Sylt was reflected both in dry and wet deposited  $\text{NH}_4^+$  (dry: 0.14 vs. 0.08  $\text{mg N m}^{-2} \text{d}^{-1}$ ,  $p < 0.05$ , wet: 1.63 vs. 1.03  $\text{mg N m}^{-2} \text{d}^{-1}$ ).

Lowest ammonium fluxes in both deposition types were observed in late winter, highest in spring and summer months (Fig. 3.2e, 3.2f). In contrast to  $\text{NO}_3^-$  deposition, dry deposition of

$\text{NH}_4^+$  is only a minor contributor to total  $\text{NH}_4^+$  deposition, 7% and 8% in List and Geesthacht, respectively.

### Molar ratios of $\text{NH}_4^+/\text{NO}_3^-$

Most of the time, molar ratios of  $\text{NH}_4^+/\text{NO}_3^-$  in total N deposition were above 1 in Geesthacht and less than 1 in List (Fig. 3.2i), indicating that ammonium deposition exceeds nitrate deposition in Geesthacht, while the opposite applies to List (Tab. 3.1). At both sites, a seasonal trend with highest molar ratios in spring/summer and lowest values in colder times can be seen in total and in wet deposition (Fig. 3.2h, 3.2i).

Due to the fact that dry deposition in List was almost devoid of ammonium, the molar ratio in dry deposition in List is  $<0.5$ , whereas it was much higher in Geesthacht: The  $\text{NH}_4^+/\text{NO}_3^-$  ratio was only  $<1$  from May to July, and approaches maximum values of 3 in winter (Fig. 3.2g).

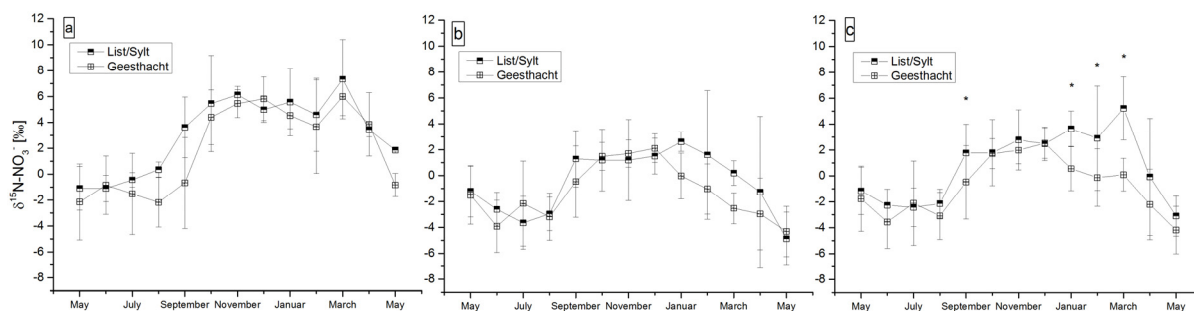
### 3.3.2. $\delta^{15}\text{N}-\text{NO}_3^-$ values

Monthly N-weighted isotope values in  $\text{NO}_3^-$  deposition during the investigation period show significantly higher values in dry ( $p < 0.01$ ) and wet ( $p < 0.05$ ) deposition in List than in Geesthacht (Tab. 3.2). Consequently, this difference is also visible in total N-weighted isotope value of total  $\text{NO}_3^-$  deposition at both sites ( $+0.7 \pm 2.3$  vs.  $-0.7 \pm 2.3\text{‰}$ , Tab. 3.2). At both sites, a seasonal trend in wet and dry deposition is visible, with highest isotope values in winter and lowest in summer times (Fig. 3.3a, 3.3b).  $\delta^{15}\text{N}$  values of dry deposition are generally higher than in wet deposition, with an average difference between these of  $\sim 3.0\text{‰}$  in List and Geesthacht.

**Table 3.2:** Mean N-weighted  $\delta^{15}\text{N}-\text{NO}_3^-$  data of wet, dry and total deposition at both sites.

Site	$\delta^{15}\text{N}-\text{NO}_3^-$ [‰]		
	Wet	Dry	Total
List	$-0.1 \pm 2.3$	$+3.1 \pm 2.3$	$+0.7 \pm 2.3$
Geesthacht	$-1.0 \pm 2.1$	$+1.9 \pm 3.0$	$-0.7 \pm 2.3$

A statistically sound comparison of monthly  $\delta^{15}\text{N-NO}_3^-$  of either wet or dry deposition (Fig. 3.3a, 3.3b) at both sites is not possible due to low sample numbers. Therefore, to come to a statistically relevant evaluation of both sites, we compared monthly N-weighted values of total  $\text{NO}_3^-$  deposition (Fig. 3.3c). We find that isotope values in List are significantly higher, especially in winter months.



**Figure 3.3:** Monthly N-weighted  $\delta^{15}\text{N-NO}_3^-$  values in dry (a), wet (b) and total (c) deposition at both study sites, asterisk: statistically significant differences between study sites.

### 3.3.3. Backward trajectories

The analysis of all computed backward trajectories indicates spatial differences in air mass origin. The clustering at both sites divides our deposition samples into 9 different clusters, which mainly differ in distance covered and direction of air masses. At both sites, most trajectories (46% in Geesthacht vs. 52% in List) are based on air masses with a mixed origin, i.e. with both a marine (North Sea/Baltic Sea) and a continental impact. However, the influence of continental air masses is considerably higher at the terrestrial site in Geesthacht than at the coastal site in List, where air masses with a distinct marine influence are more important than those with a clear continental origin (Tab. 3.3).

**Table 3.3:** Air-mass origin of cluster analysis including all backward trajectories at both sites.

Site	Marine origin	Mixed origin	Continental origin
List/Sylt	29%	52%	18%
Geesthacht	16%	46%	38%

## 3.4. Discussion

### 3.4.1. Pollution levels in List and Geesthacht

Based on the total amount of N deposition (Tab. 3.1) at both sites, annual N deposition rates (8.9 vs. 10.4 kg N ha<sup>-1</sup> yr<sup>-1</sup> in List and Geesthacht, respectively) represent a slightly lower pollution level of N sources at the coastal site List, which is in accordance with our expectations. Other studies of medium polluted study sites show similar N deposition rates (e.g. Anderson and Downing, 2006; Ayars and Gao, 2007; Thimonier et al., 2005). Last EMEP wet deposition data of a coastal site in Westerland on the island of Sylt show that our deposition data in List are in agreement with EMEP data: In 2009, total mean NH<sub>4</sub><sup>+</sup>/NO<sub>3</sub><sup>-</sup> ratio and annual wet N deposition at the station in Westerland was 1.10 and 6.4 kg ha<sup>-1</sup> yr<sup>-1</sup>, which is very close to the molar ratio (1.07) and wet N-deposition (7.3 kg ha<sup>-1</sup> yr<sup>-1</sup>) we measured during our study period in 2012/2013.

Wet N deposition has the highest contribution to the total amount (Tab. 3.1), because both sites are located in climate region with high precipitation throughout over the year. Consequently, N is scavenged from the atmosphere during precipitation events, and the temporal trend in total deposition of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> at both sites closely follows that of wet deposition, which is also evident in NH<sub>4</sub><sup>+</sup>/NO<sub>3</sub><sup>-</sup> ratios (Fig. 3.2).

The lower pollution level in List is reflected in lower NH<sub>4</sub><sup>+</sup> loads in List than in Geesthacht. Sources of NH<sub>3</sub>, which mainly stem from agricultural activities, have a much higher potential influence in the surroundings of Geesthacht. In contrast, there are fewer local NH<sub>3</sub> sources in List, and these are located in at least 15 km distance and mainly in eastern direction from the sampling site. These causes significantly lower NH<sub>4</sub><sup>+</sup> deposition in List than in Geesthacht.

NH<sub>4</sub><sup>+</sup>/NO<sub>3</sub><sup>-</sup> ratios are a reliable indicator for the detection of the relatively local contribution of industrial and agricultural sources to atmospheric N wet/bulk deposition (Anderson and Downing, 2006; Lee et al., 2012). This ratio is higher in Geesthacht (Fig. 3.2i), which is in accordance with a higher concentration of agriculture-derived NH<sub>3</sub>. Lowest NH<sub>4</sub><sup>+</sup> fluxes are observed in winter times, when less NH<sub>3</sub> is emitted due to low temperatures and due to legal restrictions on fertilizer application on fields from November to February (BdJ, 2012).



### 3.4.2. The effect of marine aerosols

Surprisingly, the lower overall pollution level in List cannot be the only explanation for differences in deposition patterns between both sites: Overall, mean  $\text{NO}_3^-$  fluxes during the study period are significantly higher in List than in Geesthacht (Tab. 3.1), which is surprising and is obviously not in accordance with the general pollution level. We will therefore discuss possible explanations for the unexpectedly high nitrate deposition.

The contribution of dry nitrate deposition to total deposition is distinctly higher in List than in Geesthacht. This cannot be explained by the pollution level, but rather by the expected chemical composition of dry deposition at the coastal site. Sea-salt is mainly present in coarse-mode and fine-mode aerosols (Wall et al., 1988). In general, sea salt aerosols interact with  $\text{NO}_3^-$ , which changes the chemical composition of aerosols (Athanasopoulou et al., 2008) and leads to enhanced nitrate incorporation in aerosols, with especially high  $\text{NO}_3^-$  contribution in coarse mode aerosols (Im et al., 2012). In the North Sea region, the sea salt contribution to particulate dry deposition is high, up to 20% were found at a coastal station in the Netherlands (van Jaarsveld and Klimov, 2011). Moreover, ship emissions can promote aerosol formation (Matthias et al., 2012), which further explains the high amount of nitrate in dry deposition in List.

The influence of sea salt on the study site in Geesthacht, more distant from the coast, is much smaller (Tsyro et al., 2011). This marine/terrestrial sea salt gradient thus explains the spatial differences in bulk dry nitrate deposition. List, which is nearly completely surrounded by the North Sea, may be particularly prone to a large influence of sea salt.

Sea salt aerosols are also scavenged from the atmosphere via wet deposition, so the impact of sea salt also explains the high wet  $\text{NO}_3^-$  loads in List. Thus, washed-out aerosol particles in wet deposition can be responsible for the almost equal nitrate load in wet deposition in List in comparison to the generally more polluted site in Geesthacht.

Backward trajectories for both sites confirm the higher marine influence at the coastal site List. Besides aerosol formation, which clearly influences nitrate deposition, this raises the question of the effect of ship emissions as a potential  $\text{NO}_x$  source. While, due to political regulation, bulk  $\text{NO}_x$  emission of anthropogenic sources in Germany and other European countries are decreasing, this is not true for ship emissions, which show an increasing trend (UBA, 2012) and are so far only strongly regulated in terms of sulphur content in fuels. This

increasing trend of  $\text{NO}_x$  emissions from ships has led to higher  $\text{NO}_3^-$  loads derived from ships in the last decades, especially in the North Sea region (Matthias et al., 2010).

Apparently, the sea salt induced formation of nitrate-bearing aerosol particles and the impact of ship emissions both on aerosol formation and as a  $\text{NO}_x$  emission source cause the unexpectedly high  $\text{NO}_3^-$  fluxes in List in comparison to Geesthacht.

### 3.4.3. Modelled and measured $\text{NH}_x$ deposition

Modelled dry N deposition data at both sites show higher fluxes than measured data. However, wet deposition CMAQ modelling data of 2008 are in a good agreement with our measurements at both sites, showing higher  $\text{NH}_4^+/\text{NO}_3^-$  ratios at the terrestrial site Geesthacht than in List.

In detail, the most profound differences are observed in dry modelled  $\text{NH}_x$  deposition fluxes, which exceed fluxes of  $\text{NO}_y$ . This is in accordance with our measurements in Geesthacht, where we indeed find that total  $\text{NH}_x$  deposition is higher, but does not comply with our measurements at the site in List. Here, we find low deposition fluxes of  $\text{NH}_x$  in contrast to  $\text{NO}_y$ , resulting in low  $\text{NH}_4^+/\text{NO}_3^-$  molar ratios in dry deposition of  $\ll 1$  (Fig. 3.2g), which is not reproduced by the model.

Concentration measurements of reduced and oxidised nitrogen compounds in air at the EMEP site in Westerland (~20 km distance to List) in 2011 show higher concentrations of  $\text{NH}_x$  than  $\text{NO}_y$  compounds, but there are no comparable deposition measurements at hand. Furthermore, the interaction of concentration and dry deposition of reduced nitrogen is rather complex, because many factors like bi-directional fluxes of  $\text{NH}_3$ , roughness of surface and the high impact of local  $\text{NH}_3$  sources alter the deposition velocity of gaseous  $\text{NH}_3$ . Literature values indicate that more than 33% of a local  $\text{NH}_3$  emission source is deposited within 20 km downwind from the source (Asman et al., 1998). Based on this value and the relative long distance (15-20 km) to local  $\text{NH}_3$  sources, this supports little influence of gaseous  $\text{NH}_3$  to dry deposition in List, especially as backward trajectories suggest that the majority of air-masses originate from areas without local  $\text{NH}_3$  emission sources (Tab. 3.3).

Moreover, other parameters like relative humidity can affect partitioning between the gas and the aerosol phase, which clearly will affect deposition in comparison to concentration measurements.

In List, the relative humidity (Tab. 3.1), and, based on EMEP measurements in Westerland, the sulphate concentration, are high. Jointly, these conditions favour the formation of fine mode  $(\text{NH}_4)_2\text{SO}_4$  (Metzger et al., 2006), if reduced nitrogen is available. Similarly, high relative humidity favours the formation of aerosol nitrate (Ansari and Pandis, 2000). As a consequence, these conditions impede the formation of  $\text{NH}_4\text{NO}_3$ , as particulate nitrate will mainly react with abundant sea salt (basically sodium chloride) to form coarse-mode  $\text{NaNO}_3$ . Furthermore, higher deposition velocity of coarse mode aerosols will lead to higher  $\text{NO}_3^-$  dry deposition, even though reduced nitrogen is available. Thus, meteorological conditions in List, favour the formation of  $\text{NaNO}_3$  and  $\text{CaNO}_3$  (Metzger et al., 2006), which can explain the low  $\text{NH}_4^+/\text{NO}_3^-$  ratios (Fig. 3.2g) at the site. This behaviour was also observed in other marine studies on dry deposition with high relative humidity (e.g. He et al., 2011).

We also assume that a part of the discrepancy of modelled data and measurements can largely be explained by the grid resolution of  $24 \times 24 \text{ km}^2$ , which might be too coarse for precise estimates of  $\text{NH}_3$  deposition close to the coast, especially as  $\text{NH}_x$  is transported over short distances in comparison to  $\text{NO}_x$ . Areas with high agricultural activity are included in the grid cell, which will lead to an overestimation of  $\text{NH}_x$  deposition fluxes.

#### 3.4.4. Seasonal variations of $\delta^{15}\text{N}$ in $\text{NO}_3^-$ deposition

$\delta^{15}\text{N}-\text{NO}_3^-$  values are in line with other reported values in wet (Elliott et al., 2007; Freyer, 1991; Russell et al., 1998) and dry deposition (Elliott et al., 2009; Yeatman et al., 2001) in similarly polluted regions. The average differences we measured between wet and dry deposition at our sites ( $\sim 3\%$ ) is in a good agreement with a study in North America (Elliott et al., 2009). Thus, the overall measurements are consistent with observations that attributed the higher values in dry deposition to isotope fractionation between particulate  $\text{NO}_3^-$ , gaseous  $\text{HNO}_3$  and dissolved nitrate, which depletes wet  $\text{NO}_3^-$  deposition relative to dry deposition (Freyer, 1991).

The seasonality of wet and dry deposition has commonly been observed worldwide in atmospheric  $\text{NO}_3^-$  studies (Kendall et al., 2008 and references therein). This typical variation in  $\delta^{15}\text{N}$  is mainly triggered by seasonality of  $\text{NO}_x$  sources and precursor reactions forming atmospheric  $\text{NO}_3^-$ . Basically,  $\text{NO}_x$  emissions by coal-fired power plants reach a maximum in winter due to highest energy demand. As this is a  $\text{NO}_x$  source with a relatively enriched

isotope signature, this leads to isotopically heavier NO<sub>x</sub> deposition in colder times. This seasonality is enhanced by biogenic soil emissions with highly depleted <sup>15</sup>N that are dominant in the vegetation period (March-October), and thus lower the δ<sup>15</sup>N in deposited NO<sub>3</sub><sup>-</sup> in warmer times.

Apart from these source effects, secondary parameters (temperature, radiation and humidity) influence δ<sup>15</sup>N, which is more pronounced in dry than in wet deposition (Elliott et al., 2009) at both sites (Tab. 3.4). The isotope exchange equilibrium between gaseous NO/NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> is temperature-dependent and leads to more enriched <sup>15</sup>N in colder times (Freyer, 1991; Freyer et al., 1993).

**Table 3.4:** Correlation coefficients (r<sup>2</sup>) and significance levels of δ<sup>15</sup>N values with NH<sub>4</sub><sup>+</sup>/NO<sub>3</sub><sup>-</sup> molar ratio of sample and mean temperature, humidity and radiation during sample times. \* indicate: ρ<0.05, \*\* indicate: ρ<0.001, N/A indicate: not available data.

Study site	Deposition type	Temperature	Humidity	Radiation	NH <sub>4</sub> <sup>+</sup> /NO <sub>3</sub> <sup>-</sup>
List	Wet	0.21**	0.05	N/A	0.38**
	Dry	0.48**	0.17*	N/A	0.20*
Geesthacht	Wet	0.21**	0.14*	0.25**	0.21**
	Dry	0.61**	0.44**	0.59**	0.17*

### 3.4.5. Marine and terrestrial drivers of δ<sup>15</sup>N

While the seasonality of isotope variations itself can be attributed to source effects and influences of atmospheric reactions (Beyn et al. 2014), it was a surprise that nitrate deposition exceeded that of Geesthacht, despite obviously lower pollution levels in List/Sylt.

To evaluate the causes for this phenomenon, we will evaluate δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> values of dry and wet deposition. The δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> values are far from showing higher δ<sup>15</sup>N values in Geesthacht we would have expected alongside with a higher pollution level. We actually found the opposite, isotope values in total were - in some months significantly - higher in List. However, the seasonal variations of different NO<sub>x</sub> sources are only one potential driver altering the δ<sup>15</sup>N values of atmospheric nitrate in same climate region (Freyer, 1991), secondary parameters can further influence deposited δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup>.

Consequently, we calculated the correlation coefficients of  $\delta^{15}\text{N-NO}_3^-$  with meteorological parameters (i.e., temperature, humidity and radiation) and with molar ratios. The high correlation coefficients indicate that meteorological parameters have a stronger impact on  $\delta^{15}\text{N}$  in Geesthacht than in List (Tab. 3.4). Contrastingly, the correlation coefficients of  $\text{NH}_4^+/\text{NO}_3^-$  ratios and isotopes in wet deposition shows higher values in List than in Geesthacht, with lower  $\delta^{15}\text{N}$  at higher molar ratios. Such changes are, as discussed above, caused by changing source contributions, so we assume that the impact of varying  $\text{NO}_x$  sources is higher in List than in Geesthacht.

There are various possible reasons for the significantly higher  $\delta^{15}\text{N}$  values and the sensitivity to source changes in List. In general,  $\text{NO}_x$  sources are not the same at both sites. The low influence of agriculture leads to lower  $\text{NO}_3^-$  loads derived from this isotopically  $^{15}\text{N}$ -depleted source in List than in Geesthacht. This spatial effect causes enriched overall  $\delta^{15}\text{N}$  in List, especially in warmer times, in contrast to Geesthacht, although more  $\text{NO}_3^-$  is deposited in List (Tab. 3.1). Furthermore, road traffic volume in List reaches its maximum in warmer times due to high tourism activity in summer (Sylt, 2013), whereas this source of low  $\delta^{15}\text{N-NO}_x$  can be regarded as non-seasonal in the urban area around Geesthacht.

However, significant isotope differences are mainly been observed in winter, and not in summer times (Fig. 3.3c), these differences are unlikely the reason of higher values in List. One might assume that  $\text{NO}_x$  from coal-fired power plants, which reach maximum output in colder times and cause enriched  $\delta^{15}\text{N}$ , has a higher impact on deposited  $\text{NO}_3^-$  in List than in Geesthacht – but backward trajectories show distinctly higher influence of marine air-masses in List and indicate a lesser impact of land-based sources on deposited  $\text{NO}_3^-$  (Tab. 3.3). This makes power plants an unlikely source for the higher values in winter.

The most common  $\text{NO}_x$  source in the North Sea region, i.e., the source region of most backward trajectories computed for List, are ship emissions. Most likely, these ship emissions - and possibly the improvements of ship engines - lead to higher isotope values at the coastal site, which is also most likely one cause for higher  $\text{NO}_3^-$  loads in List than in Geesthacht. Consequently, it seems plausible that the impact of this source on  $\delta^{15}\text{N}$  in List is higher than at the more terrestrial site. To accurately assess the influence of ship emissions on the  $\delta^{15}\text{N}$  budget, it is crucial to know its isotopic range, which, unfortunately, has not been determined.

NO<sub>x</sub> formed during the combustion process can be composed either of fuel NO<sub>x</sub>, which will lead to emission of enriched  $\delta^{15}\text{N}$ , or of thermal NO<sub>x</sub>, which stems from decomposition of atmospheric N<sub>2</sub> and will have lower  $\delta^{15}\text{N}$  values (Snape et al., 2003; Widory, 2007). Until now, the origin of NO<sub>x</sub> is not clearly classified for ship emissions, but new ship technologies aim at reduction of emitted particles amount and NO<sub>x</sub>, can cause, different, possibly higher, isotope ranges in ship NO<sub>x</sub> than road traffic: The engine technology of low NO<sub>x</sub> burner, which is based on a low temperature combustion in gas engines, were used more frequently in Europe since the end of the 1990s on ships (Kågeson, 1999). This kind of engines reduced the thermally emitted NO<sub>x</sub>. Furthermore, the higher N content in commonly used heavy oil on ships in comparison to fuels used in vehicles (EPA, 1995) may explain higher  $\delta^{15}\text{N}$  values, because more fuel N is incorporated in emitted NO<sub>x</sub>.

Additionally, the technology of selective catalytic reduction (SCR) of NO<sub>x</sub> emission, which is already increasingly used in vehicle diesel engines, is used in marine engines (Zhou and Zhang, 2014). This technology is known to emit NO<sub>x</sub> that is enriched  $\delta^{15}\text{N}$  (Felix et al., 2012). The influence of commonly used SCR technology on atmospheric NO<sub>3</sub><sup>-</sup> deposition and isotope values in terrestrial regions has been documented (Beyn et al., 2014). There are no strict NO<sub>x</sub> regulations with regards NO<sub>x</sub> emissions from ships in Europe, and this cost-intensive technology is not widely used in ship engines. Thus, the effect of SCR on the isotope range of nitrate is speculative.

Both, low NO<sub>x</sub> burner and the SCR technology, lead to high  $\delta^{15}\text{N}$  values in ship-NO<sub>x</sub> in comparison to usual road traffic NO<sub>x</sub>. This effect may be enhanced in the future, because the International Maritime Organisation (IMO) aims for a control and reduction of particulate matter, SO<sub>2</sub> and NO<sub>x</sub> emissions (IMO, 2009). Altogether, as we can clearly see a stronger impact of marine air-masses, we conclude that ship NO<sub>x</sub> emissions are most likely the main driver for higher  $\delta^{15}\text{N}$  values in deposited nitrate at the coastal study site in List, especially in times when bulk nitrate loads are relatively low due to seasonal effects.

### 3.5. Conclusions

Higher NO<sub>3</sub><sup>-</sup> loads and higher  $\delta^{15}\text{N}$ -NO<sub>3</sub><sup>-</sup> values were observed at the coastal site List in dry and wet deposition, while NH<sub>4</sub><sup>+</sup> loads are higher at the urban/terrestrial site in Geesthacht. The impact of more NH<sub>3</sub> sources close to the terrestrial site leads to higher NH<sub>4</sub><sup>+</sup> fluxes. At

the less polluted marine site, for which we assumed the lower imprint of anthropogenic  $\text{NO}_x$  sources to be mirrored in less  $\text{NO}_3^-$  deposition and more depleted  $^{15}\text{N}$  values in List, we saw surprisingly high  $\text{NO}_3^-$  fluxes and high  $\delta^{15}\text{N}$  values. A suite of marine effects can be held responsible for this: The high impact of sea-salt aerosols to the particulate phase leads to higher incorporation of  $\text{NO}_3^-$  in aerosols, which are then readily deposited. Increasing ship emissions in recent times, which affect the coastal site due to a higher influence of marine air-masses, also add to higher  $\text{NO}_3^-$  loads in List. This high impact of  $\text{NO}_x$  emissions from ships can also explain the higher isotope values in wet and dry deposition at the coastal site. The higher N fraction in heavy oil compared to vehicle fuels and the use of new technologies on ships have probably led to higher isotope values of ships in comparison to road traffic. Consequently, ship emissions are the most reliable explanation for higher  $\delta^{15}\text{N}$  values in deposited  $\text{NO}_3^-$  at marine influenced study sites.

## **Acknowledgements**

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## 4. From atmospheric nitrogen deposition to *Sphagnum* growth – an in-situ isotopic approach to N cycling in an ombrotrophic peat bog in Northern Germany

Fabian Jung, Sebastian R. Schmidt, Kai Jensen, Kirstin Dähnke

In preparation for submission

### Abstract

We investigated atmospheric inorganic nitrogen deposition, biomass of prevailing mosses *Sphagnum cuspidatum* and *Sphagnum papillosum*, and *Sphagnum* pore water in an ombrotrophic peat bog in Northern Germany to clarify whether atmospheric nitrogen inputs are the main N source for *Sphagnum* growth. We found an annual inorganic N deposition flux of 8.8 kg N kg ha<sup>-1</sup> yr<sup>-1</sup> and a total mean N isotope value of  $-0.3 \pm 4.9\text{‰}$  ( $\delta^{15}\text{N-NH}_4^+$ :  $-1.7 \pm 6.4\text{‰}$ ;  $\delta^{15}\text{N-NO}_3^-$ :  $+2.3 \pm 2.9\text{‰}$ ). Average N concentrations of the biomass of *S. cuspidatum*, which dominates in hollows, were  $1.3 \pm 0.2\%$  with a mean  $\delta^{15}\text{N}$  value of  $-5.9 \pm 1.1\text{‰}$ . *S. papillosum*, which dominates in hummocks, showed mean N concentrations of  $1.1 \pm 0.2\%$  and a mean  $\delta^{15}\text{N}$  value of  $-6.9 \pm 0.8\text{‰}$ .

Pore water concentrations did not indicate N-limitation, although N deposition load was below the N-limitation threshold of 10 kg ha<sup>-1</sup> yr<sup>-1</sup>. Significantly lower isotope values in both *Sphagnum* mosses compared to the total  $\delta^{15}\text{N}$  value in deposition ( $p < 0.01$ ) imply that main N required for annual growth of *Sphagnum* did not originate from direct atmospheric inputs, but rather from internal N cycling processes. Most likely, biological remineralization is the main N source for mosses, because a noticeable influence of <sup>15</sup>N enriched atmospheric inputs can only be observed in colder times in hummocks. The fate of isotopically enriched deposited N is not observable in our samples; so we conclude that freshly deposited N is moved downwards to the peat layer.

## 4.1. Introduction

Human activities have changed the natural N cycle dramatically since the onset of industrialization in the 19<sup>th</sup> century. Since then, huge mobilization of reactive nitrogen ( $N_R$ ) by anthropogenic activities like energy and fertilizer production has led to considerable overwhelming of natural derived  $N_R$  in the atmosphere (Galloway, 1998). The most abundant N compounds in the atmosphere are  $NO_X$  and  $NH_3$ , which consequently can be deposited to ecosystem as dry and wet deposition. Main  $NO_X$  sources are traffic and power plants; agricultural activities like animal husbandry and application of fertilizer and manure are the main sources of  $NH_3$  (Bouwman et al., 1997; Delmas et al., 1997).

The increase of N emission and associated N deposition has enormous consequences for many ecosystems, like acidification and eutrophication (Bouwman et al., 2002). Especially nutrient poor ombrotrophic peat bogs are sensitive to such changes, because they receive all nutrients from atmospheric deposition (Bobbink et al., 1998). In a typical peat bog, prevalent low pH value (~4) lead to low potential denitrification and nitrification rates (Urban and Eisenreich, 1988).

*Sphagnum* mosses are the dominant plant species in these ecosystems, which efficiently use nutrients from the atmosphere (Malmer, 1988). At low atmospheric N deposition levels in those nutrient-poor ecosystems nearly all  $N_R$  is retained in *Sphagnum*. As N deposition loads have increased constantly, in polluted areas a shift from a living peat moss layer towards the dominance of vascular plants is expected (Heijmans et al., 2002; Tomassen et al., 2003; Wiedermann et al., 2007).

One of the most important consequences of higher atmospheric N load to peat bogs is an imbalance of nutrient availability (Lamers et al., 2000). If a critical load of  $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  of atmospheric N deposition is reached, the bog ecosystems is no longer N limited for *Sphagnum* plants, so that not all deposited N is retained by *Sphagnum* mosses (Bragazza et al., 2004). At a deposition rate between  $10$  and  $20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  *Sphagnum* still accumulates N, but at high deposition rates ( $>20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) *Sphagnum* cannot ensure their filter function for the ecosystem (Lamers et al., 2000; Malmer et al., 1994; Tomassen et al., 2003). In higher polluted peat bogs ( $>10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) *Sphagnum* growth is rather limited by K and P availability (Bragazza et al., 2004). Furthermore, water-table depth is a particularly important factor in regards to *Sphagnum* growth and implicated factors like the retention capacity of N (Williams et al., 1999b).

Some *Sphagnum* studies in peat bogs focus on the influence of increasing N deposition loads to *Sphagnum* nutrient content. Higher atmospheric N loads result in increasing N concentration in tissues of peat mosses (e.g. Harmens et al., 2011; Schroder et al., 2010), but concurrent decreasing N retention capacity of mosses (Xing et al., 2011).

To conclude about the fate of atmospheric N inputs and the N requirements of mosses, the determination of N isotopes is a reliable method. Studies investigating mosses and N deposition loads at similar conditions have reported a linear relationship between  $\text{NH}_4^+/\text{NO}_3^-$  ratios in N deposition and  $\delta^{15}\text{N}$  values in mosses (Bragazza et al., 2005; Solga et al., 2005; Zechmeister et al., 2008), regardless of whether or not the critical N load is exceeded (Xiao et al., 2010). The observed values were explained by lower isotopic values of deposited  $\text{NH}_4^+$  compared to N isotopes in  $\text{NO}_3^-$  deposition (Freyer, 1978, 1991; Lee et al., 2012). Consequently, if the contribution of  $\text{NH}_4^+$  in N deposition is higher than that of  $\text{NO}_3^-$ ,  $\delta^{15}\text{N}$  values of *Sphagnum* mosses will be more  $^{15}\text{N}$  depleted. This case implicates, however, that atmospheric N deposition is the main N source for *Sphagnum* growth. In consequence, both relationships between deposition load and N concentration in mosses and between the molar ratio of  $\text{NH}_4^+/\text{NO}_3^-$  in deposition and  $\delta^{15}\text{N}$  values in mosses, supposed that N isotopes in deposition are reflected in N isotopes in mosses.

Thus, considering the influence of atmospheric nitrogen deposition to peat bogs and *Sphagnum* species, it is of advantage not only to quantify N deposition load and N concentration of mosses, but also determining N isotopes of both mosses and of N deposition can help to understand the fate of deposited N. Comparing the isotope values of N in deposition, in *Sphagnum* biomass and in pore water can give valuable information about N sources of *Sphagnum* growth and N cycling processes within the peat bogs.

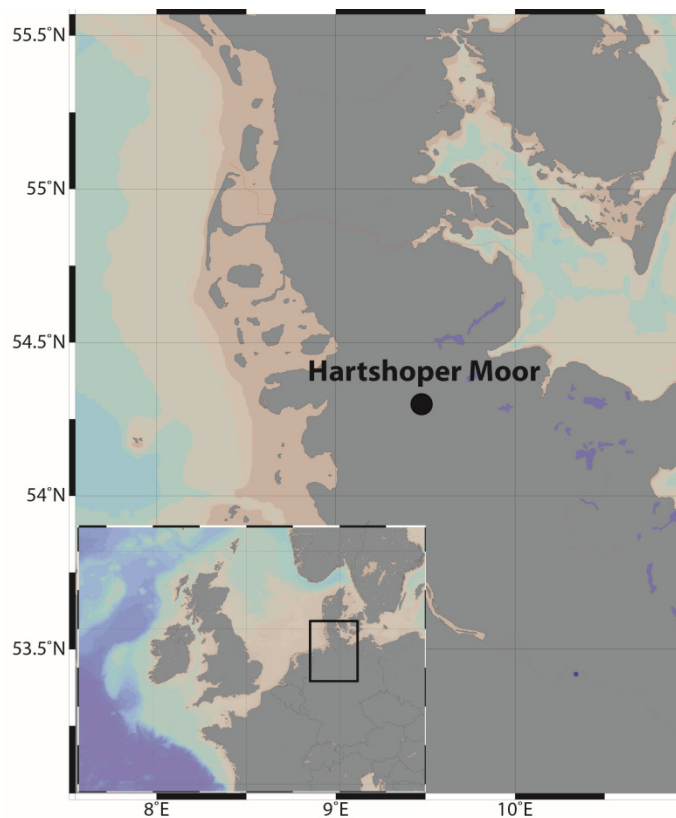
As recently reported deposition data in Northern Germany (Beyn et al., 2014) and EMEP data suggested, atmospheric nitrogen deposition loads were close to the critical N load to peat bogs. So, N deposition in that area is suggested to be the main N source for mosses.

In this paper we present data on the within year variation of N loads and N isotopes in atmospheric deposition, pore water and in the biomass of the most abundant *Sphagnum* plants in a peat bog in Northern Germany. We hypothesize that  $N_R$  added by atmospheric deposition is retained by *Sphagnum* mosses. We suppose that the  $\delta^{15}\text{N}$  value of *Sphagnum* is reflecting the N isotopes in atmospheric deposition.

## 4.2. Materials and Methods

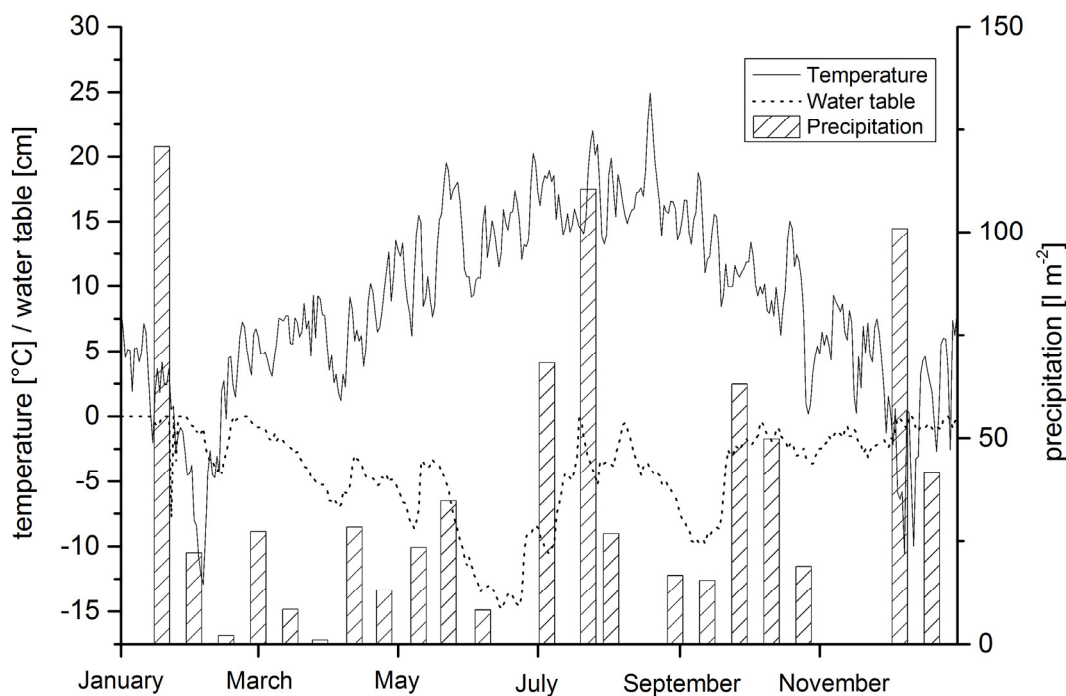
### 4.2.1. Study site

The study site has been located in the raised peat bog Hartshoper Moor in Northern Germany (Fig. 4.1), which is atmospherically affected by both agriculture and industrial sources. Livestock farming in the surroundings of the study site and road traffic are the main local atmospheric  $N_R$  sources.



**Figure 4.1:** Location of the study site in Northern Germany.

Secondary parameters (temperature, precipitation amount) (Fig. 4.2) resulting in a mean annual temperature in 2012 of  $+8.7^\circ$  and a total precipitation of  $800 \text{ l m}^{-2}$ . The trend of water table in peat bog hollows (Fig. 4.2) show lowest values during dry periods in summer and highest during both colder and wet times.



**Figure 4.2:** Trend of temperature, precipitation and water table at the sampling site in 2012.

Since at least the 16<sup>th</sup> century the peat bog has been distinctly influenced by human activities through drainage and channelling leading to lower water table. In the 20<sup>th</sup> century the area was mainly used for grazing. In the 1980s, one parcel of 7 ha was abandoned and different rewetting measures were initiated. Ditches were refilled and the discharge was restricted with a plastic sheet (Schmidt, 2013). The vegetation within this parcel is heterogeneous with relatively dry areas mainly dominated by *Molinia caerulea*, while other relatively wet patches are characterized by a microtopography typical for raised bogs. Hummocks were dominated by *S. papillosum*, *S. magellanicum* and *S. capillifolium* accompanied by *Eriophorum vaginatum* as well as *Empetrum nigrum* and *Erica tetralix*. Hollows were dominated by a relatively homogenous carpet of *S. cuspidatum*, accompanied by *S. fallax*. The dominant vascular plant is *Eriophorum angustifolium* Honck., growing loosely within the carpet.

#### 4.2.2. Sampling of plants and pore water

Usually five biomass samples of abundant plants were taken monthly between March and September 2012. Samples were carefully transferred to the laboratory where the upper 1 cm

of *Sphagnum* plants (capitula) and a part of leaves of other plants were separated, dried at +60°C for 48 h and homogenized. All samples were analysed for N content and N isotopes.

In the time between of March and September 2012 five replicates of pore water samples were collected monthly in homogenous parts in both hummocks and hollows, where *Sphagnum* mosses are abundant. It was ensured that replicates were taken always at the same point. The sampling was conducted using 50 ml syringes with soil moisture samplers (10 cm Rhizon SMS, Eijkelkamp Agrisearch Equipment, Giesbeek, Netherlands). Usually 20 ml were extracted by each sampling procedure. Samples were stored at -20°C before being analyzed for nutrient concentration and N isotopes.

### **4.2.3. Atmospheric Deposition sampling**

Samples of atmospheric deposition were taken biweekly between January and December 2012. Two bulk deposition samplers (RS200, UMS, Germany) were installed in a stand pipe at a height of 1.2 m to ensure that sun radiance, local turbulence or plants do not influence the content of the deposited sample. Samples were filtered (GF/F) and stored frozen for subsequent nutrient and isotopic analysis. Frozen samples from February were thawed and treated like other samples afterwards.

### **4.2.4. Analyses of mosses**

Aliquots of oven dried samples (3-4 mg) were weighted into tin cups for N isotope (and content) determination in a stable isotope ratio mass spectrometer (Nu Horizon, Nu Instruments Limited, UK) linked to an elemental analyser (EURO-EA 3000, Euro Vector, Italy) in continuous flow configuration. Isotope and mass calibration were conducted by the use of IAEA-600 Caffeine ( $\delta^{15}\text{N} = +1.0\text{‰}$ ) and 2,5-bis(5-tert-butyl-2-benzoxazol-2-yl) thiophene (Hekatech, Germany), respectively.

#### 4.2.5. Analysis of pore water and atmospheric deposition

Pore water and deposition samples were analysed in duplicate for nitrite, nitrate, ammonium and phosphate using an automated continuous flow system (AA3, Seal Analytical, Germany) with standard colorimetric techniques (Hansen and Koroleff, 2007).

All samples were analysed for isotopic composition of nitrate ( $\delta^{15}\text{N-NO}_3^-$ ) and ammonium ( $\delta^{15}\text{N-NH}_4^+$ ) using both the denitrifier method (Sigman et al., 2001) and the Hypobromite/Azide-method (McIlvin and Altabet, 2005; Zhang et al., 2007). Both methods are based on the isotopic analysis of nitrous oxide ( $\text{N}_2\text{O}$ ).

The denitrifier method was conducted with *Pseudomonas chlororaphis* instead of the commonly used *Ps. aureofaciens* in order to prevent the interference of mass-independent  $^{17}\text{O}$  of atmospheric nitrate. *Ps. chlororaphis* generates  $\text{N}_2\text{O}$  having nitrogen derived from  $\text{NO}_3^-$ , but oxygen primarily from  $\text{H}_2\text{O}$ . The Hypobromite/Azide-method was adapted using 5-fold amount of hypobromite amount at the oxidation step of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  due to inhibition of the reaction by organic compounds, especially by fulvic acids in pore water samples.

The sample volume for both methods was adjusted to a sample size of 10 nmol of  $\text{N}_2\text{O}$ .  $\text{N}_2\text{O}$  was extracted from the sample vials and measured with a GasBench II, coupled to an isotope ratio mass spectrometer (Delta Plus XP, Thermo Fisher Scientific, Germany). For each batch of samples using the denitrifier method two international standards (USGS34:  $\delta^{15}\text{N} = -1.8\text{‰}$ ,  $\delta^{18}\text{O} = -27.9\text{‰}$ ; IAEA-NO-3:  $\delta^{15}\text{N} = +4.7\text{‰}$ ,  $\delta^{18}\text{O} = +25.6\text{‰}$ ) and an internal standard were run. To calibrate  $\delta^{15}\text{N-NH}_4^+$  measurements three international standards (IAEA-N-1:  $\delta^{15}\text{N} = +0.4\text{‰}$ , USGS25:  $\delta^{15}\text{N} = -30.4\text{‰}$ , USGS26:  $\delta^{15}\text{N} = +53.7\text{‰}$ ) were used for each sample run. All isotopic measurements were done in replicate, typical reproducibility for  $\delta^{15}\text{N-NO}_3^-$  and  $\delta^{15}\text{N-NH}_4^+$  was better than 0.2‰ and 0.4‰, respectively.

Due to very low concentrations of  $\text{NO}_3^-$  in pore water samples, only N isotopes of  $\text{NH}_4^+$  were measured. Because each sample did not provide enough volume for the measurements, only one mixed sample (two mixed samples of hollows pore water in June and August) per month was measured in order to determine the values of  $\delta^{15}\text{N-NH}_4^+$ .

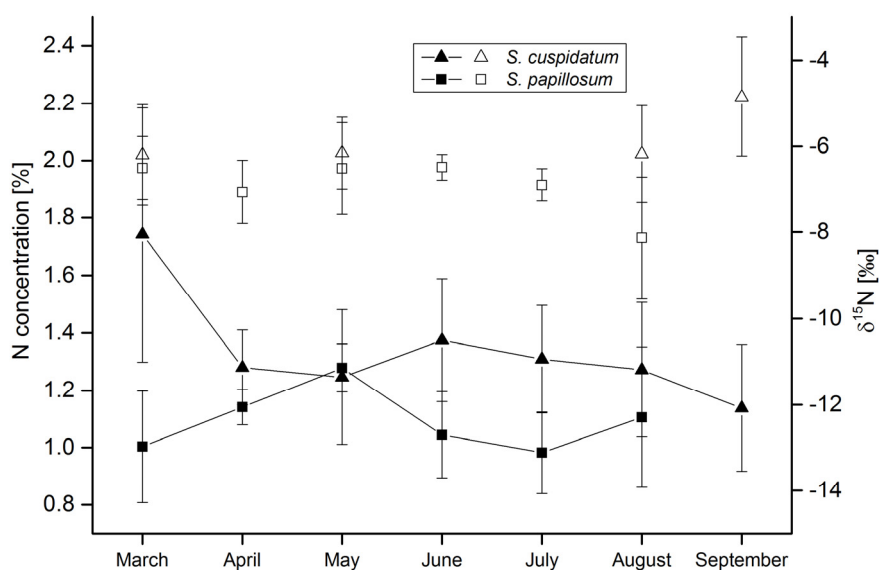
## 4.2.6. Statistical analysis

Significance tests were conducted with ANOVA to examine differences in isotope values of *Sphagnum* mosses, pore water and deposition. It was also used to compare N concentrations and N isotopes in hummocks and hollows.

## 4.3. Results

### 4.3.1. Biomass N concentrations and N isotopes

N concentrations of *S. cuspidatum* samples varied monthly between  $1.12 \pm 0.22\%$  and  $1.74 \pm 0.44\%$ , *S. papillosum* ranged from  $0.98 \pm 0.14\%$  to  $1.28 \pm 0.08\%$ . Mean N concentration for the hollow moss *S. cuspidatum* was  $1.34 \pm 0.24\%$ . In hummocks dominated by *S. papillosum* mean N content of  $1.09 \pm 0.15\%$  was found. Monthly values of N concentrations of both moss types did not show an annual trend during the investigation period (Fig. 4.3).



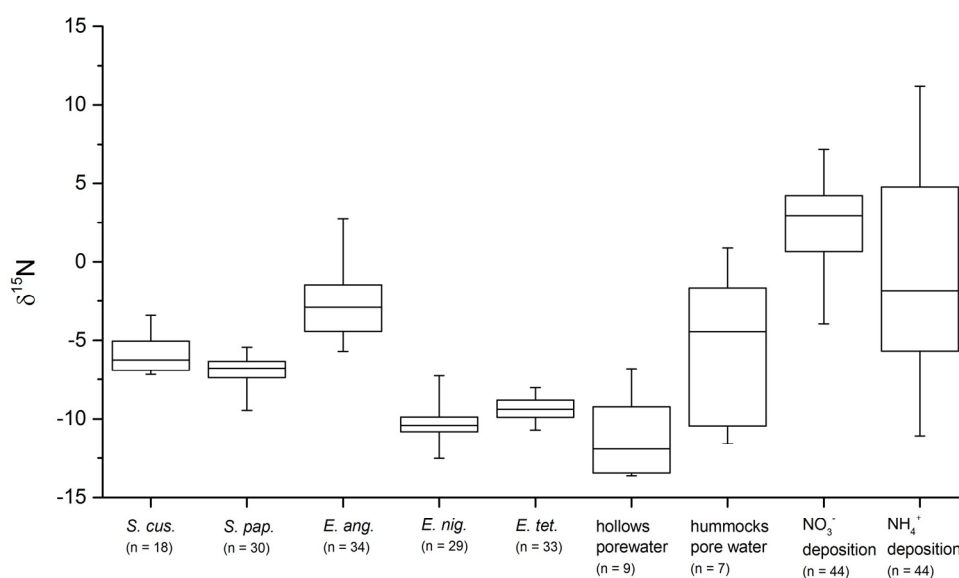
**Figure 4.3:** Monthly mean N concentrations and  $\delta^{15}\text{N}$  values of both *Sphagnum* mosses. Filled symbols indicate: N concentration (N%), open symbols indicate: isotope values ( $\delta^{15}\text{N}$ ).

N isotopes of mosses ranged from -7.2 to -3.4‰ and -9.5 to -5.4‰ in *S. cuspidatum* and *S. papillosum*, respectively (Fig. 4.4). The overall mean N isotope value in *S. cuspidatum* was  $-5.9 \pm 1.1\%$ , *S. papillosum* had an average  $\delta^{15}\text{N}$  value of  $-6.9 \pm 0.8\%$ . As N



concentrations, also  $\delta^{15}\text{N}$  values showed no significant seasonal trend in either *Sphagnum* species (Fig. 4.3).

N isotopes of dominant vascular plant *E. angustifolium* ranged from -5.7 to +2.8‰. Isotope values of *E. nigrum* and *E. tetralix* varied between -12.3 and -7.3‰ and -10.7 to -8.0‰, respectively (Fig. 4.4). The mean  $\delta^{15}\text{N}$  value of *E. angustifolium* was  $-2.8 \pm 1.4$ ‰, whereas *E. nigrum* and *E. tetralix* showed significantly lower mean values ( $p < 0.01$ ) of  $-10.4 \pm 0.7$ ‰ and  $-9.3 \pm 0.5$ ‰.

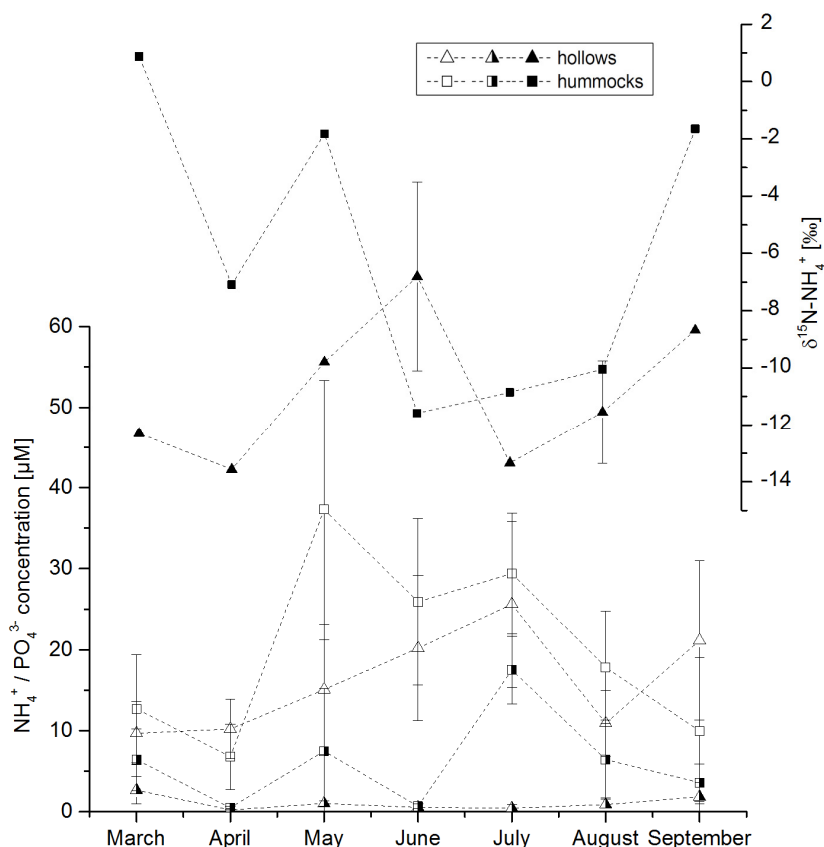


**Figure 4.4:** Isotope ranges of biomass, pore water and deposition samples. Boxes indicate inter-quartile range, whiskers indicate minimum and maximum values and center lines indicate median. n indicate: numbers of samples.

### 4.3.2. Pore water nutrient concentrations and N isotopes

Ammonium was the dominant form of dissolved N in hollows and hummocks ranging from 9.7 to 25.6  $\mu\text{M}$  and 6.8 to 37.3  $\mu\text{M}$ , respectively. Nitrate was only present at low concentrations throughout the year. The values ranged between 0.2 and 2.9  $\mu\text{M}$  in hollows and 0.7 and 2.8  $\mu\text{M}$  in hummocks. The  $\text{NO}_3^-$  concentration in hollows had a mean value of  $1.0 \pm 0.5$   $\mu\text{M}$  and  $1.6 \pm 0.6$   $\mu\text{M}$  in hummocks.  $\text{NH}_4^+$  concentrations were quite higher ( $p < 0.05$ ), showing mean values of  $15.8 \pm 7.4$   $\mu\text{M}$  and  $19.1 \pm 9.2$   $\mu\text{M}$  in hollows and hummocks, respectively. Nitrite was not detectable in all samples. Regarding the total

dissolved inorganic N, the contribution of  $\text{NH}_4^+$  was 94% in hollows and 92% in hummocks. Lowest concentrations of ammonium in both hollows and hummocks were found in March, whereas highest were observed in May and July in hummocks and hollows, respectively ( $p < 0.05$ ) (Fig. 4.5).



**Figure 4.5:** Monthly mean  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  concentrations and N isotopes of both hollows and hummocks pore water. Filled symbols indicate isotope values ( $\delta^{15}\text{N-NH}_4^+$ ), open symbols show  $\text{NH}_4^+$  concentrations and divided symbols indicate  $\text{PO}_4^{3-}$  concentrations.

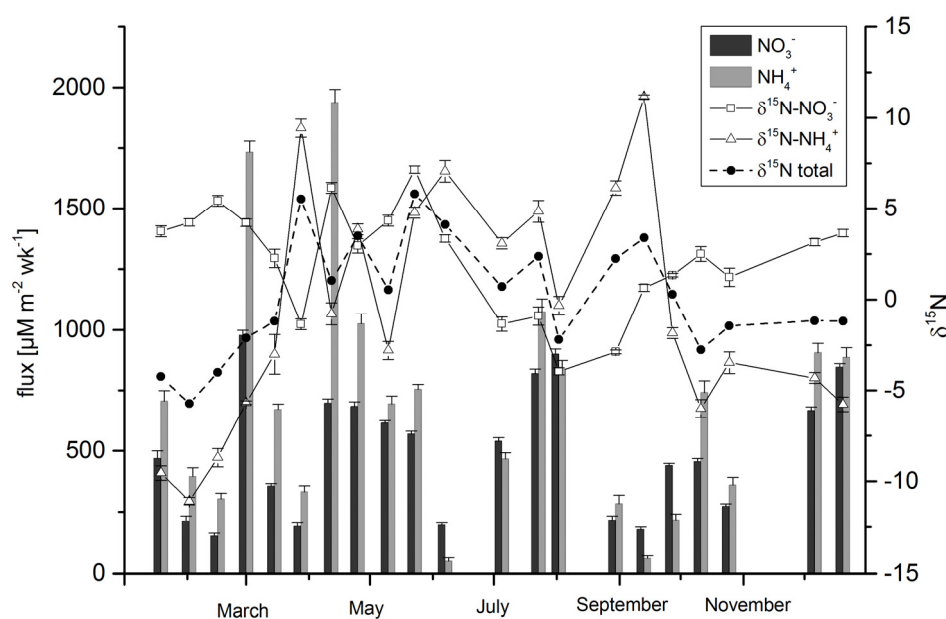
Phosphate concentrations in hollows ranged from 0.2 to 2.7  $\mu\text{M}$  and 0.5 to 17.5  $\mu\text{M}$  in hollows and hummocks, respectively (Fig. 4.5). In hollows the mean value of  $\text{PO}_4^{3-}$  was  $1.1 \pm 0.9 \mu\text{M}$ , whereas in hummocks a mean value of  $6.1 \pm 3.6 \mu\text{M}$  was observed. Concentrations in hollows were constant, while hummocks concentrations varied strongly with highest values in July and lowest in April ( $p < 0.05$ ) (Fig. 4.5).

Isotope values of ammonium were highly depleted and ranged between -13.6 and -6.8‰ in hollows. The range in hummocks was greater, where isotope values varied between -11.6 and

+0.9‰ (Fig. 4.4). Mean isotope values of ammonium were significantly higher ( $p < 0.05$ ) in hummocks ( $-6.0 \pm 5.1\%$ ) than in hollows ( $-10.9 \pm 2.5\%$ ). Regarding monthly isotopic data, the highest values were observed in June and March, the lowest in hollows and hummocks in April and June, respectively (Fig. 4.5).

### 4.3.3. Atmospheric N loads and isotopes

The annual N deposition was  $8.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  at the study site. Volume-weighted means of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were  $32.5$  and  $44.5 \text{ } \mu\text{M}$ , respectively. Hence,  $\text{NH}_4^+$  was the dominant compound in inorganic N deposition and the annual molar ratio of  $\text{NH}_4^+/\text{NO}_3^-$  was  $1.37$ .  $\text{NO}_2^-$  was always  $<1\%$  in each deposition sample. Over the annual cycle atmospheric N fluxes showed a maximum in spring and lowest fluxes in early summer and early autumn (Fig. 4.6).



**Figure 4.6:** Annual trend of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  fluxes and N isotopes in deposition samples. Bars indicate fluxes, symbols indicate isotope values.

N isotopes in deposition ranged from  $-11.1$  to  $+11.2\%$  and  $-4.0$  and  $+7.2\%$  for  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , respectively (Fig. 4.4). N weighted mean values of  $\delta^{15}\text{N}-\text{NH}_4^+$  ( $-1.7 \pm 6.4\%$ ) were significantly lower ( $p < 0.01$ ) than of  $\delta^{15}\text{N}-\text{NO}_3^-$  ( $+2.3 \pm 2.9\%$ ). Weighting both isotope values the total mean  $\delta^{15}\text{N}$  value of inorganic N deposition was  $-0.3 \pm 4.9\%$ .

Values of  $\delta^{15}\text{N-NH}_4^+$  showed a clear seasonal variation; the highest values were observed in warmer times and the lowest ones in colder times. This is opposed to the seasonal trend of  $\delta^{15}\text{N-NO}_3^-$ , where the lowest values were found in warmer times (Fig. 4.6). As being expected due to a high content of  $\text{NH}_4^+$  in N deposition, the values of total  $\delta^{15}\text{N}$  follow rather the trend of  $\delta^{15}\text{N-NH}_4^+$  values.

## 4.4. Discussion

By analysing the N concentrations and N isotopes of atmospheric deposition, *Sphagnum* biomass and pore water, we are able to test whether atmospheric  $\text{N}_R$  inputs are retained by *Sphagnum* mosses. Our results indicate that internal N cycling processes are much more important for *Sphagnum* growth than recently deposited  $\text{N}_R$ .

### 4.4.1. The nutritional status of the peat bog

In order to investigate, whether the deposited N is retained in *Sphagnum* plants in the peat bog, it is worthwhile to look at the N concentrations of prevailing *Sphagnum* species and the annual N deposition load at the site. Many studies documented that N concentrations in mosses are a reliable tool to assess the N deposition level (e.g. Harmens et al., 2011; Schroder et al., 2010).

At the site Hartshoper Moor the atmospheric N deposition load of  $8.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  is quite low for a medium polluted site in Central Europe. Other deposition studies (Beyn et al., 2014; Fowler et al., 2005b; Novak et al., 2014) showed absolute higher N deposition loads at medium polluted sites in Europe. Furthermore modelled N deposition resulted in higher N loads than the measured ones in the area of the peat bog (Simpson et al., 2011). The lower N deposition load at the site indicates a lower pollution level of atmospheric  $\text{N}_R$  species than typical medium polluted sites. The reason for that can be manifold. Around the investigated area the process of restoration is recently increasing, thus, close agricultural activities, which represent a high proportion of total N deposition at a site (Asman et al., 1998) cease to exist. However, N deposition loads usually have a high scatter between years due to changes in emissions patterns or varying meteorological conditions (Gyldenkærne et al., 2005).

Concerning the nutrient availability in the peat bog, this N load is close to the threshold of  $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  at which N-limitation in peat bogs does no longer occur. This is particularly

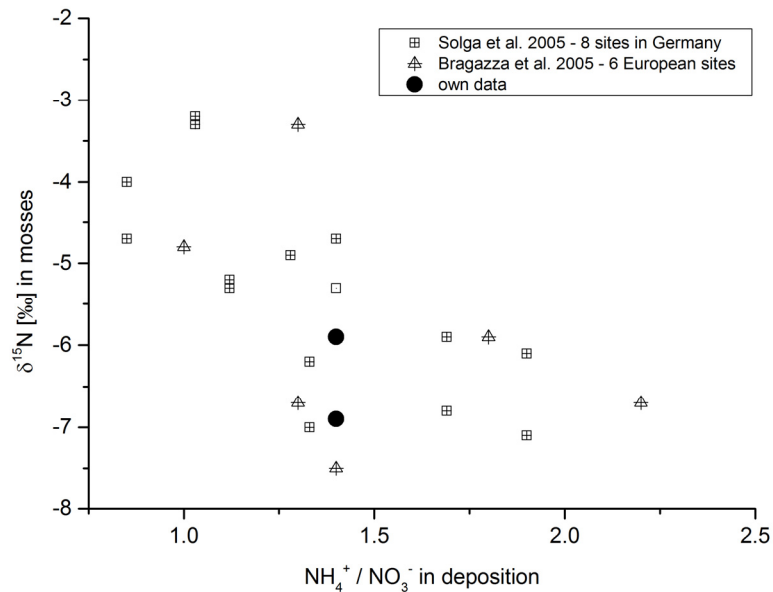
true, because organic N deposition, which includes ~10% of total N deposition in Germany (Cape et al., 2012), was not considered in our study

We tested two different approaches in order to assess the N source for *Sphagnum* growth. First, we compared the relationship between N contents in *Sphagnum* biomass and N deposition loads and second, the molar ratio of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in relation to  $\delta^{15}\text{N}$  in deposition in *Sphagnum* biomass was compared.

The annual mean N concentration of *S. cuspidatum* (1.34%) and *S. papillosum* (1.09%) in relationship to the N deposition load at our site confirmed with other observations of moss N concentration and N deposition worldwide (Bragazza et al., 2005; Pitcairn et al., 2001; Schmidt et al., 2010; Solga et al., 2005). The positive linear relationship of N concentration in mosses and N deposition load is also applicable in regions with different N deposition loads, even though the observed site is no longer N limited due to high N deposition, which is caused by metabolic adaption of *Sphagnum* plants to higher atmospheric N input (Berendse et al., 2001). Since this approach is used on a long N deposition trend, it can be supposed that *Sphagnum* plants at our site reflect the N deposition load.

Another appropriate method to assess the N source for *Sphagnum* growth is to take a look at the  $\delta^{15}\text{N}$  values of *Sphagnum* and the molar ratio of reduced and oxidised N in deposition ( $\text{NH}_4^+/\text{NO}_3^-$ ) (Solga et al., 2005). Similar to the N content vs. N deposition load approach, also this approach is often used on a large scale view on bog mosses (Zechmeister et al., 2008) and is based on the source specific  $\delta^{15}\text{N}$  values of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  deposition. In general,  $\text{NH}_4^+$  sources are  $^{15}\text{N}$  depleted and  $\text{NO}_3^-$  sources are  $^{15}\text{N}$  enriched. This is also the case at our site, where N isotopes in deposition showed higher values in  $\text{NO}_3^-$  than in  $\text{NH}_4^+$  ( $\delta^{15}\text{N}\text{-NH}_4^+$ : -1.7‰ vs.  $\delta^{15}\text{N}\text{-NO}_3^-$ : +2.3‰). The observed N isotope values represent a typical distribution for a medium polluted site (Russell et al., 1998).

Putting our data, a molar ratio of  $\text{NH}_4^+/\text{NO}_3^-$  of 1.4 and  $\delta^{15}\text{N}$  values of -5.9 and -6.9‰ for *S. cuspidatum* and *S. papillosum*, respectively, in a wider context, our data fit with previously observed relationship of the molar ratio of  $\text{NH}_4^+/\text{NO}_3^-$  in deposition and  $\delta^{15}\text{N}$  in mosses at six European sites (Bragazza et al., 2005) and at eight sites in Germany (Solga et al., 2005) (Fig. 4.7).



**Figure 4.7:** N isotopes of mosses in relation to molar ratio of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in deposition.

In summary, both approaches of the relationship between N deposition and *Sphagnum* biomass suggested that most of the deposited N is retained in *Sphagnum* mosses.

However, some other parameters that were not quite in accordance with this hypothesis indicating that the peat bog is rather P and K co-limited than N-limited. Pore water concentrations of inorganic N showed that  $\text{NH}_4^+$  is typically present at higher concentration than  $\text{NO}_3^-$  due to prevailing acidic conditions (Williams et al., 1999a). Nevertheless, in hollows and hummocks pore water concentrations of  $\text{NH}_4^+$  showed averaged volume-weighted concentrations of 15-20  $\mu\text{M}$ , which do not indicate limited conditions.

Data of P availability in the peat bog support that N was not a limiting factor. The P availability is particularly of importance in peat bogs, because a shift in nutrient availability in peat bogs from N limited to P + K co-limited conditions due to higher N supply from increasing N deposition was already observed (Bragazza et al., 2004). Furthermore, the available P is detached from atmospheric deposition, because P is not abundant in deposition; P is mostly derived by the organic substratum in peat bogs (Bates, 1992). Our  $\text{PO}_4^{3-}$  concentrations in pore water samples showed a considerable amount in hummocks only in some month; in hollows P is almost not abundant (Fig. 4.5). Thus, the ecosystem is rather P limited than N limited.

The non N-limiting conditions are supported by significantly higher  $\delta^{15}\text{N}$  values ( $p < 0.001$ ) of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition than values of both *Sphagnum* species. The mean value of total  $\delta^{15}\text{N}$  in deposition ( $-0.3\text{‰}$ ) showed about  $6\text{‰}$  higher values compared to mean  $\delta^{15}\text{N}$  values of mosses. A mentionable fractionation, which can explain the isotopic gap between *Sphagnum* biomass and N deposition, is not expectable in *Sphagnum* plants (Liu et al., 2013). Thus, the N supply for *Sphagnum* growth cannot mainly stem from direct atmospheric deposition, internal cycling processes are supposed to be much more important. The enriched N of atmospheric deposition is most likely immobilized by other organisms or processes, because isotope ranges of pore water were also significantly lower in both hollows and hummocks than values in atmospheric deposition ( $p < 0.01$ ) (Fig. 4.5, 4.6).

If *Sphagnum* plants are not the main sink for atmospheric  $\text{N}_\text{R}$ , two alternative pathways seem to be plausible. First, atmospheric  $\text{N}_\text{R}$  might be retained in pore water or it might be transported to other compartments in the peat bog. Furthermore, the dominant N source of *Sphagnum* biomass should be discussed.

#### 4.4.2. Sinks of atmospheric $\text{N}_\text{R}$

In the case, if deposited N is mostly not retained in *Sphagnum* mosses,  $\text{N}_\text{R}$  will be moved downwards into deeper soil layers. There it will be available for e.g. vascular plants (Limpens et al., 2003). Such a higher influence of deposition – derived by isotopically enriched N relative to *Sphagnum* plants – should be noticeable in the N isotope values of *Sphagnum* and vascular plants. Higher isotope ranges in dominant vascular plant *E. angustifolium* (Fig. 4.4) compared to *Sphagnum*  $\delta^{15}\text{N}$  ( $p < 0.01$ ) confirm that roots in deeper layers of the bog retained more enriched  $^{15}\text{N}$  relative to *Sphagnum* mosses (Asada et al., 2005). Additionally, vascular plants have basically a  $\text{NO}_3^-$  preference during N uptake (Falkengren-Grerup, 1995) and discriminate  $^{15}\text{N}$  during  $\text{NH}_4^+$  uptake (Evans, 2001; Handley and Scrimgeour, 1997). The remaining deposited N, which is enriched in  $^{15}\text{N}$  compared to originally substrate, is directly immobilized in peat. The process of the mobility of isotopically heavier isotope downcore to the peat layer was already observed by another study in Europe (Novak et al., 2014). This mobility is enhanced by low water tables (Blodau et al., 2006), which occur at our site in summer (Fig. 4.2). Higher N isotope values in hummocks during colder months (Fig. 4.5) are in agreement with water table dependency. However, in hollows similar characteristics cannot be observed.

A certain influence of atmospheric  $N_R$  inputs to compartments in the peat bog was only seen in hummocks pore water in colder times (March, September). At that time it appeared that hummocks were a sink for atmospheric  $N_R$ , because  $\delta^{15}N$  values in pore water (Fig. 4.5) converge to those of atmospheric  $N_R$  ( $\delta^{15}N_{total}$ , Fig. 4.6). The weak influence of atmospheric deposition on biomass growth is also noticeable in significant lower  $\delta^{15}N$  values of both *Sphagnum* plants compared to  $\delta^{15}N_{total}$  in atmospheric deposition.

#### 4.4.3. The role of remineralization as a source?

A plausible explanation for the main N supply for *Sphagnum* growth is the process of remineralization, which is supported by a study in North America (Aldous, 2002a). It concluded that the remineralized N is much more important for *Sphagnum* growth than N deposition. Other studies observed N mineralization due to higher N availability in peat bogs (Aerts et al., 1992; Williams et al., 1999a).

Considering the variations in  $NH_4^+$  concentration (Fig. 4.5), it is remarkable that highest values were observed in both hollows and hummocks in warmer times, when biological processes are relatively high. The source of this  $NH_4^+$  was not derived by direct atmospheric  $N_R$ , because in colder times atmospheric fluxes are higher than in warmer times (May-August, Fig. 4.6), the concentrations of  $NH_4^+$  in both hummocks and hollows are lowest, while in warmer times the effect is reversed. This effect might be derived from lower water tables in warmer times through evaporation, but a more meaningful explanation for increased  $NH_4^+$  concentration is the remineralization process, which can be accelerated during lower water table conditions in peat bogs (Aldous, 2002a) although the microbial activity is low in peat bogs.

Values of  $\delta^{15}N$  in pore water support the importance of remineralization processes. Mean isotope values are relatively depleted in  $^{15}N$  in hummocks and hollows compared to deposition data of  $NO_3^-$  and  $NH_4^+$ , which make recently deposited N very unlikely to be a dominant source for *Sphagnum* growth and pore water not a likely sink for deposited N. This is supported by isotope fractionation during remineralization processes, which make the product (pore water ammonium)  $\delta^{15}N$  value lower to those of substrate (biomass) (Möbius, 2013; Sanders et al., 2014). Additional to similar *Sphagnum* values, other abundant plants in wet



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patches such as *E. nigrum* and *E. tetralix* have mean  $\delta^{15}\text{N}$  values ( $-10.4 \pm 0.7\text{‰}$  and  $-9.3 \pm 0.5\text{‰}$ , respectively) being close to pore water  $\delta^{15}\text{N}$  values (Fig. 4.4).

Further, the seasonal trend of pore water concentrations and  $\delta^{15}\text{N}$  values in hummocks is influenced by the process of remineralization. At the beginning and at the end of the growing season, low temperatures lead to low biological activity and therefore less influence of  $\text{NH}_4^+$  derived by remineralization leading to lower concentrations of  $\text{NH}_4^+$  and higher N isotopes in comparison to warmer times (Fig. 4.5). Consequently, the limited influence of remineralized N in colder times led to a higher influence of N deposition resulting in higher  $\delta^{15}\text{N}$  values in hummocks pore water. This effect was decreased when warmer temperatures increased internal cycling processes mitigating the influence of atmospheric deposition. Thus, during warmer times remineralized N is the main source for available N in the peat bog.

The variations of pore water  $\delta^{15}\text{N}$  values was only observed in hummocks, where atmospheric deposition has morphologically a higher impact than in hollows, where the general nutrient pool was much greater. This low influence on hollows can be confirmed by constant  $\delta^{15}\text{N}$  values of pore water throughout the year. Another indicator for low impact of N deposition is the variation of mosses  $\delta^{15}\text{N}$  values in the investigated period, which are constantly depleted in  $^{15}\text{N}$  (Fig. 4.3).

The weak influence of atmospheric  $\text{N}_\text{R}$  inputs was confirmed by the temporal trend of  $\delta^{15}\text{N}_\text{total}$  values in deposition (Fig. 4.6). The highest values were observed in warmer times (May–August), when the lowest  $\delta^{15}\text{N}$  values were noticed in hummocks pore water samples (Fig. 4.5). Due to that anti-correlation, atmospheric N deposition was unlikely to be an important N source during that time. Due to the greater N pool of hollows, N deposition had no noticeable influence on hollows pore water.

In summary, in the investigated peat bog the process of remineralization was the main N source for biomass growth of *Sphagnum* plants. Most of the atmospheric N inputs were moved downwards to deeper layers, where atmospheric  $\text{N}_\text{R}$  was used by vascular plants or is incorporated into the peat layer.

## 4.5. Conclusion

Atmospheric N deposition plays a minor role for the growth of dominant *S. cuspidatum* and *S. papillosum* in the investigated peat bog. The dominant source for these mosses was recycled

N, which originated from the process of remineralization. Indicators for this conclusion were the highest available  $\text{NH}_4^+$  concentrations in pore water with concurrent very low  $\delta^{15}\text{N}$  values and on average ~6‰ lower values of *Sphagnum* biomass in comparison to the mean of total  $\delta^{15}\text{N}$  in deposition at warmer times. Thus,  $\delta^{15}\text{N}$  values in atmospheric deposition are not reflected in  $\delta^{15}\text{N}$  values of both *Sphagnum* mosses.

The fate of deposited N was not directly noticeable, because the peat bog was N saturated and the pool of existing N in pore water was much bigger. The noticeable influence of N deposition was only seen in times of less biological activity and only in hummocks, which have morphologically a greater influence of deposition. Enriched deposited  $^{15}\text{N}$  was moved downwards, where it was immobilized by assimilation processes to the peat layer or utilised by vascular plants.

## 5. Conclusion and Outlook

### 5.1. Conclusion

The outlined rationale and the results of this thesis provide an overview of the role of stable nitrogen isotopes in atmospheric deposition. Historical  $\text{NO}_x$  emission reduction as well as the change of  $\text{NO}_x$  source pattern could be identified in N isotopes of atmospherically deposited  $\text{NO}_3^-$ . Higher  $\delta^{15}\text{N}$  values in deposited  $\text{NO}_3^-$  compared to historical values and higher  $\delta^{15}\text{N}\text{-NO}_3^-$  values at the site with lower N pollution level are the main findings of this thesis. The cause of the observations are the implementation of catalytic converters in  $\text{NO}_x$  sources and the higher influence of  $\text{NO}_x$  emissions by ships at the marine site in List than the terrestrial site in Geesthacht. Furthermore, despite the overall reduction of N deposition for the last 30 years, atmospheric  $\text{N}_R$  inputs are not the main source for *Sphagnum* growth in a Northern Germany peat bog; the main  $\text{N}_R$  requirements for peat mosses is rather given by the process of remineralization.

Since the end of the 1980s  $\text{NO}_x$  emissions are declining due to political regulations and the implementation of  $\text{NO}_x$  reduction technologies, which consequently affect N deposition. A medium polluted site in Geesthacht was chosen in order to investigate the change. Considering the change of the  $\text{NO}_x$  emission and the known  $\delta^{15}\text{N}$  ranges of emitting  $\text{NO}_x$  sources in Germany only, the hypothesis was that both  $\text{NO}_3^-$  fluxes and  $\delta^{15}\text{N}\text{-NO}_3^-$  values decrease. Besides an expected decrease of  $\text{NO}_3^-$  deposition fluxes, a fundamental increase of N isotopes in deposited  $\text{NO}_3^-$  was observed in comparison to those from the 1980s in Germany. Backward trajectories suggest that the origin of increasing  $\delta^{15}\text{N}\text{-NO}_3^-$  values was caused by land-based sources. This is supported by a detailed view on the historical and nowadays results indicating that the differences are noticed from autumn till spring, not in summer. The values in summer can be explained by an enhanced effect of  $^{15}\text{N}$  depleted  $\text{NO}_x$  by soil emission and a mitigated effect of  $^{15}\text{N}$  enriched  $\text{NO}_x$  by power plant emissions can be observed. The implementations of catalytic converters have shifted the isotope range of power plants and land-based traffic  $\text{NO}_x$  positively and thus led to higher N isotopes in  $\text{NO}_3^-$  deposition.

The impact of lower atmospheric  $\text{N}_R$  pollution level on N deposition load and N isotopes at a coastal site compared to a terrestrial site resulted both in expectable and surprising findings. Due to higher anthropogenic imprint at the terrestrial site Geesthacht higher N loads and

higher N isotopes at this site compared to the coastal site were expected. Higher  $\text{NH}_4^+$  fluxes in dry and wet deposition at Geesthacht were found, while higher  $\text{NO}_3^-$  fluxes and higher  $\delta^{15}\text{N}-\text{NO}_3^-$  values were observed at the marine site in List. As expected, the higher impact of  $\text{NH}_3$  sources in Geesthacht explains the higher fluxes of  $\text{NH}_4^+$  at this site. But higher  $\text{NO}_3^-$  loads and concurrent higher  $\delta^{15}\text{N}-\text{NO}_3^-$  values at the coastal site reveal that  $\text{NO}_x$  pollution level is not the main driver for the observed values, because in this case a higher anthropogenic imprint would lead to higher N isotopes of deposited  $\text{NO}_3^-$  at the urban site. Due to marine air-masses reaching the site in List more frequently than ones in Geesthacht, the observed  $\text{NO}_3^-$  data are originated from marine areas. The most reliable explanation for the  $\text{NO}_3^-$  loads are  $\text{NO}_x$  emissions by ships and sea-salt aerosol impact. The cause for higher N isotope observations is derived by ship emission in general, shipping fuels and  $\text{NO}_x$  reduction technologies in ship engines. However, reduction technologies in ship engines have a smaller impact on the N isotopes in deposition, because the use of these technologies is still optional in European seas.

The consideration of N isotopes in deposition is useful for evaluating N requirements for *Sphagnum* mosses in peat bogs, since atmospheric N inputs are usually retained by them. Expected N deposition loads lead to the assumption that N Isotopes of *Sphagnum* species reflect N isotopes of deposited N ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ). Investigations of N isotopes in deposition and *Sphagnum* mosses in a raised peat bog in Northern Germany reveal that recent N deposition fluxes in the peat bog are not the main N supply for dominant *Sphagnum* mosses, because significantly higher  $\delta^{15}\text{N}$  values in total N deposition are observed than in *Sphagnum* biomass. In this raised peat bog ecosystem recycled N is incorporated into the biomass of mosses mainly; here the process of remineralization is the main  $\text{N}_R$  source for *Sphagnum* mosses.

## 5.2. Outlook & Future Work

This thesis provides new insights into N isotopes of atmospheric deposition in Central Europe, but also emerges some new challenges.

In general, the  $\text{NO}_x$  concentration affects ecosystems long before the  $\text{NO}_x$  level threatens human health. Nevertheless, technologies of  $\text{NO}_x$  reduction have primarily the aim to improve the air quality and to reduce health risks; the consequences for ecosystems are a

positive concomitant phenomenon. However, the reduction is not consistent over all NO<sub>x</sub> sources. Until now, the political regulations are mostly limited on land-based sources like road traffic and power plants, severe reduction efforts for NO<sub>x</sub> emissions by ships are missing until now in Europe. This status will probably become worse in future, because national discussions have mostly focused on the potential to reduce particulate matter and other pollutants of land-based sources (Bultjes et al., 2012). Therefore NO<sub>x</sub> emissions by ships are getting more important for N deposition in Europe. To sum up, the flux of atmospheric NO<sub>3</sub><sup>-</sup> deposition to ecosystems decreased, but with concurrent rising contribution of ship emissions.

Chapter 3 implicated that NO<sub>x</sub> emission by ships have a distinct influence on N deposition, especially in coastal regions. Since no isotope ranges of NO<sub>x</sub> emissions by ships are available, it is worthwhile in future works to this range. This can be achieved by close to source sampling of dry deposition for instance at frequently used ship tracks at the Elbe estuary.

The focus of the thesis was on the study of the inorganic fraction of N deposition. Nevertheless, the organic part in dry and wet N deposition is not negligible and in most cases bioavailable and not toxic (Cornell et al., 2003). In Germany there are only rare results of organic bulk N deposition (Cape et al., 2012). Therefore, it is of advantage to determine the organic part in a wider spatial and temporal resolution to conclude about influencing parameters of this part in Germany, which do not originate directly from fertilizer washout or from cycling processes. Quantifying organic N includes methodically the inorganic part, thus, it is possible to conclude about total atmospheric N loads to ecosystems. Furthermore, it is recommended that N deposition studies in Germany include the organic part. Nevertheless, if deposited organic N is part of future works, the time between storage and measuring has to be short, because the organic part has a higher tendency to volatilize than NH<sub>4</sub><sup>+</sup>, even when the sample is frozen (Cape et al., 2011; Keene et al., 2002).

The applied method for measuring dry deposition (passive sampling) in chapter 2 and 3 provides a good reproducibility in comparison to active sampling of particle and gaseous compounds in the Mediterranean Sea (Kouvarakis et al., 2001). Nevertheless, measured dry deposition NH<sub>4</sub><sup>+</sup> fluxes at the investigated sites are lower than modelled data. However, since N loads and isotopes of dry deposition give reliable data, there is no reason to doubt the measured data. To close this gap, it is worthwhile to verify modelling data with a widely spread dry N deposition measurements and to look more in detail into dry N deposition

measurements with a size-segregating sampling of the particulate phase and separate gaseous  $N_R$  sampling. With this kind of sampling the exact influence of sea salt aerosols to N deposition load, especially at coastal sites, can be determined. Overall, the improvements in modelling of atmospheric  $N_R$  compounds can help to estimate dry N deposition loads in more detail.

## Figure captions

- Figure 1.1: Trends in Human population and fertilizer use in the 20<sup>th</sup> century (edited after Erisman et al., 2008).
- Figure 1.2: Calculated N-Deposition flux ( $\text{mg N m}^{-2}$ ) to semi-natural ecosystems in Europe for the year 2000 (Simpson et al., 2011).
- Figure 1.3: Illustration of inorganic  $\text{N}_R$  species pathways in the atmosphere (edited after Hertel et al., 2006).
- Figure 1.4: Proportion of main sources to Germanys  $\text{NO}_X$  inventory in 2010 and their  $\delta^{15}\text{N-NO}_X$  ranges.
- Figure 2.1: Known  $\delta^{15}\text{N}$  values in  $\text{NO}_X$  emissions from natural and anthropogenic sources. Data are compiled from Ammann et al., 1999; Heaton, 1990; Li and Wang, 2008; Moore, 1977; Pearson et al., 2000.
- Figure 2.2: Location of study sites in Germany: Sampling site addressed in this study (capitals), EMEP stations considered (bold), and stations with available isotope data (underlined).
- Figure 2.3:  $\text{NH}_4^+/\text{NO}_3^-$  molar ratios (top) and  $\text{NH}_4^+$  and  $\text{NO}_3^-$  fluxes (bottom) of each sample in wet (a) and dry (b) deposition at our study site, wet and dry flux measurements implicate and error bar, which is smaller than the measurement points.
- Figure 2.4:  $\delta^{15}\text{N-NO}_3^-$  values of each wet and dry deposition sample (a) (error bars are smaller than symbol size), weekly precipitation amount (b) and daily mean temperature (c) and our study site.
- Figure 2.5: Mean backward trajectories of cluster analysis (#1 to #6) including all (161) backward trajectories and its N weighted mean  $\delta^{15}\text{N-NO}_3^-$  values (a) and seasonally dependent sample attribution to each cluster number (b).

Figure 2.6: Winter (a), spring (b), summer (c) and autumn (d)  $\delta^{15}\text{N-NO}_3^-$  values of own study site (left panel) in 2011-12 and historical sites in Germany (right panel). Box-whisker plots indicate: inter-quartile range (boxes), minimum and maximum values (whiskers) and median (center line) of wet and dry deposition samples; filled squares indicate N-weighted mean of all deposition samples and , SD at our site. Empty squares: N-weighted means and SD of bulk deposition samples at Ahrensburg (1980-83), Jülich (1979-84) and Deuselbach (1979-84) (Freyer, 1991). n: numbers of samples,  $\rho$ : imply the comparison of Geesthacht N-weighted mean and respective study sites. Asterisk: statistically significantly differences between historical and present isotope data. No statistical test was conducted with Ahrensburg data in winter (2.6a), because the number of samples (n=3) was too low for statistical analysis.

Figure 3.1: Location of the study site Geesthacht and List on Sylt.

Figure 3.2: Monthly  $\text{NO}_3^-$  (top panel) and  $\text{NH}_4^+$  (horizontal middle panel) fluxes and molar ratio of  $\text{NH}_4^+/\text{NO}_3^-$  (bottom panel) at both sites, left panel indicate (a, c, g): dry deposition, vertical middle panel (b, e, h) indicate: wet deposition, right panel indicate: total deposition (c, f, i), asterisk: statistically significant differences between study sites.

Figure 3.3: Monthly N-weighted  $\delta^{15}\text{N-NO}_3^-$  values in dry (a), wet (b) and total (c) deposition at both study sites, asterisk: statistically significant differences between study sites.

Figure 4.1: Location of the study site in Northern Germany.

Figure 4.2: Trend of temperature, precipitation and water table at the sampling site in 2012.

Figure 4.3: Monthly mean N concentrations and  $\delta^{15}\text{N}$  values of both *Sphagnum* mosses. Filled symbols indicate: N concentration (N%), open symbols indicate: isotope values ( $\delta^{15}\text{N}$ ).

Figure 4.4: Isotope ranges of biomass, pore water and deposition samples. Boxes indicate inter-quartile range, whiskers indicate minimum and maximum values and center lines indicate median. n indicate: numbers of samples.



Figure 4.5: Monthly mean  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  concentrations and N isotopes of both hollows and hummocks pore water. Filled symbols indicate isotope values ( $\delta^{15}\text{N-NH}_4^+$ ), open symbols show  $\text{NH}_4^+$  concentrations and divided symbols indicate  $\text{PO}_4^{3-}$  concentrations.

Figure 4.6: Annual trend of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  fluxes and N isotopes in deposition samples. Bars indicate fluxes, symbols indicate isotope values.

Figure 4.7: N isotopes of mosses in relation to molar ratio of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in deposition.

## Table captions

- Table 1.1: Collection of worldwide measured isotopic ranges of atmospheric  $\text{NO}_3^-$  species.
- Table 2.1:  $\text{NO}_x$  absolute and relative emission inventory of Germany in 1990 and 2010 and source specific changes - including the major sources road traffic, industry/power plants, soil volatilization and ship traffic (after UBA, 2012).
- Table 2.2: Seasonally volume-weighted mean flux of nitrate and ammonium and N-weighted mean isotopes in wet (W) and dry (D) Deposition; nw: numbers of wet deposition samples, nd: numbers of dry deposition samples.
- Table 3.1: Overview of mean meteorological parameter and mean deposition fluxes at both sites, prec. indicate: precipitation, T indicate: mean temperature, rH indicate: mean relative humidity; nw indicate: numbers of wet deposition samples, nd indicate: numbers of dry deposition samples.
- Table 3.2: Mean N-weighted  $\delta^{15}\text{N}$ - $\text{NO}_3^-$  data of wet, dry and total deposition at both sites.
- Table 3.3: Air-mass origin of cluster analysis including all backward trajectories at both sites.
- Table 3.4: Correlation coefficients ( $r^2$ ) and significance levels of  $\delta^{15}\text{N}$  values with  $\text{NH}_4^+/\text{NO}_3^-$  molar ratio of sample and mean temperature, humidity and radiation during sample times. \* indicate:  $p < 0.05$ , \*\* indicate:  $p < 0.001$ , N/A indicate: not available data.
- Table A1: Deposition data of Geesthacht.
- Table A2: Deposition data of List.
- Table A3: Deposition data of two bulk sampler in the Hartshoper Moor.
- Table A4: Pore water data of hollows and hummocks in the Hartshoper Moor.
- Table A5: Biomass data of Hartshoper Moor.

## List of abbreviations

ANOVA	One-Way Analysis of Variation
CMAQ	Community Multiscale Air Quality model
DIN	dissolved inorganic nitrogen
ECA	Emission Control Areas
EMEP	European Monitoring and Evaluation Programme
GF/F	Glass fibre filter, grad F
GDAS	Global Data Assimilation System
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory model
IAEA	International Atomic Energy Agency
IMO	International Maritime Organization
NH <sub>x</sub>	all reduced atmospheric N species
N <sub>R</sub>	reactive nitrogen
NO <sub>x</sub>	atmospheric NO and NO <sub>2</sub>
NO <sub>y</sub>	all oxidized atmospheric N species
MARPOL	International Convention for Prevention of Marine Pollution from ships
NCEP	National Centers for Environmental Prediction
ρ	level of significance (rho)
SCR	Selective Catalytic Reduction
SO <sub>x</sub>	atmospheric sulphur oxides
UBA	Umweltbundesamt
USGS	United States Geological Survey
WADOS	Wet And Dry Only deposition Sampler

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# Appendix

Following data were used for the three publications:

**Table A1:** Deposition data of Geesthacht.

Wet Deposition					Dry Deposition				
Date	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N- NO <sub>3</sub> <sup>-</sup> [‰]	Volume [l]	Date	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N- NO <sub>3</sub> <sup>-</sup> [‰]	Volume [l]
02.12.2011	97.5	137.3	+2.3	0.053	02.12.2011	11.2	12.0	+8.1	0.17
09.12.2011	28.9	47.9	+5.0	0.890	09.12.2011	11.8	16.0	+8.5	0.177
16.12.2011	26.8	33.3	+5.2	0.784	06.01.2012	63.4	36.4	+4.2	0.204
23.12.2011	46.5	45.7	+0.3	0.181	20.01.2012	26.7	23.7	+6.8	0.17
30.12.2011	49.1	73.5	+1.9	0.264	27.01.2012	15.8	12.5	+4.2	0.175
06.01.2012	16.7	28.1	+2.4	0.850	03.02.2012	18.5	18.0	+11.0	0.152
13.01.2012	45.5	54.1	+4.7	0.292	10.02.2012	15.3	13.6	+7.2	0.203
20.01.2012	46.5	68	+2.0	0.238	17.02.2012	19.7	16.8	+6.0	0.167
27.01.2012	15.1	17.4	+3.9	0.636	27.02.2012	13.6	49.0	+8.5	0.159
17.02.2012	32.2	65	+0.1	0.112	02.03.2012	18.3	16.2	+4.0	0.172
24.02.2012	98.6	171.4	+1.3	0.127	09.03.2012	14.3	21.5	+11.6	0.186
02.03.2012	84.4	148.9	+4.9	0.225	19.03.2012	17.6	13.5	+7.8	0.191
09.03.2012	60.2	96	+0.8	0.132	23.03.2012	6.6	7.5	+5.6	0.158
05.04.2012	243	389	+0.7	0.178	30.03.2012	12.7	22.6	+1.7	0.18
13.04.2012	127.9	233.0	+0.7	0.177	05.04.2012	8.3	18.8	+6.9	0.17
27.04.2012	76.5	123.0	-0.5	0.209	13.04.2012	6.5	4.3	+2.1	0.159
07.05.2012	100.3	184.3	-1.4	0.045	19.04.2012	12.1	15.7	+6.0	0.205
14.05.2012	80.4	154.7	-2.4	0.196	27.04.2012	10.5	5.7	+3.7	0.219
21.05.2012	183.9	281.2	+0.7	0.036	07.05.2012	31.8	11.5	-1.4	0.171
04.06.2012	30.4	39.5	-4.0	0.451	21.05.2012	18.1	7.4	+1.4	0.239
11.06.2012	62.9	120.1	-1.6	0.306	30.05.2012	25.4	7.9	-4.5	0.222
18.06.2012	61.1	94.4	-6.0	0.298	04.06.2012	5.6	1.4	+2.9	0.209
25.06.2012	25.1	29.7	-1.9	0.409	11.06.2012	8.5	2.1	+0.8	0.206
02.07.2012	22.1	39.3	-5.4	0.809	18.06.2012	10.3	2.1	-1.4	0.198
09.07.2012	14.6	21.8	-6.0	1.287	25.06.2012	10.9	1.9	-2.7	0.254
16.07.2012	25.7	56.9	-0.5	0.736	02.07.2012	12.3	0.5	-1.6	0.224
23.07.2012	18.6	37.7	+1.0	1.643	09.07.2012	8.9	0.4	-4.2	0.219
30.07.2012	56.8	121.3	-4.4	0.458	16.07.2012	6.9	7.3	+2.0	0.22
06.08.2012	55.8	129.8	-3.1	0.275	23.07.2012	1.5	3.5	n.a.	0.209
13.08.2012	51.1	144.8	-1.2	0.273	30.07.2012	12.2	5.3	-1.5	0.219



Table A1, continued.

Wet Deposition					Dry Deposition				
Date	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N- NO <sub>3</sub> <sup>-</sup> [‰]	Volume [l]	Date	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N- NO <sub>3</sub> <sup>-</sup> [‰]	Volume [l]
20.08.2012	18.8	59.3	-5.0	0.187	08.08.2012	7.5	4.8	-0.8	0.214
27.08.2012	85.2	218.6	-5.0	0.143	13.08.2012	2.4	7.5	n.a.	0.175
03.09.2012	35.5	102.7	+2.1	0.247	20.08.2012	5.3	6.1	-4.4	0.214
10.09.2012	46.4	84.1	0.0	0.245	28.08.2012	7.1	7.6	-1.6	0.202
17.09.2012	43.0	111.3	-0.7	0.184	03.09.2012	12.8	8.3	-3.9	0.198
24.09.2012	76.7	114.6	+2.5	0.147	10.09.2012	4.6	7.7	+1.8	0.241
01.10.2012	39.2	48.8	-4.4	0.383	17.09.2012	4.6	6.9	+2.5	0.221
08.10.2012	11.4	9.5	+2.3	1.284	25.09.2012	3.4	36.7	+4.1	0.243
15.10.2012	34.2	27.7	+0.8	0.476	01.10.2012	2.3	11.9	n.a.	0.226
05.11.2012	91.1	110.2	+1.7	0.204	08.10.2012	3.6	10.6	+6.6	0.234
12.11.2012	89.8	120.7	+2.9	0.200	15.10.2012	2.6	7.0	n.a.	0.198
19.11.2012	195.8	207.5	+0.2	0.060	22.10.2012	5.3	7.2	+2.4	0.176
26.11.2012	70.3	56.8	+0.8	0.097	29.10.2012	3.1	10.3	+4.5	0.167
03.12.2012	93.2	78.7	+1.9	0.131	08.11.2012	4.6	12.5	+7.2	0.188
10.12.2012	62.1	39.0	+0.8	0.564	12.11.2012	3.4	10.8	+6.4	0.137
17.12.2012	39.8	32.3	+2.4	0.306	19.11.2012	9.6	19.2	+5.4	0.182
24.12.2012	51.2	42.1	+3.5	0.523	27.11.2012	8.0	18.2	+4.5	0.205
31.12.2012	24.1	42.3	+2.5	0.593	03.12.2012	3.7	7.8	+5.0	0.183
07.01.2013	45.5	66.6	+0.3	0.503	11.12.2012	10.2	13.4	+7.6	0.195
14.01.2013	67.6	83.3	-2.2	0.438	20.12.2012	20.6	26.9	+4.2	0.183
28.01.2013	50.6	45.5	+0.9	0.120	04.01.2013	22.0	23.4	+6.5	0.173
04.02.2013	32.1	48.0	+2.0	0.769	10.01.2013	13.1	16.2	+3.2	0.125
11.02.2013	32.1	44.1	+1.0	0.326	16.01.2013	9.2	12.0	+4.5	0.19
25.02.2013	141.6	174.1	-1.7	0.220	24.01.2013	12.4	15.6	+4.4	0.164
11.03.2013	34.8	85.2	-4.1	0.298	28.01.2013	18.1	18.6	+5.7	0.115
25.03.2013	45.8	65.3	-2.4	0.174	07.02.2013	13.8	16.2	+8.0	0.192
15.04.2013	142.5	315.8	-0.7	0.320	14.02.2013	6.8	11.3	+4.4	0.228
22.04.2013	58.2	231.3	-5.4	0.196	25.02.2013	28.5	30.9	+0.8	0.155
29.04.2013	93.6	207.6	-5.5	0.328	13.03.2013	21.7	52.5	+5.4	0.212
13.05.2013	67.6	188.9	-4.3	0.289	25.03.2013	13.1	45.0	+7.4	0.156
20.05.2013	50.6	114.9	-3.7	0.828	15.04.2013	23.3	36.9	+5.5	0.24
27.05.2013	19.3	26.7	-6.6	1.828	29.04.2013	24.7	19.2	+2.1	0.215
03.06.2013	113.6	308.0	-6.1	0.027	13.05.2013	34.6	18.4	-1.5	0.209
17.06.2013	31.6	98.2	-1.8	0.773	29.05.2013	31.3	10.6	-0.2	0.236

## Appendix

**Table A2:** Deposition data of List.

Wet deposition					Dry deposition				
Date	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N- NO <sub>3</sub> <sup>-</sup> [‰]	Volume [l]	Date	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N- NO <sub>3</sub> <sup>-</sup> [‰]	Volume [l]
01.05.2012	65.8	82.0	-0.7	0.099	02.05.2012	23.6	0.6	-2.4	0.282
13.05.2012	91.0	131.0	-0.7	0.407	07.05.2012	18.8	0.4	-0.1	0.23
20.05.2012	103.0	56.0	-4.1	0.072	15.05.2012	36.5	4.9	+1.4	0.224
13.06.2012	62.7	56.8	-2.3	0.384	21.05.2012	29.7	0.3	-0.2	0.237
17.06.2012	45.7	48.5	-2.5	0.274	29.05.2012	58.1	0.6	-3.1	0.234
18.06.2012	11.6	24.2	-4.6	1.052	30.05.2012	24.2	6.6	-0.2	0.2
27.06.2012	18.1	25.4	-1.5	0.795	13.06.2012	24.0	9.7	-0.1	0.2
03.07.2012	31.5	39.6	-5.0	0.297	27.06.2012	54.1	2.4	-1.4	0.213
09.07.2012	8.5	25.4	-5.8	1.479	03.07.2012	10.7	1.1	-2.1	0.2
15.07.2012	36.3	31.8	-2.0	0.237	09.07.2012	20.9	1.1	-1.0	0.2
26.07.2012	11.8	11.7	-0.9	0.559	15.07.2012	53.2	3.1	-0.1	0.2
31.07.2012	21.8	40.5	-3.3	0.872	26.07.2012	71.4	4.9	-0.3	0.2
08.08.2012	23.5	35.1	-2.3	0.993	31.07.2012	25.6	1.6	-1.2	0.2
22.08.2012	26.4	44.2	-3.5	0.711	08.08.2012	56.0	2.4	-0.1	0.2
25.08.2012	52.7	94.8	-3.2	0.554	29.08.2012	84.9	5.2	+0.7	0.2
26.08.2012	6.2	15.3	-0.8	1.059	05.09.2012	42.3	3.1	+0.9	0.2
05.09.2012	38.9	32.4	-4.2	0.237	19.09.2012	53.2	2.3	+4.2	0.2
12.09.2012	39.9	26.3	+0.4	0.244	26.09.2012	9.9	2.8	+5.7	0.2
19.09.2012	18.5	18.4	+1.1	0.532	04.10.2012	28.6	3.2	+5.9	0.2
20.09.2012	16.3	10.6	+0.7	0.289	11.10.2012	16.0	0.7	+4.1	0.2
21.09.2012	19.6	28.1	-3.5	0.754	17.10.2012	22.1	1.5	+10.2	0.2
24.09.2012	21.3	12.0	+0.3	0.565	31.10.2012	43.4	7.6	+3.5	0.2
04.10.2012	30.3	22.1	+3.2	1.686	07.11.2012	31.3	4.5	+7.0	0.2
05.10.2012	15.9	8.0	+1.2	0.405	14.11.2012	75.2	45.8	+5.5	0.2
06.10.2012	15.0	5.9	-1.9	0.237	21.11.2012	38.9	12.7	+6.1	0.2
07.10.2012	17.6	9.1	-2.4	0.094	29.11.2012	34.7	5.2	+6.8	0.2
10.10.2012	8.4	3.6	-0.6	0.118	06.12.2012	20.4	2.9	+6.8	0.25
12.10.2012	42.6	29.9	-1.8	0.226	12.12.2012	22.5	4.7	+5.4	0.2
13.10.2012	35.8	29.7	+2.3	0.112	19.12.2012	95.6	20.5	+4.5	0.2
14.10.2012	55.5	57.2	+2.9	0.083	03.01.2013	126.8	18.8	+4.9	0.2
15.10.2012	35.9	27.5	+3.3	0.153	09.01.2013	37.6	4.5	+2.8	0.2
16.10.2012	43.6	38.7	+4.2	0.376	16.01.2013	25.5	1.7	+4.7	0.2
31.10.2012	38.9	36.3	+0.6	1.192	23.01.2013	24.2	6.7	+8.9	0.2
07.11.2012	26.8	25.2	+6.0	1.407	30.01.2013	50.3	15.4	+6.5	0.2
14.11.2012	42.0	16.8	+5.0	0.199	06.02.2013	29.5	6.6	+7.0	0.2
29.11.2012	47.5	39.7	+0.7	0.643	21.02.2013	45.4	16.8	+3.0	0.2

Table A2: continued.

Wet deposition					Dry deposition				
Date	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N- NO <sub>3</sub> <sup>-</sup> [‰]	Volume [l]	Date	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N- NO <sub>3</sub> <sup>-</sup> [‰]	Volume [l]
06.12.2012	96.1	54.9	+0.2	0.45	06.03.2013	64.2	25.1	+4.8	0.2
12.12.2012	27.9	11.3	-0.2	0.466	14.03.2013	24.0	5.8	+8.0	0.2
19.12.2012	60.1	35.1	+2.1	0.394	26.03.2013	40.5	17.4	+10.9	0.2
03.01.2013	47.5	30.4	+2.6	1.276	18.04.2013	47.4	15.7	+3.1	0.2
09.01.2013	51.0	16.2	+1.9	0.355	24.04.2013	26.1	4.4	+4.1	0.2
30.01.2013	37.8	30.0	+3.0	0.91	02.05.2013	32.1	2.6	+3.3	0.2
06.02.2013	24.9	9.3	+4.5	0.449	08.05.2013	41.7	3.6	+1.9	0.2
21.02.2013	86.5	54.7	-2.5	0.094	16.05.2013	41.6	5.8	+1.8	0.2
14.03.2013	70.1	44.9	+0.7	0.1					
26.03.2013	63.1	61.0	-0.7	0.061					
11.04.2013	48.2	12.4	+7.4	0.22					
18.04.2013	89.7	139.6	-3.3	0.442					
02.05.2013	124.7	244.1	-2.1	0.097					
08.05.2013	49.2	111.0	-7.0	0.259					
16.05.2013	56.8	102.5	-4.1	0.602					

Table A3: Deposition data of two bulk sampler in the Hartshoper Moor.

Date	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N-NO <sub>3</sub> <sup>-</sup> [‰]	δ <sup>15</sup> N-NH <sub>4</sub> <sup>+</sup> [‰]	Volume [l]
19.01.2012	19.2	29.4	+3.6	-9.3	3.785
	19.6	29.0	+3.8	-9.7	3.795
02.02.2012	19.0	35.4	+4.0	-10.9	0.690
	19.3	36.2	+4.4	-11.4	0.696
16.02.2012	149.8	306	+5.2	-9.0	0.060
	151.0	298	+5.6	-8.4	0.066
01.03.2012	71.2	127.4	+4.1	-5.9	0.870
	73.2	128.6	+4.3	-5.5	0.859
15.03.2012	79.2	150.1	+2.1	-3.1	0.282
	81.4	152.7	+2.4	-2.9	0.274
28.03.2012	342.9	601.1	-1.2	+9.1	0.032
	347.1	609.9	-1.6	+9.7	0.032
12.04.2012	48.1	133.6	+5.9	-0.4	0.910
	48.8	135.5	+6.3	-1.2	0.900
25.04.2012	99.3	149.0	+3.1	+3.9	0.399
	100.4	150.8	+2.9	+4.0	0.400

## Appendix

**Table A3:** continued.

Date	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N-NO <sub>3</sub> <sup>-</sup> [‰]	δ <sup>15</sup> N-NH <sub>4</sub> <sup>+</sup> [‰]	Volume [l]
10.05.2012	50.6	57.0	+4.5	-2.7	0.805
	50.8	57.4	+4.1	-2.9	0.815
23.05.2012	31.0	41.1	+7.2	+4.6	1.062
	31.4	41.7	+7.1	+4.9	1.061
07.06.2012	49.0	12.6	+3.4	+7.2	0.260
	49.7	12.8	+3.3	+7.1	0.270
05.07.2012	30.3	26.4	-1.2	+3.1	2.251
	30.4	26.2	-1.3	+3.0	2.210
23.07.2012	18.3	24.1	-0.8	+4.9	3.610
	18.5	24.4	-1.0	+4.8	3.520
02.08.2012	47.1	44.0	-3.9	-0.1	0.831
	48.3	44.7	-4.2	-0.5	0.860
30.08.2012	48.0	63.7	-2.9	+6.0	0.553
	49.1	64.0	-3.0	+6.3	0.560
13.09.2012	23.2	8.0	+0.6	+11.0	0.471
	28.9	7.9	+0.8	+11.5	0.490
27.09.2012	14.4	6.3	+1.1	-1.5	1.902
	14.1	7.6	+1.5	-2.0	1.962
11.10.2012	18.0	30.0	+2.4	-6.1	1.538
	18.9	30.3	+2.6	-5.8	1.557
25.10.2012	29.4	38.0	+1.1	-3.3	0.570
	28.5	38.5	+1.4	-3.6	0.609
06.12.2012	39.1	53.7	+2.9	-3.7	3.158
	40.0	54.1	+3.2	-5.0	3.171
20.12.2012	40.5	42.3	+3.5	-5.9	1.302
	41.0	44.1	+3.8	-5.6	1.294

**Table A4:** Pore water data of hollows and hummocks in the Hartshoper Moor.

	<b>hollows</b>				<b>hummocks</b>			
	<b>PO<sub>4</sub><sup>3-</sup></b> <b>[μM]</b>	<b>NO<sub>3</sub><sup>-</sup></b> <b>[μM]</b>	<b>NH<sub>4</sub><sup>+</sup></b> <b>[μM]</b>	<b>δ<sup>15</sup>N-</b> <b>NH<sub>4</sub><sup>+</sup></b> <b>[‰]</b>	<b>PO<sub>4</sub><sup>3-</sup></b> <b>[μM]</b>	<b>NO<sub>3</sub><sup>-</sup></b> <b>[μM]</b>	<b>NH<sub>4</sub><sup>+</sup></b> <b>[μM]</b>	<b>δ<sup>15</sup>N-</b> <b>NH<sub>4</sub><sup>+</sup></b> <b>[‰]</b>
March	1.4	0.4	15.5	-12.3	7.4	2.7	9.1	+0.9
	3.0	0.6	8.8		11.4	4.5	21.3	
	1.0	0.2	10.3		3.1	1.2	7.7	
	5.3	0.6	12.7		3.9	3.0	18.1	
	2.8	0.4	5.2					
April	0.1	0.5	11.3	-13.6	0.4	0.9	6.8	-7.1
	0.2	0.3	5.4		0.7	1.5	6.1	
	0.1	1.5	13.6		0.7	1.5	6.0	
	0.2	1.8	14.8		0.5	2.4	9.0	
	0.5	0.7	10.1		0.3	4.3	15.6	
May	1.1	0.4	30.4	-9.8	11.3	2.5	42.8	-1.8
	1.4	0.6	9.9		2.4	2.0	13.5	
	1.3	0.0	12.9		0.6	2.7	46.2	
	0.9	0.0	13.4		0.3	1.8	29.5	
	0.6	0.0	7.9		22.9	3.3	54.4	
June-1	0.6	0.7	15.2	-9.1	0.6	2.6	42.3	-11.6
	1.2	1.4	12.7		0.4	1.4	18.6	
	0.2	1.0	32.6		1.2	1.8	25.9	
	0.2	0.8	22.7		0.5	1.0	16.6	
					0.8	0.9	22.0	
June-2	0.2	1.3	18.5	-4.5				
	0.2	1.3	7.5					
	0.1	8.1	25.9					
	0.8	5.0	14.2					
	0.2	1.8	13.9					
July	1.3	6.1	7.8	-13.3				-10.9
	1.4	0.7	14.1		20.5	1.9	27.3	
	0.2	0.9	2.3		18.6	0.7	21.2	
	0.2	0.5	7.1		12.4	0.8	15.1	
	1.8	0.8	25.9		22.1	1.4	34.5	
			14.0	1.6	28.9			

Table A4: continued.

	hollows				hummocks			
	PO <sub>4</sub> <sup>3-</sup> [μM]	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N-NH <sub>4</sub> <sup>+</sup> [‰]	PO <sub>4</sub> <sup>3-</sup> [μM]	NO <sub>3</sub> <sup>-</sup> [μM]	NH <sub>4</sub> <sup>+</sup> [μM]	δ <sup>15</sup> N-NH <sub>4</sub> <sup>+</sup> [‰]
August-1	4.6	0.3	13.0	-10.3	1.1	0.5	9.4	-10.0
	0.3	0.0	8.0		13.5	0.9	24.6	
	0.5	0.5	4.6		4.9	0.6	13.3	
	1.4	0.7	8.9		9.2	0.7	25.2	
	2.6	0.0	6.7		3.5	1.4	16.6	
August-2	2.5	0.1	17.5	-12.8				
	3.4	0.2	20.5					
	2.2	0.2	11.0					
	7.3	0.6	7.6					
	1.1	0.2	13.7					
September	0.6	1.3	21.1	-8.7	2.4	0.5	15.1	-1.6
	0.9	0.3	7.0		4.2	1.0	23.1	
	0.3	0.7	31.6		1.8	0.7	6.3	
	0.6	0.6	30.0		5.1	0.6	3.0	
	0.4	0.9	20.6		2.9	0.8	2.0	

Table A5: Biomass data of Hartshoper Moor.

	<i>S. cus.</i>	<i>S. pap.</i>	<i>E. tet.</i>	<i>E. nig.</i>	<i>E. ang</i>	<i>S. cus.</i>	<i>S. pap.</i>	<i>E. tet.</i>	<i>E. nig.</i>	<i>E. ang</i>
	[%]N					δ <sup>15</sup> N [‰]				
March	1.60	1.23	0.65	0.48	0.44	-7.0	-7.5	-9.5	-10.8	-1.5
	1.71	1.17	0.62	0.40	0.38	-6.9	-5.9	-9.6	-11.1	-1.1
	1.50	0.83	0.73	0.60	0.53	-6.3	-6.8	-10.2	-10.6	-4.3
	1.72	0.79	0.68	0.50	0.35	-6.7	-6.8	-9.7	-11.1	-4.4
	2.19	1.00				-4.1	-5.7			
April	1.45	1.12	0.96	1.22	0.66		-7.2		-9.7	
	1.10	1.18	0.89	1.07	0.85		-7.4		-10.3	
	1.27	1.20	0.93	1.10	0.72		-6.0		-10.5	
	1.36	1.17	0.91	1.12	0.78		-8.0		-10.7	
	1.23	1.05	1.00	1.04	0.87		-6.8		-10.5	
May	1.66	1.21	1.11	1.14	1.90	-6.0	-6.7	-8.9	-9.5	-2.9
	1.23	1.32	1.30	1.17	2.26	-5.6	-7.1	-8.7	-9.3	-4.9
	1.07	1.26	1.40	1.16	2.14	-5.2	-5.4	-9.2	-7.3	-4.4
	1.15	1.21	1.39	1.29	2.09	-6.9	-5.5	-8.3	-10.1	-4.5
	1.14	1.41	1.23	1.26	2.15	-7.1	-7.9	-9.8	-9.4	-5.7

Table A5: continued.

	<i>S. cus.</i>	<i>S. pap.</i>	<i>E. tet.</i>	<i>E. nig.</i>	<i>E. ang</i>	<i>S. cus.</i>	<i>S. pap.</i>	<i>E. tet.</i>	<i>E. nig.</i>	<i>E. ang</i>
	[‰]N					δ <sup>15</sup> N [‰]				
June	1.40	1.00	1.20	1.29	1.44	-6.7	-9.3	-9.4	-2.2	
	1.18	1.06	1.31	1.15	1.49	-6.2	-8.0	-10.4	-2.2	
	1.59	0.90	1.36	1.52	1.46	-6.4	-8.3	-10.3	-2.0	
	1.14	0.97	1.41	1.30	1.46	-6.9	-8.8	-8.9	-2.4	
	1.58	1.30		1.40	1.71	-6.3		-9.9	-3.5	
July	1.25	1.05	1.32		1.31	-6.7	-9.4		-4.2	
	1.63	1.09	1.31		1.20	-6.3	-9.2		-0.4	
	1.21	0.76	1.19		1.30	-7.1	-9.4		-4.9	
	1.31	1.10	1.24		1.45	-7.3	-8.8		-4.7	
	1.16	0.92	1.33		1.58	-7.1	-9.9		-5.4	
August	1.20	0.87	1.12	1.04	1.08	-4.8	-8.5	-10.7	-12.3	-3.0
	1.57	1.25	0.97	1.09	1.00	-5.1	-8.1	-9.9	-11.4	-2.2
	1.11	1.22	1.09	1.02	0.94	-7.0	-8.8	-9.1	-11.3	-0.6
	1.02	0.82	1.16	1.01	1.07	-6.9	-9.5	-9.9	-10.8	-0.6
	1.46	1.37	1.07	1.05	0.98	-7.2	-5.8	-8.9	-10.3	+2.8
September	1.45					-3.4				
	0.97					-6.2				
	0.92					-5.0				
	1.29									
	1.07									

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## **Eidesstaatliche Erklärung**

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Dissertationsschrift selbst verfasst habe und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Hamburg, den

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Fabian Jung