



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



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## ABSTRACT

We investigated the isotopic composition of atmospheric NO<sub>3</sub><sup>-</sup> 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 δ<sup>15</sup>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 δ<sup>15</sup>N–NO<sub>3</sub><sup>-</sup> values: In contrast to the increasing relative importance of isotopically depleted natural NO<sub>x</sub> 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 δ<sup>15</sup>N to air mass origin from industrialized areas. Nowadays isotopically enriched NO<sub>x</sub> 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 δ<sup>15</sup>N values in nitrate deposition.

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## 1. Introduction

The increasing production of food and energy worldwide has enhanced today's anthropogenic emissions of reactive nitrogen (Nr) 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 (Table 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).

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 Nr 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 NO<sub>x</sub> emissions in Germany since 1990 (Table 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 NO<sub>x</sub> emissions, stable isotope ratios of nitrogen are useful, because isotope values of industrial NO<sub>x</sub> generally are significantly elevated over those of agricultural or natural sources (Fig. 1) (Kendall et al., 2008). For instance, δ<sup>15</sup>N–NO<sub>x</sub> values of coal-fired power plants range from +6 to +13‰ (Heaton, 1990; Kiga et al., 2000), and while vehicle emissions have a wider range (–13 to +6‰), most studies have found positive values in tailpipe exhaust, roadside denuders and

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**Table 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%
Overall	3130	1620	–48%	94%	89%	

roadside vegetation (+3.7, +5.7, and +3.8‰, respectively) (Ammann et al., 1999; Moore, 1977; Pearson et al., 2000).

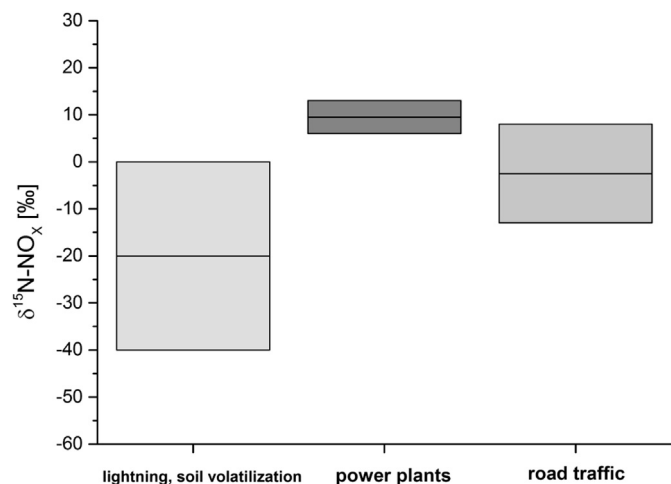
In contrast to industrial pollution, biogenic emissions from soil volatilization are isotopically depleted, with values as low as –49‰ found after fertilization (Li and Wang, 2008). As a consequence, δ<sup>15</sup>N of NO<sub>x</sub> emissions in polluted areas is considerably higher than in pristine 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 (Table 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> 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> at a medium polluted site in Northern Germany, Western Europe.

**2. Materials and methods**

**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).



**Fig. 1.** Known δ<sup>15</sup>N values in NO<sub>x</sub> 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).

**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 h) 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.

**2.3. Sample analyses**

**2.3.1. 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 (δ<sup>15</sup>N–NO<sub>3</sub>) using the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001), which is based on the isotopic analysis of bacterially produced nitrous oxide (N<sub>2</sub>O). All isotope values are corrected for the contribution of <sup>17</sup>O due to mass-dependent fractionation. To prevent the impact of mass-independent fractionation (Δ<sup>17</sup>O) of atmospheric nitrate on the δ<sup>15</sup>N values, *Pseudomonas chlororaphis* were used for the production of N<sub>2</sub>O. Unlike the commonly used strain *Pseudomonas aureofaciens*, these bacteria generate N<sub>2</sub>O, in which oxygen derives from H<sub>2</sub>O, not nitrate (Coplen et al., 2004). N<sub>2</sub>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: δ<sup>15</sup>N: –1.8‰, IAEA–NO–3: δ<sup>15</sup>N: +4.7‰) and an internal standard (δ<sup>15</sup>N: –3.0‰) were run. All isotope measurements were done in replicate, and typical reproducibility was better than 0.2‰ for <sup>15</sup>N for samples and standards.

**2.4. 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 (HYSPPLIT) (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 NO<sub>x</sub> and HNO<sub>3</sub> in the boundary layer is not more than 2 days and 1–2 days, respectively, a time frame of 72 h 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 δ<sup>15</sup>N–NO<sub>3</sub> 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 N–NO<sub>3</sub> deposition, and attributed the corresponding δ<sup>15</sup>N–NO<sub>3</sub> value of each sample to the respective cluster. We then calculated the according N-weighted mean δ<sup>15</sup>N–NO<sub>3</sub> value of each cluster.

**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.

**3.1. Wet and dry N deposition**

**3.1.1. Total nitrogen deposition**

The main reactive nitrogen compounds in both dry and wet deposition samples were NO<sub>3</sub> (38% of total N deposition,

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