Stable $^{15}$N isotopes in fine and coarse urban particulate matter

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ABSTRACT
Particulate nitrogen has far-reaching negative effects on human health and the environment, and effective strategies for reducing it require understanding its sources and formation processes. To learn about these factors, we recorded size-resolved nitrogen isotope ratios ($\delta^{15}$N) of total particulate N at an urban site in northwest Germany during a four-week measuring campaign. We observed a steady decrease in $\delta^{15}$N when going from fine to coarse particles, with values between +18‰ and −2‰. This difference based on particle size is caused by different isotope fractionation processes during particle formation: The fine particles contain ammonium nitrate, which is formed in an equilibrium process, leading to an enrichment of $^{15}$N. Moreover, fine particles are more reactive due to their larger surface areas and relatively long residence times in the atmosphere, which leads to an additional enrichment of $^{15}$N; a key step of this process likely occurs when the ammonium particles interact with ammonia from agricultural sources. In contrast to fine particles, coarse particles are formed by direct absorption of HNO$_3$ on preexisting particles; the HNO$_3$ stems from traffic emissions of NO$_x$ and subsequent oxidation in the atmospheric gas phase. Because only a small amount of isotope fractionation is associated with non-equilibrium processes during phase transitions, there is less $^{15}$N enrichment in the coarse particles. Overall, nitrogen isotopes clearly reflect the different formation processes of fine and coarse aerosol particles.

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Introduction
Climate scientists have long understood the importance of studying aerosols. Yet, the effect of aerosol particles on the radiation budget is still not fully understood, and it represents one of the biggest uncertainties in atmospheric radiation mechanisms (Pachauri and Mayer 2015). Furthermore, fine particles such as aerosols have negative effects on human health: For example, being exposed to polluted air with high levels of fine particles can affect cardiopulmonary health (Kawanaka et al. 2008).

An important gaseous precursor is ammonia, contributing to the production of fine particles and affecting air quality even in areas far from the actual sources (Koziel, Aneja, and Baek 2006; Spirig and Neftel 2006). Furthermore, ammonia is a major cause of acidification and eutrophication of ecosystems (Niederau and Jedrusiak 2005). Therefore, it is crucial to better understand the formation processes of nitrogenous particles, namely those containing nitrate and ammonium. Nitrate is present in both fine and coarse particles, where the nitrate in the coarse particles is mostly in the form of stable salts such as NaNO$_3$ and Ca(NO$_3$)$_2$ (Lee et al. 2008). In the fine particles, the nitrate is primarily found as ammonium nitrate (Kundu, Kawamura, and Lee 2010). In contrast to the nitrate, ammonium is mainly present in the fine particles, where it is produced when atmospheric ammonia neutralizes acids (Harrison and Yin 2004).

In previous studies, it has been argued that $\delta^{15}$N of particulate material allows one to identify the sources of these particles (Beyn, Matthias, and Dahnke 2014; Felix and Elliott 2014; Heaton 1990). In a study in China, Pan et al. (2016) were able to determine size-resolved $\delta^{15}$N-NH$_4$ during several haze periods and assign fossil sources. However, to use this measurement as a proxy, one must consider the effect of isotope fractionation during nucleation processes within the atmosphere. Moore (1974) showed that particulate ammonium is enriched in $^{15}$N...
compared to the ammonium in precipitation, and another study showed that these $^{15}$N ratios vary and depend on chemical reactions in the atmosphere (Walters and Michalski 2015). The isotope enrichment factors for different reactions were determined experimentally by Heaton, Spiro, and Robertson (1997), who observed, on the one hand, that unidirectional reactions lead to negative enrichment factors in the particle mass; thereby, diffusion and reaction of the lighter isotope ($^{14}$N) is favored, resulting in a product depleted in $^{15}$N. On the other hand, for reversible equilibrium reactions, they found that $^{15}$N is enriched in the product.

Considering the different formation processes of fine and coarse particles, differences in $\delta^{15}$N are expected. To understand the atmospheric processes relevant to creating $\delta^{15}$N differences in aerosol particles of different sizes, Yeatman et al. (2001) studied size-segregated aerosol particles at coastal sites in England. They described two different size-shift mechanisms responsible for the formation of coarse-mode aerosol: They found that dissolution/coagulation processes led to negative enrichment in $\delta^{15}$N, whereas dissociation/gas scavenging processes yielded positive enrichment in $\delta^{15}$N.

Given the many uncertainties about how $^{15}$N is deposited in aerosols of different sizes and origins, this study aims to improve our understanding of the nitrogen isotope fractionation processes associated with aerosol particle formation. Therefore, in order to identify the mechanisms underlying the formation of aerosol particles in urban areas, we focused on performing $\delta^{15}$N
measurements on particles that were well resolved in terms of size (fine versus coarse particles).

**Materials and methods**

**Site description**

Aerosol sampling was conducted in the city of Münster, located in northwest Germany (Figure 1). The city is situated in the Münsterland region, an area characterized by intensive agriculture, mainly livestock breeding. All samples and data were collected from 23 May 2019 through 18 June 2019 on the rooftop of the Geo 1 building of the University of Münster (51°58′08.3″ N 7°35′45.5″ E) at a height of 84 m above mean sea level (amsl). The building is located approximately 2.5 km northwest of the city center; a four-lane artery road runs directly along the building, and a major federal road passes by at a distance of 1 km to the northeast. In 2015, a manual traffic census counted an average of 28000 vehicles per day on the federal highway (Bundesanstalt für Straßenwesen 2017). The meteorological data were collected at a permanent, 15-m-high tower on the edge of the roof.

**Meteorological data**

Wind speed and wind direction were measured by a Gill WindSonic ultrasonic anemometer (99 m amsl). An MPS-system TRwS204 Total Rain weighing sensor was used to determine the amount and intensity of precipitation (85.4 m amsl). Temperature and relative humidity were measured by a Young 41382VC Relative Humidity/Temperature Probe (99 m amsl), and air pressure was quantified by a Young 61302 V Barometric Pressure Sensor (85 m amsl). All meteorological data were recorded in 0.17 Hz. Following a quality check, data were merged to 10-min averages.

**Aerosol sampling**

Size-segregated aerosols were collected over four one-week periods, resulting in four sets of samples. To obtain two parallel samples for isotope and ion analysis, two Electrical Low Pressure Impactors (ELPI) were operated simultaneously. One device was a Dekati Outdoor air ELPI with a particle size resolution of 13 stages with 50%-cutoff-size bins from 0.006 μm up to 10.00 μm and an air flow of 10 L min⁻¹ (Dekati Ltd. 2015). The suction hose had a length of 5.60 m, and the inlet was 3.34 m above the roof (87.34 m amsl). The filter substrate was tin foil (LabNeed, Tin Foil Disks, 30 mm diameter, 0.008 mm thickness), which was also cut into circles with a diameter of 25 mm and rinsed with acetone before usage. It was decided not to grease the filter substrates in both devices in order to prevent contamination of the samples. Field blank samples were taken before each measurement run. The blank foils were cut in the same way as the sample foils, rinsed with acetone, dried, inserted into the impactors, and removed directly. After completion of sample or blank collection, the substrates were promptly removed from the impactors, brought into the laboratory and stored dry in a Teflon vial at −20 °C until analysis.

**Inorganic ion and isotopic analysis**

Chemical analysis was conducted at the laboratory of the Institute of Landscape Ecology. Water-soluble ions were extracted from the aluminum foil pieces of the Outdoor air ELPI in 10 mL of deionized water and shaken horizontally for 2 hrs with 200 motions per minute. Each sample was then passed through a 0.22 μm pore size filter (Simplepure, NY + GF, 0.22 μm). For the concentrations of chloride (Cl⁻), nitrate (NO₃⁻) and sulfate (SO₄²⁻) the solutes were analyzed using an ion chromatograph (Metrohm, 883 Basic IC plus) with a detection limit 0.5 mg L⁻¹ for all ions. The concentration of ammonium (NH₄⁺) was quantified by a continuous flow analyzer (Skalar, San+ Automated Wet Chemistry Analyzer) with a detection limit of 0.2 mg L⁻¹. Due to the different stage resolution of the two impactors, the ion data had to be converted. The data generated with the Outdoor air ELPI were therefore normalized by the stage width and linearly interpolated to fit the ELPI+ stage distribution. After interpolation, the values were projected to the stage width of the ELPI+. From the values determined, the concentration was calculated in relation to the respective weekly air flow of the impactor. All data work was carried out with the open-source R (R Core Team 2020) using the R packages “openair” (Carslaw and Ropkins 2012), “zoo” (Zeileis and Grothendieck 2005), “ggepubr”
Total nitrogen isotope analyses (δ15N-TN) were carried out in the Stable Isotope Laboratory at the Institute of Geology and Paleontology using a Flash EA IsoLink interfaced to a ThermoScientific Delta V Advantage mass spectrometer (EA-IRMS). The samples from the ELPI+ collected on tin foil were used for these analyses. From each set, samples of ten stages and one blank were selected, considering sufficient particle mass concentration and ion concentration on the respective stage. The clean edge of each tin foil piece was first cut off with precision scissors, then the remaining foil containing the sample was folded and subjected to direct combustion in a single reactor packed with tungsten oxide and copper wire. Combustion temperature was set at 1020°C. The blank samples were treated in the same way. Evolved gases were separated chromatographically in the order nitrogen (N2), then carbon dioxide (CO2) and finally sulfur dioxide (SO2) and measured without further dilution. Results are reported in the standard delta notation as per mil difference from the international reference standard AIR for nitrogen isotopes:

\[
δ^{15}N(\%o) = \frac{\left(\frac{^{15}N}{^{14}N}\right)_{\text{sample}} - \left(\frac{^{15}N}{^{14}N}\right)_{\text{standard}}}{\left(\frac{^{15}N}{^{14}N}\right)_{\text{standard}}} \times 1000 \quad (1)
\]

Analytical performance was monitored with international reference materials IAEA N1, IAEA N2, and USGS 40. Reproducibility as determined by replicate measurements of reference materials was better than ±0.15 %o. All samples were corrected for blanks.

**Results and discussion**

**Influence of meteorological conditions on particle mass concentration**

We determined the particle mass concentrations to study the influence of each size class on air quality. Reliable results could not be obtained for all samples due to insufficient particle masses, especially for small diameters. Consequently, only the data of the stages 6 to 13 (Table 2) were considered. Within the respective size spectrum, we found two maxima of the aerosol mass concentrations, one at an accumulation range size range below 1 μm diameter (median of 4.21 μg m⁻³ in stage 8), which is typical for regional and long-range transport patterns (Deventer, Griessbaum, and Klemm 2013), and the other at a size just below 10 μm in diameter, representing coarse particles (median of 6.26 μg m⁻³ in stage 13), which are more typical for proximal sources (Figure 3) like road dust and soil (Minguillón et al. 2012).

In order to estimate the influence of meteorology on the aerosol particles, data from the meteorological station on the rooftop of the university building was evaluated. Apart from the first week, which was on average slightly cooler and drier than the other three weeks, the weather conditions during the measurement campaign were homogeneous (Table 1). Wind direction and wind speed were uniform, with prevailing main wind direction from southwest (Table 1 and Figure 2). Thus, the...
meteorological station was likely not affected by different sources of substances (gases or particles) due to rotating wind directions. The long-range transported air masses were, therefore, of oceanic origin and were influenced by local sources in the Münster area, mainly by emissions from agriculture and traffic (Gietl and Klemm 2009).

In a study in urban Russia, Stulov, Plaude, and Monakhova (2010) found that in all particle size classes, the particle number concentration depends strongly on wind speed, while it does not depend much on precipitation. Therefore, small changes in total precipitation during our measurement period should have only a minor effect on the particle number concentration. However, the relative humidity of air does influence the composition of the aerosol particles. In contrast to most other species, the sulfate content increases with increasing air humidity (>50%), since aqueous-phase processing plays an increasingly important role (Sun et al. 2013). At the same time, the nitrate and ammonium content change insignificantly, which such that a higher portion of sulfate is present in air masses with higher relative humidity. During our measurement period, the relative humidity showed only a minor week-to-week variability, making the data comparable (Table 1).

Overall, any differences in particle mass concentration and composition were most likely not caused by changing meteorological conditions.

**Inorganic ion analysis**

To identify the sources of the particulate matter at the urban site, we determined the matter’s anion concentrations. We found that the ions accounted for up to 39% of the total particle mass, on a median (Table 2). Taken together, the concentration of all four detected ions had the highest median in stage 8 (1.06 μg m⁻³) and the lowest in stage 13 (0.08 μg m⁻³). In more detail, nitrate was present in all stages, with peaks in stage 8 (up to 0.92 μg m⁻³) and stage 12 (up to 0.33 μg m⁻³) and a median of 0.09 μg m⁻³ across stages 6 to 13 (Figure 4b). The minimum value above the detection limit of 0.02 μg m⁻³ was observed in stage 6. The ammonium concentration was high in the small-diameter stages and decreased rapidly from stage 10 on (Figure 4a). The largest value (0.20 μg m⁻³) was found in stage 8 (Figure 4a). The median value of the NH₄⁺ concentration for stages 6 to 13 was 0.03 μg m⁻³. A similar pattern was also evident for sulfate: stage 8 displayed the maximum value of 0.67 μg m⁻³, whereas stage 12 showed the minimum value of 0.02 μg m⁻³. The median across all weeks for stages 6 to 13 was at 0.11 μg m⁻³. The concentration of chloride was very small and mostly below the detection limit of 0.02 μg m⁻³, with a median value of 0.01 μg m⁻³ (Figure 4c).

Overall, the chemical composition we determined is consistent with previous findings on the formation and composition of aerosol particles in the literature. Certain precursor gases are required for the formation of secondary fine particulate matter, especially gases such as sulfur oxides (SOₓ), nitrogen oxides (NOₓ) and ammonia...
The composition of inorganic ion species we found indicates that these gases are also the main precursors in Münster. Ammonia and inorganic acid gases, which are released from livestock, poultry farming, and from the use of liquid manure, can impair air quality through the formation of secondary particles in the fine dust range of PM2.5 (Koziel, Aneja, and Baek 2006).

The Münsterland region is an important agricultural region in Germany. With its milk, beef and pork production, it is one of the most important refining regions, and poultry farming has also increased significantly in recent years (Lammers and Becker 2014). The ammonia and ammonium deposition in the Münsterland region is over 18 kg N per hectare per year, twice the national average (Niederau and Jedrusiak 2005). The main sources of ammonia are intensive livestock farming and the application of liquid manure as fertilizer. The oxidation of sulfur dioxide and nitrogen oxides produces sulfuric acid (H2SO4) and nitric acid (HNO3). Ammonia neutralizes these acids in the atmosphere, forming ammonium sulfate and ammonium nitrate (Schiferl et al. 2014). In an ammonium-rich environment, such as the measuring site, the sulfate reacts primarily to form ammonium sulfate (Behera and Sharma 2010). The remaining ammonia is converted to ammonium nitrate. The pattern of ammonium concentration often corresponds to the sum of sulfate and nitrate in the fine particle fractions (Seinfeld and Pandis 2016).

**Figure 4.** Concentration of cations and anions in the respective sample week. (a) Particulate NH4+; (b) particulate NO3; (c) particulate Cl; (d) particulate SO42-.
Stages 5 to 10 contained, on average, more sulfate than nitrate. Most of the sulfuric acid present reacted to form ammonium sulfate and ammonium bisulfate, and the remaining ammonia was available for ammonium nitrate formation. Yet, ammonium nitrate concentrations have been shown to be enhanced in the Münster area by emissions from livestock farming (Gietl and Klemm 2009). While sulfate concentrations in Western Europe have generally decreased in recent years, ammonium concentrations have remained relatively constant. According to the German Environment Agency (2019), sulfur dioxide emissions in Germany decreased by 94.3% from 1990 to 2017, whereas nitrogen oxide emissions decreased by 59% and ammonia emissions only decreased by 10.9%. Thus, nitrate has become increasingly important in the fine aerosol range (Wang et al. 2019).

In contrast to sulfate and ammonium, the nitrate concentrations within our weekly samples were also high in the larger particle classes. The low ammonium values in the larger stages indicate that nitrate is not present as ammonium nitrate in the coarse particle range. While previous studies have shown that nitrate is often present in coarse particles (Harrison and Yin 2004; Pakkanen 1996), there is no primary particle source for coarse particulate nitrate. Nonetheless, gaseous nitrogen species as gaseous nitric acid or fine particles containing nitrate can interact with existing coarse particles (Pakkanen 1996), and nitrate also attaches itself as a coating to already existing particles. Components of coarse particles could be abrasion from traffic, wind-eroded soil and sea spray (Liu and Harrison 2011) Sea salt particles in particular can interact with anthropogenic nitrate during their transport via urban areas, which may be the case in Münster, as Gietl and Klemm (2009) found that the main wind direction from the southwest advects humid oceanic air masses with high sea salt content to Münster. There, sea salt can react with acidic pollutants whereas HCl volatilizes, leading to a reduction of the chloride concentration in aerosol particles. Aged sea salt that is present in the coarse particle range is thus greatly reduced in chloride (Crilley et al. 2017; Hoffman, Laskin, and Finlayson-Pitts 2004; Schiferl et al. 2014). Such chloride depletion was also confirmed in our measurement data, as hardly any chloride was detected across all size classes.

Isotopic fractionation processes in fine and coarse aerosol particles

Nitrogen isotope measurements were only obtained for 26 samples due to sample limitations, but the results reveal a striking trend (Figure 5). The fine particles were highly enriched in $^{15}$N, while as the D50% of the particles increased, particulate matter became more and more depleted in $^{15}$N. Namely, the particle classes with D50% between 0.15 and 0.60 μm showed $\delta^{15}$N values between $+11\%_{\text{o}}$ and $+18\%_{\text{o}}$, whereas the values of the coarse particle classes between 1.6 and 3.6 μm ranged from $-2\%_{\text{o}}$ to $+4\%_{\text{o}}$. Unfortunately, we could only obtain one reliable sample in stage 10 (D50% = 0.940 μm) to observe the transition of $\delta^{15}$N between fine and coarse particle fractions. The isotope ratio in this sample showed an intermediate position (8.43 %o) between the fine and coarse particles (Figure 5).

In order to make assumptions about the origins of aerosol particles, previous studies have measured the isotope signatures of the precursor gases of particles. Felix et al. (2013) studied isotope ratios of ammonia in the USA. They recorded $^{15}$N-NH$_3$ values between $-56\%_{\text{o}}$ and $-23\%_{\text{o}}$ for volatilized livestock waste and values between $-15\%_{\text{o}}$ and $-2\%_{\text{o}}$ for fossil fuels. In 1990, Heaton determined the isotope ratios of NO$_x$ emitted by cars (-13 %o to $-2\%_{\text{o}}$) and NO$_x$ emitted by coal-fired power plants ($+6\%_{\text{o}}$ to $+13\%_{\text{o}}$). More recent $^{15}$N-NO$_x$ values for gasoline powered vehicles has been reported to range between $-13\%_{\text{o}}$ and 9 %o and for diesel powered vehicles between $-21\%_{\text{o}}$ and $-2\%_{\text{o}}$ (Walters, Goodwin, et al. 2015; Walters, Goodwin, et al. 2015). The broader range of values from the more recent studies can be explained by the increased use of selective catalytic reducers. The catalytic reduction of NO$_x$ increases the $\delta^{15}$N-NO$_x$ values.
relative to the generated NO\textsubscript{x} (Walters, Goodwin, et al. 2015).

However, a recent study by Pan et al. (2020) found that passive collections provided mean $^{15}$N-NH\textsubscript{3} values that were almost 15 \textperthousand lower than those obtained with active sampling. This implies that many previous studies using passive measurement methods to collect NH\textsubscript{3} may have obtained biased values.

Moreover, one cannot consider the isotope ratios in (condensed) aerosols as a direct consequence of different source signatures of the respective precursor gases. In 1977, Moore reported that chemical and physical processes in the atmosphere change the isotopic composition. For example, while the $\delta^{15}$N value of NH\textsubscript{3} indicates the signature of the system prior to further processes, the $\delta^{15}$N in precipitation or aerosols represents the result of phase-change and removal mechanisms; heterogeneous reactions in which the condensed phase is removed leads to a fractionation of the N isotopes in the ammonia system (Moore 1977). Elliott et al. (2019) conclude in their review article that due to the many NO\textsubscript{x} reactions taking place in the atmosphere, it is not easily possible to relate the $^{15}$N of the deposited atmospheric NO\textsubscript{3}\textsuperscript{-} to that of the emitted NO\textsubscript{x}. A combination of source and isotope effects is therefore the most likely driver of the large fluctuations reported for the deposition of NO\textsubscript{3} and NH\textsubscript{4}\textsuperscript{+} isotopes in environmental systems (Elliott et al. 2019).

According to Vodička et al. (2019), organic compounds are mostly depleted in heavier isotopes because the underlying non-equilibrium process favors the lighter isotopes in the reaction products. For inorganic species, however, the equilibrium effect is usually predominant. Equilibrium isotope effects occur during reversible chemical reactions or phase changes. In these reactions, the heavier isotope is bound in the most stable compounds with the lowest total energy. Several studies have indicated that $^{15}$N is depleted in the precursor gases and enriched in precipitation, especially in aerosol particles (Heaton, Spiro, and Robertson 1997; Moore 1977; Ti et al. 2018; Vodička et al. 2019); this fractionation effect was further quantified by Heaton, Spiro, and Robertson (1997). They exposed filters with ammonium sulfate to an atmosphere enriched with ammonia gas, and they exposed filters with ammonium nitrate to nitric acid vapor. The calculated enrichment factor ($\varepsilon$), defined as $\delta_{\text{ion}} - \delta_{\text{gas}}$ is $+33$ \textperthousand for the NH\textsubscript{3}/NH\textsubscript{4}\textsuperscript{+} system and $+21$ \textperthousand for HNO\textsubscript{3}/NO\textsubscript{3}\textsuperscript{-}. Pan et al. (2016) found $^{15}$N-NH\textsubscript{4}\textsuperscript{+} values between $-37.1$ \textperthousand and 5.8 \textperthousand in fine particles during haze periods in an urban area in China. In order to draw conclusions about the precursor gases, they used the enrichment factor by Heaton, Spiro, and Robertson to determine hypothetical $\delta^{15}$N-NH\textsubscript{3} ratios. This enabled them to confirm fossil sources in the majority of cases. If we apply these factors to our data, we can likewise draw conclusions about the precursor gases. Assuming that only ammonia plays a significant role as a precursor gas for fine particles, we calculated $\delta^{15}$N-NH\textsubscript{3} values between $-24.6$ \textperthousand and $-15.5$ \textperthousand for the particles with a D50% between 0.15 and 0.94 \textmu m at our site, which is consistent with the signatures measured by Felix et al. (2013) in areas with high livestock production. Even if the latest findings of Pan et al. (2020) are taken into account and a bias of $-15$ \textperthousand is considered for the values of Felix et al. (2013), this assumption still applies quite well. By further assuming that nitrogen oxides are the main precursor of nitrate in the coarse particles, we then subtracted the respective enrichment factor from our values (Heaton, Spiro, and Robertson 1997), resulting in $\delta^{15}$N-NO\textsubscript{x} values between $-22.7$ \textperthousand and $-17.19$ \textperthousand. These values are considerably lower than those determined by Heaton (1990) for $\delta^{15}$N-NO\textsubscript{x} from precursors. Thus, the fractionation effect observed in the laboratory matches the isotope ratios we observed in the fine particles when we assume ammonia as a precursor. However, as the isotope values for the coarse particles cannot be represented by the laboratory values, this approach does not explain the wide range of isotope values found here between the different particle size classes. The values vary between $+18$ \textperthousand in the fine particle classes and $-2$ \textperthousand in the coarse classes.

Mkoma et al. (2014) observed a similar order of magnitude in aerosol particles with higher $\delta^{15}$N-TN ratios in fine particles than in coarse particles, i.e., average values of 17.4 \textperthousand for PM\textsubscript{2.5} and 12.1 \textperthousand for PM\textsubscript{10}. Also, Freyer (1991) reported higher $\delta^{15}$N values for NO\textsubscript{3}\textsuperscript{-} in fine aerosol particles ($<3.5 \mu m$) than in coarse particles ($>3.5 \mu m$). Under conditions comparable to those in our study during summer, respective values ranged, on average, from $+4.2$ \textperthousand to $-1.4$ \textperthousand.

Assuming that NH\textsubscript{3} and NO\textsubscript{x} cycles are not coupled (Moore 1977), the respective dominance of these species in the different size classes and the underlying processes represent the reasons for the observed wide range in $\delta^{15}$N. Therefore, the two formation pathways for particulate nitrogen seem to differ in their degree of isotope fractionation.

Direct absorption of HNO\textsubscript{3} into existing aerosols can enhance the nitrate content of particles in the coarse range (Freyer 1991); this presumption is supported by the ion composition of the coarse particles,
which likely consist of aged sea salt (Schiferl et al. 2014). Nitric acid is highly hydrophilic and deposits very quickly onto existing surfaces, and nitric acid is enriched in $^{15}\text{N}$ in relation to its precursor gases, because equilibrium fractionation occurs during the oxidation of NO$_x$ (Savard et al. 2017). In a study that quantified the net isotope effect of gas-to-particle conversion from NO$_x$ to NO$_3^-$, Chang et al. (2018) used a model calculation and determined an isotope effect of 15.33 $\%_\text{o} \pm 4.90 \%_\text{o}$ for an urban, high-traffic area in China. If this isotope effect is applied to the isotope ratios of the presumed predecessor gases, i.e., NO$_x$ for the coarse particles, hypothetical values for the particles can be calculated. Adding this isotope effect to the $\delta^{15}\text{N}$-NO$_x$ values reported for traffic by Heaton (1990) result in $\delta^{15}\text{N}$-NO$_3^-$ values around 0 $\%_\text{o}$, which correspond well to values obtained in this study for the coarse particles. Once absorbed, NO$_x$ rarely evaporates again; in non-equilibrium processes such as this (absorption), the isotopic fractionation is very low (Vodička et al. 2019). Consequently, we can exclude an additional enrichment in $^{15}\text{N}$ in the coarse particle spectrum. Furthermore, coarse particles are more likely to be deposited and more frequently washed out by rain (Freyer 1991). Such coarse particles are enriched in $^{15}\text{N}$ compared to the precursor gas, but to a much lesser degree than fine particles are.

Regarding N fractionation in fine particles, the fine particles mainly consist of semi-volatile ammonium nitrate, and the degree of isotopic fractionation is determined by the chemical equilibrium between gas phase and aqueous or solid phase (Savard et al. 2017). A shift in the dissociation equilibrium leads to the partwise evaporation of NH$_4$NO$_3$. Thereby, the lighter $^{14}\text{N}$ isotope is preferred, which leads to a $^{15}\text{N}$ enrichment in the residual fraction of the particulate nitrate.

Elliott et al. (2019) conclude that the combined effects of source changes, seasonal variations in reaction chemistry and temperature-dependent fractionation factors exert an influence on the isotope ratios. The seasonal $\delta^{15}\text{N}$-NO$_3^-$ and $\delta^{15}\text{N}$-NH$_4^+$ values are generally lower in the summer months and higher in the winter months and the combustion of fossil fuels influences the $\delta^{15}\text{N}$ values to a higher extent in the colder months. However, we cannot track this seasonality due to the sole measurement campaign in summer.

Due to the constant availability of NH$_3$ at our measuring site, it is likely that dissociation occurs and ammonium nitrate forms, such that $^{15}\text{N}$ progressively accumulates in the aerosol particles. Furthermore, the formation of ammonium sulfate influences the $\delta^{15}\text{N}$ of total nitrogen; namely, as soon as a chemical balance is reached, NH$_4^+$ stabilizes with higher $^{15}\text{N}$ values than the precursor gas NH$_3$ (Heaton, Spiro, and Robertson 1997). Given the high ammonium sulfate content in our samples, this effect contributes to the higher $\delta^{15}\text{N}$ for the fine particle fraction. In addition, fine particles are more reactive due to their larger surface-to-volume ratios, and they have a longer residence time in the atmosphere than coarse particles. All these factors lead to higher $\delta^{15}\text{N}$ values in the fine particle fraction (Vodička et al. 2019), which the observed data from this study confirms. Thus, our findings support the hypothesis that the observed differences in $\delta^{15}\text{N}$ result from fractionation processes rather than from particles that came from different sources.

Despite this overall agreement, artifacts cannot be excluded from our results. Due to the long residence time of the filters in the device, further reactions cannot be completely excluded. Volatilization of NO$_3^-$ from the impactation surface can lead to further accumulation of $^{15}\text{N}$ in the remaining material, a process that has been shown to be potentially relevant for filters (Freyer 1991). Appel, Tokiwa, and Haik (1981) also showed that inert filters such as Teflon are affected by negative errors due to the volatilization of NH$_4$NO$_3$ and the volatilization of HNO$_3$. However, we do not consider these processes to be prominent in our case, since the differences in $\delta^{15}\text{N}$ ratios are substantial for fine versus coarse particles.

Furthermore, particle losses cannot be excluded due to the length of the suction hose. According to Kumar et al. (2008), however, the losses for particles larger than 0.02 $\mu$m are moderate. Since the losses should also have no influence on the isotope ratios, we also assume this influence to be negligible.

**Conclusion**

During summer, the atmospheric nitrogen budget in Münster is characterized by high ammonia concentrations resulting from agriculture in the surrounding Münsterland and high nitrate emissions caused by traffic in the city. As clearly shown, $\delta^{15}\text{N}$ values reported for total nitrogen are not uniform across the size range of particulate matter. Size-resolved collection and analytical strategies such as the ones applied here are necessary to understand the complex chemical processes that occur during the formation of atmospheric particles. In particular, our size-resolved sample collection routine allows for a greater size resolution of particles upon which $\delta^{15}\text{N}$ can be determined. The difference in $\delta^{15}\text{N}$ between fine and coarse particles is greater than shown by previous
models and laboratory experiments, and this difference results from different fractionation processes that occur during particle formation. In both fine and coarse particles, these processes lead to an enrichment of the heavier $^{15}$N isotope; however, the fine particles are subject to equilibrium exchange processes that lead to a further enrichment in $^{15}$N. Furthermore, fine particles’ higher reactivity due to their larger surface areas and their longer residence times in the atmosphere account for the observed large difference in $\delta^{15}$N for fine and coarse particles. Our results show that there is no distinct difference in the formation processes of fine and coarse particles, and the gradual decrease of the $\delta^{15}$$N$-TN values from fine to coarse particles suggests a smooth transition from the dominant fractionation processes in fine particles to those in coarse particles. Nonetheless, this study is a feasibility study. Further measurements are required for a better understanding of the isotope fractionation processes of atmospheric nitrogen compounds in order to improve our understanding of a possible temperature dependence of these processes as well as the influence of other sources such as seasonal agricultural activity, measurement campaigns during various seasons of the year including winter should be performed. Furthermore, determining the $\delta^{15}N$ for individual species of nitrogen (nitrate, ammonium, organic N) with a high particle size resolution and of the precursor gases (nitrogen oxides, ammonia) would be of great value.

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