Seasonal study of stable carbon and nitrogen isotopic composition in fine aerosols at a Central European rural background station

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Abstract. Determinations of stable carbon isotope ratios (δ13C) of total carbon (TC) and nitrogen isotope ratios (δ15N) of total nitrogen (TN) were carried out for fine aerosol particles (PM1) collected on a daily basis at a rural background site in Košetice (Central Europe) between 27 September 2013 and 9 August 2014 (n=146). We found a seasonal pattern for both δ13C and δ15N. The seasonal variation in δ15N was more pronounced, with 15N-depleted values (av. 13.1±4.5‰) in winter and 15N-enriched values (25.0±1.6‰) in summer. Autumn and spring are transition periods when the isotopic composition gradually changed due to different sources and the ambient temperature. The seasonal variation in δ13C was less pronounced but more depleted in 13C in summer (-27.8±0.4‰) compared to winter (-26.7±0.5‰).

Major controls of the seasonal dependencies were found based on a comparative analysis with water-soluble ions, organic carbon, elemental carbon, trace gases and meteorological parameters (mainly ambient temperature). A comparison of δ15N with NO3-, NH4+ and organic nitrogen (OrgN) revealed that although a higher content of NO3- was associated with a decrease in δ15N values in TN, NH4+ and OrgN had the opposite influences. The highest concentrations of nitrate, mainly represented by NH4NO3, originated from the emissions from biomass burning, leading to lower δ15N values of approximately 14% in winter. During spring, the percentage of NO3- in PM1 decreased, and 15N enrichment was probably driven by equilibrium exchange between the gas and aerosol phases (NH3(g) ↔ NH4+(p)) as supported by the increased ambient temperature. This equilibrium was suppressed in early summer when the NH4+/SO42- molar ratios reached 2, and nitrate partitioning in aerosol was negligible. During summer, kinetic reactions probably were the primary processes as opposed to gas-aerosol equilibrium on a nitrogen level. However, summertime δ15N values were some of the highest observed, probably suggesting the aging of ammonium sulfate and OrgN aerosols. Such aged aerosols can be coated by organics in which 13C enrichment takes place by photooxidation process. This result was supported by the positive correlation of δ13C with temperature and ozone, as observed in the summer season.
During winter, we observed an event with the lowest $\delta^{15}N$ and highest $\delta^{13}C$ values. The winter Event 36 was connected with prevailing southeast winds. Although higher $\delta^{13}C$ values probably originated from biomass burning particles, the lowest $\delta^{15}N$ values were associated with agriculture emissions of NH$_3$ under low temperature conditions that were below 0°C.

1. Introduction

Key processes in the atmosphere, which are involved with climate changes, air quality, rain events (Fuzzi et al., 2015) or visibility (Hyslop, 2009), are strongly influenced by aerosols. Because these processes are still insufficiently understood, they are studied intensively. One approach to explore chemical processes taking place in atmospheric aerosols is the application of stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope ratios. These isotopes can provide unique information on source emissions together with physical and chemical processes in the atmosphere (Gensch et al., 2014; Kawamura et al., 2004), as well as atmospheric history (Dean et al., 2014). Isotopic composition is affected by both primary emissions (e.g., Heaton, 1990; Widory, 2006) and secondary processes (e.g., Fisseha et al., 2009b; Walters et al., 2015a). Both $\delta^{13}C$ and $\delta^{15}N$ values are influenced by kinetic and equilibrium isotope fractionation that takes place in the atmosphere. In the case of nitrogen, $^{15}N$ is generally depleted in gas phase precursors (ammonia, nitrogen oxides) but is more enriched in ions (NH$_4^+$, NO$_3^-$) in rainfall and most enriched in particulate matter and dry deposition (Heaton et al., 1997). In the case of carbon, the major form is organic carbon (OC), which is composed of large numbers of organic compounds where isotope fractionations via the kinetic isotope effect (KIE) usually dominating the partitioning between gas and aerosol (liquid/solid) phases (Gensch et al., 2014).

Many studies have been conducted on $\delta^{13}C$ and $\delta^{15}N$ in particulate matter (PM) in Asia (e.g., Kundu et al., 2010; Pavuluri et al., 2015b; Pavuluri and Kawamura, 2017) and America (e.g., Martinelli et al., 2002; Savard et al., 2017). However, only few studies have been performed in Europe. European isotope studies on aerosols mainly involve the analysis of $\delta^{15}N$ in NO$_3^-$ and/or NH$_4^+$. Widory (2007) published a broad study on $\delta^{15}N$ in TN in PM10 samples from Paris, focusing on seasons (winter vs. summer) with some specific sources. Freyer (1991) reported the seasonal variation in $\delta^{15}N$ of nitrate in aerosols and rainwater as well as gaseous HNO$_3$ at a moderately polluted urban area in Jülich (Germany). Yeatman et al. (2001a, 2001b) conducted analyses of $\delta^{15}N$ in NO$_3^-$ and NH$_4^+$ at two coastal sites from Weybourne, England, and Mace Head, Ireland, focusing on the effects of possible sources and aerosol size segregation on their formation processes and isotopic enrichment. More recently, Ciężka et al. (2016) reported one-year observations of $\delta^{15}N$ in NH$_4^+$ and ions in precipitation at an urban site in Wroclaw, Poland, whereas Beyn et al. (2015) reported seasonal changes in $\delta^{15}N$ in NO$_3^-$ in wet and dry deposition at a coastal and an urban site in Germany to evaluate nitrogen pollution levels.
Studies on $\delta^{13}$C at European sites have been focused more on urban aerosols. Fisseha et al. (2009) used stable carbon isotopes to determine the sources of urban carbonaceous aerosols in Zurich, Switzerland, during winter and summer. Similarly, Widory et al. (2004) used $\delta^{13}$C of TC, together with an analysis of lead isotopes, to study the origin of aerosol particles in Paris (France). Górka et al. (2014) used $\delta^{13}$C in TC together with PAH analyses for the determination of sources of PM10 organic matter in Wroclaw, Poland, during vegetative and heating seasons. Masalaite et al. (2015) used an analysis of $\delta^{13}$C in TC on size-segregated urban aerosols to elucidate carbonaceous PM sources in Vilnius, Lithuania. Fewer studies have been conducted on $\delta^{13}$C in aerosols in rural and remote areas of Europe. In the 1990s, Pichlmayer et al. (1998) conducted an isotope analysis in snow and air samples for the characterization of pollutants at high-alpine sites in Central Europe. Recently, Martinsson et al. (2017) published seasonal observations of $\delta^{13}$C in TC of PM10 at a rural background station in Vavihu in southern Sweden based on 25 weekly samples.

These $\delta^{13}$C and $\delta^{15}$N studies show the potential of these isotopes to characterize aerosol types and the chemical processes that take place in them. To broaden this isotope approach over the European continent, we present seasonal variations in $\delta^{13}$C of total carbon (TC) and $\delta^{15}$N of total nitrogen (TN) in the PM1 fraction of atmospheric aerosols at a rural background site in Central Europe. To the best of our knowledge, this is the first seasonal study of these isotopes in this location, and it is one of the most comprehensive isotope studies of a fine fraction of aerosols.

2. Materials and methods

2.1. Measurement site

The Košetice observatory is the specialized workplace of the Czech Hydrometeorological Institute (CHMI), which is focused on monitoring the quality of the environment (Váňa and Dvorská, 2014). The site is located in the Czech Highlands ($49^{°}34'24.13''$ N, $15^{°}4'49.67''$ E, 534 m ASL) and is surrounded by an agricultural landscape and forests, out of range of major sources of pollution with a very low frequency of traffic. The observatory is officially classified as a Central European rural background site, which is part of the EMEP, ACTRIS, and GAW networks. A characterization of the station in terms of the chemical composition of fine aerosols during different seasons and air masses is presented by Schwarz et al. (2016) and longtime trends by Mbengue et al. (2018) and Pokorná et al. (2018). As part of a monitoring network operated by the CHMI, the site is equipped with an automated monitoring system that provides meteorological data (wind speed and direction, relative humidity, temperature, pressure, and solar radiation) and the concentrations of gaseous pollutants ($\text{SO}_2$, CO, NO, NO$_2$, NOx, and O$_3$).
2.2. Sampling and weighing

Aerosol samples (n = 146) were collected for 24 h every two days from September 27, 2013, to August 9, 2014, using a Leckel sequential sampler SEQ47/50 equipped with a PM1 sampling inlet. Some gaps in sampling were caused by outages and maintenance to the sampler. The sampler was loaded with pre-baked (3 h, 800°C) quartz fiber filters (Tissuequartz, Pall, 47 mm), and the flow rate of 2.3 m³/h was used. In addition, field blanks (n = 7) were also taken for an analysis of the contribution of absorbable organic vapors.

The mass of PM1 was measured by gravimetric analysis of each quartz filter before and after the sampling with a microbalance that had ±1 µg sensitivity (Sartorius M5P, Sartorius AG, Göttingen, Germany). The weighing of samples was performed at 20±1 °C and 50±3 % relative humidity after equilibration for 24 h.

2.3. Determination of TC, TN and their stable isotopes

For the TC and TN analyses, small filter discs (area 0.5 cm², 1.13 cm² or 2.01 cm²) were placed in a pre-cleaned tin cup, shaped into a small marble using a pair of tweezers, and introduced into the elemental analyzer (EA; Flash 2000, Thermo Fisher Scientific) using an autosampler. Inside the EA, samples were first oxidized in a quartz column heated at 1000°C, in which tin marble burns (~1400°C) and oxidizes all carbon and nitrogen species to CO₂ and nitrogen oxides, respectively. In the second quartz column, heated to 750°C, nitrogen oxides were reduced to N₂. Evolved CO₂ and N₂ were subsequently separated on a gas chromatographic column, which was installed in EA, and measured with a thermal conductivity detector for TC and TN. Parts of CO₂ and N₂ were then transferred into an isotope ratio mass spectrometer (IRMS; Delta V, Thermo Fisher Scientific) through a ConFlo IV interface to monitor the δ¹⁵N/¹⁴N and δ¹³C/¹²C ratios.

An acetanilide external standard (from Thermo-electron-corp.) was used to determine the calibration curves before every set of measurements for the calculation of the right values of TC, TN and their isotopic ratios. The δ¹⁵N and δ¹³C values of the acetanilide standard were 11.89‰ (relative to the atmospheric nitrogen) and -27.26‰ (relative to Vienna Pee Dee Belemnite standard), respectively. Subsequently, the δ¹⁵N of TN and δ¹³C of TC were calculated using the following equations:

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

\[
\delta^{13}C = \left( \frac{^{13}C/^{12}C}_{sample}/^{13}C/^{12}C_{standard} - 1 \right) \times 1000
\]
2.4. Ion chromatography

Quartz filters were further analyzed by using a Dionex ICS-5000 (Thermo Scientific, USA) ion chromatograph (IC). The samples were extracted using ultrapure water with conductivity below 0.08 µS/m (Ultrapur, Watrex Ltd., Czech Rep.) for 0.5 h using an ultrasonic bath and 1 h using a shaker. The solution was filtered through a Millipore syringe filter with 0.22-µm porosity. The filtered extracts were then analyzed for both anions (SO$_{4}^{2-}$, NO$_{3}^{-}$, Cl$^{-}$, NO$_{2}^{-}$ and oxalate) and cations (Na$^{+}$, NH$_{4}^{+}$, K$^{+}$, Ca$^{2+}$ and Mg$^{2+}$) in parallel. The anions were analyzed using an anion self-regenerating suppressor (ASRS 300) and an IonPac AS11-HC (2 x 250 mm) analytical column and detected with a Dionex conductivity detector. For cations, a cation self-regenerating suppressor (CSRS ULTRA II) and an IonPac CS18 (2 m x 250 mm) analytical column were used together with a Dionex conductivity detector. The separation of anions was conducted using 25 mM KOH as an eluent at a flow rate of 0.38 ml/min, and the separation of cations was conducted using 25 mM methanesulfonic acid at 0.25 ml/min.

The sum of nitrate and ammonium nitrogen was in good agreement with measured TN (Fig. S1 in Supplementary Information (SI)), and based on the results of TN, NO$_{3}^{-}$ and NH$_{4}^{+}$, organic nitrogen (OrgN) was also calculated using following equation (Wang et al., 2010): OrgN = TN – 14*[NO$_{3}^{-}$/62 + NH$_{4}^{+}$/18].

2.5. EC/OC analysis

Online measurements of organic and elemental carbon (OC and EC) in aerosols were provided in parallel to the aerosol collection on quartz filters mentioned above by a field semionline OC/EC analyzer (Sunset Laboratory Inc., USA) connected to a PM1 inlet. The instrument was equipped with a carbon parallel-plate denuder (Sunset Lab.) to remove volatile organic compounds to avoid a positive bias in the measured OC. Samples were taken at 4 h intervals, including the thermal-optical analysis, which lasts approximately 15 min. The analysis was performed using the shortened EUSAAR2 protocol: step [gas] temperature [°C]/duration [s]: He 200/90, He 300/90, He 450/90, He 650/135, He-Ox. 500/60, He-Ox. 550/60, He-Ox. 700/60, He-Ox. 850/100 (Cavalli et al., 2010). Automatic optical corrections for charring were made during each measurement, and a split point between EC and OC was detected automatically (software: RTCalc526, Sunset Lab.). Instrument blanks were measured once per day at midnight, and they represent only a background instrument signal without any reflection on concentrations. Control calibrations using a sucrose solution were made before each change of the filter (ca. every 2$^{nd}$ week) to check the stability of instruments. The 24 h averages with identical measuring times, such as on quartz filters, were calculated from acquired 4 h data. The sum of EC and OC provided the TC concentrations, which were consistent with TC values measured by EA (see Fig. S2 in SI).
2.6. Spearman correlation calculations

Spearman correlation coefficients ($r$) were calculated using R statistical software (ver. 3.3.1). Correlations were calculated for the annual dataset (139 samples), separately for each season (autumn - 25, winter - 38, spring - 43, and summer - 33 samples), and the winter Event (7 samples). Data from the winter Event were excluded from the annual and winter datasets for the correlation analysis. Correlations with p-values over 0.05 were taken as statistically insignificant.

3. Results and discussion

The time series of TN, TC and their isotope ratios ($\delta^{15}$N and $\delta^{13}$C) for the whole measurement campaign are depicted in Fig. 1. Sampling gaps in autumn and at the end of spring are caused by servicing or outages of the sampler; however, 146 of the samples between September 27, 2013, and August 9, 2014, are enough for a seasonal study. In Fig. 1, the winter Event is highlighted, which has divergent values, especially for $\delta^{15}$N, and is discussed in detail in section 3.4.

Table 1 summarizes the results for the four seasons: autumn (Sep–Nov), winter (Dec–Feb), spring (Mar–May) and summer (Jun–Aug). The higher TN concentrations were observed in spring (max. 7.59 $\mu$gN m$^{-3}$), while the higher TC concentrations were obtained during the winter Event (max. 13.6 $\mu$gC m$^{-3}$). Conversely, the lowest TN and TC concentrations were observed in summer (Fig. 1).

Figure 2 shows relationships between TC and TN and their stable isotopes for one year. The correlation between TC and TN is significant ($r=0.70$), but during higher concentration events, this dependence can be split due to the different origins of these components. The highest correlations between TC and TN were obtained during transition periods in autumn (0.85) and spring (0.80). Correlations between TC and TN in winter (0.43) and in summer (0.37) were weaker but still statistically significant ($p<0.05$). As seen in the TC/TN ratios (Table 1), seasonal TC/TN averages fluctuate, but their medians have similar values for autumn, winter and spring, while the summer value is higher (3.45) and roughly points to different aerosol composition in comparison with other seasons. However, seasonal differences between TC/TN ratios are not as large as those in other works (e.g., Agnihotri et al., 2011), and thus, this ratio itself does not provide much information about aerosol sources.

The correlation between $\delta^{13}$C and $\delta^{15}$N (Fig. 2, right) is also significant but negative ($-0.71$). However, there is a statistically significant correlation for spring only ($-0.54$), while in other seasons, correlations
are statistically insignificant (autumn: -0.29, winter: -0.11 and summer: 0.07). This result shows that significant and related changes in the isotopic composition of nitrogen together with carbon occur especially in spring, while there are stable sources of particles during winter and summer. The winter Event measurements show the highest $\delta^{13}$C values and the lowest $\delta^{15}$N values, but they are still in line with the linear fitting of all annual data (Fig. 2, right).

### 3.1. Total nitrogen and its $\delta^{15}$N

The $\delta^{15}$N values are stable in winter at approximately 15‰, with the exception of the winter Event, which deviated by an average of 13‰. In summer, the $\delta^{15}$N shows strong enrichment of $^{15}$N in comparison with winter, resulting in an average value of 25‰. During the spring period, we observe a slow increase in $\delta^{15}$N from April to June (Fig. 1), indicating a gradual change in nitrogen chemistry in the atmosphere. During autumn, a gradual change is not obvious because of a lack of data in a continuous time series. Year round, $\delta^{15}$N ranged from 0.6‰ to 28.2‰. Such a large range may originate from the limited number of main compounds containing nitrogen in aerosols, which is specifically present in the form of NO$_3^-$, NH$_4^+$ and/or organic nitrogen (OrgN), and thus, the final $\delta^{15}$N value in TN can be formulated by the following equation:

$$\delta^{15}\text{N}_{\text{TN}} = \delta^{15}\text{N}_{\text{NO}_3^-}*f_{\text{NO}_3^-} + \delta^{15}\text{N}_{\text{NH}_4^+}*f_{\text{NH}_4^+} + \delta^{15}\text{N}_{\text{OrgN}}*f_{\text{OrgN}}$$

where $f_{\text{NO}_3^-} + f_{\text{NH}_4^+} + f_{\text{OrgN}} = 1$ and $f$ represents the fractions of nitrogen from NO$_3^-$, NH$_4^+$ and OrgN in TN, respectively. The highest portion of nitrogen is contained in NH$_4^+$ (54 % of TN year-round), followed by OrgN (27 %) and NO$_3^-$ (19 %). While the NH$_4^+$ content in TN is seasonally stable (51-58 %, Table 1), the NO$_3^-$ content is seasonally dependent – higher in winter, similarly balanced in spring and autumn, and very low in summer, when the dissociation of NH$_4$NO$_3$ plays an important role, and its nitrogen is partitioned from the aerosol phase to the gas phase (Stelson et al., 1979).

The seasonal trend of $\delta^{15}$N in TN, with the lowest values in winter and highest in summer, has been observed in other studies from urban Paris (Widory, 2007), rural Brazil (Martinelli et al., 2002), East Asian Jeju Island (Kundu et al., 2010) and rural Baengnyeong Island (Park et al., 2018) sites in Korea. However, different seasonal trends of $\delta^{15}$N in TN in Seoul (Park et al., 2018) show that such seasonal variation does not always occur.

Figure 3 shows changes in $\delta^{15}$N values as a function of the main nitrogen components in TN, with different colors for different days. There are two visible trends for a type of nitrogen. Although $^{15}$N is more depleted with increasing contents of NO$_3^-$ in TN, the opposite is true for NH$_4^+$ and OrgN. The strongest dependence of most of the bulk data is expressed by a strong negative correlation between $\delta^{15}$N and the share of NO$_3^-$ in TN (Fig. 3). In all cases, the dependence during the winter Event is
completely opposite to the rest of the bulk data (Fig. 3) showing different processes on $\delta^{15}$N formation, which is highlighted by a very strong positive correlation between $\delta^{15}$N and NO$_3^-$-N/TN (0.98). This point will be discussed in section 3.4.

Considering the individual nitrogen components, several studies (Freyer, 1991; Kundu et al., 2010; Yeatman et al., 2001b) show seasonal trends of $\delta^{15}$N of NO$_3^-$, with the lowest $\delta^{15}$N in summer and the highest in winter. Savard et al. (2017 and references therein) summarized four possible reasons for this seasonality of $\delta^{15}$N in NO$_3^-$, that is, (i) changes in emissions strength, (ii) influence of wind directions in the relative contributions from sources with different isotopic composition, (iii) the effect of temperature on isotopic fractionation and (iv) chemical transformations of nitrogen oxides over time with a lower intensity of sunlight, which can lead to higher $\delta^{15}$N values of atmospheric nitrate during winter months, as shown by Walters et al. (2015a). In the case of our data, mixing of all of these factors probably had an influence on the nitrate isotopic composition during different parts of the year.

Conversely, Kundu et al. (2010) reported higher $\delta^{15}$N values of NH$_4^+$ in summer than in winter and generally reported higher $\delta^{15}$N values in NH$_4^+$ than in NO$_3^-$ except for winter. In sum, the contribution of NH$_4^+$ to $\delta^{15}$N overwhelms the contribution of NO$_3^-$ to $\delta^{15}$N. Additionally, TN is composed of NH$_4^+$, NO$_3^-$ and OrgN. In Fig. 3, we can observe the enrichment of $^{15}$N in TN in summer when the lowest NO$_3^-$ contribution occurs. Thus, higher values of $\delta^{15}$N in TN in summer are mainly caused by NH$_4^+$ originating from (NH$_4$)$_2$SO$_4$, OrgN and ammonium salts of organic acids.

Furthermore, in summer, we observed one of the largest enrichments of $^{15}$N in TN aerosols in comparison with other studies (Kundu et al., 2010 and references therein), which may be due to several reasons. First, the works mentioned above mainly studied total suspended particles (TSP) aerosols; however, we focus on the fine PM1 fraction, which should be more reactive than the coarse fraction and consequently result in a higher abundance of $^{15}$N during the gas/particle portioning of NH$_3$ and NH$_4^+$. Second, the fine aerosol fraction of the Aitken mode persists for a longer period of time in the atmosphere than the coarse fraction, which is also a factor leading to higher $^{15}$N enrichment. Indeed, Mkoma et al. (2014) reported average higher $\delta^{15}$N in TN in fine aerosols (17.4‰, PM2.5) in comparison with coarse aerosols (12.1‰, PM10), and Freyer (1991) also reported higher $\delta^{15}$N in NO$_3^-$ (4.2‰ to 8‰) in fine aerosols (< 3.5 µm) in comparison with the coarse mode (-1.4‰ to 5.5‰). Third, a shorter sampling time in this work (24 h) leads to the collection of samples with episodic values (see the winter Event) that would be averaged (overlapped) over a longer time resolution (e.g., weekly samples).

Similarly, as in this study, the highest $\delta^{15}$N values in TN were observed in a few studies from the Indian region (Aggarwal et al., 2013; Bikkina et al., 2016; Pavuluri et al., 2010) where biomass burning is
common, and ambient temperatures are high. Therefore, in addition to the above reasons, temperature also plays a significant role in $^{15}$N enrichment. This point will be discussed in more detail in section 3.3.

Figure 4 shows the $\delta^{15}$N in TN as a function of NO$_3^{-}$. The $\delta^{15}$N shows a peak at approximately 14±1‰ with increasing nitrate concentrations. Assuming that NO$_3^{-}$ in the fine aerosol fraction consists predominantly of NH$_4$NO$_3$ (Harrison and Pio, 1983), it can be stated that nitrate at the Košetice site is a source of nitrogen, with $\delta^{15}$N values at approximately 14‰, which is similar to the winter values of $\delta^{15}$N in NO$_3^{-}$ in other studies. Specifically, Kundu et al. (2010) reported a winter average value of $\delta^{15}$N in NO$_3^{-}$ at +15.9‰ from a Pacific marine site at Gosan Island, South Korea, whereas Freyer (1991) reported +9.2‰ in a moderately polluted site from Jülich, Germany. Yeatman et al. (2001) reported approximately +9‰ from a Weybourne coastal site, UK. Park et al. (2018) reported 11.9‰ in Seoul and 11.7‰ from a rural site in Baengnyeong Island, Korea.

Considering the $\delta^{15}$N of nitrogen oxides, which are common precursors of particulate nitrate, we can see that the $\delta^{15}$N of nitrogen oxides generated by coal combustion (Felix et al., 2012; +6 to +13‰, Heaton, 1990) or biomass burning (+14‰, Felix et al., 2012) are in a same range with our $\delta^{15}$N during the period of enhanced concentrations of NO$_3^{-}$. These $\delta^{15}$N values of nitrogen oxides are also significantly higher than those from vehicular exhaust (-13 to -2‰, Heaton, 1990; -19 to +9‰, Walters et al., 2015b) or biogenic soil (-48 to -19‰, Li and Wang, 2008). Thus, $\delta^{15}$N values of approximately 14‰ (Fig. 4) are probably characteristic of fresh emissions from heating (both coal and biomass burning) because these values are obtained during the domestic heating season.

The exponential curves in Fig. 4 represent a boundary in which the $\delta^{15}$N values are migrating as a result of enrichment or depletion of $^{15}$N, which is associated with removal or loading of NO$_3^{-}$ in aerosols. These curves represent two opposite chemical processes, with a match at approximately 14‰, which showed a strong logarithmic correlation ($r=0.96$ during winter Event, green line, and -0.81 for the rest of points, black line, Fig. S3). These results indicate a significant and different mechanism by which nitrogen isotopic fractionation occurs in aerosols. In both cases, the decrease in nitrate leads to exponential changes in the enrichment or depletion of $^{15}$N from a value of approximately 14‰. In the case of enrichment, in addition to a higher proportion of NH$_4^{+}$ than NO$_3^{-}$, the dissociation process of NH$_3$NO$_3$ can cause an increase in $^{15}$N in TN during a period of higher ambient temperatures, as hypothesized by Pavuluri et al. (2010).

OrgN has not been widely studied compared to particulate NO$_3^{-}$ and NH$_4^{+}$, although it represents a significant fraction of TN (e.g., Jickells et al., 2013; Neff et al., 2002; Pavuluri et al., 2015). Figure 5 shows the relationship between $\delta^{15}$N in TN and OrgN. Organic nitrogen consists organic compounds containing nitrogen in water soluble and insoluble fractions. The majority of samples have a
concentration range of 0.1-0.5 µg m\(^{-3}\) (gray highlight in Fig. 5), which can be considered as background OrgN at the Košetice site. During the domestic heating season with the highest concentrations of NO\(_3^-\) and NH\(_4^+\), we can observe a significant increase in OrgN with \(\delta^{15}\text{N}\) again at approximately 14‰, which implies that the isotopic composition of OrgN is determined by the same process during maximal NO\(_3^-\) concentrations, that is, emissions from domestic heating. In the case of emissions from combustion, OrgN originates mainly from biomass burning (Jickells et al., 2013 and references therein), and thus, elevated concentrations of OrgN (together with high NO\(_3^-\) and NH\(_4^+\) conc.) may refer to this source. On the other hand, looking at the trend of OrgN/TN in dependence on \(\delta^{15}\text{N}\) (Fig. 3), it is more similar to the trend of NH\(_4^+\)/TN than NO\(_3^-\)/TN. Thus, it can be assumed that changes in the \(\delta^{15}\text{N}\) in OrgN in samples highlighted as a gray area in Fig. 5 are probably driven more by the same changes in NH\(_4^+\) particles, and especially in summer with elevated OrgN in TN (Table 1).

### 3.2. Total carbon and its \(\delta^{13}\text{C}\)

The \(\delta^{13}\text{C}\) of TC ranged between -25.4‰ and -28.9‰ (Fig. 6), which is similar but broader than the range reported at a rural background site in Vavihill (southern Sweden, range -26.7 to -25.6‰, Martinsson et al. (2017)), urban Wroclaw (Poland, range -27.6 to -25.3‰, Górka et al. (2014)), and different sites (urban, coastal, forest) in Lithuania (East Europe, Masalaite et al., 2015, 2017) but similar to those published by Fisseha et al. (2009) in Zurich. However, our \(\delta^{13}\text{C}\) values are smaller than those reported for coastal TSP aerosols from Okinawa (East Asia, range -24.2 to -19.5‰, Kunwar et al. (2016)) or rural Tanzania (Central-East Africa, range -26.1 to -20.6‰ in PM2.5, Mkoma et al. (2014)). In fact, similar or different \(\delta^{13}\text{C}\) values are widely reported in the northern and southern hemispheres (Cachier, 1989), which can be explained by different distributions of C3 and C4 plants (Martinelli et al., 2002), the influence of marine aerosols (Ceburnis et al., 2016), as well as different anthropogenic sources (e.g., Widory et al., 2004). The \(\delta^{13}\text{C}\) values at the Košetice site fall within the range common to other European sites. The \(\delta^{13}\text{C}\) values are significantly smaller than those of \(\delta^{15}\text{N}\) due to a higher number of carbonaceous compounds in the aerosol mixture whose isotope ratio overlaps each other. However, it is possible to distinguish lower \(\delta^{13}\text{C}\) values in summer (Table 1), which may indicate a contribution from higher terrestrial plant emissions. Similarly, Martinsson et al. (2017) reported lower \(\delta^{13}\text{C}\) values in summer in comparison with other seasons, which they explain by high biogenic aerosol contributions from C3 plants.

A comparison of \(\delta^{13}\text{C}\) with TC in Fig. 6 shows an enhanced enrichment of \(^{13}\text{C}\) at higher TC concentrations. The lowest \(\delta^{13}\text{C}\) values were observed in field blank samples (mean -29.2‰, n=7), indicating that the lowest summer values in particulate matter were close to gas phase values. A similar dependence of \(\delta^{13}\text{C}\) on the TC concentration was observed by Fisseha et al. (2009), whereby winter \(^{13}\text{C}\)
enrichment was associated with WSOC (water soluble organic carbon) that originated mainly from wood combustion. Similarly, at the Košetice station, different carbonaceous aerosols were observed during the heating season (Oct.–Apr.) than in summer (Mbengue et al., 2018; Vodička et al., 2015), whereby winter aerosols were probably affected by not only biomass combustion but also burning of coal (Schwarz et al., 2016), which can result in higher carbon contents and more $^{13}$C enriched particles (Widory, 2006). However, relatively low $\delta^{13}$C values in our range (up to -28.9‰) are caused by not only sources of TC but also a the fact that fine particles are more $^{13}$C depleted in comparison with coarse particles (e.g., Masalaite et al., 2015; Skipitytė et al., 2016). Furthermore, based on the number of size distribution measurements at the Košetice site, larger particles were observed in winter in comparison with summer, even in the fine particle fraction (Zíková and Ždímal, 2013), which can also have an effect on lower $\delta^{13}$C values in summer.

### 3.3. Temperature dependence and correlations of $\delta^{15}$N and $\delta^{13}$C with other variables

Tables 2 and 3 show Spearman's correlation coefficients (r) of $\delta^{15}$N and $\delta^{13}$C with different variables that may reflect some effects on these isotopes. In addition to year-round correlations, correlations for each season, as well as for the Event, are presented separately.

Correlations of $\delta^{15}$N in winter and summer are often opposite (see e.g., for TN -0.40 in winter vs. 0.36 in summer, for NH$_4^+$ -0.42 in winter vs. 0.40 in summer), indicating that changes in aerosol chemistry at the nitrogen level are different in these seasons. Similarly, the contradictory dependence between $\delta^{15}$N and TN in summer and winter was observed by Widory (2007) on PM10 samples from Paris and was connected with secondary processes affecting the nitrogen chemistry that follows two distinct pathways between $^{15}$N enrichment (summer) and depletion (winter).

From a meteorological point of view, a significant correlation of $\delta^{15}$N with temperature has been obtained, indicating the influence of temperature on the nitrogen isotopic composition. Dependence of $\delta^{15}$N in TN on temperature (Fig. 7) is opposite to that observed by Ffreyer (1991) for $\delta^{15}$N in NO$_3$; however, it is same to that observed by Ciężka et al. (2016) for $\delta^{15}$N in NH$_4^+$ from precipitation. These authors concluded that the isotope equilibrium exchange between nitrogen oxides and particulate nitrates is temperature dependent and could lead to more $^{15}$N enriched NO$_3^-$ during the cold season (Freyer et al., 1993; Savard et al., 2017). Although Savard et al. (2017) reported a similar negative $\delta^{15}$N in NH$_4^+$ dependence at temperatures in Alberta (Canada), such as for NO$_3^-$, most studies (e.g., Kawashima and Kurahashi, 2011; Kundu et al., 2010) reported the opposite temperature dependence for $\delta^{15}$N in NH$_4^+$ because the NH$_3$ gas concentrations are more abundant during warm weather.
conditions, and thus, isotopic equilibrium exchange $\text{NH}_3(g) \leftrightarrow \text{NH}_4^+(p)$ leading to $^{15}\text{N}$ enrichment in particles is more intensive.

All the considerations mentioned above indicate that a final relationship between $\delta^{15}\text{N}$ in TN and temperature is driven by the prevailing nitrogen species, which is $\text{NH}_4^+$ in our case. A similar dependence was reported by Pavuluri et al. (2010) between temperature and $\delta^{15}\text{N}$ in TN in Chennai (India), where $\text{NH}_4^+$ strongly prevailed. They found the best correlation between $\delta^{15}\text{N}$ and temperature during the colder period (range 18.4-24.5°C, avg. 21.2°C); however, during warmer periods, this dependence was weakened. In our study, we observed the highest correlation of $\delta^{15}\text{N}$ with temperature in autumn ($r=0.58$, temp. range -1.9 to 13.9°C, avg. 6.6°C), followed by spring ($r=0.52$, temp. range 1.5-18.7°C, avg. 9.3°C), but there was even a negative but insignificant correlation in summer ($r=-0.21$, temp. range: 11.8-25.5°C, avg. 17.7°C). This result indicates that temperature plays an important role in the enrichment/depletion of $^{15}\text{N}$; however, it is not determined by a specific temperature range but rather the conditions for repeating the process of "evaporation/condensation", as shown by the comparison with the work of Pavuluri et al. (2010). It is likely that isotopic fractionation caused by the equilibrium reaction of $\text{NH}_3(g) \leftrightarrow \text{NH}_4^+(p)$ reaches a certain level of enrichment under higher temperature conditions in summer.

In summer, $\delta^{15}\text{N}$ correlates positively with $\text{NH}_4^+$ ($r=0.40$) and $\text{SO}_4^{2-}$ (0.51), indicating a link with $(\text{NH}_4\text{H}_2\text{SO}_4)$ that is enriched by $^{15}\text{N}$ due to aging. Figure 8 shows a decreasing molar ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ with increasing $^{14}\text{N}$ enrichment, especially during spring, indicating a gradual uptake of ammonia in the gas phase to aerosol phase. With a decreasing $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio, there is also a visible decrease in the nitrate content in aerosols (Fig. 8). However, when the $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio approaches a value below 2, there is not enough available ammonia in the gas phase, leading to the exclusion of nitrate from the aerosol phase, as well as to the disruption of the thermodynamic equilibrium between $\text{NH}_3(g) \leftrightarrow \text{NH}_4^+(p)$, which previously led to $^{15}\text{N}$ enrichment in the particles. In this context, we note that 25 out of 33 summer samples have molar $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios below 2, and the remaining samples are approximately 2, although the average relative abundance of $\text{NO}_3^-$ in PM1 in those samples is very low (ca. 1.7%).

Recently, Silvern et al. (2017) reported that organic aerosols can play a role in modifying or retarding the achievement of $\text{H}_2\text{SO}_4-\text{NH}_3$ thermodynamic equilibrium at $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios of less than 2, even when sufficient amounts of ammonia are present in the gas phase. Thus, an interaction between sulfates and ammonia may be hindered such that organics coated with aged aerosols preferentially react (Liggio et al., 2011). Indeed, we observed a positive (and significant) correlation between temperature and $\delta^{13}\text{C}$ ($r=0.39$) only in summer, whereas $\delta^{15}\text{N}$ vs. temperature is negative (-0.21), suggesting that the thermodynamic equilibrium between $\text{NH}_3(g)$ and nitrogen in particles was minimal or replaced by the influence of organics in this season. Ammonia measurements directly at the Košetice site were carried...
out until 2001, and they showed that the NH$_3$ concentrations in summer and winter were comparable (http://portal.chmi.cz/files/portal/docs/uooco/isko/tab_roc/2000_enh/CZE/kap_18/kap_18_026.html), which indirectly support the above hypothesis.

The summer positive correlations of $\delta^{13}$C with ozone ($r=0.66$) and temperature ($0.39$) indicate oxidation processes that can indirectly lead to carbon isotope enrichment. This result is also supported by the fact that the content of oxalate in PM$_1$, measured by IC, was twice as high in spring and summer than in winter and autumn. The influence of temperature on $\delta^{13}$C in winter is opposite to that in the summer. The winter negative correlation (-0.35) probably points to the evolution of more fresh emissions from domestic heating with higher contents of $^{13}$C during lower temperatures.

The whole year temperature dependence on $\delta^{13}$C is the opposite of that observed for $\delta^{15}$N (Fig. 7, left), suggesting more $^{13}$C-depleted products in summer. This result is probably connected with different carbonaceous aerosols during winter (anthropogenic emissions from coal, wood and biomass burning with the enrichment of $^{13}$C) in comparison with the summer season (primary biogenic and secondary organic aerosols with lower $\delta^{13}$C). The data of $\delta^{13}$C in Fig. 7 are also more scattered, which indicates that in the case of carbon, the isotopic composition depends more on sources than on temperature.

Correlations of $\delta^{13}$C with OC are significant in all seasons; they are strongest in spring and weakest in summer (Table 3). Correlations of $\delta^{13}$C with EC, whose main source is combustion processes from domestic heating and transportation, are significant ($r=0.61-0.88$) only during the heating season (autumn–spring, see Table 3), while in summer, the correlation is statistically insignificant (0.28). Thus, the isotopic composition of aerosol carbon at the Košetice station is not significantly influenced by EC emitted from transportation, otherwise the year-round correlation between $\delta^{13}$C and EC would also be significant in summer. This result is consistent with positive correlations between $\delta^{13}$C and gaseous NO$_2$, as well as particulate nitrate, which is also significant from autumn to spring, and this result is also supported by the negative correlation of $\delta^{13}$C with the EC/TC ratio ($r=-0.51$), which is significant only in summer.

It should be mentioned that the wind directions during the campaign were similar, with the exception of the winter season, when southeast (SE) winds prevailed (see Fig. S4 in SI). We did not observe any specific dependence of isotopic values on wind directions, except for the Event.
3.4. **Winter Event**

The winter Event represents a period between January 23 and February 5, 2014, when enrichment of $^{13}$C and substantial depletion of $^{15}$N occurred in PM1 (see Figs. 1 and 9 for details). We do not observe any trends of the isotopic compositions of $\delta^{15}$N and $\delta^{13}$C with wind directions, except for the period of the Event and one single measurement on 18th December 2013. Both the Event and the single measurement are connected to SE winds through Vienna and the Balkan Peninsula (Fig. 10). More elevated wind speeds with very stable SE winds are observed on the site with samples showing the most $^{15}$N depleted values at the end of the Event (Fig. 9). Stable weather conditions and the homogeneity of the results indicate a local or regional source, which is probably associated with emissions of sulfates (Fig. S5), which are not sufficiently mixed at this time.

Although the Event contains only 7 samples, high correlations are obtained for $\delta^{15}$N and $\delta^{13}$C (Tables 2 and 3). Generally, correlations of $\delta^{15}$N with several parameters during the Event are opposite to those of the four seasons, indicating the exceptional nature of these aerosols from a chemical point of view. During the Event, $\delta^{15}$N correlates positively with NO$_3^-$ ($r=0.96$) and NO$_3^-$-N/TN (0.98), with large values of $\delta^{15}$N at approximately 14‰, which we previously interpreted as the emissions from domestic heating by coal and/or biomass burning. Positive correlations of $\delta^{15}$C with oxalate and potassium (both 0.93) and the negative correlation with temperature (-0.79) also show that the Event is associated with emissions from combustion.

In contrast, we find that most $\delta^{15}$N values with a depletion of $^{15}$N are associated with enhanced NH$_4^+$ contents (70-80 %) and the almost total absence of NO$_3^-$ nitrogen (see Figs. 3 and 4). Although some content of OrgN is detected during the Event (Fig. 3), the correlation between $\delta^{15}$N and OrgN/TN is not significant (Table 2). This result shows that nitrogen with the lowest $\delta^{15}$N values is mainly connected with NH$_4^+$, which is supported by a strong negative correlation between $\delta^{15}$N and NH$_4^+$/TN (-0.86).

Assuming that nitrogen in particles mainly originates from gaseous nitrogen precursors via gas-to-particle conversion (e.g., Wang et al., 2017) during the Event, we should expect the nitrogen to originate mainly from NH$_3$ with depleted $^{15}$N but not nitrogen oxides. Agricultural emissions from both fertilizer application and animal waste are such sources of NH$_3$ emissions (Felix et al., 2013). Considering possible agriculture emission sources, there exist several collective farms, with both livestock (mainly cows, Holsteins cattle) and crop production in the SE direction from the Košetice observatory – namely, Agropodnik Košetice (in 3.4 km distance), Agrodam Hořepník (6.8 km) and Agrosev Červená Řečice (9.5 km). Skipityt et al. (2016) reported lower $\delta^{15}$N values of TN (+1 to +6‰) for agriculture-derived particulate matter of poultry farms, which are close to our values obtained during the Event.
The $\delta^{15}N$ values from the Event are associated with an average temperature of below 0°C (Figs. 7 and 9). Savard et al. (2017) observed the lowest values of $\delta^{15}N$ in NH$_3$ with temperatures below -5°C, and the NH$_4^+$ particles that were simultaneously sampled were also isotopically lighter compared to the samples collected under higher temperature conditions. They interpreted this result as the preferential dry deposition of heavier isotopic $^{15}$NH$_3$ species during the cold period, whereas the remaining lighter $^{14}$NH$_3$ species in the atmosphere, lead to lighter NH$_4^+$ in particles. Moreover, the removal of NH$_3$ by dry deposition also leads to a non-equilibrium state between the gas and aerosol phases. Such an absence of equilibrium exchange of NH$_3$ between the gas and liquid/solid phases is supported by a NH$_4^+$/SO$_4^{2-}$ molar ratio below 2 for the three most $^{15}$N depleted samples (Fig. 8). In such conditions, nitrate partitioning in PM is negligible, and unidirectional reactions of lighter NH$_3$ isotope with H$_2$SO$_4$ in the atmosphere are strongly preferred due to the kinetic isotope effect, which is (after several minutes) followed by enrichment of the nitrogen due to the newly established equilibrium (Heaton et al., 1997).

Based on laboratory experiments, Heaton et al. (1997) estimated the isotopic enrichment factor between gas NH$_3$ and particle NH$_4^+$, $\varepsilon_{\text{NH}_4-\text{NH}_3}$, to be $+33\%$. Savard et al. (2017) reported an isotopic difference ($\Delta \delta^{15}N$) between NH$_3$ (g) and particulate NH$_4^+$ as a function of temperature, whereas $\Delta \delta^{15}N$ for a temperature of approximately 0°C was approximately 40%. In both cases, after subtraction of these values (33 or 40%) from the $\delta^{15}N$ values of the measured Event, we obtain values between approximately -28 to -40%, which are in a range of $\delta^{15}N$-NH$_3$ (g) measured for agricultural emissions. These values are especially in good agreement with $\delta^{15}N$ of NH$_3$ derived from cow waste (ca. -22 to -38%, Felix et al., 2013).

Thus, in case of the Event, we probably observe PM representing a mixture of aerosols from household heating characterized by higher amounts of NO$_3^-$ and $\delta^{14}N$ in TN (ca. 14%), which are gradually replaced by $^{15}$N-depleted agricultural aerosols. Results of the whole process from low temperatures that first support dry deposition of NH$_3$ followed by unidirectional (kinetic) reaction of lighter isotope NH$_3$(g) $\rightarrow$ NH$_4^+$(p) originate mainly from agricultural sources in the SE direction from the Košetice station.

If the four lowest values of $\delta^{15}N$ mainly represent agricultural aerosols, then the $\delta^{13}C$ values from the same samples should also be characteristic of agricultural sources. In this case, the $\delta^{13}C$ values ranging from -25.4 to -26.2% belong to the most $^{13}$C enriched fine aerosols at the Košetice site. However, similar $\delta^{13}C$ values were reported by Widory (2006) for particles from coal combustion. Skipityté et al. (2016) reported a mean value of $\delta^{13}C$ in TC (-23.7±1.3‰) for PM1 particles collected on a poultry farm, and they suggested the litter as a possible source for the particles. Thus, in the case of $\delta^{13}C$ during the Event we observed, emissions either from domestic heating and/or agricultural sources are responsible for the $^{13}$C values.
4. Summary and Conclusions

Based on the analysis of year-round data of stable carbon and nitrogen isotopes, we extracted some important information on the processes taking place in fine aerosols during different seasons at the Central European station of Košetice. Seasonal variations were observed for $\delta^{13}$C and $\delta^{15}$N, as well as for TC and TN. The supporting data (i.e., ions, EC/OC, meteorology, trace gases) revealed characteristic processes that led to changes in the isotopic compositions on the site.

The main and gradual changes in nitrogen isotopic composition occurred in spring. During early spring, domestic heating with wood stoves is still common, with high nitrate concentrations in aerosols, which decreased toward the end of spring. Additionally, temperature slowly increases, and the overall situation leads to thermodynamic equilibrium exchange between gas ($\text{NO}_x$-$\text{NH}_3$-$\text{SO}_2$ mixture) and aerosol ($\text{NO}_3^-$-$\text{NH}_4^+$-$\text{SO}_4^{2-}$ mixture) phases, which causes $^{15}$N enrichment in aerosols. Enrichment of $^{15}$N ($\Delta \delta^{15}$N) from the beginning to the end of spring was approximately $+10\%$. Gradual springtime changes in isotopic composition were also observed for $\delta^{13}$C, but the depletion was small, and $\Delta \delta^{13}$C was only about $-1.4\%$.

In summer, we observed the lowest concentrations of TC and TN; however, there was an enhanced enrichment of $^{15}$N, which was probably caused by the aging of nitrogen aerosols, where ammonium sulfate is subjected to isotopic fractionation via equilibrium exchange between $\text{NH}_3(g)$ and $\text{NH}_4^+(p)$. Based on a $\text{NH}_4^+$/$\text{SO}_4^{2-}$ molar ratio of less than 2, we concluded that summer aerosols become more acidic, and thus, kinetic isotopic fractionation took place via the equilibrium exchange of nitrogen species. However, summer values of $\delta^{15}$N were still among the highest compared with those in previous studies, which can be explained by several factors. First, a fine aerosol fraction (PM1) is more reactive, and its residence time in the atmosphere is longer than coarse mode, leading to $^{15}$N enrichment in aged aerosols. Second, summer aerosols, compared to other seasons, contain a negligible amount of nitrate, contributing to a decrease in the average value of $\delta^{15}$N of TN. On the other hand, we observed an enrichment of $^{13}$C only in summer, which can be explained by the photooxidation processes of organics and is supported by the positive correlation of $\delta^{13}$C with temperature and ozone. Despite this slow enrichment process, summertime $\delta^{13}$C values were the lowest compared to those in other seasons and referred predominantly to organic aerosols of biogenic origin. The role of organics in summer may also have an effect on the aforementioned $^{15}$N enrichment due to thermodynamic equilibrium.

In winter, we found the highest concentrations of TC and TN. Lower winter $\delta^{15}$N values were apparently influenced by fresh aerosols from combustion, which were strongly driven by the amount of nitrates (mainly NH$_4$NO$_3$ in PM1), and led to an average winter value of $\delta^{15}$N approximately $14\%$. Winter $\delta^{13}$C values were more enriched than summer values, and they were connected mainly to emissions from coal and (mostly) biomass burning for domestic heating.

We observed an aerosol event in winter, which was characterized by temperatures below the freezing point, stable southeast winds, and a unique isotope signature with a depletion of $^{15}$N and enrichment of...
The winter Event characterized by 15N depletion was probably caused by the dry deposition of NH3 (with heavier isotope) during cold weather, and with decreasing concentrations of NO3-. However, it was completely opposite to a summertime decrease in nitrate, which led to an enrichment of 15N. In the case of the most depleted 15N event, nitrate was suppressed to partition in aerosol and gas phases with unidirectional reactions of isotopically light ammonia and sulfuric acid resulting in (NH4)2SO4, which originated mainly from agriculture emissions in this case.

This study revealed a picture of the seasonal cycle of δ15N in aerosol TN at the Košetice site. In the case of carbon, the seasonal cycle of δ13C values was not so pronounced because they mainly depend on the isotopic composition of primary sources, which often overlapped, and because secondary reactions were influenced by the kinetic isotopic effect, while phase transfer probably did not play a crucial role.

Acknowledgements

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Skipitytė, R., Mašalaitė, A., Garbaras, A., Mickienė, R., Ragažinskienė, O., Baliukonienė, V.,


Table 1: Seasonal and entire campaign averages ± standard deviations, (medians in brackets) of different variables.

<table>
<thead>
<tr>
<th></th>
<th>Autumn</th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Year</th>
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<td>N of samples</td>
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<td>45</td>
<td>43</td>
<td>33</td>
<td>146</td>
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<tr>
<td>TC [µg m⁻³] (from EA)</td>
<td>3.61±1.61 (3.30)</td>
<td>4.76±2.44 (3.88)</td>
<td>3.78±2.03 (3.04)</td>
<td>2.71±0.76 (2.68)</td>
<td>3.81±2.03 (3.35)</td>
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<tr>
<td>TN [µg m⁻³]</td>
<td>1.56±1.18 (1.33)</td>
<td>1.67±0.96 (1.45)</td>
<td>2.00±1.62 (1.47)</td>
<td>0.81±0.29 (0.82)</td>
<td>1.56±1.22 (1.26)</td>
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<td>δ¹³C [%ε]</td>
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<td>-26.7±0.5 (-26.7)</td>
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<td>TC/PM1 [%]</td>
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<td>33±8 (32)</td>
<td>38±15 (35)</td>
<td>31±6 (30)</td>
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<td>TN/PM1 [%]</td>
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<td>11±3 (12)</td>
<td>17±4 (17)</td>
<td>9±2 (9)</td>
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<td>NO₃⁻/N/TN [%]</td>
<td>21±6 (21)</td>
<td>25±8 (28)</td>
<td>22±8 (21)</td>
<td>5±3 (4)</td>
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<tr>
<td>NH₄⁺/N/TN [%]</td>
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<td>51±9 (49)</td>
<td>58±7 (60)</td>
<td>57±6 (57)</td>
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<td>OrgN/TN [%]</td>
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<td>25±8 (23)</td>
<td>20±8 (19)</td>
<td>39±6 (38)</td>
<td>27±10 (25)</td>
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<tr>
<td>TC/TN</td>
<td>2.77±1.10 (2.60)</td>
<td>3.34±1.66 (2.68)</td>
<td>2.33±0.98 (2.34)</td>
<td>3.60±1.23 (3.45)</td>
<td>3.01±1.38 (2.61)</td>
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Table 2: Spearman correlation coefficients ($r$) of $\delta^{15}$N with various tracers. Only bold values are statistically significant (p-values < 0.05).

<table>
<thead>
<tr>
<th>$\delta^{15}$N vs.</th>
<th>Autumn</th>
<th>Winter*</th>
<th>Spring</th>
<th>Summer</th>
<th>Year*</th>
<th>Event</th>
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<td>NO$_3$-N/TN</td>
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<td>OrgN</td>
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<td>Cl$^-$</td>
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<tr>
<td>NO$_2$ (gas)</td>
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<td>NO$_2$/NO (gas)</td>
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<td>-0.82</td>
<td>0.14</td>
<td>-0.76</td>
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<tr>
<td>Temp.</td>
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<td>0.52</td>
<td>-0.21</td>
<td>0.77</td>
<td>-0.43</td>
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*Event data are excluded from winter and year datasets.
Table 3: Spearman correlation coefficients (r) of δ\textsubscript{13}C with various tracers. Only bold values are statistically significant (p-values < 0.05).

<table>
<thead>
<tr>
<th>δ\textsubscript{13}C vs.</th>
<th>Autumn</th>
<th>Winter*</th>
<th>Spring</th>
<th>Summer</th>
<th>Year*</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC</td>
<td>0.64</td>
<td>0.63</td>
<td>0.91</td>
<td>0.39</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>EC</td>
<td>0.61</td>
<td>0.74</td>
<td>0.88</td>
<td>0.28</td>
<td>0.84</td>
<td>0.46</td>
</tr>
<tr>
<td>EC/TC</td>
<td>0.06</td>
<td>0.06</td>
<td>0.13</td>
<td>-0.51</td>
<td>0.32</td>
<td>-0.32</td>
</tr>
<tr>
<td>TC/PM1</td>
<td>-0.16</td>
<td>-0.05</td>
<td>-0.40</td>
<td>0.22</td>
<td>-0.09</td>
<td>0.32</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>0.74</td>
<td>0.52</td>
<td>0.71</td>
<td>0.12</td>
<td>0.76</td>
<td>0.39</td>
</tr>
<tr>
<td>NH\textsubscript{4}*</td>
<td>0.84</td>
<td>0.59</td>
<td>0.80</td>
<td>0.42</td>
<td>0.66</td>
<td>0.75</td>
</tr>
<tr>
<td>Oxalate</td>
<td>0.34</td>
<td>0.62</td>
<td>0.71</td>
<td>0.65</td>
<td>0.25</td>
<td>0.93</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>0.80</td>
<td>0.64</td>
<td>0.73</td>
<td>0.41</td>
<td>0.34</td>
<td>0.54</td>
</tr>
<tr>
<td>K*</td>
<td>0.84</td>
<td>0.63</td>
<td>0.70</td>
<td>0.47</td>
<td>0.76</td>
<td>0.93</td>
</tr>
<tr>
<td>Cl*</td>
<td>0.44</td>
<td>0.62</td>
<td>0.68</td>
<td>0.44</td>
<td>0.76</td>
<td>0.25</td>
</tr>
<tr>
<td>CO (gas)</td>
<td>0.21</td>
<td>0.53</td>
<td>0.60</td>
<td>0.32</td>
<td>0.37</td>
<td>0.68</td>
</tr>
<tr>
<td>O\textsubscript{3} (gas)</td>
<td>-0.41</td>
<td>-0.26</td>
<td>0.14</td>
<td>0.66</td>
<td>-0.33</td>
<td>0.11</td>
</tr>
<tr>
<td>NO\textsubscript{2} (gas)</td>
<td>0.67</td>
<td>0.38</td>
<td>0.70</td>
<td>0.18</td>
<td>0.69</td>
<td>0.32</td>
</tr>
<tr>
<td>NO\textsubscript{2}/NO (gas)</td>
<td>0.72</td>
<td>0.65</td>
<td>0.67</td>
<td>0.68</td>
<td>0.78</td>
<td>0.96</td>
</tr>
<tr>
<td>Temp.</td>
<td>-0.33</td>
<td>-0.35</td>
<td>-0.20</td>
<td>0.39</td>
<td>-0.57</td>
<td>-0.79</td>
</tr>
</tbody>
</table>

\*Event data are excluded from winter and year datasets.
Figures:

Fig. 1: Time series of $\delta^{15}$N together with TN (top) and $\delta^{13}$C together with TC (bottom) in PM1 aerosols at the Košetice station. The gray color highlights an Event with divergent values, especially for $\delta^{15}$N.

Fig. 2: Relationships between TC and TN (left) and their stable carbon and nitrogen isotopes (right). The color scale reflects the time of sample collection. The gray circle highlights the winter Event measurements.
Fig. 3: Changes in $\delta^{15}N$ depending on fraction of individual nitrogen components (NO$_3$-N, NH$_4$-N, and OrgN) in TN. The color scale reflects the time of sample collection.

Fig. 4: Relationships of $\delta^{15}N$ in TN vs. NO$_3$ concentrations. The larger circles indicate higher NH$_4^+$ concentrations. The color scale reflects the time of sample collection.
Fig. 5: Relationships of δ¹⁵N in TN vs. OrgN concentrations. The larger circles indicate higher sums of $\text{NO}_3^- + \text{NH}_4^+$ concentrations. The color scale reflects the time of sample collection, and the highlighted portion is a concentration range between 0.1-0.5 µg m$^{-3}$. 

NO$_3^- + \text{NH}_4^+$ concentrations. The color scale reflects the time of sample collection, and the highlighted portion is a concentration range between 0.1-0.5 µg m$^{-3}$. 

Fig. 5: Relationships of δ¹⁵N in TN vs. OrgN concentrations. The larger circles indicate higher sums of $\text{NO}_3^- + \text{NH}_4^+$ concentrations. The color scale reflects the time of sample collection, and the highlighted portion is a concentration range between 0.1-0.5 µg m$^{-3}$. 

Fig. 5: Relationships of δ¹⁵N in TN vs. OrgN concentrations. The larger circles indicate higher sums of $\text{NO}_3^- + \text{NH}_4^+$ concentrations. The color scale reflects the time of sample collection, and the highlighted portion is a concentration range between 0.1-0.5 µg m$^{-3}$. 

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Discussion started: 12 September 2018
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Fig. 6: Relationship between TC and $\delta^{13}$C. The color scale reflects the time of sample collection.
Fig. 7: Relationships between temperature and $\delta^{13}$C in TC (left) and $\delta^{15}$N in TN (right). The color scale reflects the total radiation.
Fig. 8: Relationships between $\delta^{15}$N in TN and molar ratios of NH$_4^+$/SO$_4^{2-}$ in particles. The larger circle indicates a higher nitrate content in PM1. The color scale reflects the time of sample collection.
Fig. 9: Time series of $\delta^{15}$N, TN, $\delta^{13}$C, TC and meteorological variables (temperature, wind speed and direction, 1 h time resolution) during the Event, which is highlighted by a gray color.
Fig. 10: NOAA HYSPLIT (Stein et al., 2015) 24 h backward air mass trajectories at 500 m above ground level for the observation site from 30 Jan until 5 Feb 2014 (right).