Response to anonymous Referee RC1

Firstly, we would like to thank the referee for his positive criticism and valuable review which has enabled us to improve our paper. Based on the reviewer comments, we thought about different views of the issue and we also re-wrote some parts of the manuscript. Answers for reviewer's comments are following below.

The paper of Vodicka et al. aimed at elucidating particulate matter and their gaseous precursor sources by interpreting results of isotope analysis. The study is based on a year-round data set and, therefore, trying to discern seasonal differences and processes taking place in different seasons. The analytical approach to the measurement results is highly commendable where authors try to make sense of various relationships between the variables. By large the interpretations are justified although several of them are highly speculative and aiming to fit the data or simply shallow. Graphics of the paper is very well prepared and clear utilising three or four dimensions in 2D graph. The paper is certainly recommended for publication in Atmospheric Chemistry and Physics, but additional work is required by removing ambiguities, speculations and making the interpretations more coherent.

Major comments

The major comment is the lack of coherent interpretation arising from unified approach to isotope effect and fractionation processes. Physico-chemical properties are the result of quantum mechanical effects with heavier isotopes (like C13 and N15) possessing lower vibrational energy levels and making stronger bonds and vice versa for lighter isotopes. Also, lighter isotope species have lower vapour pressures resulting in faster phase transitions. Condensation of isotope-light species would make the product of lower isotope ratio while evaporation would make it higher. Formation/evaporation of ammonium nitrate is, indeed, a reversible reaction, but not necessarily in equilibrium from isotope point of view because of competition effect with sulfate for ammonium. Particulate matter products, like ammonium sulfate or nitrate only consume a small fraction of their respective gaseous species pool (1-10%) with a possible exception of nitric acid (which is a product itself). Hence, isotope-heavy product does not necessarily involve heavy precursors, but instead isotope-heavy fraction of gaseous precursors due to the above considerations.

Response: Thank you for this comment. It provides some general information that were missing in our manuscript. Based on this, we decided to extend the Introduction chapter to the following paragraph: *"Isotopes are furthermore altered mainly by kinetic and/or equilibrium fractionation processes. Kinetic isotope effects (KIE) occur mainly during unidirectional (irreversible) reactions but also diffusion or during reversible reactions that are not yet at equilibrium (Gensch et al., 2014). Owing to KIE, reaction products (both gasses and particles) are depleted in the heavy isotope relatively to the reactants, and this effect is generally observed in organic compounds (Irei et al., 2006). If the partitioning between phases is caused by non-equilibrium processes (such as e.g. absorption), the isotopic fractionation is small and lower than that caused by chemical reactions (Rahn and Eiler, 2001). Equilibrium isotope effects occur in reversible chemical reactions or phase changes if the system is in equilibrium. Under such conditions, the heavier isotope is bound into the compounds where the total energy of the system is minimized and the most stable. Equilibrium effects are typical for inorganic species and usually temperature dependent."*

Particles of different size ranges do not induce isotope effects, but are rather a result of chemical transformations or being produced by different emission sources, e.g. traffic produces mainly nanoparticles, while solid fuel combustion produce wide range of particle depending on the size of the source (industrial scale versus domestic).

Response: We agree with the reviewer that just different particle size itself does not induce isotope effects on these particles, and we even do not say such statement in the paper so we are sorry if some part of text sounds so. We also agree with reviewer that in first round different emission sources have effect both on particle size and isotopic composition, which is valid especially for δ^{13}C values. But moreover, size of particles has an effect on different reactivity of these particles – e.g. compounds in small particles react more often than bigger one because their effective surface for reactions is larger. Submicron particles of accumulation mode also persist longer time in atmosphere so isotopic effects also take longer time than on coarse particles and may differ in the resulting isotope composition. The above implies that even if the same isotope effects occur on the particles, the indirect properties resulting from the particle size can lead to a different isotopic composition during particle chemical/physical transformations. And this is what we try to describe in the article.
For details, see answer for specific comment related to line 275 to effect of size on nitrogen isotope contents, and answer for specific comment related to line 366 due to carbon.

It would very useful to consider isotope mixing approach in interpreting the results which would eliminate unnecessary associations, e.g. dC13 and EC (which is a relatively small fraction of TC). The authors, indeed, consider isotope mixing in few cases which is encouraged to do more frequently.

Response: Regarding to associations between δ^{13}C and EC we answered in specific comment related to line 454 (see below).

Regarding to multi-isotope approach, we extended Introduction chapter about examples of studies using multi isotope analyses – see following text:

"Recently, the multiple isotope approach was applied in several studies by using δ^{13}C and δ^{15}N measurements. Specifically, the δ^{13}C and δ^{15}N composition of aerosol (along with other supporting data) was used to identify the sources and processes on marine sites in Asia (Bikkina et al., 2016; Kunwar et al., 2016; Miyazaki et al., 2011; Xiao et al., 2018). Same isotopes were used to determine the contribution of biomass burning to organic aerosols in India (Boreddy et al., 2018) and in Tanzania (Mkoma et al., 2014), or to unravel the sources of aerosol contamination at Cuban rural and urban coastal sites (Morera-Gómez et al., 2018). These studies show the potential advantages of δ^{13}C and δ^{15}N isotope ratios to characterize aerosol types and to reveal the underlying chemical processes that take place in them."

Lastly, not all of the observations or measurement results should be strictly interpreted as some may be spurious or based on small subset of data and highly uncertain. Insignificant correlations should not even be noted with numbers, they are meaningless.

A: Thank you for this comment. Actually, we had much bigger correlation matrix and we choose only correlations which were somehow interesting and also make sense for following interpretations. These value are summarized in Tables 2 and 3.

Regarding statistical significance/insignificance, this is determined based on p-value. Results are statistically significant if p-value is less than 0.05 in case of our study, and how it is used in case of many similar studies. However, the significance level of 0.05 is just a convention, and it is not entirely appropriate to omit the results of insignificant correlations just based on p-value. In fact, applying this discriminatory value is the subject of many disputations between statisticians, and using of p-value was even banned in some scientific journals (e.g. Siegfried, 2015, on-line).
In some cases, the difference between statistically significant and insignificant correlation can be very small - see for example the correlation of $\delta^{13}C$ with winter temperature (-0.35, p=0.0328 => significant) and autumn temperature (-0.33, p=0.1063 => insignificant) (Table 3). In other cases, this difference can be much greater, and comparison of such differences has meaning. We agree it is not necessary to comment insignificant correlations and in this sense we removed all insignificant correlations from text. However, we would like to keep these values in Tables 2 and 3 because it can be interesting for some readers, and it can be a good compromise of this situation.

Minor comments

Line 12. A study of stable carbon...

Response: Reworded

Line 15. 146 daily samples suggest 40% data coverage which is rather low for continuous sampling.

Response: We agree that the original formulation could be confusing. Sampling was performed every second day with 24-h time resolution and in this sense we changed this part of sentence from *"…collected on a daily basis at a rural background site…"* to *"…collected every two days with a 24 h sampling period at a rural background site… "*.

Line 17. Autumn and spring were transition periods...(use past tense as the study refers to the past).

Response: Changed

Line 18. changing sources instead of different.

Response: Changed

Line 21. "Controls" can be used when processes are exactly known. “A comparative analysis with .... has revealed major associations which enlightened about certain processes affecting isotopic composition”.

Response: The sentence was reformulated in sense of comment to the following text:
“A comparative analysis with water-soluble ions, organic carbon, elemental carbon, trace gases and meteorological parameters (mainly ambient temperature) has shown major associations with the isotopic compositions, which enlightened the affecting processes.”

Line 32. “...of nitrogen species.”, instead of “on nitrogen level”.

Response: Changed

Line 36. The winter event has occurred in prevailing southeast air masses.

Response: Reformulated

Line 43. “Aerosols have a strong impact on key processes in the atmosphere associated with climate change, air quality, rain patterns and visibility”.

Response: First sentence of introduction was reformulated in sense of comment. Thank you.

Line 47. Unique insights instead of information.

Response: Changed

Line 49. Is atmospheric history any different from physical and chemical processes in the atmosphere? What is meant specifically by history?

Response: We didn't mean different chemical and physical processes during history of atmosphere but different chemical origin of chemical compounds in atmosphere which is "signed" e.g. by changes of $\delta^{15}N$ of NO3 in ice cores (see cited paper Dean et. al, 2014).
In this sense we changed end of sentence to: “*atmospheric composition in history*”.

Line 51. altered instead of influenced.

Response: Changed

Line 52. Delete "in case of nitrogen" and "in the case of carbon".

Response: These phrases were removed during rewriting of Introduction chapter.

Line 60. Americas or North&South America.

Response: Changed to “Americas”

Line 63. focusing on seasonality.

Response: Changed

Line 85. ...and to reveal undergoing chemical processes.

Response: Changed

Line 86. to broaden the approach over the European....

Response: Changed

Line 89. First study in the location or region? Surely authors must be certain about their location/station.

Response: We meant Central European region, so we changed word *"location"* to *"region"*.

Line 95. ...observatory is a key station of the Czech..., focusing on air quality and environmental monitoring.

Response: Reformulated. Thank you.

Line 99. with very low traffic density.

Response: Changed

Line 110-112. Were 146 samples obtained as a result of continuous or strategic sampling? Unclear sampling strategy or low data coverage. Please explain. Perhaps "Some temporal gaps were caused by sampler maintenance or power outages resulting in 146 samples during a year-long study".

Response: We are sorry that our text was little bit confusing. Sampling was not made continuously day by day but every second day (it means 24 h of sampling followed by 24 h gap). Such kind of sampling was made based on strategic decision before starting of campaign. Even so we had three bigger gaps caused by sampler maintenance or power outages.
We reformulated sentences on lines 110-112 to make a text clearer. Instead of "*Aerosol samples (n = 146) were collected for 24 h every two days from September…*" we used "*Aerosol samples were collected two days for 24 h from September…*".
The sentence "*Some gaps in sampling were caused by outages and maintenance to the sampler*." was changed to "*Some temporal gaps were caused by sampler maintenance or power outages resulting in 146 samples during the almost year-long study.*".

Line 113. sampled at a flow rate of 2.3 m3/h.

Response: Changed to: *"...operated at the flow rate at a 2.3 m^3/h."*

Line 119. The PM1 mass was measured gravimetrically with a microbalance (....) in a controlled environment (....).

Response: The paragraph was rephrased and shortened in a sense of comment. Thank you.

Line 135. Thermo Electron Corp.

Response: Corrected

Line 136. ...for calculating TC, TN and their isotope values.

Response: Reformulated

Line 152. measured, not detected.

Response: Changed

Line 175. ...instrument response without filter exposure.

Response: Reformulated

Line 184. ...for the annual dataset (139) and separately for each season and winter event.

Response: Corrected

Line 186. ...for the correlation analysis as their distinctly high concentrations and isotopic values might have affected the results.

Response: Sentence was completed in a sense of comment. Thank you.

Line 193. Statistically, 146 sample may be sufficient, indeed, but specific season(s) may not be typical, unless known to be such from previous studies.

Response: Seasonal comparison with other years provide e.g. work of Mbengue et al. (2018) (also cited in our work), which is published 4 years survey of EC/OC together with other variables (e.g. temperature) between years 2013-2016 directly at the Košetice station. It shows that a period from this work is not seasonally atypical during last years of observation.

Line 203. ..., but the relationship split during high concentration events due to divergent sources.

Response: Reformulated. Thank you!

Line 208. ...and characteristic of significant shift in chemical composition.

Response: End of sentence was changed in terms of comment.

Line 211. Use past tense as the study has been conducted in the past.

Response: Sentence changed to past tense

Line 209-211. Little difference does provide information on sources and quite contrary suggest that they were similar throughout the year in terms of BC production. The split contribution in each season may be different as suggested by isotope ratios, but overall the mixture of the sources seems to produce a steady trend.

Response: Station Košetice is a background site where the aerosol is more homogeneous than e.g. at an urban site, which can be reason for little seasonal differences of TC/TN ratio. However, previous studies from this station (Mbengue et al., 2018; Schwarz et al., 2016; Vodička et al., 2015) show that long-term concentrations of EC (and thus BC) are different in winter and summer, and sources are not similar throughout the year in terms of EC production. Different summer EC sources are consistent with a slightly higher summer TC/TN ratio than other seasons. In this sense, we changed the text to following:

"As seen in Table 1, the seasonal averages of TC/TN ratios fluctuate, but their medians have similar values for autumn, winter and spring. The summer TC/TN value is higher (3.45) and characteristic of a significant shift in chemical composition, which is in line with previous studies at the site (Schwarz et al., 2016)*. However, seasonal differences in the TC/TN ratios were not as large as those in other works (e.g., Agnihotri et al., 2011), and thus, this ratio itself did not provide much information about aerosol sources."*

Line 215. Do not report what was insignificant as it may mislead readers. "This result highlights significant shift in carbonaceous matter sources and corresponding isotope values in spring while during other seasons the sources were rather stable".

Response: Thank you for this comment. Instead of original sentence we used above suggested one by the reviewer. We also deleted values of insignificant correlation coefficients in text.
Original sentence
"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."
was changed to

“However, there is a statistically significant correlation for spring only (-0.54), while in other seasons, correlations are statistically insignificant. This result highlights a significant shift in the sources of carbonaceous aerosols and their isotope values in spring while the sources were rather stable during other seasons.”

Line 217. Lack of correlation during particular season is due to stability of sources while the variability between samples is similar in all seasons. Authors may look at the fractional variability of isotope ratios in each season as it seems that relative variability of dC13 is a lot larger than dN15.

Response: We agree with the review that lack of correlations during seasons is due to stability of sources in this period, and in this sense we also changed the sentence on line 215 (see previous comment).
In case of reviewer suggestion related to fractional variability of isotope ratios, we are not sure by its meaning because variability of $\delta^{15}N$ is larger than variability of δ^{13}C.

Line 224. ...which increased by an average of 13permile.

Response: We changed original word *"deviated"* to *"showed"* instead of reviewer proposed *"increase"* because change is from 15 to 13‰. Whole sentence is following: *“The $\delta^{15}N$ values are stable in winter at approximately 15‰, with an exception of the winter Event, which showed by an average of 13‰.”*

Line 232. What is the purpose of the formula if not solved for fractions (which is impossible given one equation and at least two unknowns).

Response: The reason for showing this formula is to give readers an idea before discussion about contribution of different nitrogen compounds to δ^{15}N of TN and also to discussion about results presented in Fig. 3. However, because it is an equation with general information character, we decided to move this equation to the Introduction chapter.

Line 236. What does it mean similarly balanced if NO3 was higher in winter?

Response: The original sentence was: *“...higher in winter, similarly balanced in spring and autumn, and very low in summer...”*. We wrote that similarly balanced were values in spring and autumn, not in spring and winter. However, we split this text to two following sentences to make this part of document clearer.

“...the highest in winter, and somewhat lower in spring and autumn. In summer when the dissociation of NH_4NO_3 plays an important role the NO_3^- content is very low and its nitrogen is partitioned from the aerosol phase to gas phase.”

Line 258. (a) changes in NOx emissions

Response: Changed

Line 262. “Considering our study, it was most likely that all of the factors contributed to a certain extent to isotopic composition throughout the year”.

Response: Original sentence was changed as follows: *“In our study, it is most likely that all these factors contributed, to a certain extent, to the nitrogen isotopic composition of NO_3^- throughout the year.”*

Line 266. In summary,.... If enrichment of N15 occurs during lowest NO3 contribution it can be inferred that NO3 is depleted in N15. Is this inference consistent through the year?

Response: In our study, we observed the highest enrichment of $\delta^{15}N$ in TN during summer when NO_3 concentrations are lowest. However, during winter Event when NO_3 contribution was also on the lowest level, $\delta^{15}N$ in TN was contrariwise most depleted (see Figs.3 and 4). This Event shows that that exceptions may occur and we can’t generalize. So, in our study, the inference, which you are proposing in comment, is not consistent throughout whole measurement campaign.

Line 275. Size fraction has no impact if the most of nitrogen containing particles reside in submicron range. Life-time has no impact either if coarse particles do not contain appreciable amount of nitrogen. If they do, what compounds that would be and how did they end up in coarse particles. If those compounds appeared in coarse particles by condensation then nitrogen was mainly concentrated on the surface and consequently coarse particles would be as reactive as fine ones.

Response: Nitrogen from NO_3 is contained in sufficient amounts both in fine and coarse fractions (e.g. Ondráček et al., 2011; Pakkanen, 1996; Schwarz et al., 2012), not only in submicron range. As summarized by e.g. Kundu et al. (2010), coarse mode contains predominantly non-volatile nitrogen in a form of $NaNO_3$ or $Ca(NO_3)_2$, whereas fine mode consists mainly from semi-volatile nitrogen from NH_4NO_3 and also in form of ammonium sulfate and bisulfate. If we have non-volatile nitrates in coarse fraction and predominantly NH_4NO_3 in fine fraction, where dissociation of NH_4NO_3 play an important role in enrichment of nitrogen, so it leads to some effect on the isotope composition depending on the particle size fraction. Yeatman et al. (2001) proposed presence of two different size-shift processes: dissociation/gas scavenging and dissolution/coagulation. Dissolution/coagulation processes appear to exhibit negative isotopic enrichment of nitrogen and shift both NH_4^+ and NO_3 to the coarse mode, whereas dissociation/gas scavenging processes appear to exhibit positive enrichment factors. All this is supported also by the works of Mkoma et al. (2014) and Freyer (1991) who observed a higher enrichment of ^{15}N in the fine fraction of the aerosol in comparison with coarse one. Last but not least, fine aerosol has larger particle surface/volume ratio than coarse one which can suggest higher reactivity of smaller particles.
Above arguments lead us to the fact that we have in this case the opposite view than reviewer.

Line 277. Aitken mode contributes negligibly to PM1 mass making this argument very weak. Unless authors can quantitatively prove it otherwise.

Response: Thank you for this notice. We made a mistake in this part. Instead of Aitken mode, we should write Accumulation mode there because this mode contributes by a main part to PM1 mass and also persist the longest time in the atmosphere. In text, we changed word *"Aitken"* to *"accumulation"*.

Line 303. Not all of gaseous precursor mass is ending up in NH4NO3, but preferentially heavier part. Authors must consider kinetic fractionation, otherwise conclusions are biased or unfounded.

Response: It is clear that during incorporation of nitrogen from gas phase to aerosol phase play a role both equilibrium and kinetic fractionation. Equilibrium fractionation is related to bond stability of nitrogen isotope whereas kinetic fractionation is related to the "speed" of isotope. First time, nitrogen incorporation is probably driven by kinetic fractionation because lighter isotopes react faster, but later heavier isotopes form a more stable bonds during equilibrium fractionation. In fine fraction of aerosol, we have nitrates almost exclusively in a form of NH_4NO_3 which undergo to dissociation to NH_4^+ and NO_3^- in water – this state is reversible and equilibrium fractionation is preferred in such system.
Nevertheless, Ciężka et al. (2016) suggested a possible kinetic exchange reactions between NH_3 and NH_4^+ as one of three possible processes affecting nitrogen isotopic composition, especially for fossil fuels combustions during the heating season. Also Deng et al. (2018) reported the kinetic nitrogen fractionation factors between gaseous and aqueous ammonia with statement that, when the removal of degassed ammonia is not efficient, ammonia may dissolve back to the fluid, which may significantly shift the nitrogen isotope behavior from kinetic isotope fractionation toward equilibrium isotope fractionation. Indeed, all this suggests that kinetic fractionation is likely to affect the isotopic composition of fresh particles from combustion having lower $\delta^{15}N$ than in spring or summer, and before they are affected by equilibrium fractionation.
Originally, on line 303, we did not present equilibrium fractionation as a dominant process, but we only compared known values of the isotopic composition of nitrogen oxides for different sources.
Since it is difficult to determine exact contribution of these fractionations to the final value of the heavier isotope in the aerosol, we do not discuss exactly, however, we added following two sentences to consider an influence of kinetic fractionation in a first steps of gas-aerosol transformation: *"Because of the only slight difference between above reported $\delta^{15}N$ of nitrogen oxides and our $\delta^{15}N$ of TN during maximal NO_3^- events, the isotope composition is probably influenced by the process of kinetic isotopic fractionation in fossil fuel combustion samples during heating season as referred by Ciężka et al. (2016) as one of three possible processes."*

Line 317. If ratio goes up during evaporation, NH4NO3 must have had lower ratio which makes sense for highly volatile compound. One could hypothesize that ammonium N15 ratio is the same in ammonium sulfate and ammonium nitrate, but as compounds are of different volatility that is unlikely, because volatile particulate compounds originate from lighter (more depleted) precursors than less volatile compounds which originate from heavier precursors.

Response: We agree with the reviewer that ammonium ^{15}N ratio is NOT same in ammonium sulfate and ammonium nitrate and we didn't hypothesized opposite view in paper. On line 317 we wrote '*...the dissociation process of NH_4NO_3 can cause an increase in ^{15}N in TN during a period of higher ambient temperatures...*' which is supposed to be okay, because evaporation of more volatile ammonia from NH_4NO_3 comes more easily during the higher temperature and the lighter isotope is released into the gaseous phase with a higher probability.

Line 332. “Thus it can be considered...

Response: Changed to *“considered”.*

Line 342. more depleted, not "smaller".

Response: This part of text was removed during revisions.

Line 349. What does it mean "smaller"? Lower, more negative? That is not because of overlap, but source specific ratios which in case of organic carbon are largely negative.

Response: We are sorry for a confused formulation that may imply that we compare the negative values of δ^{13}C in comparison with δ^{15}N. However, it is not so because we know that strongly negative δ^{13}C values originate from chosen carbon standard (PDB). Originally, we wanted to say that the range of TC δ^{13}C values is significantly smaller than a range of TN δ^{15}N values.
Based on this, we changed original sentence: *“The δ^{13}C values are significantly smaller than those of δ^{15}N…”* to *"The range of TC δ^{13}C values is significantly narrower than that of TN δ^{15}N…"*

Line 366. Wrong conclusion as mentioned in major comments. Fine particle sources are different from coarse particle sources. The ratio can only become more depleted in the atmosphere due to condensation of depleted precursors and even then condensation prefers heavier molecules, not lighter.

Response: The conclusion on line 366 that fine particles have lower δ^{13}C values than coarse particles was consistent with the Masalaite et al. (2015) and Skipitytė et al. (2016) studies referred in the same sentence on line 367, but is probably inappropriately formulated. We agree with reviewer that aerosol sizes itself cannot induce isotope effect and differences are caused e.g. by different aerosol sources. In this sense, we changed the sentence on line 366 from the original *“…relatively low δ^{13}C values in our range (up to -28.9‰) are caused by not only sources of TC but also a fact that fine particles are more ^{13}C depleted in comparison with coarse particles (e.g., Masalaite et al., 2015; Skipitytė et al., 2016).”* to the following: *“relatively low δ^{13}C values in our range (up to -28.9‰) are caused because fine particles have lower δ^{13}C values in comparison with coarse particles probably due to different sources of TC. (e.g., Masalaite et al., 2015; Skipitytė et al., 2016).”*

Line 389. “The aforementioned studies concluded that the isotope equilibrium exchange...

Response: Changed.

Line 397. resulting relationship, not final.

Response: Changed

Line 401. Very narrow temperature range can produce unreliable relationships. The temperature range in this study is far more impressive.

Response: Thank you, we agree that temperature range is one of benefit of our study. (min. in winter -9.8°C to max. in summer +25.5°C results in Δ 35.3°C). It is visible that if we account data from whole year (and so we take the full temperature range) we have stronger correlation between $\delta^{15}N$ and temperature than just for individual seasons.
In cases of statistically significant seasonal correlations during autumn and spring we have following temperature ranges and correlations: autumn $\Delta T=15.8°C$, $r=0.58$; spring $\Delta T=17.2°C$, $r=0.52$. Pavuluri et al. (2010), whose work we compare, observed a strong correlation ($r^2 = 0.58$) for a temperature range of $\Delta T=6.1°C$, which is a stronger correlation for a narrower temperature range than in our case. This gives an assumption that even during the narrower temperature range in the work of Pavuluri et al. (2010), we can get a relationship which is reliable for our comparison.
We did not make any revisions in MS related to this comment.

Line 413. What is the actual process of aging? Isn't it just the production of ammonium sulfate? Sure, production is two step: first bisulfate, than sulfate. It is obvious that decreasing molar ratio corresponds to lower nitrate, because ammonium nitrate can only be produced if at least bisulfate has been produced. When nitrate is not competing for ammonium due to higher temperature, sulfate can become fully neutralized.

Response: We don't guess that process of aging is just production of ammonium sulfate without its further modifications. Surely, formation of sulfate through bisulfate is a major way, however, changes are not stopped after formation of sulfate. First, when the ammonium sulfate is in a solution the ions do not bond each other but they are in a form of NH_4^+ and SO_4^{2-}. At the same time, NH_3 from gas phase is absorbed into the droplet. During evaporation of water and part of ammonia, the lighter ammonia is evaporated more and aerosol is enriched by heavier NH_4^+. It implies, the older the aerosol the more ^{15}N in ammonium sulfate. Second, as shown by recent research (Weber et al., 2016) sulfate is probably not a definitive compound that is not undergo to further changes in time. There probably exist an equilibrium between sulfate and bisulfate which can also affect subsequent changes in gas/particle partitioning of ammonia. Based on this, we added following sentences to related paragraph in subsection 3.3:
"Finally, summer values of NH_4^+/SO_4^{2-} molar ratio below 2 indicate that SO_4^{2-} in aerosol particles at high summer temperatures may not be completely saturated with ammonium but it can be composed from mixture of $(NH_4)_2SO_4$ and NH_4HSO_4 (Weber et al., 2016). The equilibrium reaction between these two forms of ammonium sulfates related to temperature oscillation during a day and due to vertical mixing of the atmosphere is a probable factor which leads to increased values of $\delta^{15}N$ in early summer."

Line 436. Oxidation by ozone indeed makes organic matter enriched in heavier carbon, because ozone attacks unsaturated bonds and those involving lighter carbon are preferentially broken releasing "light" CH3 fragments making the bulk matter heavier.

Response: Thank you for this supportive comment. At the end of sentence we added new following reference related to enrichment of ^{13}C by photochemical processing of aqueous aerosols – see

Pavuluri and Kawamura (2016) in references – and we also modified the sentence to following: *“As seen in Table 3, summertime positive correlations of δ^{13}C with ozone (r=0.66) and temperature (0.39) indicate oxidation processes that can indirectly lead to an enrichment of ^{13}C in organic aerosols that are enriched with oxalic acid (Pavuluri and Kawamura, 2016).”*

Line 444. “...depleted products in summer”. Is this contradictory to the above paragraph?

Response: It seems in contradictory to the above paragraph, however, these are two different things. Even if summer ^{13}C is most depleted compared to other seasons (probably due to different sources) there is a possible indirect oxidation process for their enrichment. Based on correlation analysis, this process is relevant only in summer, however, this enrichment is not strong enough to reach average δ^{13}C values during other seasons. The time series in Fig. 1 show the lowest δ^{13}C values in a mid of June and slowly increasing enrichment of ^{13}C during rest of summer, which also support this process.
We did not make any revisions in MS related to this comment.

Line 454. EC is a minor fraction of TC, so correlations are a bit pointless as EC isotope content contributes little to the TC isotope content.

Response: It is true that EC is a minor fraction of TC, however, in case of our data EC contributes by 19% on average during all seasons, which is not negligible. Interpretations of the results related to EC are supported also by other correlations, namely between δ^{13}C and NO_2, NO_3^- and EC/TC ratio, so we believe that it is not pointless. However, it is possible that these results can be biased by lower content of EC in TC thus we modified part of last sentence at the end of related paragraph as follows: “*This result can be biased by the fact that EC constitutes on average 19% of TC during all seasons. However, it is consistent with positive correlations between δ^{13}C and gaseous NO_2, as well as particulate nitrate, which is also significant in autumn to spring. This result is also supported by the negative correlation between δ^{13}C and EC/TC ratio (r=-0.51), which is significant only in summer.”*

Line 476. Sulfate cannot be emitted, reword.

Response: Changed to “*formation of sulfates*”

Line 507. Dry deposition of fine particulate matter is negligible making this assertion pure speculation. Dry deposition of ammonia can only occur on surfaces - were these frosted surfaces? Confusing interpretation, please reword.

Response: Thank you for this comment. It is right that dry deposition of fine particulate matter is negligible, however, in mentioned part of text we discussed possible dry deposition of gaseous ammonia. Moreover, given sentence is a reference to observations of Savard et al. (2017). Throughout the Event, the temperature was below 0°C (see Fig.9), so frosted surfaces could be possible on the ground surface, which can support deposition but also decrease fluxes of ammonia from e.g. water surfaces or soil. Also the results indicate that during the Event gradually rose deficit of ammonia and after some time the main source of ammonia were probably agricultural emissions from farms whose emissions of NH_3 are not as affected by low temperatures. Nevertheless, because we did not measure ammonia fluxes during the campaign, the conclusions on dry deposition heavier isotope of ammonia may sound little bit speculative (as the reviewer mentioned). In this sense we changed text in subsection 3.4 and in Conclusions.

New text in subsection 3.4. (original lines 507-511): *"They interpreted the result as a preferential dry deposition of heavier isotopic $^{15}NH_3$ species during the cold period, whereas lighter $^{14}NH_3$ species preferentially remains in the atmosphere. However, cold weather can also lead to a decline of ammonia fluxes from aerosol water surfaces, soil, etc. (Roelle and Aneja, 2002), which generally result in a deficit of ammonia in the atmosphere. Emissions from farms are not as limited by low temperature and are thus a main source of ammonia in this deficiency state. The removal of NH_3 leads to a non-equilibrium state between the gas and aerosol phases."*

New text in Conclusions (original lines 577-582): *"The winter Event characterized by ^{15}N depletion was probably caused by preferential unidirectional reactions between isotopically light ammonia, originated mainly from agriculture emissions, and sulfuric acid, resulting in $(NH_4)_2SO_4$ and NH_4HSO_4. This process was probably supported by long-term cold weather leading to a deficiency of ammonia in the atmosphere (due to dry deposition and/or low fluxes), and subsequent suppression of nitrate to partitioning in aerosol."*

Table 2&3. Omit insignificant correlation as they are meaningless.

Response: We would like to keep all the values in Tables 2 and 3, however, we removed insignificant correlations from the text - see our responses for major comments in more details.

References:

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

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Abstract. A study of the stable carbon isotope ratios ($\delta^{13}C$) of total carbon (TC) and the nitrogen isotope ratios ($\delta^{15}N$) of total nitrogen (TN) were carried out for fine aerosol particles (PM1) collected every two days with a 24 h sampling period at a rural background site in Košetice (Central Europe) from September 27, 2013, to August 9, 2014 (n=146). We found a seasonal pattern for both $\delta^{13}C$ and $\delta^{15}N$. The seasonal variation in $\delta^{15}N$ was characterized by lower values (av. 13.1±4.5‰) in winter and higher values (25.0±1.6‰) in summer. Autumn and spring were transition periods when the isotopic composition gradually changed due to the changing sources and the ambient temperature. The seasonal variation in $\delta^{13}C$ was less pronounced but more depleted in ^{13}C in summer (-27.8±0.4‰) as compared to winter (-26.7±0.5‰).

A comparative analysis with water-soluble ions, organic carbon, elemental carbon, trace gases and meteorological parameters (mainly ambient temperature) has shown major associations with the isotopic compositions, which enlightened the affecting processes. A comparison of $\delta^{15}N$ with NO_3^-, NH_4^+ and organic nitrogen (OrgN) revealed that although a higher content of NO_3^- was associated with a decrease in the $\delta^{15}N$ of TN, NH_4^+ and OrgN caused increases. The highest concentrations of nitrate, mainly represented by NH_4NO_3, related to the emissions from biomass burning, leading to an average $\delta^{15}N$ of TN (13.3‰) in winter. During spring, the percentage of NO_3^- in PM1 decreased. An enrichment of ^{15}N was probably driven by the equilibrium exchange between the gas and aerosol phases ($NH_3(g) \leftrightarrow NH_4^+(p)$), which is supported by the increased ambient temperature. This equilibrium was suppressed in early summer when the molar ratios of NH_4^+/SO_4^{2-} reached 2, and the nitrate partitioning in aerosol was negligible due to the increased ambient temperature. Summertime $\delta^{15}N$ values were among the highest, suggesting the aging of ammonium sulfate and OrgN aerosols. Such aged aerosols can be coated by organics in which ^{13}C enrichment takes place by the photooxidation process. This result was supported by a positive correlation of $\delta^{13}C$ with ambient temperature and ozone, as observed in the summer season.

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During winter, we observed an event with the lowest $\delta^{15}N$ and highest $\delta^{13}C$ values. The winter *Event* occurred in prevailing southeast air masses. Although the higher $\delta^{13}C$ values probably originated from biomass burning particles, the lowest $\delta^{15}N$ values were probably associated with agriculture emissions of NH_3 under low temperature conditions ($\leq$ 0°C).

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1. Introduction

Aerosols have a strong impact on key processes in the atmosphere associated with climate change, air quality, rain patterns and visibility (Fuzzi et al., 2015; Hyslop, 2009). 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 insight on source emissions along with physical and chemical processes in the atmosphere (Gensch et al., 2014; Kawamura et al., 2004), as well as atmospheric composition in history (Dean et al., 2014). However, studies based on single isotope analysis have their limitations (Meier-Augenstein and Kemp, 2012). Those include an uncertainty when multiple sources or different processes are present, whose measured delta values may overlap (typically in the narrower $\delta^{13}C$ range). Another factor are isotope fractionation processes which may constrain the accuracy of source identification (Xue et al., 2009). Using isotope analysis on multiple phases (gas and particulate matter) or multiple isotope analysis can overcome these problems and may be useful to constrain the potential sources/processes.

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Generally, 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). Isotopes are furthermore altered mainly by kinetic and/or equilibrium fractionation processes. Kinetic isotope effects (KIE) occur mainly during unidirectional (irreversible) reactions but also diffusion or during reversible reactions that are not yet at equilibrium (Gensch et al., 2014). Owing to KIE, reaction products (both gasses and particles) are depleted in the heavy isotope relatively to the reactants, and this effect is generally observed in organic compounds (Irei et al., 2006). If the partitioning between phases is caused by non-equilibrium processes (such as e.g. absorption), the isotopic fractionation is small and lower than that caused by chemical reactions (Rahn and Eiler, 2001). Equilibrium isotope effects occur in reversible chemical reactions or phase changes if the system is in equilibrium. Under such conditions, the heavier isotope is bound into the compounds where the total energy of the system is minimized and the most stable. Equilibrium effects are typical for inorganic species and usually temperature dependent. Regarding to the isotopic distribution in individual phases, ^{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 the most enriched in particulate matter and dry deposition (Heaton et al., 1997; Ti et al., 2018). Total

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Deleted: 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 nitrogen usually consists of the three main components, 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:

$\delta^{15}N_{TN} = \delta^{15}N_{NO3}*f_{NO3} + \delta^{15}N_{NH4}*f_{NH4} + \delta^{15}N_{OrgN}*f_{OrgN}$

where $f_{NO3} + f_{NH4} + f_{OrgN} = 1$ and f represents the fractions of nitrogen from NO_3^-, NH_4^+ and OrgN in TN, respectively.

Total carbon in aerosol is usually divided into elemental carbon (EC) and organic carbon (OC), where OC forms the major part of TC (e.g., Mbengue et al., 2018). Although EC is more or less inert to chemical changes, slightly different $\delta^{13}C$ in EC originating from primary emissions are described (Kawashima and Haneishi, 2012). OC represents a wide variety of organic compounds which can originate from different sources with different ^{13}C content resulting in different $\delta^{13}C$ values in bulk of emissions. Changes in isotopic ratio of $\delta^{13}C$ in OC (and thus also TC) can subsequently affect chemical reactions where isotope fractionations via the kinetic isotope effect (KIE) usually dominate the partitioning between gas and aerosol (liquid/solid) phases (e.g. Zhang et al., 2016).

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 the Americas (e.g., Martinelli et al., 2002; Savard et al., 2017). Recently, the multiple isotope approach was applied in several studies by using $\delta^{13}C$ and $\delta^{15}N$ measurements. Specifically, the $\delta^{13}C$ and $\delta^{15}N$ composition of aerosol (along with other supporting data) was used to identify the sources and processes on marine sites in Asia (Bikkina et al., 2016; Kunwar et al., 2016; Miyazaki et al., 2011; Xiao et al., 2018). Same isotopes were used to determine the contribution of biomass burning to organic aerosols in India (Boreddy et al., 2018) and in Tanzania (Mkoma et al., 2014), or to unravel the sources of aerosol contamination at Cuban rural and urban coastal sites (Morera-Gómez et al., 2018). These studies show the potential advantages of $\delta^{13}C$ and $\delta^{15}N$ isotope ratios to characterize aerosol types and to reveal the underlying chemical processes that take place in them.

Only few studies on $\delta^{13}C$ and $\delta^{15}N$ isotope ratios have been performed in Europe, which are moreover often based on single isotope analysis. Regarding the isotopes of nitrogen, Widory (2007) published a broad study on $\delta^{15}N$ in TN in PM10 samples from Paris, focusing on seasonality (winter vs. summer) with some specific sources. Freyer (1991) reported the seasonal variation in the $\delta^{15}N$ 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 the 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 the nitrogen pollution levels.

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Studies on δ^{13}C at European sites have been focused more on urban aerosols. Fisseha et al. (2009) used stable carbon isotopes of the different carbonaceous aerosol fractions (TC, black carbon, and water soluble and insoluble OC) to determine the sources of urban aerosols in Zurich, Switzerland, during winter and summer. Similarly, Widory et al. (2004) used δ^{13}C of TC, along with an analysis of lead isotopes, to study the origin of aerosol particles in Paris (France). Górka et al. (2014) used δ^{13}C in TC in conjunction with PAH analyses for the determination of the sources of PM10 organic matter in Wroclaw, Poland, during vegetative and heating seasons. Masalaite et al. (2015) used an analysis of δ^{13}C in TC on size-segregated urban aerosols to elucidate carbonaceous PM sources in Vilnius, Lithuania. Fewer studies have been conducted on δ^{13}C in aerosols in rural and remote areas of Europe. In the 1990s, Pichlmayer et al. (1998) conducted a multiple isotope analysis of δ^{13}C in OC, δ^{15}N in NO_3^- and δ^{34}S in SO_4^{2-} 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 δ^{13}C in TC, along with the ^{14}C/^{12}C isotope ratio of PM10 at a rural background station in Vavihill in southern Sweden based on 25 weekly samples.

To broaden the multiple isotope approach over the European continent, we present seasonal variations in δ^{13}C of TC and δ^{15}N of 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 region, 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 a key station of the Czech Hydrometeorological Institute (CHMI), focusing on air quality and environmental monitoring (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 very low traffic density. 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 (SO_2, CO, NO, NO_2, NO_x and O_3).

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2.2. Sampling and weighing

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

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The PM1 was measured gravimetrically (each filter before and after the sampling) with a microbalance that had ±1 µg sensitivity (Sartorius M5P, Sartorius AG, Göttingen, Germany) in a controlled environment (20±1 °C and 50±3 % relative humidity after filter equilibration for 24 h).

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2.3. Determination of TC, TN concentrations and their stable isotopes

For the measurements of total carbon (TC) and nitrogen (TN) and their stable isotope ratios, small filter discs (area 0.5 cm^2, 1.13 cm^2 or 2.01 cm^2) 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 the tin marble burns and oxidizes all the carbon and nitrogen species to CO_2 and nitrogen oxides, respectively. In the second quartz column, heated to 750°C, nitrogen oxides were reduced to N_2. Evolved CO_2 and N_2 were subsequently separated on a gas chromatographic column, which was installed in EA, and measured with a thermal conductivity detector for TC and TN. CO_2 and N_2 were then transferred into an isotope ratio mass spectrometer (IRMS; Delta V, Thermo Fisher Scientific) through a ConFlo IV interface to monitor the $^{15}N/^{14}N$ and $^{13}C/^{12}C$ ratios.

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An acetanilide external standard (from Thermo Electron Corp.) was used to determine the calibration curves before every set of measurements for calculating TC, TN and their isotope values. The $\delta^{15}N$ and $\delta^{13}C$ 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 $\delta^{15}N$ of TN and $\delta^{13}C$ of TC were calculated using the following equations and the final δ values are expressed in relation to the international standards:

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

$$\delta^{13}C\ (‰) = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard} - 1]*1000$$

2.4. Ion chromatography

The loads on the quartz filters was 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 measured 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 in conjunction 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.

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The sum of nitrate and ammonium nitrogen showed a good agreement with the 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 the following equation (Wang et al., 2010): OrgN = TN – 14*[NO_3^-/62 + NH_4^+/18].

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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 semi-online 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 response without filter exposure. Control calibrations using a sucrose solution were made before each change of the filter (ca. every 2nd week) to check the stability of instruments. The 24 h averages with identical measuring times, such as on quartz filters, were calculated from the acquired 4 h data. The sum of EC and OC provided TC concentrations, which were consistent with the TC values measured by EA (see Fig. S2 in SI).

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2.6. Spearman correlation calculations

Spearman correlation coefficients (r) were calculated using R statistical software (ver. 3.3.1). The correlations were calculated for the annual dataset (n=139) and separately for each season (autumn: 25, winter: 38, spring: 43, and summer: 33), and winter event (7). Data from the winter *Event* were excluded from the annual and winter datasets for the correlation analysis as their distinctly high concentrations and isotopic values might have affected the results. 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 (δ^{15}N and δ^{13}C) for the whole measurement campaign are depicted in Fig. 1. Some sampling gaps were caused in autumn and at the end of spring by servicing or outages of the sampler. However, 146 of the samples from September 27, 2013, to August 9, 2014 are sufficient for a seasonal study. In Fig. 1, the winter *Event* is highlighted, which has divergent values, especially for δ^{15}N, and is discussed in detail in section 3.4.

Table 1 summarizes the results for 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 µgN m^{-3}), while the higher TC concentrations were obtained during the winter *Event* (max. 13.6 µgC m^{-3}). Conversely, the lowest TN and TC concentrations were observed in summer (Tab. 1).

Figure 2 shows the relationships between the TC and TN concentrations and their stable isotopes for one year. The correlation between TC and TN is significant (r=0.71), but the relationship split during high concentration events due to divergent sources. 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 summer (0.37) were weaker but still statistically significant ($p<0.05$). As seen in Table 1, the seasonal averages of TC/TN ratios fluctuate, but their medians have similar values for autumn, winter and spring. The summer TC/TN value is higher (3.45) and characteristic of a significant shift in chemical composition, which is in line with previous studies at the site (Schwarz et al., 2016). However, seasonal differences in the TC/TN ratios were not as large as those in other works (e.g., Agnihotri et al., 2011), and thus, this ratio itself did not provide much information about aerosol sources.

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The correlation between $\delta^{13}C$ and $\delta^{15}N$ (Fig. 2, right) is also significant but negative (-0.69). However, there is a statistically significant correlation for spring only (-0.54), while in other seasons, correlations are statistically insignificant This result highlights a significant shift in the sources of carbonaceous aerosols and their isotope values in spring while the sources were rather stable during other seasons The winter *Event* measurements show the highest $\delta^{13}C$ and lowest $\delta^{15}N$ values, but a linear fit does not show a significant differences as compared to rest of the 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 an exception of winter *Event*, which showed 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 observed 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. The range of $\delta^{15}N$ was from 0.6‰ to 28.2‰ year round Such a wide range may arise from a limited number of nitrogen-containing species and/or components in aerosols, which are specifically present in the forms of NO_3^-, NH_4^+ and/or organic nitrogen (OrgN). The highest portion of nitrogen is contained in NH_4^+ (54 % of TN year-round), followed by OrgN (27 %) and NO_3^- (19 %). Although the NH_4^+ content in TN is seasonally stable (51-58 %, Table 1), the NO_3^- content is seasonally dependent; the highest in winter, and somewhat lower in spring and autumn. In summer when the dissociation of NH_4NO_3 plays an important role the NO_3^- content is very low and its nitrogen is partitioned from the aerosol phase to gas phase (Stelson et al., 1979).

The seasonal trend of $\delta^{15}N$ of 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 $\delta^{15}N$ of 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 for most bulk data is expressed by a strong negative correlation between $\delta^{15}N$ and the fraction 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), suggesting the presence of different processes for $\delta^{15}N$

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values, which is characterized by a strong positive correlation between $\delta^{15}N$ and NO_3^--N/TN (0.98). This point will be discussed in section 3.4.

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Considering the individual nitrogen components, several studies (Freyer, 1991; Kundu et al., 2010; Yeatman et al., 2001b) showed 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 $\delta^{15}N$ of NO_3^-; namely, (i) changes in NO_X emissions, (ii) influence of wind directions in the relative contributions from sources with different isotopic compositions, (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 our study, it is most likely that all these factors contributed, to a certain extent, to the nitrogen isotopic composition of NO_3^- throughout the year.

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Conversely, Kundu et al. (2010) reported higher $\delta^{15}N$ values of NH_4^+ in summer than in winter and reported higher $\delta^{15}N$ values of NH_4^+ than NO_3^-, except for winter season. In sum, the contribution of NH_4^+ to $\delta^{15}N$ overwhelms that of NO_3^-. Additionally, TN is composed of NH_4^+, NO_3^- and OrgN. In Figure 3, we can observe an enrichment of ^{15}N in TN in summer when the lowest NO_3^- contribution occurs. Thus, higher $\delta^{15}N$ values of TN in summer are mainly caused by higher abundances of NH_4^+ originating from $(NH_4)_2SO_4$, OrgN and ammonium salts of organic acids.

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Furthermore, we observed one of the largest enrichments of ^{15}N of TN in summer aerosols as compared to previous studies (Kundu et al., 2010 and references therein), which may be explained by several reasons. First, the previous studies mainly focused on total suspended particles (TSP); however, we focused on the fine fraction (PM1), whose surface should be more reactive due to a larger surface area per unit of aerosol mass than the coarse fraction and consequently result in a higher abundance of ^{15}N during the gas/particle portioning between NH_3 and NH_4^+. Second, fine accumulation mode particles have a longer residence time in the atmosphere than the coarse mode fraction, which is also a factor that results in an enrichment of ^{15}N. Indeed, Mkoma et al. (2014) reported average higher $\delta^{15}N$ of TN in fine (17.4‰, PM2.5) than coarse aerosols (12.1‰, PM10). Freyer (1991) also reported higher $\delta^{15}N$ of 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 interval of our work (24 h) leads to more chance to collect episodic samples such as the winter *Event*, which could not be clearly detected due to averaged (overlapped) aerosols over a longer sampling period (e.g., weekly samples).

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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 the common source, 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 $\delta^{15}N$ of TN as a function of NO_3^- concentration. Samples with the highest NO_3^- concentrations (>6 µg m^{-3}, n=5) show an average $\delta^{15}N$ of 13.3±0.7‰ . Assuming that NO_3^- in the fine aerosol fraction consists predominantly of NH_4NO_3 (Harrison and Pio, 1983), it can be stated that ammonium nitrate is a source of nitrogen at the Košetice site, with $\delta^{15}N$ values at approximately 13.3‰, 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 of $\delta^{15}N$ of 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 the 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). Because of the only slight difference between above reported $\delta^{15}N$ of nitrogen oxides and our $\delta^{15}N$ of TN during maximal NO_3^- events, the isotope composition is probably influenced by the process of kinetic isotopic fractionation in fossil fuel combustion samples during heating season as referred by Ciężka et al. (2016) as one of three possible processes. Thus, $\delta^{15}N$ values around 13.3‰ (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 $\delta^{15}N$ values are migrating as a result of the enrichment or depletion of ^{15}N, which is associated with the removal or loading of NO_3^- in aerosols. These curves represent two opposite chemical processes, with a match at approximately 13.3‰, 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 13.3‰. In the case of enrichment, in addition to a higher proportion of NH_4^+ than NO_3^-, the dissociation process of NH_4NO_3 can cause an increase in ^{15}N of TN during a period of higher ambient temperatures, as hypothesized by Pavuluri et al. (2010).

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OrgN has not been widely studied as 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 δ^{15}N of 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 δ^{15}N again at approximately 13.3‰, which implies that the isotopic composition of OrgN is determined by the same source. 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 (as well as 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 δ^{15}N (Fig. 3), it is more similar to the trend of NH_4^+-N/TN than NO_3^--N/TN. Thus, it can be considered that the changes in the δ^{15}N of 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 δ^{13}C

The δ^{13}C of TC ranged from -28.9 to -25.4‰ (Fig. 6) and the lowest δ^{13}C we 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. Our δ^{13}C values are within the range reported for particulate TC (-29‰ to -15‰) as summarized by Gensch et al. (2014). The lowest values are associated with fine particles after combustion and transport (Ancelet et al., 2011; Widory, 2006) while the highest values are associated with the coarse fraction and carbonate contribution (Kawamura et al., 2004). This broad range can be explained by the influence of marine aerosols (Ceburnis et al., 2016), different anthropogenic sources (e.g., Widory et al., 2004), as well as different distributions of C3 and C4 plants (Martinelli et al., 2002) resulting in different δ^{13}C values in the northern and southern hemispheres (Cachier, 1989). The δ^{13}C values at the Košetice site fall within the range common to other European sites. For example, 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)), different sites (urban, coastal, forest) in Lithuania (East Europe, Masalaite et al., 2015, 2017), as well as urban Zurich (Switzerland, Fisseha et al. (2009)).

The range of TC δ^{13}C values is significantly narrower than that of TN δ^{15}N due to a higher number of carbonaceous components in the aerosol mixture whose isotope ratio overlaps one another. However, it is possible to distinguish lower δ^{13}C values in summer (Table 1), which may indicate a contribution from higher terrestrial plant emissions. Similarly, Martinsson et al. (2017) reported lower δ^{13}C values

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Deleted: 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 δ^{13}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 δ^{13}C values are widely reported in the northern and southern hemispheres

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A comparison of δ^{13}C with TC in Fig. 6 shows an enhanced enrichment of ^{13}C at higher TC concentrations. The lowest δ^{13}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.

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A similar dependence of $\delta^{13}C$ on the TC concentration was observed by Fisseha et al. (2009), where winter ^{13}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). Moreover, winter aerosols at the Košetice site were probably affected by not only biomass burning but also coal burning (Schwarz et al., 2016), which can result in higher carbon contents and more ^{13}C-enriched particles (Widory, 2006). 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. Thus, the relatively low $\delta^{13}C$ values in our range (up to -28.9‰) are because fine particles have lower $\delta^{13}C$ values in comparison with coarse particles probably due to different sources of TC. (e.g., Masalaite et al., 2015; Skipitytė et al., 2016).

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 isotope distributions. 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 (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 aerosol chemistry at the nitrogen level is different in these seasons. Similarly, the contradictory dependence between $\delta^{15}N$ and TN in summer and winter was observed by Widory (2007) in PM10 samples from Paris. Widory (2007) connected this result with different primary nitrogen origin (road-traffic emissions in summer and no specific source in winter) and following secondary processes associated with isotope fractionation during degradation of atmospheric NOx leading to two distinct pathways for ^{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. The dependence of $\delta^{15}N$ of TN on temperature (Fig. 7) is similar to that observed by Ciężka et al. (2016) for $\delta^{15}N$ of NH_4^+ from precipitation; however, it is the opposite of that observed by Freyer (1991) for $\delta^{15}N$ of NO_3^-. The aforementioned studies 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

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All the considerations mentioned above indicate that a resulting relationship between δ^{15}N of TN and temperature is driven by the prevailing nitrogen species, which is NH_4^+ in our case. A similar dependence was reported by Pavuluri et al. (2010) between temperature and δ^{15}N of TN in Chennai (India), where NH_4^+ strongly prevailed. They found the best correlation between δ^{15}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 δ^{15}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 (temp. range: 11.8-25.5°C, avg. 17.7°C). This result indicates that ambient temperature plays an important role in the enrichment/depletion of ^{15}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 NH_3(g) ↔ NH_4^+(p) reaches a certain level of enrichment under higher temperature conditions in summer.

In summer, δ^{15}N correlates positively with NH_4^+ (r=0.40) and SO_4^{2-} (0.51), indicating a link with $(NH_4)_2SO_4$ that is enriched by ^{15}N due to aging. Figure 8 shows an enrichment of ^{15}N as a function of the molar ratio of NH_4^+/SO_4^{2-}. The highest NH_4^+/SO_4^{2-} ratios, showing an ammonia rich atmosphere, were observed during winter, late autumn and early spring along with high abundance of NO_3^- that is related to favorable thermodynamic conditions during heating season and enough ammonia in the atmosphere. Gradual decreasing molar ratios of NH_4^+/SO_4^{2-} during spring indicate a gradual increase of ambient temperatures and therefore worsened thermodynamic conditions for NO_3^- formation in aerosol phase, which was accompanied by a visible decrease in the nitrate content in aerosols (Fig. 8). The increase of temperatures finally leads to the NH_4^+/SO_4^{2-} ratio reaching 2 at the turn of spring and summer. Finally, summer values of NH_4^+/SO_4^{2-} molar ratio below 2 indicate that SO_4^{2-} in aerosol particles at high summer temperatures may not be completely saturated with ammonium but it can be composed from mixture of $(NH_4)_2SO_4$ and NH_4HSO_4 (Weber et al., 2016). The equilibrium reaction between these two forms of ammonium sulfates related to temperature oscillation during a day and due to vertical mixing of the atmosphere is a probable factor which leads to increased values of δ^{15}N in early summer. Ammonia measurements, that were carried out at the Košetice site until 2001, showed that NH_3

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concentrations in summer were slightly higher than in winter (http://portal.chmi.cz/files/portal/docs/uoco/isko/tab_roc/2000_enh/CZE/kap_18/kap_18_026.html), which supports temperature as a main factor influencing NH_4^+/SO_4^{2-} ratio at Košetice. In this context, we noticed that 25 out of 33 summer samples have molar ratios of NH_4^+/SO_4^{2-} below 2, and the remaining samples are approximately 2, and the relative abundance of NO_3^- in PM1 in those samples is very low (ca. 1.7 %).

Deleted: Figure 8 shows a decreasing molar ratio of NH_4^+/SO_4^{2-} with increasing ^{15}N enrichment, especially during spring, indicating a gradual uptake of ammonia in the gas phase to aerosol phase. With a decreasing NH_4^+/SO_4^{2-} molar ratio, there is also a visible decrease in the nitrate content in aerosols (Fig. 8). However, when the NH_4^+/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 $NH_3(g) \leftrightarrow NH_4^+(p)$, which previously led to ^{15}N enrichment in the particles. In this context, we note that 25 out of 33 summer samples have molar NH_4^+/SO_4^{2-} ratios below 2, and the remaining samples are approximately 2, although the average relative abundance of 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 H_2SO_4-NH_3 thermodynamic equilibrium at NH_4^+/SO_4^{2-} molar ratios of less than 2, even when sufficient amounts of ammonia are present in gas phase. Thus, an interaction between sulfates and ammonia may be hindered due to the preferential reaction with aged aerosols coated with organics (Liggio et al., 2011). In thermodynamic equilibrium, partitioning between gas (NH_3) and aerosol (NH_4^+) phases should result in even larger $\delta^{15}N$ values of particles in summer, however, measurements show a different situation. Summer $\delta^{15}N$ values are highest but further enrichment was stopped. Moreover, we observed a positive (and significant) correlation between temperature and $\delta^{13}C$ (r=0.39) only in summer, whereas the correlation coefficient of $\delta^{15}N$ vs. temperature is statistically insignificant, suggesting that while values of $\delta^{15}N$ reached their maxima, the $\delta^{13}C$ can still grow with even higher temperatures due to the influence of organics in summer season.

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As seen in Table 3, summertime positive correlations of $\delta^{13}C$ with ozone (r=0.66) and temperature (0.39) indicate oxidation processes that can indirectly lead to an enrichment of ^{13}C in organic aerosols that are enriched with oxalic acid (Pavuluri and Kawamura, 2016). This result is also supported by the fact that the content of oxalate in PM1, 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 summer. The negative correlation (-0.35) in winter probably indicates more fresh emissions from domestic heating (probably coal burning) with higher $\delta^{13}C$ values during cold season.

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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 $\delta^{13}C$) (Vodička et al., 2015). 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.

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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 sources are combustion processes from

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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 suggest that transportation is significant source of EC in summer. This result can be biased by the fact that EC constitutes on average 19% of TC during all seasons. However, it is consistent with positive correlations between $\delta^{13}C$ and gaseous NO_2, as well as particulate nitrate, which is also significant in autumn to spring. 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.

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It should be mentioned that the wind directions during the campaign were similar, with the exception of 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*.

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3.4. Winter *Event*

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The winter *Event* represents the period from January 23 to February 5, 2014, when an 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 December 18, 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 the formation of sulfates (Fig. S5).

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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 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). Before the *Event*, we also observed the highest values of $\delta^{15}N$ at approximately 13.3‰, which we previously interpreted as an influence of the emissions from domestic heating via coal and/or biomass burning. Positive correlations of $\delta^{13}C$ with oxalate and potassium (both 0.93) and the negative correlation with temperature (-0.79) also suggest that the *Event* is associated with fresh emissions from burning sources.

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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 % of TN) and almost absence of NO_3^- nitrogen (see Figs. 3 and 4). Although some

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content of OrgN is detected during the *Event* (Fig. 3), the correlation between δ^{15}N and OrgN/TN is not significant (Table 2). This result suggests that nitrogen with the lowest δ^{15}N values is mainly connected with NH_4^+, which is supported by a strong negative correlation between δ^{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 could expect the nitrogen originated mainly from NH_3 with depleted ^{15}N but not nitrogen oxides. Agricultural emissions from both fertilizer application and animal waste are important sources of NH_3 (Felix et al., 2013). Considering possible agriculture emission sources, there exist several collective farms, with both livestock (mainly cows, Holstein cattle) and crop production in the SE direction from the Košetice observatory – namely, Agropodnik Košetice (3.4 km away), Agrodam Hořepník (6.8 km) and Agrosev Červená Řečice (9.5 km). Skipitytė et al. (2016) reported lower δ^{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* (Fig. 9).

The δ^{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 δ^{15}N of 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 the result as a preferential dry deposition of heavier isotopic $^{15}NH_3$ species during the cold period, whereas lighter $^{14}NH_3$ species preferentially remains in the atmosphere. However, cold weather can also lead to a decline of ammonia fluxes from aerosol water surfaces, soil, etc. (Roelle and Aneja, 2002), which generally result in a deficit of ammonia in the atmosphere. Emissions from farms are not as limited by low temperature and are thus a main source of ammonia in this deficiency state. The removal of NH_3 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 considered to cause the NH_4^+/SO_4^{2-} molar ratios below 2 for the three most ^{15}N depleted samples (Fig. 8). However, under such conditions, nitrate partitioning in PM is negligible. It should be mentioned, that a deficiency of ammonia in atmosphere during the winter Event leads to completely opposite δ^{15}N values than in summer (see section 3.3) even if molar ratios NH_4^+/SO_4^{2-} are below 2 in both cases.

Unidirectional reactions of isotopically lighter NH_3 with H_2SO_4 in the atmosphere are strongly preferred by the kinetic isotope effect, which is, after several minutes, followed by enrichment of $^{14}NH_3$ 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^+, $\varepsilon_{NH4\text{-}NH3}$, 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 δ^{15}N values of the measured *Event*, we obtain values from approximately -40 to -28‰, which are in a range of δ^{15}N-

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NH$_3$ (g) measured for agricultural emissions. These values are especially in good agreement with δ^{15}N of NH$_3$ derived from cow waste (ca. -38 to -22‰, Felix et al., 2013).

Thus, during the course of the winter *Event*, we probably observed PM representing a mixture of aerosols from household heating characterized by higher amounts of NO$_3^-$ and low value (8.2‰) of δ^{15}N of TN, which are gradually replaced by ^{15}N-depleted agricultural aerosols. The whole process occurred under low temperature conditions that was first initiated by a deficiency of NH$_3$ followed by an unidirectional (kinetic) reaction of isotopically lighter NH$_3$(g) → NH$_4^+$(p), in which NH$_3$ is mainly originated from agricultural sources SE of the Košetice station.

If the four lowest values of δ^{15}N mainly represent agricultural aerosols, then it can be suggested that the δ^{13}C values from the same samples should originate from same sources. During the winter *Event*, the δ^{13}C values ranging from -26.2 to -25.4‰ belong to the most ^{13}C enriched fine aerosols at the Košetice site. However, similar δ^{13}C values were reported by Widory (2006) for particles from coal combustion (-25.6 to -24.6‰). Skipitytė et al. (2016) reported a mean value of δ^{13}C of TC (-23.7±1.3‰) for PM1 particles collected on a poultry farm, and suggested the litter as a possible source for the particles. Thus, in the case of δ^{13}C values that we observed during the winter *Event* are probably caused by emissions from domestic heating than from agricultural sources. This is also supported by increased emissions of SO$_2$ from coal combustion to formation of sulfates.

4. Summary and Conclusions

Based on the analysis of year-round data of stable carbon and nitrogen isotopes, we extracted 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 δ^{13}C and δ^{15}N, as well as for TC and TN concentrations. 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, the temperature slowly increases and the overall situation leads to thermodynamic equilibrium exchange between gas (NO$_x$-NH$_3$-SO$_2$ mixture) and aerosol (NO$_3^-$- NH$_4^+$- SO$_4^{2-}$ mixture) phases, which causes an enrichment of ^{15}N in aerosols. Enrichment of ^{15}N (Δδ^{15}N) from the beginning to the end of spring was approximately +10‰. Gradual springtime changes in isotopic composition were also observed for δ^{13}C, but the depletion was small, and Δδ^{13}C was only -1.4‰.

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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 nitrogenous aerosols, where ammonium sulfate and bisulfate is subjected to isotopic fractionation via equilibrium exchange between NH_3(g) and NH_4^+(p) when NH_4^+/SO_4^{2-} molar ratio was less than 2. 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 particles, 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. Although the summer $\delta^{15}N$ values were the highest further ^{15}N enrichment was minimized at this season. 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.

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_4NO_3 in PM1), and led to an average winter value (13.3±0.7‰) of $\delta^{15}N$ of TN. Winter $\delta^{13}C$ values were more enriched than summer values, which are involved with the emissions from biomass and coal burning for domestic heating.

We observed an aerosol event in winter, which was characterized by low temperatures below the freezing point, stable southeast winds, and a unique isotope signature with a depletion of ^{15}N and enrichment of ^{13}C. The winter *Event* characterized by ^{15}N depletion was probably caused by preferential unidirectional reactions between isotopically light ammonia, originated mainly from agriculture emissions, and sulfuric acid, resulting in $(NH_4)_2SO_4$ and NH_4HSO_4. This process was probably supported by long-term cold weather leading to a deficiency of ammonia in the atmosphere (due to dry deposition and/or low fluxes), and subsequent suppression of nitrate to partitioning in aerosol. The majority of yearly data showed a strong correlation between $\delta^{15}N$ and ambient temperature, demonstrating an enrichment of ^{15}N via isotopic equilibrium exchange between the gas and particulate phases. This process seemed to be one of the main mechanisms for ^{15}N enrichment at the Košetice site, especially during spring. The most ^{15}N-enriched summer and most ^{15}N-depleted winter samples were limited for the partitioning of nitrate between gas and aerosols.

This study revealed a picture of the seasonal cycle of $\delta^{15}N$ in aerosol TN at the Košetice site. The seasonal $\delta^{13}C$ cycle was not so pronounced because they mainly depend on the isotopic composition of primary sources, which often overlapped. Although photochemical secondary oxidation reactions are

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

	Autumn	**Winter**	**Spring**	**Summer**	**Year**
N of samples	25	45	43	33	146
TC [µg m^{-3}] (from EA)	3.61±1.61 (3.30)	4.76±2.44 (3.88)	3.78±2.03 (3.04)	2.71±0.76 (2.68)	3.81±2.03 (3.35)
TN [µg m^{-3}]	1.56±1.18 (1.33)	1.67±0.96 (1.45)	2.00±1.62 (1.47)	0.81±0.29 (0.82)	1.56±1.22 (1.26)
δ^{13}C [‰]	-26.8±0.5 (-26.9)	-26.7±0.5 (-26.7)	-27.1±0.5 (-27.0)	-27.8±0.4 (-27.7)	-27.1±0.6 (-27.0)
δ^{15}N [‰]	17.1±2.4 (16.9)	13.1±4.5 (15.2)	17.6±3.5 (17.3)	25.0±1.6 (25.1)	17.8±5.5 (16.9)
TC/PM1 [%]	28±6 (26)	33±8 (32)	38±15 (35)	31±6 (30)	33±11 (31)
TN/PM1 [%]	11±3 (11)	11±3 (12)	17±4 (17)	9±2 (9)	12±4 (12)
NO_3^--N/TN [%]	21±6 (21)	25±8 (28)	22±8 (21)	5±3 (4)	19±10 (20)
NH_4^+-N/TN [%]	51±6 (51)	51±9 (49)	58±7 (60)	57±6 (57)	54±8 (54)
OrgN/TN [%]	28±8 (26)	25±8 (23)	20±8 (19)	39±6 (38)	27±10 (25)
TC/TN	2.77±1.10 (2.60)	3.34±1.66 (2.68)	2.33±0.98 (2.34)	3.60±1.23 (3.45)	3.01±1.38 (2.61)

Table 2: Spearman correlation coefficients (r) of δ^{15}N with various tracers. Only bold values are statistically significant (p-values < 0.05).

δ^{15}N vs.	**Autumn**	**Winter***	**Spring**	**Summer**	**Year***	**Event**
TN	-0.30	**-0.40**	**-0.70**	**0.36**	**-0.54**	**0.93**
TN/PM1	**-0.63**	**-0.50**	-0.02	**0.37**	**-0.35**	0.36
NO_3^--N/TN	-0.39	-0.04	**-0.73**	-0.26	**-0.77**	**0.98**
NH_4^+-N/TN	0.16	-0.30	**0.60**	**0.52**	**0.42**	**-0.86**
OrgN/TN	0.20	**0.38**	0.20	-0.33	**0.51**	-0.71
NO_3^-	**-0.41**	**-0.35**	**-0.80**	-0.03	**-0.78**	**0.96**
NH_4^+	-0.22	**-0.42**	**-0.61**	**0.40**	**-0.44**	0.75
OrgN	-0.26	-0.27	**-0.56**	0.30	**-0.25**	0.71
SO_4^{2-}	-0.07	**-0.38**	-0.30	**0.51**	0.03	-0.57
Cl^-	-0.37	-0.18	**-0.74**	**-0.37**	**-0.74**	**0.99**
O_3 (gas)	**0.45**	0.14	0.15	-0.02	**0.40**	-0.71
NO_2 (gas)	**-0.53**	**-0.34**	**-0.72**	0.20	**-0.64**	**0.86**
NO_2/NO (gas)	**-0.51**	-0.26	**-0.82**	0.14	**-0.76**	**0.82**
Temp.	**0.58**	0.30	**0.52**	-0.21	**0.77**	-0.43

*Event data are excluded from winter and year datasets.

Table 3: Spearman correlation coefficients (r) of $\delta^{13}C$ with various tracers. Only bold values are statistically significant (p-values < 0.05).

$\delta^{13}C$ vs.	**Autumn**	**Winter***	**Spring**	**Summer**	**Year***	**Event**
OC	**0.64**	**0.63**	**0.91**	**0.39**	**0.75**	0.75
EC	**0.61**	**0.74**	**0.88**	0.28	**0.84**	0.46
EC/TC	0.06	0.06	0.13	**-0.51**	**0.32**	-0.32
TC/PM1	-0.16	-0.05	**-0.40**	0.22	-0.09	0.32
NO_3^-	**0.74**	**0.52**	**0.71**	0.12	**0.76**	0.39
NH_4^+	**0.84**	**0.59**	**0.80**	**0.42**	**0.66**	0.75
Oxalate	0.34	**0.62**	**0.71**	**0.65**	**0.25**	**0.93**
SO_4^{2-}	**0.80**	**0.64**	**0.73**	**0.41**	**0.34**	0.54
K^+	**0.84**	**0.63**	**0.70**	**0.47**	**0.76**	**0.93**
Cl^-	**0.44**	**0.62**	**0.68**	**0.44**	**0.76**	0.25
CO (gas)	0.21	**0.53**	**0.60**	0.32	**0.37**	0.68
O_3 (gas)	**-0.41**	-0.26	0.14	**0.66**	**-0.33**	0.11
NO_2 (gas)	**0.67**	**0.38**	**0.70**	0.18	**0.69**	0.32
NO_2/NO (gas)	**0.72**	**0.65**	**0.67**	**0.68**	**0.78**	**0.96**
Temp.	-0.33	**-0.35**	-0.20	**0.39**	**-0.57**	**-0.79**

*Event data are excluded from winter and year datasets.

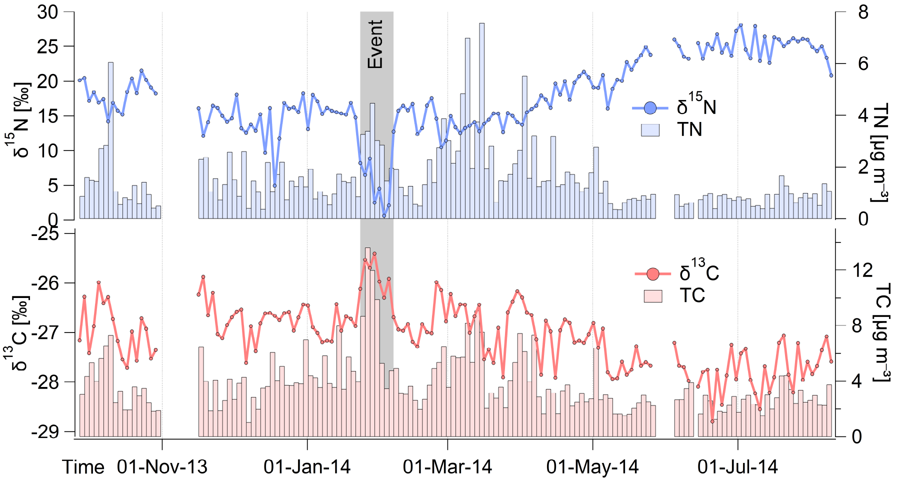

Fig. 1: Time series of $\delta^{15}N$ along with TN (top) and $\delta^{13}C$ as well as TC (bottom) in PM1 aerosols at the Košetice station. The gray color highlights an *Event* with divergent values, especially for $\delta^{15}N$.

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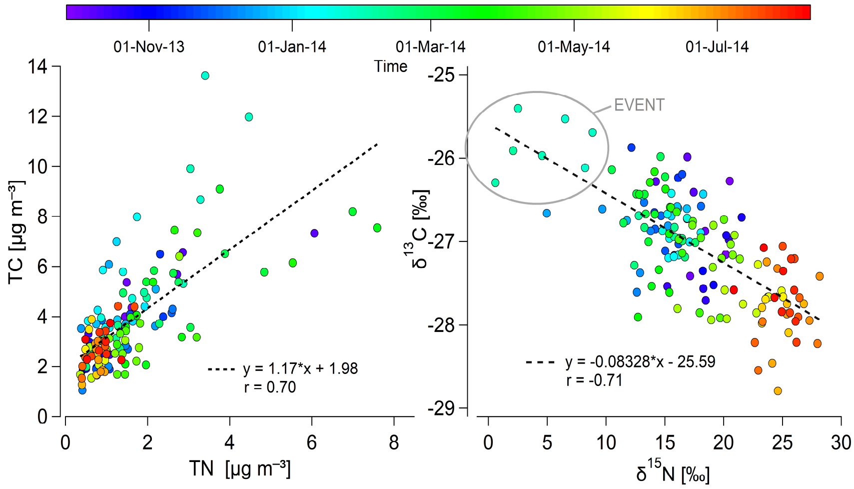

Fig. 2: Relationships between TC and TN (left) and their stable carbon and nitrogen isotopes (right). The color scale reflects the time of sample collection. The gray circle highlights the winter *Event* measurements.

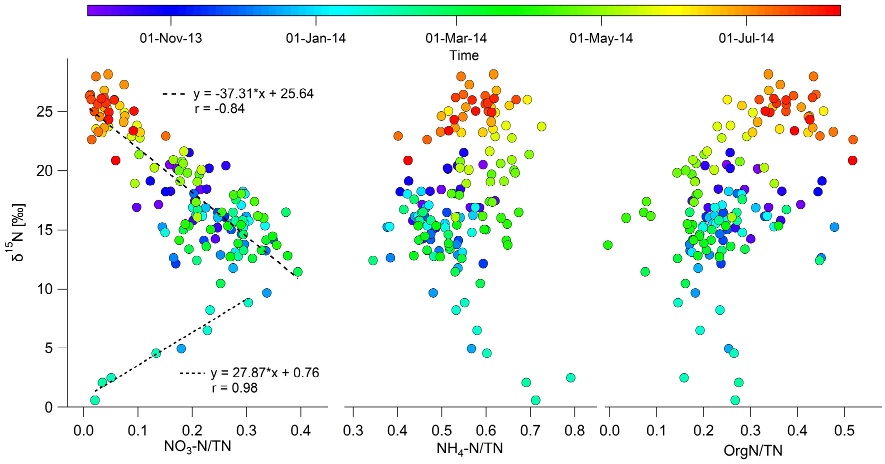

Fig. 3: Changes in δ^{15}N depending on fraction of individual nitrogen components (NO$_3$-N, NH$_4$-N, and OrgN) in TN. The color scale reflects the time of sample collection.

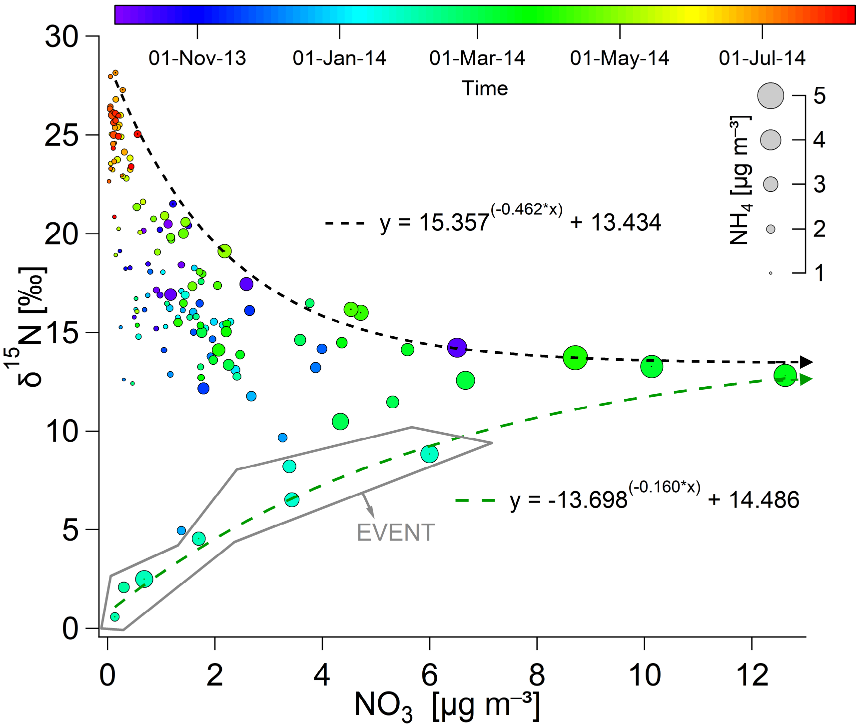

Fig. 4: Relationships of δ^{15}N of TN vs. NO_3^- concentrations. The larger circles indicate higher NH_4^+ concentrations. The color scale reflects the time of sample collection.

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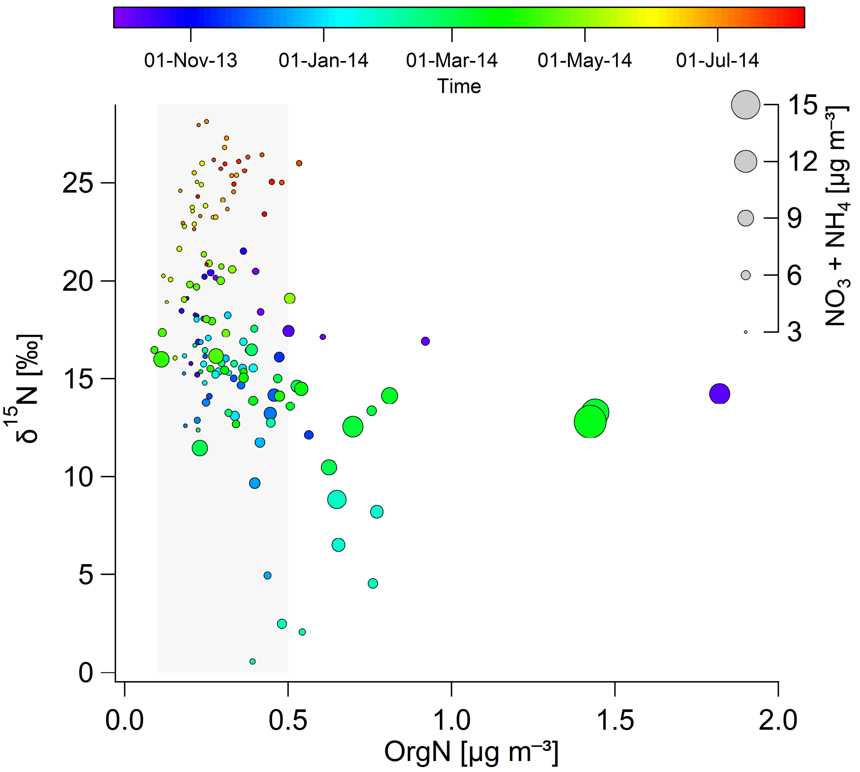

Fig. 5: Relationships of $\delta^{15}N$ of TN vs. OrgN concentrations. The larger circles indicate higher sums of NO_3^-+ NH_4^+ concentrations. The color scale reflects the time of sample collection, and the highlighted portion is a concentration range between 0.1-0.5 µg m^{-3}.

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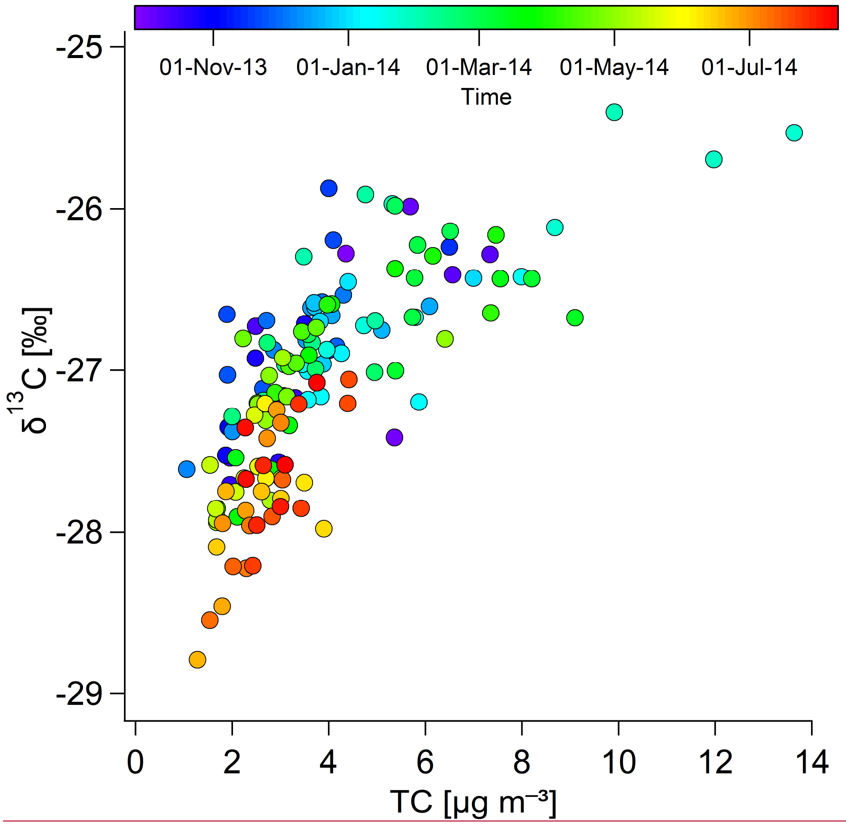

Fig. 6: Relationship between TC and $\delta^{13}C$. The color scale reflects the time of sample collection.

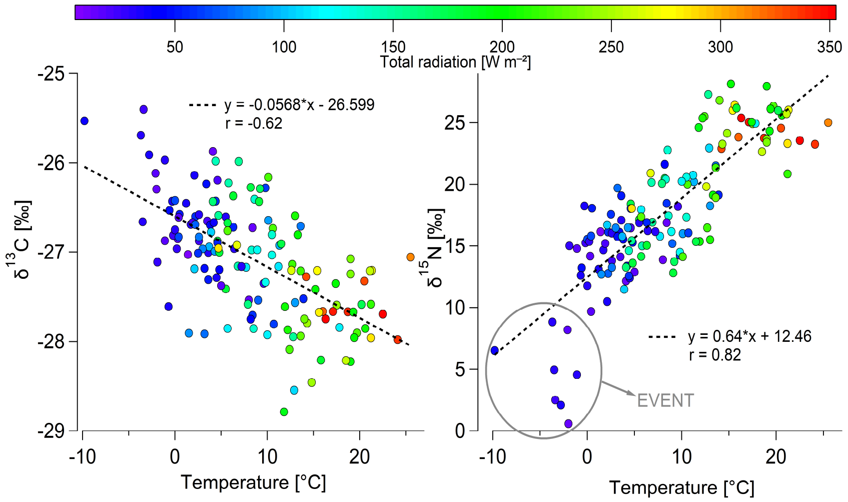

Fig. 7: Relationships between temperature and $\delta^{13}C$ of TC (left) and $\delta^{15}N$ of TN (right). The color scale reflects the total radiation.

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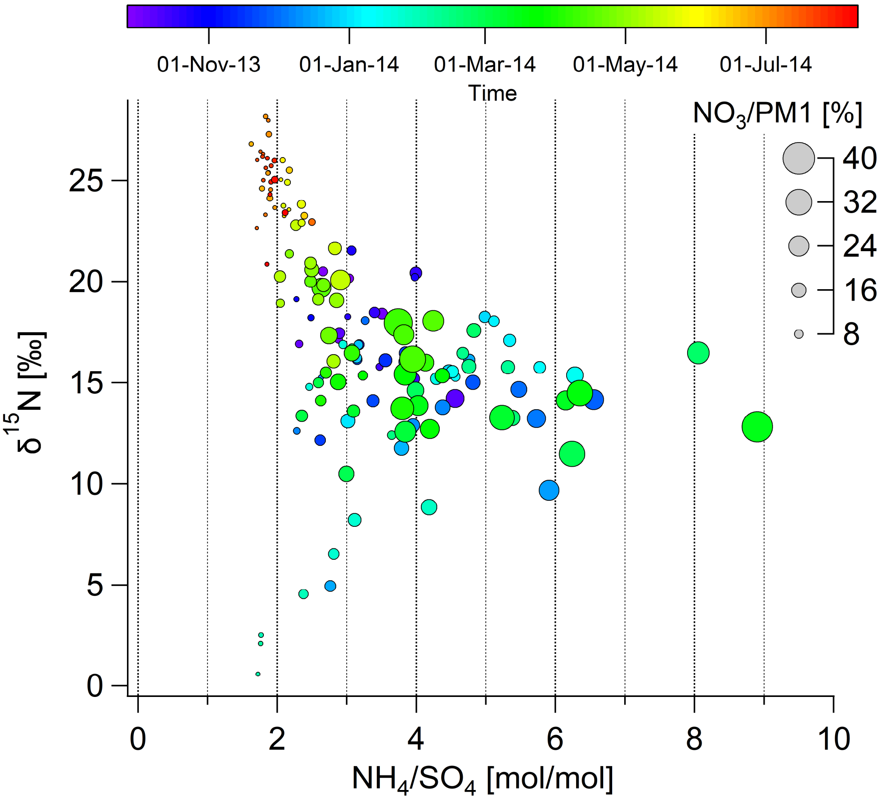

Fig. 8: Relationships between δ^{15}N of TN and molar ratios of NH$_4^+$/SO$_4^{2-}$ in particles. The larger circle indicates higher nitrate content in PM1. The color scale reflects the time of sample collection.

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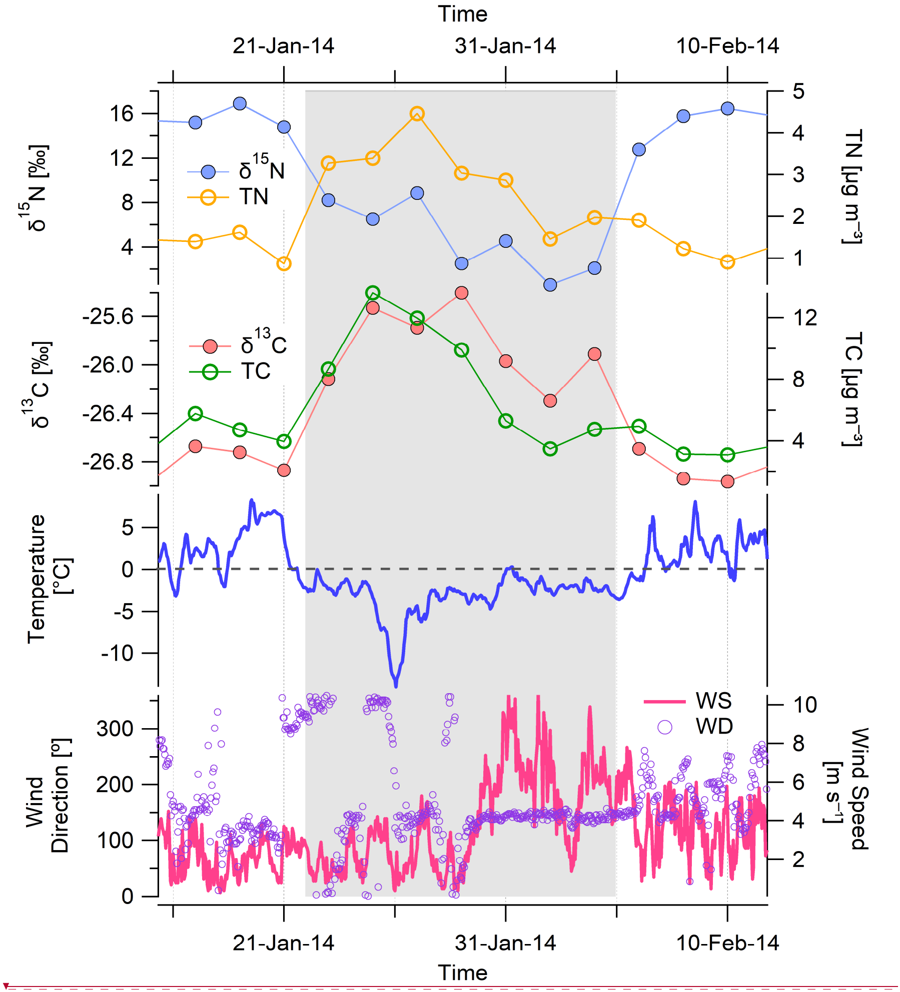

Fig. 9: Time series of $\delta^{15}N$, TN, $\delta^{13}C$, TC and meteorological variables (temperature, wind speed and direction, 1 h time resolution) during the *Event*, which is highlighted by the gray color.

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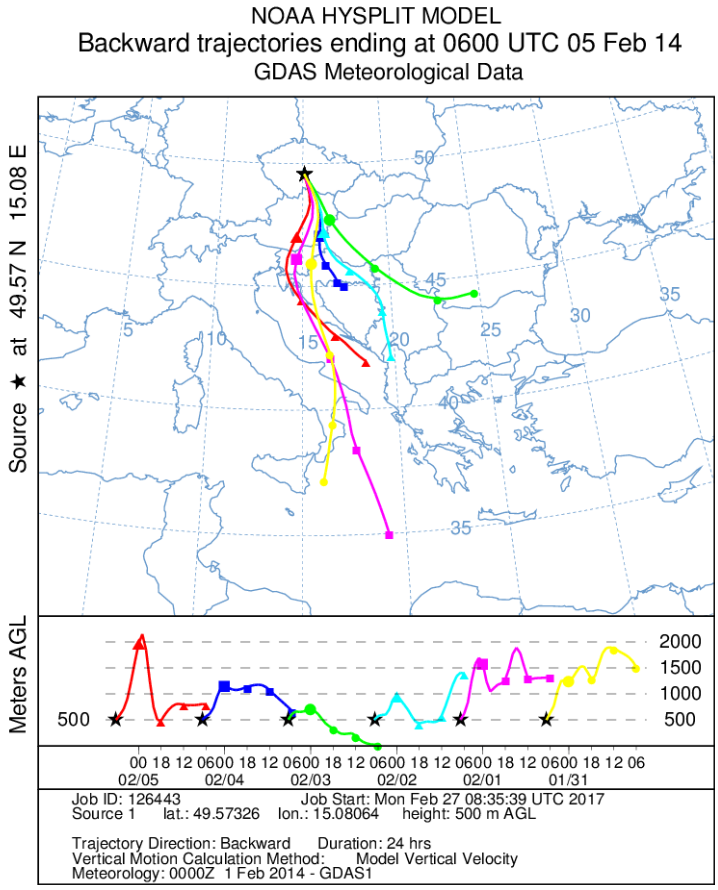

Fig. 10: NOAA HYSPLIT (Stein et al., 2015) 24 h backward air mass trajectories at 500 m above ground level for the observation site from 30 Jan until 5 Feb 2014 (right).

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), and thus, the final δ^{15}N value in TN can be formulated by the following equation:

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