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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal study of stable carbon and nitrogen isotopic composition in fine aerosols at a Central European rural background station" *by* Petr Vodička et al.

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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

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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 δ13C 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 δ13C 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 δ13C and δ15N measurements. Specifically, the δ13C and δ15N 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 δ13C and δ15N 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.

Response: 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 δ13C 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 δ15N 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 m3/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 δ15N is larger than variability of δ13C.

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‰Ẇhole sentence is following: “The δ15N 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 dis-

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cussion about contribution of different nitrogen compounds to δ15N 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 NH4NO3 plays an important role the NO3- 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 NO3- 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 δ15N in TN during summer when NO3 concentrations are lowest. However, during winter Event when NO3 contribution was also on the lowest level, δ15N 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 NO3 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 NaNO3 or Ca(NO3)2, whereas fine mode consists mainly from semi-volatile nitrogen from NH4NO3 and also in form of ammonium sulfate and bisulfate. If we have non-volatile nitrates in coarse fraction and predominantly NH4NO3 in fine fraction, where dissociation of NH4NO3 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 NH4+ and NO3 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 15N 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 NH4NO3 which undergo to dissociation to NH4+ and NO3- in water – this state is reversible and equilibrium fractionation is preferred in such system. Nevertheless, CiÄŹÅijka et al. (2016) suggested a possible kinetic exchange reactions between NH3 and NH4+ 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 δ15N 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 δ15N of nitrogen oxides and our δ15N of TN during maximal NO3- 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 CiÄŹÅijka 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 15N 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 NH4NO3 can cause an increase in 15N in TN during a period of higher ambient temperatures...’ which is supposed to be okay, because evaporation of more volatile ammonia from NH4NO3 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 δ13C in comparison with δ15N. However, it is not so because we know that strongly negative δ13C values originate from chosen carbon standard (PDB). Originally, we wanted to say that the range of TC δ13C values is significantly smaller than a range of TN δ15N values. Based on this, we changed original sentence: “The δ13C values are significantly smaller than those of δ15N. . .” to "The range of TC δ13C values is significantly narrower than that of TN δ15N. . ."

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 δ13C values than coarse particles was consistent with the Masalaite et al. (2015) and SkipitytÄŮ 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 δ13C 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 13C depleted in comparison with coarse particles (e.g., Masalaite et al., 2015; SkipitytÄŮ et al., 2016).” to the following: “relatively low δ13C values in our range (up to -28.9‰ are caused because fine particles have lower δ13C values in comparison with coarse particles probably due to different sources of TC. (e.g., Masalaite et al., 2015; SkipitytÄŮ 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 δ15N 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 ΔT=15.8°C , r=0.58; spring ΔT=17.2°C, r=0.52. Pavuluri et al. (2010), whose work we compare, observed a strong correlation (r2 = 0.58) for a temperature range of ΔT=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 NH4+ and SO42-. At the same time, NH3 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 NH4+. It implies, the older the aerosol the more 15N 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 NH4+/SO42- molar ratio below 2 indicate that SO42- in aerosol particles at high summer temperatures may not be completely saturated with ammonium but it can be composed from mixture of (NH4)2SO4 and NH4HSO4 (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 δ15N 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 13C 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 δ13C with ozone (r=0.66) and temperature (0.39) indicate oxidation processes that can indirectly lead to an enrichment of 13C 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 13C 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 δ13C values during other seasons. The time series in Fig. 1 show the lowest δ13C values in a mid of June and slowly increasing enrichment of 13C 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 δ13C and NO2, NO3- 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 δ13C and gaseous NO2, as well as particulate nitrate, which is also significant in autumn to spring. This result is also supported by the negative correlation between δ13C 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 NH3 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 15NH3 species during the cold period, whereas lighter 14NH3 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 NH3 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 15N depletion was probably caused by preferential unidirectional reactions between isotopically light ammonia, originated mainly from agriculture emissions, and sulfuric acid, resulting in (NH4)2SO4 and NH4HSO4. 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: Agnihotri, R., Mandal, T. K., Karapurkar, S. G., Naja, M., Gadi, R., Ahammed, Y. N., Kumar, A., Saud, T. and Saxena, M.: Stable carbon and nitrogen isotopic composition of bulk aerosols over India and northern Indian Ocean, Atmos. Environ., 45(17), 2828–2835, doi:10.1016/j.atmosenv.2011.03.003, 2011.

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