

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.

Anonymous Referee #2

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This paper presents seasonal variations of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ in ambient aerosol collected in Košetice (Central Europe) between 27 September 2013 and 9 August 2014. The authors show an impressive series of measurements aiming to investigate sources and processing of the fine fraction of aerosol at a rural background site. This study using two-isotope analysis is very suitable for this goal.

The use of multiple isotope ratios for the study of atmospheric pollution and the chemistry of organic compounds in the atmosphere is a newly emerging tool. The manuscript contributes to scientific progress within the scope of the journal; therefore, it is suitable to be published for discussions in ACP. Both description and discussion

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of measurements are well founded. Unfortunately, the presentation is not on the same level, therefore it needs to be substantially improved before publishing.

General comments:

1) The authors discuss the benefits of using isotopes in the atmospheric research. These can give some hints to information, which is not available from concentration measurements, such as the impact of sources vs. processing on measured delta values. I miss though a discussion on the current limitations of using isotope ratio measurements for the above mentioned purpose. This omission might be the reason why the interpretation sounds sometimes so futile.

Example: Lines 262-263 'In the case of our data, mixing of all of these factors probably had an influence on the nitrate isotopic composition during different parts of the year.' Reformulate!

2) The introduction should make the reader aware of the importance of using multiple isotopes (literature sources are required), e.g. for constraining potential sources. The sentence on the Lines 85-86 is too late and too less. A proper foreword would bring more structure in the discussion from Lines 59-83. Here the authors must clearly differentiate between single and multiple isotope analyses.

3) Separate Spearman from Pearson correlation coefficients. For that purpose, label them for each use (e.g. in Line 203).

4) Name the described variables throughout the manuscript!

Some examples: Line 122: Replace 'Determination of TC, TN and their stable isotopes' by 'Determination of TC, TN concentrations and their stable isotope ratios'

Line 123: Replace 'For the TC and TN analyses' by 'For the TC and TN concentration and isotopic ratio measurements'

5) Vague statements should be replaced by precise explanations throughout the paper.

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An example: Line382: specify the 'secondary processes'

6) Generally: swap the negative numbers in ranges. The lower numbers stay first.

Examples: Line520 -40 to -28permil and Line522 -38 to -22permil

Specific comments:

Lines54-57: Reformulate! The OC/EC ratios are very different in aerosol, depending on its sources. Moreover, make more sentences of this single one. Differentiate between equilibrium and kinetic isotopic effect. Guide the reader through that by giving some information on corresponding fractionation (non-equilibrium partitioning causes much lower fractionation than chemical reactions. Contrarily, equilibrium fractionation might be significant).

Line87: No need to introduce TC and TN. It happened already in Lines12-13

Line127: I don't understand. Is the oven temperature 1000°C? How can the marble burn, if that needs 1400°C?

Line131: What does 'parts' means? Give the approximate fraction in %.

Lines135-139: Mention that the final delta values are expressed relatively to the international standards and not to the 'working' standard.

Line146: The loads on the quartz filter are meant here of course.

Lines198-200: Move these sentences to the first paragraph, they don't belong to Fig.1.

Lines218-219: Reformulate: 'but they are still in line with the linear fitting of all annual data'. This is not appropriate.

Lines290-291: Reformulate! Either state that the samples containing the highest NO₃-concentration show a d₁₅N of..., or fit a histogram plot showing a peak of measurements with NO₃- concentrations higher than... at a delta value of 14+/-1 permil.

Lines300-307: The paragraph should be moved upward to Fig. 3.

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Lines338-349: Completely rearrange! Suggestion: start with a statement 'The measured TC d₁₃C ranged between.... These values are ... (in which part?) situated in the reported ranges... (here give an overall range. for that take the information from e.g. the review by gensch et al. 2014). This broad range can be explained by... (plants, marine, combustion sources... whatever). (At this point bring the similarity to other european reported values).'

Line349: Replace 'The d₁₃C values are significantly smaller than those of d₁₅N due to' by 'The range of TC d₁₃C values is significantly smaller than that of TN d₁₅N due to'

Lines358-359: This comparison is confusing: what do you mean? Similar to what? Do you refer the first or the second sentence?

Lines365-370: Change the order of these two sentences. Describe first the observations and then give the explanation.

Line 375: Replace 'these isotopes' with 'isotope distributions'.

Lines379-380: Not the changes in aerosol chemistry are different, but the chemistry itself.

Lines386-391: Change the order of the first two sentences. The third one describes the first not the second one.

Lines415-422: Lack of clarity! Reformulate, by bringing some structure in it: starting at high NH₄/SO₄ down to 2 and lower than 2! For each range: particle components, processes (e.g. NH₃ deficit in gas phase at ratios <2), seasonal dependence.

Lines429-434: Too abrupt! Start with the observation of similar gaseous NH₃ in summer and winter. Describe what a thermodynamic equilibrium would mean for the particles and how would this be reflected in the delta values. Measurements show a different situation -> more organics in summer...

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Lines482-484: Very confuse sentence. Reformulate!

Lines570-574: The winter observation should stay before the summer ones. In that way, the flow is more coherent (e.g. no need to explain lower values of TN d15N when there are high fraction of nitrates.).

Editorial revisions:

The used English is not optimal. I do not give any editorial advises! My only suggestion is that this manuscript MUST be carefully revised by a native speaker. The work is too good to risk to make the reader hostile due to the language.

The manuscript is 'peppered' with:

1) Wrong prepositions

- Lines43-44 'Key processes in the atmosphere, which are involved WITH climate changes, air quality, rain events (Fuzzi et al., 2015) or visibility (Hyslop, 2009), are strongly influenced by aerosols. ' - Lines391-392 ' Although Savard et al. (2017) reported a similar negative d15N in NH4+ dependence AT temperatures in Alberta (Canada),...' Also the word order is wrong.

2) Unhandy expressions

- Lines325-328:' During the domestic heating season with the highest concentrations of NO3and NH4+, we can observe a significant increase in OrgN with $\delta^{15}\text{N}$ again at approximately 14‰ which implies that the isotopic composition of OrgN is determined by the same process during maximal NO3-concentrations, that is, emissions from domestic heating.'

3) Long, confusing sentences

Lines361-365 or Lines391-396. In these cases it helps to divide into more clear sentences.

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