

## ***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 RC2

We would like to thank the reviewer for his valuable and helpful comments. Based on this, we have changed a part of the manuscript which led to an improvement in the final text. Responses to specific comments are below.

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

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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 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!

Response: Thank you for this comment. We added following text referring to the current limitations of using isotope ratio measurements in first paragraph of Introduction chapter. "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  $\delta^{13}\text{C}$  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." Specific text on lines 262-263 were changed to the following sentence: "In our study, it is most likely that all these factors contributed, to a certain extent, to the nitrogen isotopic composition of  $\text{NO}_3^-$  throughout the year."

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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.

Response: We extended Introduction chapter about examples of studies using multi isotope analyses. The sentence from the lines 85-86 we slightly modified and moved at the end of this paragraph. New text related to studies with multiple isotope measurements in Introduction chapter is following: "Recently, the multiple isotope approach was applied in several studies by using  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  measurements. Specifically, the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  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  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotope ratios to characterize aerosol types and to reveal the underlying chemical processes that take place in them." We also added data on other isotope analyzes (if were performed) to distinguish single- and multi-isotope studies in paragraph related to European studies

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

Response: Thank you for this comment. We identified in text few Pearson's correlation coefficients (connected with Figures 2, 3 and 7) instead of Spearman's ones. Although each of these coefficients provides different information (Pearson benchmarks linear relationship, Spearman benchmarks monotonic relationship), the values in our work are same or similar (e.g. for TC vs. TN is  $r(P)$ : 0.70 and  $r(S)$ : 0.71). Based on this, we decided to use only Spearman correlation coefficients in this work. Changes

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were made in Figures 2, 3 and 7, and related text (original lines 203, 213). Currently, Spearman's correlations are used throughout the document so there is no need to differentiate it from Pearson's correlations.

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'

Response: For a text clarification, there were changed variables description on following lines: 122, 123, 202, 205, 290, 545,

5) Vague statements should be replaced by precise explanations throughout the paper. An example: Line 382: specify the 'secondary processes'

Response: We are sorry for vague statements. We rephrased the text as below. Statement on line 382 was based on work of Widory (2007). We changed the previous sentence to following: "Similarly, the contradictory dependence between  $\delta^{15}\text{N}$  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  $^{15}\text{N}$  enrichment (summer) and depletion (winter)."

R: 6) Generally: swap the negative numbers in ranges. The lower numbers stay first. Examples: Line 520 -40 to -28permil and Line 522 -38 to -22permil

Response: Ranges of negative numbers were swapped on original lines 338, 520, 522 and 533. Thank you for your notice.

Specific comments: Lines 54-57: 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

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that by giving some information on corresponding fractionation (non-equilibrium partitioning causes much lower fractionation than chemical reactions. Contrarily, equilibrium fractionation might be significant).

Response: We changed the Introduction chapter with the text related to isotopes in carbonaceous aerosols and we also inserted a new paragraph on isotope fractionation:

New text related to carbonaceous aerosols: “ 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  $\delta^{13}\text{C}$  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  $^{13}\text{C}$  content resulting in different  $\delta^{13}\text{C}$  values in bulk of emissions. Changes in isotopic ratio of  $\delta^{13}\text{C}$  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).”

New paragraph related to isotope fractionation: “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.”

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

Response: Edited and only shortcuts were kept.

Line127: I don't understand. Is the oven temperature 1000  $^{\circ}\text{C}$ ? How can the marble burn, if that needs 1400  $^{\circ}\text{C}$ ?

Response: Theory is that burning tin should locally increase temperature around the sample to approximately 1400 $^{\circ}\text{C}$ , however, this is not so important and it can be also confusing so we deleted temperature 1400 $^{\circ}\text{C}$  from the MS.

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

Response: At this point, there is an auto-dilution system on the ConFlo IV interface, which is applied to each gas species matching sample and reference gas intensities. This dilution is automatic and the device dynamically reacts to the sample volume. Therefore, it is not possible to specify the exact part of the sample. For this reason, we decided to shorten the sentence to the following form: “Parts of  $\text{CO}_2$  and  $\text{N}_2$  were then transferred into an isotope ratio mass spectrometer (IRMS; Delta V, Thermo Fisher Scientific) through a ConFlo IV interface to monitor  $^{15}\text{N}/^{14}\text{N}$  and  $^{13}\text{C}/^{12}\text{C}$  ratios.”

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

Response: That's a good point. Sentence before equations was extended to following form: ‘Subsequently,  $\delta^{15}\text{N}$  of TN and  $\delta^{13}\text{C}$  of TC were calculated using the following equations and the final  $\delta$  values are expressed in relation to the international standards.’

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

Response: Yes, you are right that the loads on quartz filters was analyzed. The sentence was changed in this sense.

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

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Response: You are right, these sentences belong to Table 1 so we just changed link to Fig.1 to Tab.1 at the end of this paragraph.

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

Response: The sentence was reworded to the following: "The winter Event measurements show the highest  $\delta^{13}\text{C}$  and the lowest  $\delta^{15}\text{N}$ , but a linear fit does not show a significant differences as compared to rest of the data (Fig. 2, right)."

Lines290-291: Reformulate! Either state that the samples containing the highest  $\text{NO}_3^-$  concentration show a  $\delta^{15}\text{N}$  of..., or fit a histogram plot showing a peak of measurements with  $\text{NO}_3^-$  concentrations higher than... at a delta value of  $14\pm 1$  permil.

Response: Thank you for this comment. You are right that statement on lines 290-291 "The  $\delta^{15}\text{N}$  shows a peak at approximately  $14\pm 1\text{‰}$ ." is not exact, and is the result of estimation based on exponential curves in Figure 4. So newly, we took samples with  $\text{NO}_3^-$  concentrations higher than  $6 \mu\text{g}/\text{m}^3$  ( $n=5$ ) and we calculated an average  $\delta^{15}\text{N}$  value from these samples. It results in new value of  $\delta^{15}\text{N}$  ( $13.3\pm 0.7\text{‰}$ ), we used this calculated value instead of  $14\pm 1\text{‰}$  in whole text. New text on lines 290-291 is following: "Samples with the highest  $\text{NO}_3^-$  concentrations ( $>6 \mu\text{g}/\text{m}^3$ ,  $n=5$ ) show an average  $\delta^{15}\text{N}$  of  $13.3\pm 0.7\text{‰}$ "

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

Response: The paragraph on lines 300-307 relates to the previous one, where the results in Figure 4 are commented. For this reason, we would like keep this paragraph in the current position.

Lines338-349: Completely rearrange! Suggestion: start with a statement 'The measured TC  $\delta^{13}\text{C}$  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,

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marine, combustion sources... whatever). (At this point bring the similarity to other european reported values).'

Response: Thank you for this suggestion. Based on this, paragraph was rearranged as below: "The  $\delta^{13}\text{C}$  of TC ranged from  $-28.9$  to  $-25.4\text{‰}$  (Fig. 6) and the lowest  $\delta^{13}\text{C}$  we observed in field blank samples (mean  $-29.2\text{‰}$   $n=7$ ), indicating that the lowest summer values in particulate matter were close to gas phase values. Our  $\delta^{13}\text{C}$  values are within the range reported for particulate TC ( $-29\text{‰}$  to  $-15\text{‰}$  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  $\delta^{13}\text{C}$  values in the northern and southern hemispheres (Cachier, 1989). The  $\delta^{13}\text{C}$  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  $-25.6\text{‰}$  Martinsson et al. (2017)), urban Wroclaw (Poland, range  $-27.6$  to  $-25.3\text{‰}$  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))."

Line349: Replace 'The  $\delta^{13}\text{C}$  values are significantly smaller than those of  $\delta^{15}\text{N}$  due to' by 'The range of TC  $\delta^{13}\text{C}$  values is significantly smaller than that of TN  $\delta^{15}\text{N}$  due to'

Response: The sentence was changed based on the comment as bellow: "The range of TC  $\delta^{13}\text{C}$  values is significantly narrower than that of TN  $\delta^{15}\text{N}$  due to..."

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

Response: The comparison was between first and third sentence. Second sentence

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was moved to first paragraph of section 3.2, so now it should be clearer. See first paragraph of subsection 3.2 in the revised MS.

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

Response: The order of sentences was changed. See end paragraph of subsection 3.2 in the revised MS.

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

Response: Replaced

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

Response: Word "changes" was deleted.

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

Response: The order of sentences was changed.

Lines415-422: Lack of clarity! Reformulate, by bringing some structure in it: starting at high  $\text{NH}_4/\text{SO}_4$  down to 2 and lower than 2! For each range: particle components, processes (e.g.  $\text{NH}_3$  deficit in gas phase at ratios  $<2$ ), seasonal dependence.

Response: Thank you for your suggestion. Based on this comment, we decided to completely change this paragraph to the following: "Figure 8 shows an enrichment of  $^{15}\text{N}$  as a function of the molar ratio of  $\text{NH}_4^+/\text{SO}_4^{2-}$ . The highest  $\text{NH}_4^+/\text{SO}_4^{2-}$  ratios, showing an ammonia rich atmosphere, were observed during winter, late autumn and early spring along with high abundance of  $\text{NO}_3^-$  that is related to favorable thermodynamic conditions during heating season and enough ammonia in the atmosphere. Gradual decreasing molar ratios of  $\text{NH}_4^+/\text{SO}_4^{2-}$  during spring indicate a gradual increase of ambient temperatures and therefore worsened thermodynamic

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conditions for  $\text{NO}_3^-$  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  $\text{NH}_4^+/\text{SO}_4^{2-}$  ratio reaching 2 at the turn of spring and summer. Finally, summer values of  $\text{NH}_4^+/\text{SO}_4^{2-}$  molar ratio below 2 indicate that  $\text{SO}_4^{2-}$  in aerosol particles at high summer temperatures may not be completely saturated with ammonium but it can be composed from mixture of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  (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  $\delta^{15}\text{N}$  in early summer. Ammonia measurements, that were carried out at the Košetice site until 2001, showed that  $\text{NH}_3$  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](http://portal.chmi.cz/files/portal/docs/uoco/isko/tab_roc/2000_enh/CZE/kap_18/kap_18_026)) which supports temperature as a main factor influencing  $\text{NH}_4^+/\text{SO}_4^{2-}$  ratio at Košetice. In this context, we noticed that 25 out of 33 summer samples have molar ratios of  $\text{NH}_4^+/\text{SO}_4^{2-}$  below 2, and the remaining samples are approximately 2, and the relative abundance of  $\text{NO}_3^-$  in  $\text{PM}_{10}$  in those samples is very low (ca. 1.7 %)."

Lines429-434: Too abrupt! Start with the observation of similar gaseous  $\text{NH}_3$  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...

Response: Thank you for this notice. We moved the sentence, about similar gaseous  $\text{NH}_3$  concentrations in summer and winter at the Košetice site, to paragraph above (see response to previous comment). The lines have been reformulated into the following form: " In thermodynamic equilibrium, partitioning between gas ( $\text{NH}_3$ ) and aerosol ( $\text{NH}_4^+$ ) phases should result in even larger  $\delta^{15}\text{N}$  values of particles in summer, however, measurements show a different situation. Summer  $\delta^{15}\text{N}$  values are highest but further enrichment was stopped. Moreover, we observed a positive (and significant) correlation between temperature and  $\delta^{13}\text{C}$  ( $r=0.39$ ) only in summer, whereas the cor-

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relation coefficient of  $\delta^{15}\text{N}$  vs. temperature is statistically insignificant, suggesting that while values of  $\delta^{15}\text{N}$  reached their maxima, the  $\delta^{13}\text{C}$  can still grow with even higher temperatures due to the influence of organics in summer season.”

Lines482-484: Very confuse sentence. Reformulate!

Response: The sentence is reworded to the following: “During the Event,  $\delta^{15}\text{N}$  correlates positively with  $\text{NO}_3^-$  ( $r=0.96$ ) and  $\text{NO}_3^-/\text{N/TN}$  (0.98). Before the Event, we also observed the highest values of  $\delta^{15}\text{N}$  at approximately 13.3‰ which we previously interpreted by the emissions from domestic heating via coal and/or biomass burning.”

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  $\delta^{15}\text{N}$  when there are high fraction of nitrates.).

Response: In summary and conclusions, we wanted to discuss all seasons for the first time. After summary related to seasonal data follow conclusions related to winter Event. This is reason why the winter data are discussed after summer data. It seems more logic to us if the winter Event summary follows winter data than to discuss first about winter, then continue about summer season, and after that return to discuss about the winter Event. So we prefer not to move this paragraph.

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.

Response: We are sorry for inconvenience with English. In fact, the text was checked by the professional language service before the first submission so we expected it should be alright. As the final step after this review process, we sent again the manuscript for English corrections to Sean Mark Miller who is a native speaker and professional corrector.

The manuscript is 'peppered' with: 1) Wrong prepositions - Lines43-44 'Key processes

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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  $\delta^{15}\text{N}$  in  $\text{NH}_4^+$  dependence AT temperatures in Alberta (Canada),...’ Also the word order is wrong.

Response: Text with above mentioned prepositions was changed. Lines43-44: “Aerosols have a strong impact on key processes in the atmosphere associated with climate change...” Lines391-392: “Although Savard et al. (2017) reported a similar negative temperature dependence for  $\delta^{15}\text{N}$  in  $\text{NH}_4^+$  in Alberta (Canada), ...”

2) Unhandy expressions - Lines325-328: ‘ During the domestic heating season with the highest concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , we can observe a significant increase in OrgN with  $\delta^{15}\text{N}$  again at approximately 14‰ which implies that the isotopic composition of OrgN is determined by the same process during maximal  $\text{NO}_3^-$  concentrations, that is, emissions from domestic heating.’

Response: Sentence on lines325-328 was shortened to: “During the domestic heating season with the highest concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , we can observe a significant increase in OrgN with  $\delta^{15}\text{N}$  again at approximately 13.3‰ which implies that the isotopic composition of OrgN is determined by the same source.”

3) Long, confusing sentences Lines361-365 or Lines391-396. In these cases it helps to divide into more clear sentences.

Response: We divided above mentioned long sentences and also others in the revised MS. Newly for line 361-365: “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  $^{13}\text{C}$  enriched particles (Widory, 2006).” Newly for lines 391-396: “Although Savard et al. (2017) reported a similar negative temperature dependence for  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  in Alberta (Canada),

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most studies reported a positive temperature dependence for  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  that is stronger than that for  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  (e.g., Kawashima and Kurahashi, 2011; Kundu et al., 2010). The reason is that  $\text{NH}_3$  gas concentrations are higher during warmer conditions, and thus the isotopic equilibrium exchange reaction, i.e.,  $\text{NH}_3(\text{g}) \leftrightarrow \text{NH}_4^+(\text{p})$ , which leads to  $^{15}\text{N}$  enrichment in particles, is more intensive.”

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