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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.

Anonymous Referee #1

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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.

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).

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.

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.

Minor comments

Line 12. A study of stable carbon…

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

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

Line 18. changing sources instead of different.

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”.

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

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

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

Line 47. Unique insights instead of information.

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

Line 51. altered instead of influenced.

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

Line 60. Americas or North&South America.

Line 63. focusing on seasonality.

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

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

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

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

Line 99. with very low traffic density.

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”.

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

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

Line 135. Thermo Electron Corp.

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

Line 152. measured, not detected.

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

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

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

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.

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

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

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

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.

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”.

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.

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

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).

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

Line 258. (a) changes in NOx emissions

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”.

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?

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.

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

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.

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.

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

Line 342. more depleted, not "smaller".

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.

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.

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

Line 397. resulting relationship, not final.

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

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.

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.

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

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.

Line 476. Sulfate cannot be emitted, reword.

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.

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

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