Dear Dr. Jan Kaiser and Dr. Jochen Rudolph,

Thank you for your thought-provoking comments on our manuscript. All comments you raised have been seriously taken into account when we revised the manuscript. We also extend our thanks to reviewer #1 and Dr. Merched Azzi for their comments on our work.

Below are our answers to your questions and corresponding revisions on the manuscript.

Review comments

The paper presents a method for determining nitrogen isotope ratios ($\delta^{15}N$) for total nitrogen (TN) in particulate matter (PM). The advantage of this method is that it seems to be simple and very precise. The disadvantage is that TN in PM consists of several components. Therefore the value of $\delta^{15}N$ measurements in TN as additional constraint for determining the origin of TN is somewhat limited. The authors try to resolve this by using an isotope model (IsoSource). However, considering the large number of possible sources for TN, the system (described by Eq.1 in the paper) even with the additional constraint of $\delta^{15}N$ measurements in TN, is still underdetermined. Consequently a correct mathematical solution will result in a space of possible solutions, not a single solution and not even a best solution since, without additional assumptions or introducing (often inherent) boundary conditions, all solutions for an underdetermined system are equally valid. One may argue (see comments of Referee 1) that consequently the scientific value of the information in this paper is very limited. I do not completely agree. A paper thoroughly evaluating possibilities and limitations of an approach to identify the sources for TN in PM based on a simple, precise method for $\delta^{15}N$ measurements in TN could be of substantial scientific interest, especially when based on two data sets from locations impacted by very different types of sources for TN. Unfortunately, in its current form, the paper provides little additional insight. The main problems are:

i) There is no explanation of the additional constraints, assumptions and boundary conditions that are used to determine best solutions and the various uncertainty ranges given in by Figure 4 and Table 2.

ii) There are several factors that can create uncertainty in the solutions: a) The problem of an underdetermined system, b) The uncertainty of $\delta^{15}N$ values for the various sources of TN in PM, c) The variability of chemical composition and $\delta^{15}N$ within the two sample sets. The potential value of the used approach depends on a) uncertainty arising from b) can (at least in principle) be reduced by conducting more detailed studies of $\delta^{15}N$ in emissions and isotope effects for atmospheric reactions. The variability arising from c) could actually be useful information since it would provide insight into contributions from different source types under different conditions. Unfortunately, the paper does not provide any quantitative insight to which extent a) the fundamental limitation impacts the reliability of source apportionment based on measurements of δ^{15}N in TN. The qualitative statements and conclusions that isotope ratio measurements and combinations of different types of isotope ratio measurements can provide new insight and constraints are nothing new.

Answer:

Thanks for your appreciation of our work and very insightful comments on the system of bulk N in $PM_{2.5}$*. We recognized that the presentation of mass-balance equations (described by Equations 1 and 2 in the initial manuscript), being used to resolve the system, is clearly underdetermined. The main reason is that the mathematical solution based on the IsoSource mixing model cannot take into account the uncertainties associated with multiple sources, fractionation and isotope signatures (Moore & Semmens, 2008; Davis et al., 2015). In this study, uncertainties include the* $\delta^{15}N$ *variabilities in* $PM_{2.5}$ *and major N sources, isotopic effects during the* NH_3 *(g) ↔* NH_4^+ *(p) equilibrium. Uncertainties in these variabilities could not be considered and quantified in the model of IsoSource. However, a Bayesian isotope mixing model called stable isotope analysis in R (SIAR) can incorporate the above uncertainties and avoid the limitations of IsoSource model. The SIAR model runs in R statistical computing program and uses a Bayesian framework to establish a logical prior distribution based on Dirichlet distribution for estimating possible proportional source contribution, and then to determine the probability distribution for the contribution of each source to the mixture (Evans et al., 2000; Parnell &Jackson, 2008).*

In revision, we recompiled the mean and SD values (needed in the SIAR model) of source $\delta^{15}N$ *data (both Table S1 and Fig. 1 were updated), re-calculated the proportional contributions of each source by using the SIAR model (see detailed descriptions in Lines 358-382, and estimation results in Fig. 3 and Table 2), also re-wrote relevant contents in the section of 4.3 in Discussions (Lines 359-383). Therefore, both the solution and results of source apportionment are more accurately and properly presented by using the SIAR model. This work also makes a new exploration of natural isotope method shifting from a qualitative tool (since 1950s)to a quantitative one for tracing atmospheric N sources.*

iii) In their isotope models for the sample set from a remote location the authors use a fixed offset of 33‰ to adjust for isotope fractionation resulting from distribution of NH_3/NH_4^+ between gas and PM phase. However, the actual isotope fractionation for N in NH_3/NH_4^+ between gas and PM phase will depend on the fraction of total NH_3/NH_4^+ over NH_4^+ in PM. The results shown in Figure 3 seem to be consistent with this fundamental principle. Consequently the use of a given fixed value for background samples and no correction for urban samples seems somewhat arbitrary and this may substantially impact the results of source apportionment.

Answer:

Thank you for pointing this out. To date, isotope effects for atmospheric $NH_3 \leftrightarrow NH_4^+$ *equilibrium in the field circumstances remain very incomplete. The value of 33‰ is the only empirical one evaluated for* ^{15}N *enrichment in particulate* NH_4^+ *(Heaton et al., 1997). Experimental works have been also conducted on the isotope fractionations of* NH_3 *volatilization (e.g., Li et al., 2012), while it is uncertain which factors can be used to make the corrections of isotope effects.*

As you pointed out, the isotope fractionations for N in NH_3/NH_4^+ *between gas and PM phase will depend on the fraction of total* NH_3/NH_4^+ *over* NH_4^+ *in PM. Both the ratio of* NH_3 *(g) to* NH_4^+ *(p) and the equilibrium are strongly regulated by environmental factors such as temperature, humidity, the availability of ambient acid gases relative to* NH_3 *(as reflected by Fig. 2 in our revision), etc. Further studies are needed to verify the relationships between the isotope fractionations and the ratio of* NH_3 *(g) to* NH_4^+ *(p), which may be a reasonable and feasible factor to correct isotope effects.*

In the revised manuscript, we assigned an uniform isotope effect of 33‰ for all background samples when running in the SIAR model, but we also stressed further studies should resolve the uncertainty that isotope effects for $NH_3 \leftrightarrow NH_4^+$ *equilibrium may vary among samples and between sites. We have incorporated your important comments into the sections of Discussion, please check Lines 348-356, 444-446.*

iv) The dependence shown in Figure 3 seems interesting. However I do not understand the use of $NH_4^+/(NO_3^- + 1/2SO_4^{2-})$ as x-axis. Based on stoichiometry it should be $NH_4^+/(NO_3^- + 2SO_4^{2-})$. I am not sure how this would change the dependence shown Figure 3, but in any case a dependence such as the one in Figure 3 can also result from varying contributions from a source emitting NO_2 enriched in $\delta^{15}N$ or a source of NH_3 depleted in $\delta^{15}N$ and so on.

Answer:

Thank you for pointing this out. The stoichiometry should be expressed as $n\text{-}NH_4^+/(n\text{-}NO_3^- + 2*n\text{-}SO_4^{2-})$*, in which* $n\text{-}NH_4^+$ *is the actual molecular concentrations of* NH_4^+ *in* $PM_{2.5}$*, while the* $(n\text{-}NO_3^- + 2*n\text{-}SO_4^{2-})$ *indicates the expected concentrations of* NH_4^+ *that can be fixed by* NO_3^- *and* SO_4^{2-} *in* $PM_{2.5}$*. We have re-calculated the ratios and updated the correlation (please check in Table 1, Fig.2 of our revised manuscript). The ratios of* $n\text{-}NH_4^+/(n\text{-}NO_3^- + 2 \times n\text{-}SO_4^{2-})$ *were* 0.8 ± 0.4 *in* $PM_{2.5}$ *of Beijing, which clearly indicated a fully fixation of* NH_4^+ *by existing* NO_3^- *and* SO_4^{2-} *in* $PM_{2.5}$*, thus supported our assumption of negligible isotope effects for* NH_4^+ *of* $PM_{2.5}$ *at Beijing. In the revision, we re-organized the discussions on the above mechanism in Lines 306-318 for Beijing site and Lines 334-347 for the background site.*

These problems need to be addressed quantitatively. After all, the results of source apportionment are numbers and the value of these numbers depends on quantitative understanding of uncertainties. If the authors are able and willing to revise the paper accordingly, a substantially revised manuscript may be considered for publication.

Answer:

As we explained above, using the SIAR model did allow a more reasonable estimation and a more appropriate consideration of the uncertainties. We appreciate having this opportunity to revise this manuscript with your very helpful comments.

In a revised manuscript the authors should pay more attention to avoiding very unusual English phrases and the use of correct grammar as well as providing all necessary details to allow the reader to fully understand what is presented in the tables and figures. In the current version I often had to guess what is shown. I would also like to point out that I find the introduction to be too long, especially since the experimental part also includes several "introductory type" statements. Since a publishable revised version will substantially differ from the current one I will not going into details. In summary, in its current form the paper should not be published in ACP, however a thoroughly revised version could be reconsidered for publication in ACP.

Answer:

We have tried to correct and improve the quality of English in whole manuscript, especially the section of Introduction has been substantially improved and shortened. The 4.1 and 4.2 sections of the Discussion has been re-organized. The captions of tables and figures were also re-written to be fully understandable. We also invited Dr. Chandra M Pavuluri, who is an atmospheric chemist on organic aerosols, to correct the English and discuss the revisions.

References:

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