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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Source apportionment of atmospheric ammonia before, during, and after the 2014 APEC summit in Beijing using stable nitrogen isotope signatures" *by* Y. Chang et al.

Anonymous Referee #2

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Manuscript ID: acp 2016-432 Title: Source apportionment of atmospheric ammonia before, during, and after the 2014 APEC summit in Beijing using stable nitrogen isotope signatures The authors have presented data which increases the inventory of isotopic signatures of ammonia emission sources, an area lacking in data. The authors have characterized isotopic signatures of NH3 emissions sources in China, a region of the world where this has not been done, and the data agrees closely with data obtained in other areas of the world. This data can be employed by researchers to quantify NH3 emissions contributing to ambient atmosphere. This is valuable as many NH3 emission sources are nonpoint sources making them difficult to quantify. Using the nitrogen isotope signatures the authors have estimated urban source contribution before and

after a major event in Beijing in which air quality measures were employed during the event. The authors provide isotopic evidence that vehicles are a major contributor to urban NH3 concentrations and the isotopic signature in the city changed to reflect the reduction in vehicle emissions resulting from air quality measures. The estimation of other source contributions is likely confounded by potentially overlapping source signatures and this should be more adequately addressed by the authors. This a novel approach to assessing NH3 source contributions in an urban setting and the authors have presented the data in a clear and concise manner. If the major and minor issues below are addressed, I believe the manuscript could be accepted to ACP.

Major comments:

Source apportionment

The authors use an isotope mixing model to predict NH3 source apportionment. The endmember signatures used in the model are vehicles, fertilizer, livestock waste, and human waste. The authors provide evidence that the vehicle endmember signature is significantly different from the other three endmembers but the other endmembers signatures are similar and with more sampling it is likely that these signatures will overlap. This is because the three sources are essentially the same "volatilized NH3" source and if the literature data is taken into consideration, these sources' signatures are observed to overlap. I don't think the authors have a viable case for assigning the source signatures they present to each source. I do however believe they could combine the "volatilized NH3" sources as one endmember and vehicles as another endmember. While this would only provide insight to vehicle source apportionment, I think it is a more realistic approach. If the authors keep the mixing model as is, they need to explain the caveats associated with the estimates of the "volatilized NH3" sources and include error analysis. Rather than reporting specific values a range should be reported that represents the deviation and error involved in the calculations.

Vehicle sampling Unlike the US, a major urban NH3 source in China is human waste

which has been found to have a δ15N-NH3 value of $\sim$ -41 to -30 permil in this study. The vehicle exhaust in this study was sampled in a tunnel not directly from tailpipe. Most highly trafficked tunnels have ventilation systems that flush the tunnel with ambient air constantly. If the urban ambient air NH3 is mainly from waste and the tunnels are flushed with ambient air, this mixing would lower the δ15N value of the NH3 sampled at the tunnel. Do these tunnels have ventilation systems? Could mixing with ambient air confound the δ15N vehicle signal?

Line 119: All three filters from a sampling event were combined for single analysis. Why? Was there not enough N for analysis? This doesn't allow for reporting of the deviation, if any among samplers. Did the authors evaluate deviation among samplers? If so this should be included.

Line 166: When sampling exhaust from septic tanks the authors state "However, the δ15N-NH3 values of daily samples varied widely ($\pm$10 per mil), suggesting that the isotope fractionation may occur during the process of sampling/storage. After many tests by trial and error, we found that a sampling period of 2 hours could provide sufficient N-NH3 as well as avoid potential fractionation" It seems the daily samples would be more representative of the source and the fractionation that is occurring is representative of the source. The magnitude of fractionation is going to change under varying environmental conditions but this is a symptom of the source type and should be evaluated as the range in source signature.

Line 284: The authors state "However, although also sampled in a closed environment, the δ15N values of municipal solid waste demonstrate a much greater variation (-37.6 to -29.9‰, which may be due to the variable composition of solid waste" There are many more factors that may alter the fractionation during volatilization (e.g. pH, temperature, wind, moisture...) This again emphasizes the inability to use single source signatures for sources that are all a product of volatilized ammonia.

Line 400: The authors state "However, as a direct product of NO re-

duction on the catalyst surface of TWCs (2NO+5H2$\rightarrow$2NH3+2H2O and/or 2NO+2CO+3H2$\rightarrow$2NH3+2CO2), NH3 emitted from light-duty vehicle exhausts can be expected to have similar δ15N-values to vehicle-emitted NOx." This reasoning is not sound. NO produced may have a different original δ15N value then the NH3 being used in the TWC and the fractionation factor of the two different compounds caused by the TWC process could be very different. There is not valid evidence to state that the δ15N of vehicle NOx and NH3 would be the same.

Minor comments Line 28: APEC should not be abbreviated Line 51: delete "extensive" Line 160: "don't" should be replaced with "doesn't" Line 198: "A" should be deleted Lin3 229: The wording "far ahead" is not the appropriate descriptor here and should be changed.

Figure 3: The x-axis labeling isn't sufficient. Are the boxes in order of sampling period? If so provide the timeframe on the axis

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