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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric chemistry of nitrogenous aerosols in Northeast Asia: biological sources and secondary formation" *by* C. M. Pavuluri et al.

Anonymous Referee #2

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This manuscript reports results obtained from analysis of total nitrogen, water soluble total nitrogen, the stable nitrogen isotope composition of these fractions, nitrate, ammonium and several organic tracers in a set of 21 aerosol samples collected over a period of one year at an urban site in Sapporo, Japan. The authors have already published two other manuscripts arising from this sample set, but the foci of those manuscripts are significantly different from the work presented here. The work is mostly well described and the majority of the data appear sound. I do feel that some additional details concerning analytical methods (particularly the potential for isotopic fractionation during water soluble total nitrogen isotope composition analysis) are necessary.

The interpretation of the trends in nitrogen species' concentrations and isotopic composition through regression analysis with other parameters is not entirely convincing and this section of the manuscript is also rather long and repetitive. The authors might like to consider condensing this text in a revised version.

Specific comments:

TN extraction and analysis – please add the volumes of Milli-Q water (line 113) and 0.05M KOH (line 115) used. Was the "50 μL of water extract" a sub-sample of the 200 μL of re-dissolved extract mentioned on line 116?

Potential isotopic fractionation during δ15N analysis of WSTN – I am not convinced by the authors' argument that similarity in temporal trends can be used to rule out fractionation during analysis of WSTN. A constant fractionation would preserve the temporal trend but still change the isotope ratio. Can more information be supplied to support this please?

Concentrations of TN and WSTN – there are problems with the values given on lines 199 & 200. Firstly the maximum concentration for WSTN is significantly higher than the equivalent for TN (should the WSTN value actually be 1,520 ng m-3 ?). Secondly, average values for these parameters are completely different to those given for the same parameters in Table 1. Why?

Limits of detection / quantitation – the authors must quote the limits of detection for their measured and calculated parameters. Several times in Sections 3.2 and 3.3 the lower limit of concentration ranges are quoted as "0.00 ng m-3", but this cannot be correct. There are no analytical methods capable of detecting complete absence of an analyte. The lower limits of these concentration ranges should be quoted as "< X ng m-3", where X is the relevant limit of detection.

Possible influence of biomass burning – I found the repeated references to "anthropogenic emissions including biomass burning" or "biogenic sources including biomass

burning" through the manuscript to be rather unclear and poorly explained. The authors measured levoglucosan (generally considered to be a good indicator of biomass burning) as one of their organic tracers. In their correlation analysis (which I comment on below), they found no significant correlation between WSON and levoglucosan for these samples (line 311). This implies to me that there is no evidence for a significant contribution to WSON from biomass burning and yet the references to "including biomass burning" continue throughout the manuscript (e.g. line 329). How do the authors justify this? In one of their related manuscripts (Pavuluri et al., 2015), it is suggested that levoglucosan may have been degraded in these samples, but this does not appear to be mentioned here. Might this be the reason for the lack of significant correlation? Since they have measured sodium and potassium ion concentrations in these samples (Pavuluri et al., 2015), the authors might calculate non-seasalt potassium concentrations as an alternative tracer for biomass burning.

Correlation analysis – several things trouble me about the authors' approach to this. Firstly, I can find no indication of which correlation method was used. Since at least one of the parameters investigated (sucrose) is very obviously not normally distributed, I urge the use of a non-parametric correlation method such as Spearman's Rank Correlation. Secondly, the authors reporting of correlations based on correlation coefficients is very poor. I would strongly recommend that they select a single confidence limit to define a "significant" correlation and avoid the use of phrases such as "WSON well correlates with ... SOA tracers (r = 0.61) ...." (lines 321-322) where correlation coefficients are below this confidence limit. The statement "WION showed ... positive correlation (although weak) with all biogenic SOA tracers" really is misleading. The highest correlation coefficient for these tracers in Table 3 is 0.26, which implies (assuming Pearson's correlation was used) that α-pinene explains $\sim$7% of the variation in WION. This "correlation" is not weak, it is non-existent. Finally, a number of times in Section 3.4.1, the authors make statements about the co-variations in parameters with season based on Figure 4, but in many cases these variations are not clear because the data in panels a), b) and f) are plotted as stacked bars. If the authors really want to

convince the reader that these relationships exist, I recommend that they include some x-y plots of the parameters concerned.

Outliers – this is another case of the authors not giving full details of what they have done. On what basis did they decide that outliers existed in the data (Dixon's test, Grubb's test or another test)? Which points were removed? What does "correlation ... slightly improved" actually mean?

Methanesulphonate – since MSA is a degradation product of dimethylsulphide and neither compound contains N, it might be appropriate for the authors to explain the significance of any potential relationships between MSA and WION (line 380).

Technical corrections:

Line 123 – change start of sentence to "We also measured ..." Line 131 – change "beyond 0.5" to "greater than 0.5". Line 226 – change "subject for chemical aging" to "subject to chemical aging". Line 392 – insert subscripted "TN" at δ15N.

References:

Pavuluri, C. M., Kawamura, K., Mihalopoulos, N., and Fu, P.: Characteristics, seasonality and sources of inorganic ions and trace metals in North-east Asian aerosols, Environmental Chemistry, 12, 338-349, 10.1071/EN14186, 2015.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 12617, 2015.