Authors' Responses to Referee #2 Comments

We thank the anonymous referee #2 thoughtful comments, which are very helpful to improve our manuscript. Based on the reviewer's comments, we revise the manuscript.

Anonymous Referee #2

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.

Response: We appreciate the critical comments.

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?

Response: Following the reviewer's suggestion, we include the volumes of Milli Q water (~15 ml) and KOH solution (~0.5 ml) in the revised MS. Yes, 50 µL water extract is a sub-sample of 200 µL of re-dissolved extract. To avoid any confusion to the reader, we clearly state it in the revised MS.

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?

Response: No, we do not agree with the reviewer's veiw. If the evaporative loss of N species, e.g., NH_3, is significant, $\delta^{15}N$ of the remained WSTN should be significantly varied in proportionate to the loss of WSTN, because of isotopic fractionation caused by NH_4^+-NH_3 exchange (phase partitioning) reaction (Hoefs, 2009). Under equilibrium conditions, $\delta^{15}N$ values of NH_4^+ become higher than those of NH_3, where the isotopic enrichment factor ($\varepsilon_{NH4+-NH3}$) is estimated to be +33‰ (Heaton et al., 1997). On the contrary, if the loss of WSTN is mainly due to sticking to the glass walls, the isotopic fractionation may not be significant. Therefore, no abnormal deviation in $\delta^{15}N_{WSTN}$ temporal trend and its comparability to that of $\delta^{15}N_{TN}$ suggest that the evaporative loss of N species and thus the impact of WSTN loss on its $\delta^{15}N$ are not important. We describe these points in the revised MS.

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?

Response: Yes, there was a typo. The maximum concentration of WSTN is 1520 ng m^{-3}. We correct it in the revised MS.

The range and averages given in the text represent the whole data set (n = 21) obtained during the study period (September 2009 to October 2010) whereas Table 1 presents the seasonal: autumn (n = 8), winter (n = 3), spring (n = 5) and summer (n = 5), and annual (n = 19) averages. To avoid such ambiguity, we give the sample numbers in Table 1 in the revised MS.

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.

Response: We agree with the reviewer’s opinion that there are no analytical methods capable of detecting the complete absence of an anlyte. However, we reported 0.00 ng m^{-3} for organic carbon contents (ON, WSON and WION) because (i) the measured parameters; TN, WSTN, NO_3^- and NH_4^+, were detected in each and every sample, (ii) the detection limit of EA (Carlo Erba NA1500), caused by just sensitivity of the detector, is very small (0.4 mgN; Neiuwenhuize et al., 1994), and (iii) the blank levels in TN measurement were 0.0 mgN.

Since we measured TN, WSTN and inorganic ions following the standard analytical procedures of EA, TOC analyzer and IC and those instrument detection limits are well known, we focussed only on the estimation of analytical precision in their measurements. Using the propagating errors of each parameter, we estimate the precisions of ON, WSON and WION that are being noted in the revised MS. The blank levels in TN measurement and the detection limit of EA are also be included in the revised MS. According to the reviewer’s opinion, we also replace the expression of “0.00 ng m^{-3}“ with a phrase of “below detection limit (BDL)” in the revised MS.

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.

Response: Following the reviewer’s suggestion, we take care to avoid any repetetion of the text and references to sources in the revised MS. Also, we exclude some sentences in the results and discussion section in order to make the text concise in the revised MS.

In fact, based on radiocarbon and organic tracers as well as measurements of inorganic ions and MODIS fire detections, Pavuluri et al. (2013; 2015) found that the contributions from biomass burning emissions to Sapporo aerosols are significant. In the present study, the obtained results of nitogenous aerosols and their comparison with literature suggest that WSON in Sapporo aerosols has been contributed from multiple sources including biomass burning. The importance of biomass burning contribution to WSON is supported by its positive correlation with levoglucosan. As noted by the reviewer, the weak correlation of WSON with levoglucosan may be caused, in part, by decomposition of levoglucosan (Hoffmann et al., 2010) in spring and summer (Pavuluri et al., 2015). We add these points in the revised MS. The influence of biomass burning emissions on nitrogen, including WSON loading is further supported by isotopic signatures of TN and WSTN in Sapporo aerosols. Please see section 3.5 of the MS. Therefore, we believe that the interpretation of significant contribution of WSON from biomass burning emissions is logical.

However, it is difficult to provide further evidence based on linear relationship between WSON and non-sea-salt potassium, as suggested by the rviewer, because the higher concentrations of Na$^+$ in autumn aerosols have been attributed to microbial activities (Pavuluri et al., 2015) and hence, it is not possible to estimate the nss-K$^+$. Further, the higher concentrations of K$^+$ in spring and summer have also been attributed to a minor contributions from biogenic emissions in addition to the significant contributions from biomass burning (Pavuluri et al., 2015).

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 ~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.

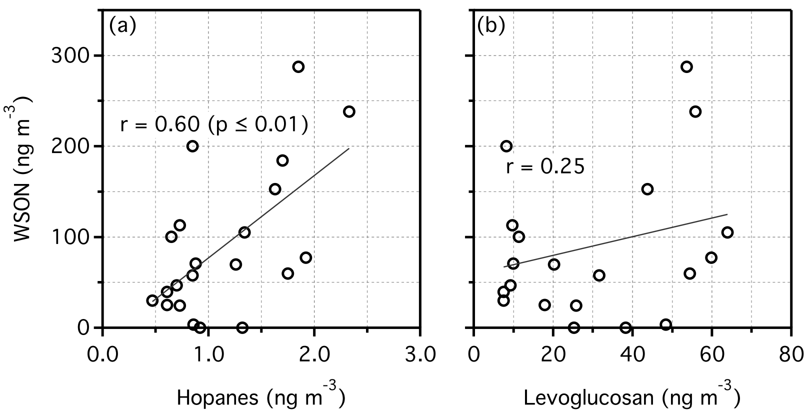
Response: Following the reviewer's recommendation, we conducted the Spearman's rank correlation analysis to estimate the relations of WSON and WION with source tracers. Also, we selected single confidence limit (0.05 level) to define the significant correlation. The obtained results are given in Table R1 below. We replace the data in Table 3 with these results and also take care in using the phrases in the description in section 3.4 of the revised MS.

Table R1. Spearman's rank correlation of WSON and WION with source tracers in Sapporo aerosols during the study period ($n = 21$). Significant correlation coefficients at 0.05 level are shown in bold.

Source tracer	Correlation coefficient (ρr)	
	WSON	WION
Hopanes	**0.48**	**-0. 50**
Levoglucosan	0.18	**-0.57**
Sucrose	-0.02	**0.38**
Isoprene-SOA tracers	-0.12	**0.50**
α-Pinene-SOA tracers	0.21	0.14
β-Caryophylinic acid	0.06	0.30
MSA$^-$	0. 09	**0.59**

In order to show the linear relations between WSON and source tracers, we provide their scatter plots shown in Figure R1 given below as Fig. 5 in the revised MS. Although linear relations of WSON with α-pinene SOA tracers and MSA^- during spring and summer are not statistically significant, the Spearman's rank correlations ($r = 0.71$ and $r = 0.62$, respectively) are found to be significant ($p \leq 0.05$). This point is to be added in the revised MS.

(i) During whole campaign period (n = 21)



(ii) During spring and summer (n = 10)

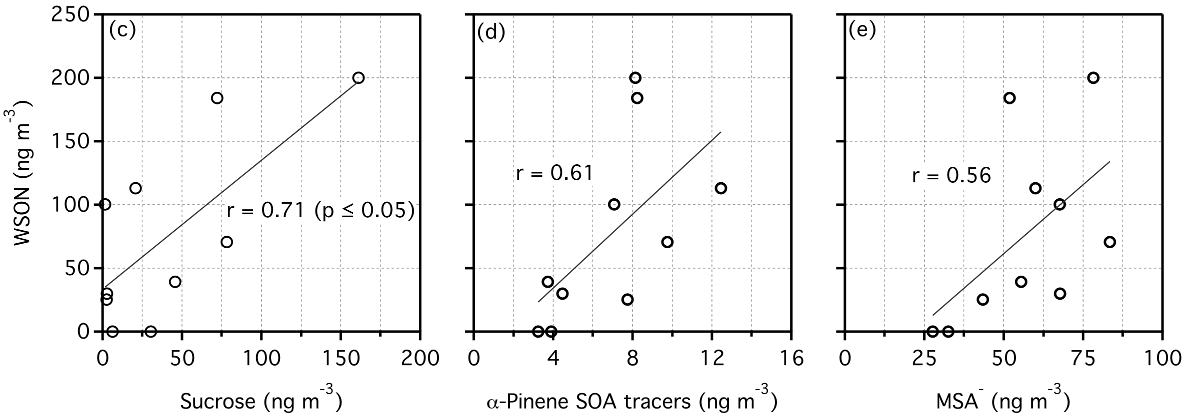


Figure R1. Linear relations of WSON with (a) hopanes (C_{27}-C_{32} hopanoid hydrocarbons) and (b) levoglucosan during campaign period (n = 21) and with (c) sucrose, (d) α-pinene-SOA tracers (sum of 3-hydroxyglutaric, pinonic, pinic and 3-methyl-1,2,3-butanetricarboxylic acids), and (e) MSA^- in spring and summer (n = 10) in Sapporo aerosols.

In fact, we found the correlation coefficients estimated by Spearman's rank correlation analysis between WION and biogenic SOA tracers such as isoprene SOA and MSA^- for the total data set (n = 21) (please see Table R1) and also between WION and β-caryophyllinic acid ($r = 0.62$) in spring and summer (n = 10) to be moderate and statistically significant. We note these points in the revised MS. Therefore, we strongly believe that our hypothesis of secondary production of WION from biogenic SOA based on the relations between WION and source tracers is logical and justifiable. However, in order to fully understand the source(s) of WION in the atmosphere, we need to conduct further studies in different locale, which is a subject of future research. We also note this point in the revised MS.

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?

Response: The values of data points higher than that of 1.5 × interquartile range are considered to be statistical outliers. However, as we found significant Spearman's rank correlations between WION and biogenic SOA tracers, except for α-pinene-SOA tracers, (Table R1) we felt that such description is not so important and be excluded in the revised MS.

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).

Response: MSA^- is produced in the atmosphere by photochemical oxidation of dimethyl sulfide (DMS) (Bates et al., 1992) that emits from terrestrial higher plants (Geng and Mu, 2006), soil in forests (Yi et al., 2010) and phytoplankton bloom in oceans (Bates et al., 1992). Therefore, MSA^- can be considered as a tracer to understand the importance of secondary production of WSON and WION from biogenic organic compounds, although both DMS and MSA^- do not contain nitrogen. We note these points in the revised MS.

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.

Response: We take all the suggested corrections in the revised MS.

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.

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