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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nitrogen speciation in various types of aerosol in spring over the northwestern Pacific Ocean" *by* L. Luo et al.

Anonymous Referee #1

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Anthropogenic activity is increasing nitrogen inputs to the oceans particularly downwind of fast growing economies such as in Asia and there is evidence that the deposition of this nitrogen to marine waters may be sufficient to cause a deleterious effect. This paper includes as noted later one very impressive illustration of this. This paper adds further information on deposition in this region and is therefore valuable although I would suggest it needs a few modification before final publication. One important general point that I think may need to be included in this paper is a discussion of the relationship between fog, aerosol and precipitation. There have now been several papers, at least some of which are referenced here, that illustrate that fogs are relatively regular occurrences in this region and may be important vectors of nitrogen deposition. This paper contributes further to this information. It is clear that fogs can contain high

concentrations of many components and I think that has been known for many years from other settings such as the acid rain debate. However, although fogs can be sampled by aerosol collectors, or indeed by specialist fog samplers, I am not really sure if it is appropriate to compare aerosols collected under normal conditions and under fogs, since fog seem to me to be somewhere between rain and aerosol. Gas exchange processes between water(fog) droplets and aerosol particles may be different and hence if the observed differences in composition between fogs and other aerosols (e.g. 3.2, 3.3 Table 2) represent differences in sources, cycling or simply that they are different types of atmospheric particles. It is also not really clear to me how to convert concentrations to fluxes since conventional deposition velocities are not appropriate. This comment does not invalidate any of the information here, but just to caution that any comparison needs to be done carefully. Specific comments Page 25587 Line 8 Sampling only when "cruising", presumably meaning the ship is moving forward, does not of itself guarantee clean sampling – it is about wind direction in relation to that ship's movement. Page 25589 Line 9 it is probably worth adding a reference for seawater composition RA calculation – this is really deriving the acidity from an ion balance calculation which is OK but does ignore other ions such as bicarbonate which may be there at higher pH. It's also not quite clear why a ratio rather than a cations-anions approach is preferable so I would suggest this approach needs bit of explanation and justification. Line 20 I assume the WSON error estimate is an average because it must vary from sample to sample. Section 2.3 It is important in any calculation of this type to emphasise the uncertainty in deposition velocities, particularly where wind speed and size distribution are not well known as here – a recent paper by Baker et al 2013 (DOI: 10.1002/gbc.20062) illustrates some of the difficulties in this.

Page 25592 Line 11 dust is highly variable as these authors know well, so 5 samples is a small basis for producing average values. The authors seem to be using 1000ng/m3 as a threshold for dusty samples (see also the end of section 3.1) but I don't think this is stated. Line 15-20 the discussion of Al solubility here is difficult to follow, partly because Fig 3 does not contain an explicit Al solubility and also because of the earlier

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noted difficulty of really understanding their RA term.

Page 25594 Line 1-14 There are clearly several sources of Ca and K including sea-water and dust but I suspect that beyond stating this, the authors could shorten this section and remove some vague speculation. Line 15-20 The tabulated data is in nM/m3 and yet figure 5 is in nequiv/m3 with no explanation. I would do everything in one unit and this affects the statements on ammonium/sulphate ion balances. It is probably worth noting the importance of ammonia emissions in Asia which supply this neutralising ammonia.

Page 25596 Line 15-20 rates of NOx oxidation may also be important. Line 23- line 2 p25597 include references to explain the sources of the Jeju data and as noted before I am not really sure that it is simple to compare fog and aerosol in this way. They are obviously different but there are several possible explanations of why.

P25597 Line 9-11. Without some knowledge of particle size I don't think you can say whether sulphuric or nitric acid is neutralised by ammonium, you simply have the ratio of ammonium to nitrate+2xsulphate on a molar basis. Line 20-30 Concentrations differences for WSON between aerosols and fog do not tell you about scavenging I think and the different WSON % of TN suggests different source regions to me. Section 3.3.3 As the authors show these aerosols are not at all "background" but quite contaminated so I would suggest changing the naming. The discussion of WSON sources in section 3.3.3 seems to assume there is one single source and to confuse the reader by arguing for no marine source (line 9) and a marine source (line 26). There are multiple sources of WSON (see for example Cape et al., 2011 review in atmospheric research). The discussion on p25600 line 0-8 about sources of nitrate and ammonium from seawater I think is a bit confusing – it is very hard to see seawater as a significant source of nitrate and ammonium to aerosols, and I do not really understand the reasons for arguing for a source of ammonium and nitrate from photolysed marine DON.

Section 3.4 Others have done this kind of comparison of WSON and TN (e.g Jickells

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et al DOI: 10.1098/rstb.2013.0115) and argue that it suggests most of the WSON is anthropogenic, do these authors have a different interpretation? Note that the rain and aerosol data bases are different so the different %WSON may be sampling biases. The list of references at the top of p25601 could probably go to the figure caption.

P25602 the estimation that nitrogen deposition from the atmosphere exceeds river and offshore inputs is a startling illustration of the importance of these inputs in this region and might be highlighted. The comparison of impacts on productivity might best be made with "new" not total primary production rates.

Section 4 seems to be a summary not a conclusion.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 25583, 2015.