

The original reviewer comments are given in black text. Responses to these comments are given throughout this document in blue text. Sections added or significantly altered in the manuscript are given in “underlined blue text in quotations”.

## **Interactive comment on “Ammonia in the summertime Arctic marine boundary layer: sources, sinks and implications” by G. R. Wentworth et al.**

**M.T. Johnson (Referee)**

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Wentworth et al present a neat study of the ocean-atmosphere and aerosol-gas phase partitioning of ammonium/ammonia in the high Arctic, considering the interactions with melt-ponds and seabird and fire emissions. As they point out, observations of the multiphase ammonia system at high latitudes are few and far between so this dataset represents a considerable addition to our knowledge and understanding of the system. The modelling element, which demonstrates the potential significance of point sources of ammonia, in particular seabird colonies adds a useful extra dimension to the study.

The data and arguments are clearly presented and for the most part very easy to follow and the findings are insightful and scientifically reasonable.

Apart from some adding some more details to the methods and other minor comments/corrections listed below I recommend publication of this manuscript as-is.

As a point of interest the authors may wish to explore briefly the hypothesis presented in Johnson and Bell, 2008 (<http://www.publish.csiro.au/?paper=EN08030>), which suggests that away from strong local sources of ammonia, the gas phase concentration is likely to be controlled by the partial pressure of ammonia over the aerosol (akin to the compensation point concept applied by Wentworth et al to the ocean / melt pond surface). As level of neutralisation goes up, the partial pressure (compensation point) increases. This therefore suggests that the reason that NH<sub>3</sub> is higher in the summer not simply because of the seabird emissions but additionally due to the lack of aerosol acidity to take it up, therefore 'pushing' it into the ocean. The reverse situation was postulated in Johnson and Bell 2008 - whereby acidic sulfate emissions in the remote marine boundary layer would reduce the compensation point over the aerosol and lead to a consequent emission from the ocean, but the principle is basically the same.

We agree with this assessment and thank the referee for pointing out the Johnson and Bell (2008) study. We have clarified in the text that low sulphate loading allows seabird NH<sub>3</sub> emissions to remain in the gas-phase (i.e. “pushing” it into the ocean):

“Lastly, Johnson and Bell (2008) show that a sufficiently neutralized sulphate aerosol will tend to ‘push’ gas-phase NH<sub>3</sub> into the ocean in the aerosol-gas-ocean system, also consistent with Fig. 3.” (inserted into Page 29989, line 15)

Specific comments/corrections:

p29977 - expand on T dependence - not just solubility but also acid-base partitioning is strongly T dependent, making it a 'double whammy' effect

The following sentence has been expanded to clarify the impact on  $\text{NH}_3$ -to- $\text{NH}_4^+$  partitioning:

“Colder SST reduces the emission potential due to increased solubility of  $\text{NH}_3$  (because of both reduced  $\text{NH}_{3(\text{aq})}$  volatility and increased partitioning of  $\text{NH}_{3(\text{aq})}$  to  $\text{NH}_{4^+(\text{aq})}$ ); hence, at higher latitudes the open ocean is more likely to act as a net sink (Johnson et al., 2008).” (inserted into Page 29977, line 10)

p22978 - re lifetime and transport - the authors should also consider the lifetime and potential for transport of aerosol  $\text{NH}_4$  - could this have more of an influence?

The impact of  $\text{NH}_4^+$  transport from southern latitudes has little impact on  $\text{NH}_x$  in the summertime Arctic boundary layer. This is due, in part, to a polar dome that makes long-range transport to the Arctic surface layer inefficient during the summer (Stohl, 2006). In addition, most of the  $\text{NH}_x$  is gas-phase  $\text{NH}_3$  providing further evidence that the role of  $\text{NH}_4^+$  transport is minor with respect to the summertime Arctic  $\text{NH}_x$  budget near the surface.

Methods (p22980 - 29981) - some clarification needed for the uninitiated to this method:

-why use  $\text{H}_2\text{O}_2$  in the acceptor stream? Why not use a typical acid for ammonia trapping - oxalic acid,  $\text{HCl}$  or similar?

The instrument's sampling interface is designed to collect both acidic and alkaline gases.  $\text{H}_2\text{O}_2$  is used to increase the collection efficiency of  $\text{SO}_2$  (by oxidizing it to  $\text{SO}_4^{2-}$ ). Previous studies that characterize the AIM-IC system have found that an acidic denuder solution is not required to achieve high collection efficiency of  $\text{NH}_3$  (Hsu and Clair, 2015; Markovic et al., 2012). Furthermore, acidifying the denuder solution would reduce the solubility of acidic gases (e.g.  $\text{HNO}_3$ ,  $\text{HONO}$ , organic acids). This has been clarified in the text:

“...dissolved in a 2 mM  $\text{H}_2\text{O}_2$  solution (to enhance the solubility of  $\text{SO}_2$ )” (inserted in Page 29980, line 4).

-samples collected by hygroscopic growth - surely these are less than 2.5uM not larger than 2.5 uM? The >2.5 uM fraction of aerosol has been impacted 'out' of the sampler?

Yes, we have corrected the text to read:

“The remaining  $\text{PM}_{2.5}$  particles have sufficient inertia to pass through the denuder into a supersaturation chamber where they are collected as an aqueous solution via hygroscopic growth.” (Page 29980, line 5)

-is there a 22m line for each of the denuder and supersaturation chamber? What is it's diameter/what is it made of? Is this part of the system continuous flow i.e. are the 10ml samples collected in the lab manually and fed into the ICs? What is the flow rate? How is the volume of sample collected in the supersaturation chamber related to concentration in the atmosphere?

Yes – there are separate 22 m lines for each of the denuder and supersaturation chamber. Dissolved (aqueous) samples are continuously pulled through the lines (diameter of 0.8 mm) into four 5 mL syringes (one each for cation gas, cation particle, anion gas, and anion particle analysis). These syringes are controlled automatically by a stepper motor and pull at a rate of 5 mL hr<sup>-1</sup> each (so the flow rate through each sample line is 10 mL hr<sup>-1</sup>, since each line feeds only two syringes). After one hour of sampling the syringes are automatically injected onto both a cation IC and anion IC for quantification of dissolved ions. The mole loading on each syringe is related back to an atmospheric concentration by use of a calibration curve (converting IC peak area to moles) and average air flow during sample time (to give units of mole m<sup>-3</sup>).

-Seawater/melt pond NH<sub>x</sub> - a bit more detail on the method would be useful – what working reagent mix was used, what was the working reagent to sample volume ratio? How long were samples incubated for after inoculation with working reagent?

The working reagent was composed of 500 mL borate buffer (20 g sodium tetraborate decahydrate dissolved in 500 mL of deionized water), 2.5 mL of sodium sulfite solution (1 g of sodium sulfite dissolved in 125 mL of deionized water) and 25 mL of a phthalaldehyde solution (1 g of phthalaldehyde dissolved in 25 mL 95%-ethanol). For analysis 1.2 mL of working reagent was combined with 5 mL of sample and incubated for 3.5 hours.

How were matrix effects and background fluorescence accounted for in the calibration/ analysis?

Matrix effects and background fluorescence were accounted for using standard additions and blanks (seawater in borate buffer only), respectively. The procedures and equations are outlined in Holmes et al. (1999). The authors found that matrix effects were less than 5% of the fluorescence signal in seawater at high dissolved organic concentrations. Furthermore, the matrix effect and the background are corrected for.

It is stated that melt pond samples were analysed within 10hrs but seawater ones within 1 hr - why difference? Was this 10 hrs til inoculation or 10 hours incubation after inoculation with working reagent?

There was sometimes a delay for analysis of melt pond samples due to a lack of personnel as well as incubation tubes. The same operator was responsible for performing multiple analyses on melt pond water. The 10 hrs was the time until inoculation – the incubation period was the same as for seawater (3.5 hours).

Potentially all such methodological details could be put into the supplementary material.

We prefer not to include all these details in the manuscript as they are readily available in previous publications for both the AIM-IC (Hsu and Clair, 2015; Markovic et al., 2012) and

seawater  $\text{NH}_x$  method (Holmes et al., 1999). Since the focus of the manuscript is not method development there would be little added value to including all these details in the text.

p29988 - discussion of Fig 3 and the fluxes is a little brief and rather unfocussed. Maybe better in the discussion, expanded on a little?

The discussion has been expanded to include the following:

“Net fluxes were exclusively downwards (net deposition into the ocean and melt ponds) due to the relative abundances of  $\text{NH}_{3(g)}$  and  $\text{NH}_4^+_{(aq)}$  in these surface pools as well as cold surface temperatures as suggested by Johnson et al., (2008).” (inserted into Page 29988, line 3)

p29989 - sentence beginning 'On the other hand...' is a bit hard to follow – suggest replace 'nanoequivalents' with 'concentration' and move '( $\text{NH}_x$  napprox  $\text{NH}_3$ )' to after 'SO<sub>4</sub><sup>2-</sup>'.

Agreed – we switched around the wording as suggested.

Also on this page - the discussion of neutralisation could do to be tightened up a bit -  $\text{NH}_4:\text{SO}_4 = 1$  isn't 'neutralised' - given a simple system of simply  $\text{H}_2\text{SO}_4$  and  $\text{NH}_4$ , neutral pH should be achieved at  $\text{NH}_4:\text{SO}_4 = 2:1$ , not 1:1. However, I would argue that pH 7 always counts as neutralised, whatever the  $\text{NH}_4:\text{SO}_4$  ratio is? There are obviously other sources of acidity which can affect pH as well as  $\text{NH}_4/\text{SO}_4$  neutralisation.

Throughout the manuscript we define the  $\text{NH}_4^+:\text{SO}_4^{2-}$  ratio with units of equivalents (so the ratio is  $\text{NH}_4^+$  moles to  $2*\text{SO}_4^{2-}$  moles, such that it already accounts for the double charge of sulphate). In other words, a ratio of 1 equates a fully neutralized sulphate aerosol. An aerosol with  $\text{NH}_4^+:\text{SO}_4^{2-}$  ratio (in equivalents) approaching 1 can still have an acidic pH. We have updated the manuscript to clarify how we chose to define the ratio:

“During the first third of the cruise (before 18 July), gas-phase  $\text{NH}_3$  was also low and neutralization (i.e. the ratio  $\text{NH}_4^+:\text{SO}_4^{2-}$  in units of equivalents) was ambiguous due to numerous values near or below detection limit.” (Page 29988, line 26).

The concept of a particle being acidic (pH << 7) despite a  $\text{NH}_4^+:\text{SO}_4^{2-}$  equivalents ratio approaching 1 is also clarified:

“For example, a deliquesced ammonium sulphate particle containing  $20 \text{ neq m}^{-3}$  of  $\text{SO}_4^{2-}$  and  $19.98 \text{ neq m}^{-3}$   $\text{NH}_4^+$  at 85% RH will have a pH of ~3.1 under equilibrium conditions despite having an  $\text{NH}_4^+:\text{SO}_4^{2-}$  equivalents ratio of 0.999.” (inserted Page 29989, line 6)

Figure 1 - what does purple colour mean? (I guess it means no data) - please clarify in legend

Correct – it means periods without AIM-IC data due to: 1) instrument troubleshooting, 2) invalid measurements from ship activity (validity criteria outlined on page 29981, line 11) or 3)  $\text{NH}_3$  measurements below the detection limit (only 2 instances). This has been clarified in the figure legend.

## References

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