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

**Anonymous Referee #2**
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This is a comprehensive paper with interesting results. Although a bit long/wordy in places, the text is clear and easy to follow. I recommend publication if the comments below are addressed.

General Comments: I see no reason to present these gas and aerosol composition data using mass units. Converting mass to moles would make for a more intuitive dataset and enable comparison with recent publications such as Johnson et al (2008).

The main rationale behind using $ng\ m^{-3}$ versus $nmol\ m^{-3}$ is two-fold: 1) the flux calculations (in $ng\ m^{-2}\ s^{-1}$) are more intuitive with $ng\ m^{-3}$, and 2) several publications of sea-air $NH_3$ exchange (Asman et al., 1999; Greenaert et al., 1998) also use mass units. Furthermore, terrestrial $NH_3$ flux studies use units of $ng\ m^{-2}\ s^{-1}$ (e.g. Zhang et al., 2010) so we chose to report our fluxes in these units for consistency with the broader $NH_3$ flux community. The conversion from mass to moles is simple (divide by 17.03) such that a reader could easily convert be the two.

Inlet location: There are two issues that need to be addressed. Firstly, how far forward is the inlet? The text is a little vague: "mounted to the hull near the bow of the ship". This is particularly important when it comes to choosing the wind sector to exclude/include data. If the inlet is very close to the bow +/-90 degrees is probably ok. If it is further back, I'd recommend a more stringent wind sector.

The inlet was about 4 m back from the bow of the ship – for reference, the length of the *CCGS Amundsen* is 98 m. This has been clarified in the text:

"These components were contained within an aluminum inlet box that was mounted to the hull near the bow of the ship (about 4 m back of the bow)." (inserted on page 29980, line 8)

Secondly, if the inlet height was only 1 m above the deck then adverse wind/wave conditions could have caused substantial contamination of the signals. Sea spray generated by the ship plunging into the waves tends to come right up over the bow in these conditions. I assume the conditions in summer were benign but this should be stated more explicitly. In future I recommend mounting the inlet higher up, above the wave spray zone!

We agree the potential for contamination by ship-generated sea spray could be an issue in certain circumstances (e.g. significant waves, while breaking ice). There were several factors that would mitigate this effect during the cruise: 1) relatively benign conditions (as the referee pointed out),

and 2) a $PM_{2.5}$ impactor atop the inlet which removes coarse mode sea salt particles generated by ship/wave action. In addition, $NH_x$ is such a minor constituent of seawater that ship-generated sea salt would not affect the $NH_3$ or $NH_4^+$ dataset. Also, Fig. 4 reveals $SO_4^{2-} \approx NH_4^+$ on an equivalent basis suggesting there is negligible sea salt $SO_4^{2-}$, otherwise $SO_4^{2-}$ would be greater than $NH_4^+$.

We have briefly clarified the issue of the ship-generated sea spray in the manuscript:

"Influence from ship-generated sea spray was likely minimal due to the benign nature of the summertime Arctic Ocean, in addition to the $PM_{2.5}$ impactor designed to remove coarse particles." (inserted on page 29980, line 9)

We placed the inlet box near deck level for logistical and safety reasons. The set-up and troubleshooting of the components inside the inlet box is time-consuming and finicky so is much easier at deck level. Also, visual checks of the inlet box had to be performed every several hours which would have been impossible (due to safety) during icebreaking, inclement weather, or choppy seas had the inlet box been elevated out of arms reach. Also, the impactor was swapped regularly (every few days) to prevent build-up of sea salt on its surface, although visible accumulation was never observed.

Specific Comments:

Page 29976, Line 18: What does 'area-wide nature' mean?

It means the emissions are spread over a large area and hence more difficult to calculate or estimate, relative to point sources (e.g. tailpipes, smokestacks). This has been clarified in the text:

"…however, large uncertainties exist for these values due to the area-wide nature (emissions spread over a large spatial extent) and poor characterization of many sources." (inserted on page 29976, line 18)

Page 29981, Line 19: As far from the side of the ship or as far from the side of the melt pond? Please specify.

From the side of the melt pond. Personnel were lowered onto the sea ice for melt pond sampling. This has been clarified in the text:

"The water was sampled as far from the side of the melt pond as possible" (inserted on Page 29981, line 19)

Section 3.2: Sulphate neutralisation. I would like to see some scatter plots (or a correlation analysis) of gas phase NH3 vs particulate NH4 and gas phase NH3 vs the degree of aerosol neutralisation (NH4:SO4 ratio). Assuming the analysis in Figure 5 is correct, the cruise data should follow a similar trend – i.e. higher NH4 concentrations/greater aerosol neutralisation when gas phase NH3 concentrations increased.

Since there is typically a much higher loading of $NH_3$ than both $NH_4^+$ and $SO_4^{2-}$, the $NH_4^+$ concentrations should not correlate with $NH_3$ concentrations. This is because the sulphate is already saturated with $NH_4^+$ so any additional increase in $NH_3$ will not result in a noticeable increase in $NH_4^+$.

A similar trend occurs with neutralization ratio. As the ratio of $NH_4^+$:$SO_4^{2-}$ equivalents approaches 1 it is not very sensitive to $NH_3$ concentrations. This is shown in the plot below of $NH_4^+$:$SO_4^{2-}$ versus $NH_3$ (NOTE: this figure is a molar ratio, so the ratio approaches 2 for a fully neutralized aerosol). Errors bars represent a very conservative estimate of uncertainty ($\pm$ (30% + detection limit)).

For the points of low $NH_3$ mixing ratios (<100 pptv) there is insufficient $NH_3$ to neutralize the $SO_4^{2-}$ (molar ratio less than 2). However, above this approximate threshold the ratio is insensitive to $NH_3$ since the sulphate is already neutralized. We chose not to include this figure in the manuscript for two reasons: 1) $NH_4^+$ and $SO_4^{2-}$ approach detection limits so uncertainties regarding their ratio is large resulting in unrealistic molar ratios above two, and 2) it is redundant with the analysis of Fig. 4 (since $NH_4^+ \approx SO_4^{2-}$ the $SO_4^{2-}$ is roughly neutralized).
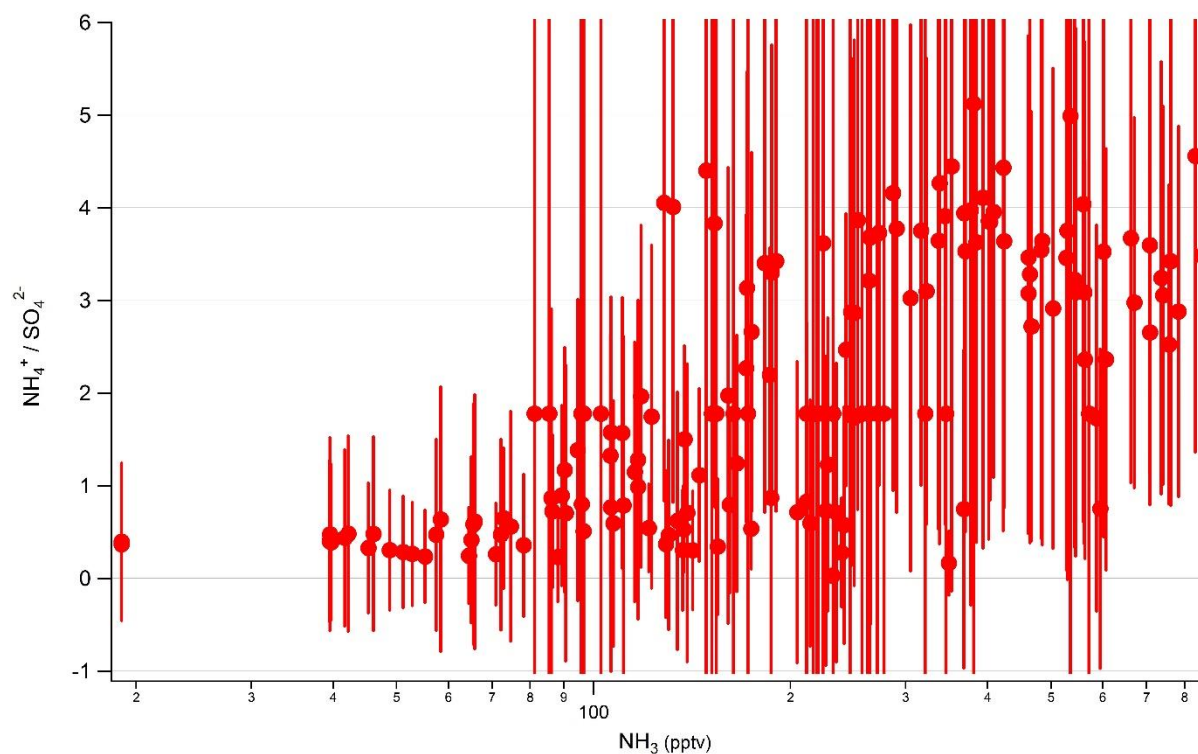


Figure 5: Surely it should be 2*NH4/nssSO4? This would give a neutral value of 1. I think a ratio of NH4/2*nssSO4 will give a much lower value when the aerosol is neutralised.

Throughout the manuscript we have defined the $NH_4^+$:$SO_4^{2-}$ ratio using the units of neq m$^{-3}$, which is the nmol m$^{-3}$ value multiplied by the charge of the species in question (e.g. 1 nmol m$^{-3}$ $SO_4^{2-}$ = 2 neq m$^{-3}$). Therefore a fully neutralized $SO_4^{2-}$ aerosol has an equivalent ratio of

$NH_4^+:SO_4^{2-} = 1$, meaning there is 1 equivalent ($\equiv$1 mole) of $NH_4^+$ for every 1 equivalent ($\equiv$0.5 moles) of $SO_4^{2-}$.

Also, has there ever been a comparison between AIMS-IC and High Vol filter samplers? In other words, could High Vol. particulate NH4 measurements be confounded if gas phase NH3 concentrations were high? This is worthy of discussion given the inclusion of High Vol. data in Figure 5.

Hsu and Clair (2015) compared $PM_{2.5}$ composition data ($NH_4^+$, $SO_4^{2-}$, $NO_3^-$) of a co-located AIM-IC and Partisol $PM_{2.5}$ Sampler (similar to a Hi-Vol sampler). The authors found the Hi-Vol underestimated $NH_4^+$ relative to the AIM-IC due to volatilization of $NH_4NO_3$ deposited on the filter of the Partisol sampler. However, this effect is likely negligible at Alert due to low summertime temperatures (~0 ℃) and small mass loadings of $NH_4NO_3$.

The Hi-Vol samplers at Alert do not have a denuder upstream of the filter used to capture $PM_{2.5}$. It is possible that acidic $PM_{2.5}$ collected on the filter may become more neutralized over time if there was high $NH_3$ levels in the air flowing over the filters. As the reviewer suggested this may increase the $NH_4^+:SO_4^{2-}$ on the filter such that it overestimates the average $NH_4^+:SO_4^{2-}$ ratio in ambient $PM_{2.5}$. However, this would require high levels of $NH_3$ which is consistent with our interpretation of the Hi-Vol data: that is suggests significant regional source(s) of $NH_3$.

These issues of under and overestimation of $NH_3$ by Hi-Vol samplers has been added to the text:

"In warm environments volatilization of $NH_4NO_3$ off of filters can cause an underestimation of $NH_4^+$, but this is not expected to be an issue at Alert due to cold weather and low loadings of $NH_4NO_3$." (inserted Page 29989, line 11)

"However, there is no denuder upstream of the Hi-Vol filters to remove $NH_3$ so the observed $NH_4^+:SO_4^{2-}$ ratio (Fig. 5) may be higher than for ambient $PM_{2.5}$. This effect is difficult to characterize, but if it is important then it is still evidence for the abundance of $NH_3$ in the summertime Arctic boundary layer" (inserted Page 29989, line 15)

Page 29990, Line 15: The Bouwman flux estimate uses a seawater NHx climatology and, crucially, assumes that the atmospheric NH3 concentration is zero. This leads to an overestimate of the oceanic NH3 emissions. Using a different flux estimate would make the discrepancy in NH3 mixing ratio between the model and the data even greater than stated. It would be worth including reference to the recent paper by Paulot et al (GBC, 2015), which demonstrates this overestimate using different NH3 emission schemes within the GEOS-Chem model.

We agree with this assessment and have included an additional sentence further explaining the recent Paulot et al. (2015) work:

"Paulot et al. (2015) recently showed the oceanic emissions from this original inventory are roughly a factor of 3 too high since the initial inventory assumes atmospheric $NH_3$ is equal to zero." (inserted Page 29990, line 16)

Section 3.4: Implications for N-deposition. This is an interesting discussion, but it feels incomplete as no attempt is made to include the particulate NH4 deposition. The particulate NH4 contribution is likely to be from the same source (i.e. volatile gas phase NH3 is emitted from seabird colonies. Some neutralises whatever SO4 aerosol is present, and the rest remains in the gas phase).

The deposition plots in Fig. 8 represent total (wet and dry) $NH_x$ deposition and do include $NH_4^+$ deposition. The majority of $NH_x$ deposition results from wet/dry deposition of $NH_3$; $NH_4^+$ deposition is minor in comparison. We agree that the majority of $NH_4^+$ likely stems from the same source as gas-phase $NH_3$ (as the referee points out). We have clarified the minor contribution of $NH_4^+$ in the text:

"The majority of $NH_x$ deposition is caused by $NH_3$ as opposed to $NH_4^+$." (inserted page 29994, line 26)

Page 29995, Line 25: Typo – remove the word 'a' from between 'slightly' and 'higher'

Thank you – we have removed the typo.

References

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