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.

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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 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$_3$ 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$_3$ 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$_3$ 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 NH$_3$-to-NH$_4^+$ partitioning:

“Colder SST reduces the emission potential due to increased solubility of NH$_3$ (because of both reduced NH$_3$(aq) volatility and increased partitioning of NH$_3$(aq) to NH$_4^+$$(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 NH$_4^+$ - could this have more of an influence?

The impact of NH$_4^+$ transport from southern latitudes has little impact on NH$_3$ 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 NH$_3$ is gas-phase NH$_3$ providing further evidence that the role of NH$_4^+$ transport is minor with respect to the summertime Arctic NH$_3$ budget near the surface.

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

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

The instrument’s sampling interface is designed to collect both acidic and alkaline gases. H$_2$O$_2$ is used to increase the collection efficiency of SO$_2$ (by oxidizing it to 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 NH$_3$ (Hsu and Clair, 2015; Markovic et al., 2012). Furthermore, acidifying the denuder solution would reduce the solubility of acidic gases (e.g. HNO$_3$, HONO, organic acids). This has been clarified in the text:

“…dissolved in a 2 mM H$_2$O$_2$ solution (to enhance the solubility of SO$_2$)” (inserted in Page 29980, line 4).
samples collected by hygroscopic growth - surely these are less than 2.5 uM 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 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$^{-1}$ each (so the flow rate through each sample line is 10 mL hr$^{-1}$, 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$^{-3}$).

- Seawater/melt pond NHx - 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 phthaldialdehyde solution (1 g of phthaldialdehyde 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).

Poteantially 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 NH$_4$ 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 NH$_3$(g) and 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 '(NHx napprox NH3) to after 'SO$_4^{2-}$'.

Agreed – we switched around the wording as suggested.

Also on this page - the discussion of neutralisation could do to be tightened up a bit - NH4:SO4
= 1 isn’t ‘neutralised’ - given a simple system of simply H2SO4 and NH4, neutral pH should
be acheived at NH4:So4 = 2:1, not 1:1. However, I would argue that ph 7 always counts as
neutralised, whatever the NH4:SO4 ratio is? There are obviously other sources of acidity which
can affect pH as well as NH4/SO4 neutralisation.
Throughout the manuscript we define the NH$_4^+$:SO$_4^{2-}$ ratio with units of equivalents (so the ratio is NH$_4^+$ moles to 2*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 NH$_4^+$: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 NH$_3$ was also low and neutralization (i.e. the ratio NH$_4^+$: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 NH$_4^+$:SO$_4^{2-}$ equivalents ratio approaching 1 is also clarified:

“For example, a deliquesced ammonium sulphate particle containing 20 neq m$^{-3}$ of SO$_4^{2-}$ and 19.98 neq m$^{-3}$ NH$_4^+$ at 85% RH will have a pH of ~3.1 under equilibrium conditions despite having an NH$_4^+$: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) NH$_3$ measurements below the detection limit (only 2 instances). This has been clarified in the figure legend.

References


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 between 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\textsubscript{2.5} impactor atop the inlet which removes coarse mode sea salt particles generated by ship/wave action. In addition, NH\textsubscript{3} is such a minor constituent of seawater that ship-generated sea salt would not affect the NH\textsubscript{3} or NH\textsubscript{4}\textsuperscript{+} dataset. Also, Fig. 4 reveals SO\textsubscript{4}\textsuperscript{2-} $\approx$ NH\textsubscript{4}\textsuperscript{+} on an equivalent basis suggesting there is negligible sea salt SO\textsubscript{4}\textsuperscript{2-}; otherwise SO\textsubscript{4}\textsuperscript{2-} would be greater than NH\textsubscript{4}\textsuperscript{+}.

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\textsubscript{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)
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 NH₃ than both NH₄⁺ and SO₄²⁻, the NH₄⁺ concentrations should not correlate with NH₃ concentrations. This is because the sulphate is already saturated with NH₄⁺ so any additional increase in NH₃ will not result in a noticeable increase in NH₄⁺.

A similar trend occurs with neutralization ratio. As the ratio of NH₄⁺:SO₄²⁻ equivalents approaches 1 it is not very sensitive to NH₃ concentrations. This is shown in the plot below of NH₄⁺:SO₄²⁻ versus NH₃ (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 (± (30% + detection limit)).

For the points of low NH₃ mixing ratios (<100 pptv) there is insufficient NH₃ to neutralize the SO₄²⁻ (molar ratio less than 2). However, above this approximate threshold the ratio is insensitive to NH₃ since the sulphate is already neutralized. We chose not to include this figure in the manuscript for two reasons: 1) NH₄⁺ and SO₄²⁻ 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 NH₄⁺ ≈ SO₄²⁻ the SO₄²⁻ is roughly neutralized).
Figure 5: Surely it should be $2\times\text{NH}_4/\text{nssSO}_4$? This would give a neutral value of 1. I think a ratio of $\text{NH}_4/2\times\text{nssSO}_4$ will give a much lower value when the aerosol is neutralised.

Throughout the manuscript we have defined the $\text{NH}_4^+:\text{SO}_4^{2-}$ 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$^{-3}$ $\text{SO}_4^{2-} = 2$ neq m$^{-3}$). Therefore a fully neutralized $\text{SO}_4^{2-}$ aerosol has an equivalent ratio of $\text{NH}_4^+:\text{SO}_4^{2-} = 1$, meaning there is 1 equivalent (≡1 mole) of $\text{NH}_4^+$ for every 1 equivalent (≡0.5 moles) of $\text{SO}_4^{2-}$.

Also, has there ever been a comparison between AIMS-IC and High Vol filter samplers? In other words, could High Vol particulate $\text{NH}_4$ measurements be confounded if gas phase NH$_3$ 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 ($\text{NH}_4^+$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$) 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 $\text{NH}_4^+$ relative to the AIM-IC due to volatilization of NH$_3$NO$_3$ deposited on the filter of the Partisol sampler. However, this effect is likely negligible at Alert due to low summertime temperatures (~0 °C) and small mass loadings of NH$_3$NO$_3$.

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$_4^{2-}$ ratio 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$_4$NO$_3$ 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$_4$NO$_3$.” (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 NH$_x$ climatology and, crucially, assumes that the atmospheric NH$_3$ concentration is zero. This leads to an overestimate of the oceanic NH$_3$ emissions. Using a different flux estimate would make the discrepancy in NH$_3$ 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 NH$_3$ 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 NH$_4$ deposition. The particulate NH$_4$ contribution is likely to be from the same source (i.e. volatile gas phase NH$_3$ is emitted from seabird colonies. Some neutralises whatever SO$_4$ 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 NH₃ deposition is caused by NH₃ as opposed to NH₄⁺.” (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


Ammonia in the summertime Arctic marine boundary layer: Sources, Sinks and Implications

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Abstract

Continuous hourly measurements of gas-phase ammonia (NH₃(g)) were taken from 13 July to 7 August 2014 on a research cruise throughout Baffin Bay and the eastern Canadian Arctic Archipelago. Concentrations ranged from 30-650 ng m⁻³ (40-870 pptv) with the highest values recorded in Lancaster Sound (74°13’ N, 84°00’ W). Simultaneous measurements of total ammonium ([NH₄⁺]), pH and temperature in the ocean and in melt ponds were used to compute the compensation point (χ), which is the ambient NH₃(g) concentration at which surface-air fluxes change direction. Ambient NH₃(g) was usually several orders of magnitude larger than both χₒcean and χ_MP (<0.4-10 ng m⁻³) indicating these surface pools are net sinks of NH₃. Flux
calculations estimate average net downward fluxes of 1.4 and 1.1 ng m\(^{-2}\) s\(^{-1}\) for the open ocean and melt ponds, respectively. Sufficient NH\(_3(g)\) was present to neutralize non-sea salt sulphate (nss-SO\(_4^{2-}\)) in the boundary layer during most of the study. This finding was corroborated with a historical dataset of PM\(_{2.5}\) composition from Alert, NU (82°30’ N, 62°20’ W) wherein the median ratio of NH\(_4^+/\text{nss-SO}_4^{2-}\) equivalents was greater than 0.75 in June, July and August. The GEOS-Chem chemical transport model was employed to examine the impact of NH\(_3(g)\) emissions from seabird guano on boundary-layer composition and nss-SO\(_4^{2-}\) neutralization. A GEOS-Chem simulation without seabird emissions underestimated boundary layer NH\(_3(g)\) by several orders of magnitude and yielded highly acidic aerosol. A simulation that included seabird NH\(_3\) emissions was in better agreement with observations for both NH\(_3(g)\) concentrations and nss-SO\(_4^{2-}\) neutralization. This is strong evidence that seabird colonies are significant sources of NH\(_3\) in the summertime Arctic, and are ubiquitous enough to impact atmospheric composition across the entire Baffin Bay region. Large wildfires in the Northwest Territories were likely an important source of NH\(_3\), but their influence was probably limited to the Central Canadian Arctic. Implications of seabird-derived N-deposition to terrestrial and aquatic ecosystems are also discussed.

1 Introduction

Ammonia (NH\(_3(g)\)) is the dominant alkaline gas in the atmosphere and is an important component of the global nitrogen cycle. Its transport and deposition can have harmful effects for N-sensitive ecosystems such as eutrophication, loss of biodiversity and soil acidification (Krupa, 2003). The presence of NH\(_3(g)\) can impact climate by increasing rates of new particle formation via stabilization of sulphuric acid clusters (Kirkby et al., 2011). Gas-phase NH\(_3\) is also able to partition to acidic fine particulate matter (PM\(_{2.5}\)) to form particulate-phase ammonium (NH\(_4^+(p)\)), which alters various aerosol properties, such as scattering efficiency (Martin et al., 2004), hygroscopicity (Petters and Kreidenweis, 2007), ice nucleating ability (Abbatt et al., 2006) and heterogeneous chemistry occurring on surfaces (Fickert et al., 1999).

As a result, the accurate quantification of the magnitude and location of NH\(_3(g)\) sources is important for chemical transport models (CTMs). The major anthropogenic source is agriculture (fertilization and animal husbandry) with biomass burning, transport and industry being minor contributors (Reis et al., 2009). Natural sources include soils, vegetation, oceans and animal excreta (Sutton et al., 2013). Estimates for the annual global emissions of NH\(_3(g)\)
range from 35-54 Tg N yr\(^{-1}\); 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. In remote marine environments, the ocean is thought to be the dominant source of NH\(_3\)(g) to the marine boundary layer and delivers an estimated 6-8 Tg N yr\(^{-1}\) to the atmosphere globally (Sutton et al., 2013). The dominant sources of oceanic NH\(_x\) (≡NH\(_3\) + NH\(_4^+\)) include remineralisation of organic matter by bacteria and phytoplankton excretion (Carpenter et al., 2012). However, NH\(_x\) is an extremely labile nutrient for microbes such that assimilation by phytoplankton and bacteria prevents significant accumulation in surface waters. Nonetheless, there exists a pool of dissolved ammonia (NH\(_3\)(sw)) available for exchange with the atmosphere.

In order to compute sea-air NH\(_3\) fluxes, simultaneous measurements of both atmospheric NH\(_3\)(g) and oceanic NH\(_x\) are required. These measurements are extremely challenging due to low ambient concentrations and complications arising from making ship-based measurements (e.g. proximity to human activity can cause artefacts). As a result, to our knowledge only six previous studies have simultaneously quantified both [NH\(_3\)(g)] and oceanic [NH\(_x\)], leading to extremely large uncertainties for both the direction and magnitude of global sea-air NH\(_3\) fluxes (Asman et al., 1994; Geernaert et al., 1998; Gibb et al., 1999; Johnson et al., 2008; Quinn et al., 1988, 1990). Johnson et al. (2008) provided the most recent dataset and summarized the previous studies to show that the open ocean can be both a net source and a net sink of NH\(_3\)(g), with sea surface temperature (SST) being a key determinant for the direction of flux. Colder SST reduces the emission potential due to increased solubility of NH\(_3\) (because of both reduced NH\(_3\)(aq) volatility and increased partitioning of NH\(_3\)(aq) to NH\(_4^+\)(aq)); hence, at higher latitudes the open ocean is more likely to act as a net sink (Johnson et al., 2008). Of the six previous studies, only Johnson et al. (2008) quantified NH\(_3\) fluxes above the Arctic Circle (66°33’ N) during a summer time study in the Norwegian Sea. Therefore additional measurements of sea-air NH\(_3\) fluxes in the High Arctic are invaluable for improving constraints on oceanic NH\(_3\) emissions.

During the summertime, freshwater melt ponds are a ubiquitous feature on top of melting Arctic sea ice and can comprise up to 80% of the sea ice surface (Lüthje et al., 2006). These melt ponds form from melting sea ice and are anywhere from a few cm to over 1 m deep. They are chemically distinct from the bulk ocean owing to their low salinity and physical separation from the ocean mixed layer by sea ice or stratification. To our knowledge, no studies to date have attempted to quantify melt pond-air NH\(_3\)(g) fluxes despite the abundant presence of melt ponds in the summertime Arctic.
Quantifying sea-air and melt pond-air NH$_3$ exchange in the Arctic will help elucidate the role these processes play as either sources or sinks in the Arctic nitrogen cycle. Many terrestrial Arctic ecosystems are N-limited and highly sensitive to perturbations in N-input (Shaver and Chapin III, 1980), thus Arctic soils and vegetation are unlikely to represent important sources of atmospheric ammonia. Major sources at lower latitudes include agriculture, vegetation, transport and industry (Reis et al., 2009; Sutton et al., 2013) but these are expected to contribute minimally north of the Arctic Circle. Since the lifetime of NH$_3$(g) is typically less than 24 h, long-range transport from lower latitudes is likely not important (Lefer et al., 1999). Substantial NH$_3$ emissions have been measured from both seabird guano (Blackall et al., 2007) and seal excreta (Theobald et al., 2006) so large colonies may be relevant point sources throughout the Arctic region. Biomass burning can also inject significant quantities of NH$_3$ into the free troposphere and/or boundary layer (Bouwman et al., 1997). Although vegetation in the high Arctic is sparse, there can be large wildfires in boreal regions, and emissions may be transported poleward. The potential for the ocean and melt ponds to act as sources to the atmosphere will depend on the relative importance of sources and sinks within the atmosphere and the aqueous systems.

NH$_3$ emission to the atmosphere can affect the extent of non-sea salt sulphate (nss-SO$_4^{2-}$) neutralization, which has implications for N-transport (Lefer et al., 1999). Therefore, it is important to also consider the relative abundances of atmospheric NH$_x$ and nss-SO$_4^{2-}$. The dominant source of the latter in the summertime Arctic is oxidation of dimethylsulphide (DMS) emitted from the Arctic Ocean (Leaitch et al., 2013; Sharma et al., 1999, 2012). Measurements of PM$_{2.5}$ composition in the summertime Arctic marine boundary layer are rare (e.g. Chang et al., 2011; Leck et al., 2001). Previous chemical transport model (CTM) studies with GEOS-Chem predict highly acidic aerosol (i.e. nss-SO$_4^{2-} >>$ NH$_x$) with negligible amounts of NH$_3$(g) throughout the summertime Arctic boundary layer (Breider et al., 2014).

The region for this study is the eastern Canadian Arctic Archipelago where ship-based atmospheric (NH$_3$(g), NH$_4^+$, SO$_4^{2-}$) and oceanic ([NH$_x$], pH, SST) measurements were taken over a 4-week period in July and August, 2014. To our knowledge, this study presents the first measurements of NH$_3$(g) in the Canadian Arctic. Motivated by a lack of atmospheric and oceanic measurements in the region, as well as substantial uncertainties in sea-air and melt pond-air NH$_3$ fluxes, the specific goals of this study were to:
1) Simultaneously quantify NH$_3$(g) and oceanic/melt pond [NH$_3$] to infer surface-air NH$_3$ fluxes

2) Assess the relative abundances of NH$_3$(g), NH$_4^+(p)$ and SO$_4^{2-}(p)$ to determine the extent of SO$_4^{2-}(p)$ neutralization

3) Elucidate the major sources and sinks of atmospheric NH$_3$ throughout the summertime Arctic marine boundary layer

4) Evaluate whether atmospheric NH$_3$ deposition could be an important N-input to aquatic and terrestrial Arctic ecosystems

2 Materials and Methods

2.1 2014 CCGS Amundsen Cruise

Measurements were taken aboard the Canadian Coast Guard Ship *Amundsen* between 13 July and 7 August 2014 as part of the Network on Climate and Aerosols: Addressing Key Uncertainties in Remote Canadian Environments (NETCARE). The CCGS *Amundsen* departed from Québec City, Québec on 8 July 2014 and sailed throughout the Eastern Canadian Archipelago heading as far north as 81.47 °N eventually reaching Kugluktuk, Nunavut on 13 August 2014. A detailed map of the ship’s route for this leg is shown in Fig. 1 along with the ship’s position at the start of selected days. All times are given in co-ordinated universal time (UTC).

2.2 Atmospheric Measurements

Ambient levels of water-soluble ions in PM$_{2.5}$ (NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$) and their precursor gases (NH$_3$, SO$_2$, and HNO$_3$) were measured using the Ambient Ion Monitor-Ion Chromatograph (AIM-IC) system (Model 9000D, URG Corp., Chapel Hill, NC). The AIM-IC is a continuous on-line system which provides simultaneous gas-phase and particle-phase measurements with hourly time resolution. The system has been adapted to locate the gas and particle separation and collection hardware as close as possible to the inlet sampling point (Markovic et al., 2012).

Ambient air is pulled through a PM$_{2.5}$ impactor to remove coarse (>2.5 μm in diameter) particles at a flow of 3 L min$^{-1}$. Air then enters a parallel plate wet denuder where water-soluble gases are dissolved in a 2 mM H$_2$O$_2$ solution (to enhance the solubility of SO$_2$) which is continuously flowing across the denuder membranes. The remaining PM$_{2.5}$ particles with diameter larger than 2.5 μm have sufficient inertia to pass through the denuder into a supersaturation chamber.
where they are collected as an aqueous solution via hygroscopic growth. 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). The height of the inlet was 1 m above the deck. 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 such particles. The aqueous solutions collected in the inlet box were pulled down a 22 m sample line through a conduit leading to the IC systems which were housed in a laboratory below deck. Half of each ~10 mL aqueous aliquot (representing 1 hour of sampling) was then separately injected onto both a cation IC and anion IC for quantification of water-soluble ions.

The IC systems (ICS-2000, Dionex Inc., Sunnyvale, CA) were operated using CS17/AS11-HC analytical columns, CG17/AG11-HC guard columns and TCC-ULP1/TAC-ULP1 concentrator columns for improved detection limits. Reagent-free gradient elution schemes and suppressed conductivity were also employed. Aqueous standards of known concentration were prepared via serial dilution of commercially available mixed standards (Dionex Corp., Sunnyvale, CA) containing 6 cations (P/N 040187) and 7 anions (P/N 056933). Manual injection of these standards yielded reasonable ($R^2 > 0.99$) six-point calibration curves.

During the campaign, three zero air overflow experiments were performed to quantify the background signal of each analyte measured during AIM-IC ambient sampling. For each experiment the inlet was overflowed with high purity zero air (AI 0.0 UZ-T, PraxAir, Toronto, ON) at 4.5 L min$^{-1}$ for 18 hours. The average peak area during the final 8 hours of each experiment was used as a background and subtracted from each ambient measurement. Detection limits were calculated by taking 3 times the standard deviation of each analyte peak area during the final 8 hours of each zero air overflow. This value was then converted to either a mixing ratio or mass loading assuming standard temperature and pressure (STP). Detection limits for species of interest during the cruise were 29 ng m$^{-3}$ (NH$_3$), 17 pptv (SO$_2$), 8 pptv (HNO$_3$), 12 ng m$^{-3}$ (NH$_4^+$), 36 ng m$^{-3}$ (SO$_4^{2-}$), and 64 ng m$^{-3}$ (NO$_3^-$). For the convenience of flux calculations, NH$_3$ values are reported in ng m$^{-3}$ (at STP 100 ng m$^{-3}$ NH$_3$ ≈ 130 pptv).

Standard meteorological parameters were measured using a Vaisala HMP45C212 sensor for temperature, an RM Young model 61205V transducer for pressure, and an RM Young Model 05103 wind monitor for wind speed and direction located at the bow ship of the ship at a height of 8.2 - 9.4 m above the deck. Data were averaged to 1-hour to match the time resolution of the AIM-IC. In order to remove any influence from activities aboard the ship, gas-phase
measurements are only reported if the following conditions were met: 1) average hourly ship speed \( > 4 \) knots \((\approx 7.4 \text{ km h}^{-1})\), 2) average hourly apparent wind direction \( \pm 90^\circ \) of the bow, and 3) standard deviation of apparent wind direction \( < 36^\circ \). Similar cut-offs for speed and wind direction have been used in previous studies of \( \text{NH}_3 \) in the marine boundary layer (e.g. Johnson et al., 2008; Norman and Leck, 2005).

### 2.3 Surface Measurements

A total of 37 surface ocean and 9 melt pond samples were collected throughout the study. Melt pond samples were collected directly into a cooler jug using an electrical pump fixed on a telescopic arm. The water was sampled as far from the side of the melt pond as possible, between 1-2 m depending on the size of the melt pond. Temperature was measured in situ with a VWR high precision thermometer and total aqueous \([\text{NH}_3]\) was determined within 10 h of sampling using a fluorometric technique that has been optimized for low concentrations and complex matrices (Holmes et al., 1999). The method detection limit was 20 nM. Surface ocean samples were obtained with a Rosette sampler equipped with GO-FLOW bottles and a CTD (Seabird Electronics SBE911+) recording temperature. Total aqueous \([\text{NH}_3]\) was determined as above within 1 hour of sampling. Surface water temperature along the ship’s track was continuously measured by a thermosalinograph (Seabird Electronics SBE 45) connected to the seawater inlet. For the purposes of flux calculations, the ocean pH and salinity were assumed to be \(8.1\) and \(35 \text{ g kg}^{-1}\), respectively, which are representative for the region of interest (Takahashi et al., 2014). These assumptions have been made previously and were not found to be a major source of uncertainty when calculating sea-air \( \text{NH}_3 \) fluxes (Johnson et al., 2008).

The melt pond pHs were measured using a pH-meter within four hours of sampling. A three point calibration of the pH probe (Orion™ Model 91-72, Thermo Scientific) was performed using commercially available pH 4.01, 7.00 and 10.00 buffers. Salinity of the melt ponds were determined with a WTW Cond 330i handheld conductivity meter.

### 2.4 Flux Calculations

The direction of sea-air \( \text{NH}_3 \) fluxes can be assessed by comparing ambient measurements of \( \text{NH}_3(g) \) to the atmospheric mixing ratio predicted from Henry’s Law equilibrium calculations using seawater \([\text{NH}_3]\) and surface temperature measurements (e.g. Asman et al., 1994; Johnson et al., 2008; Quinn et al., 1988, 1996). This equilibrium \( \text{NH}_3 \) concentration signifies the ambient value at which the net flux changes direction, and is known as the compensation point (denoted
In other words, one expects a net downwards flux if ambient NH\textsubscript{3}\textsubscript{(g)} exceeds \(\chi\) and a net upward flux if it is below \(\chi\). The magnitude of these fluxes are commonly computed using the “two-phase” model first developed by Liss and Slater (1974), which describes the sea-air transfer of gases as being controlled by molecular diffusion on either side of the interface. The transfer of NH\textsubscript{3} across this interface is predominantly dictated by the air-side transfer velocity, given the relatively high water solubility of NH\textsubscript{3} (Liss, 1983). Hence, the equation to calculate sea-air NH\textsubscript{3} fluxes is:

\[
F_{\text{NH}_3} = k_g \cdot (\chi - \text{NH}_3\text{,(g)}) \cdot 17.03
\]  
(1)

where \(F_{\text{NH}_3}\) is the sea-air flux of NH\textsubscript{3} (ng m\textsuperscript{-2} s\textsuperscript{-1}), \(k_g\) is the air-side transfer velocity (m s\textsuperscript{-1}), \text{NH}_3\text{,(g)} is the measured ammonia concentration (nmol m\textsuperscript{-3}), \(\chi\) is the compensation point (nmol m\textsuperscript{-3}), and the molecular weight of 17.03 g mol\textsuperscript{-1} is to convert nmol to ng. Numerous parameterizations exist for \(k_g\) with varying degrees of complexity (Johnson, 2010). Here we adopt the approach established by Duce et al. (1991):

\[
k_g = \frac{\mu}{770 + 45 \cdot MW^{1/3}}
\]  
(2)

where \(\mu\) is the wind speed (m s\textsuperscript{-1}) and MW is the molecular weight of the gas of interest (17.03 for NH\textsubscript{3}). Although simple, this parameterization has been used previously to estimate sea-air NH\textsubscript{3} fluxes (e.g. Johnson et al., 2008) and has been shown to be in good agreement (within 20 \%) with a more complex scheme, particularly at lower wind speeds (Johnson, 2010). The following equation is used to calculate \(\chi\):

\[
\chi = K_H \cdot [\text{NH}_3\text{,(sw)}]
\]  
(3)

where \(K_H\) is the Henry’s law constant (dimensionless) and [\text{NH}_3\text{,(sw)}] is the concentration of dissolved ammonia in the surface pool (nmol m\textsuperscript{-3}). The temperature-dependent equation for \(K_H\) is (McKee, 2001):

\[
K_H = \frac{1}{17.93 \cdot \frac{T}{273.15} \cdot e^{(4092/T) - 9.70}}
\]  
(4)

where \(T\) is the surface temperature (in K). The following equation is used to relate the NH\textsubscript{3}\text{,(sw)} to the concentration of total dissolved NH\textsubscript{x} ([\text{NH}_x\text{,(sw)}]), which is the value actually measured by the procedure outlined in section 2.3:
\[
\frac{[NH_3(sw)]}{[NH_4(H_2O)]]} = \frac{[NH_4(H_2O)] \cdot K_a}{10^{-pH} + K_a}
\]  

(5)

where \( K_a \) is the acid dissociation constant of \( \text{NH}_4^+ \). The \( pK_a = -\log(K_a) \) is calculated according to Bell et al. (2008), which provides an empirical correction for salinity (\( S, \) dimensionless) at a given temperature (\( T, \) in °C):

\[
pK_a = 10.0423 + 0.003071 \cdot S - 0.031556 \cdot T
\]  

(6)

Equations (2) and (4) closely follow that of Johnson et al. (2008) but are sufficiently similar to analogous approaches for calculating \( K_H \) and \( k_g \) used in other sea-air \( \text{NH}_3 \) exchange studies (e.g. Asman et al., 1994; Gibb et al., 1999; Quinn et al., 1992). Johnson (2004) reported that fluxes calculated with these various schemes usually agree within 2%. Melt pond-air exchange was also examined using Eqs. (1) to (6).

2.5 GEOS-Chem

The GEOS-Chem chemical transport model (www.geos-chem.org) is used to aid in the interpretation of the atmospheric measurements. We use GEOS-Chem version 9-02 at 2°x2.5° resolution globally, and with 47 vertical layers between the surface and 0.01 hPa. The assimilated meteorology is taken from the NASA Global Modelling and Assimilation Office (GMAO) Goddard Earth Observing System version 5.11.0 (GEOS-FP) assimilated meteorology product. Boundary layer mixing uses the non-local scheme implemented by Lin and McElroy (2010). Our simulations use 2014 meteorology and allow a 2-month spin-up prior to the simulation.

The GEOS-Chem model includes a detailed oxidant-aerosol tropospheric chemistry mechanism as originally described by Bey et al. (2001). Simulated aerosol species include sulphate-nitrate-ammonium (Park et al., 2004; Park et al., 2006), carbonaceous aerosols (Park et al., 2003; Liao et al., 2007), dust (Fairlie et al., 2007; Fairlie et al., 2010) and sea salt (Alexander et al., 2005). The sulphate-nitrate-ammonium chemistry uses the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007), which partitions ammonia and nitric acid between the gas and aerosol phases. For our simulations, the natural \( \text{NH}_3 \) emissions are from Bouwman et al. (1997) and biomass burning emissions are from the Quick Fire Emissions Dataset (QFED2) (Darmenov and da Silva, 2013), which provides daily open fire emissions at 0.1° x 0.1° resolution. Anthropogenic \( \text{NH}_3 \) emissions are from Bouwman et al. (1997). The model includes
natural and anthropogenic sources of SO$_2$ (van Donkelaar et al., 2008; Fischer et al., 2011) and DMS emissions based on the Nightingale (2000) formulation and oceanic DMS concentrations from Lana et al. (2011). Oxidation of SO$_2$ occurs in clouds by reaction with H$_2$O$_2$ and O$_3$ and in the gas phase with OH (Alexander et al., 2009) and DMS oxidation occurs by reaction with OH and NO$_3$.

GEOS-Chem simulates both wet and dry removal of aerosols and gases. Dry deposition follows a standard resistance in series scheme (Wesley, 1989) with an aerosol dry deposition velocity of 0.03 cm s$^{-1}$ over snow and ice (Fischer et al., 2011). Wet removal in GEOS-Chem takes place in large-scale clouds and convective updrafts (Liu et al., 2001). In-cloud scavenging of hydrophilic species takes place at temperatures warmer than 258K, and hydrophobic black carbon and dust are also removed at temperatures colder than 258K (Wang et al., 2011).

2.6 FLEXPART-WRF

FLEXPART-WRF (Brioude et al., 2013, website: flexpart.eu/wiki/FpLimitedareaWrf) is a Lagrangian particle dispersion model based on FLEXPART (Stohl et al., 2005) that is driven by meteorology from the Weather Research and Forecasting (WRF) Model (Skamarock et al., 2005). Here we use FLEXPART-WRF run in backward mode to study the emissions source regions and transport pathways influencing ship-based ammonia measurements. A WRF simulation for the summer 2014 NETCARE campaign was performed using WRF 3.5.1 with initial and boundary conditions provided by the operational analysis (0.25° x 0.25° resolution) from European Centre for Medium-Range Weather Forecasts (ECMWF). Parameterizations and options for the WRF simulations are given in Table 1. The WRF model was run from 1 July 2014 to 13 August 2014 and nudged to ECMWF winds, temperature, and humidity every 6 hours above the atmospheric boundary layer. The WRF run was evaluated using meteorological measurements made onboard the Amundsen and from Polar-6 aircraft flights during this period. FLEXPART-WRF was run in backward mode to produce retroplume output that is proportional to the residence time of the particles in a given volume of air. Runs were performed using the location of the ship, with one model run performed every 15 minutes while the ship was in the model domain (13 July-13 August 2014). For each run, 100,000 particles were released at the ship location (100 m extent horizontally and vertically) and the FLEXPART-WRF was run backwards for 7 days prior to release. The output provides retroplume information (the residence time of air prior to sampling) which is used to calculate
the potential emission sensitivites (PES) integrated over the seven days prior to sampling by instruments aboard the Amundsen.

3 Results and Discussion

3.1 Surface-Atmosphere NH₃ Fluxes

Figure 1 shows the ambient NH₃(g) concentrations measured by the AIM-IC throughout the cruise. Measured values of NH₃(g) range between 30-650 ng m⁻³ with the highest values occurring in Lancaster Sound as the ship was steaming eastward into Baffin Bay. Only two measurements of NH₃ were below the detection limit (29 ng m⁻³) throughout the entire cruise. NH₃ consistently exceeded 100 ng m⁻³ during later parts of the cruise along the eastern shores of Ellesmere Island and western shores of Greenland. Lower values (<100 ng m⁻³) were observed at the beginning of the campaign along the eastern shores of Baffin Island.

Measurements of NH₃(g) in the marine boundary layer at northern latitudes (>50°N) are sparse; however the concentrations measured in this study are within the few previously reported ranges for the regions above 50 °N. Johnson et al. (2008) reported NH₃(g) between 20-300 ng m⁻³ in the Norwegian Sea during spring and summer, but a lower range (20-90 ng m⁻³) in the northern North Sea in winter. In the southern North Sea, Asman et al. (1994) measured higher values (30-1500 ng m⁻³) in a study lasting from February to October.

The relevant measurements needed to calculate χ for both the open ocean and melt ponds are listed in Tables S1 and S2, respectively. Only four unique co-ordinates are listed for the nine melt pond samples because multiple melt ponds were sampled at each location. Roughly half of the surface ocean samples had [NH₃] below the detection limit (20 nM) and in general values were significantly lower than in the melt ponds. Open ocean samples ranged from <20 to 380 nM whereas seven of the nine melt pond samples were between 640 to 1260 nM (with the other two below detection limit). These concentrations and their spatial variability are typical for the region during summer (Martin et al. 2010).

Parameters listed in Tables S1 and S2 were input into Eqs. (3) to (6) to calculate χ for both the surface ocean and melt pond samples. For samples with [NH₃] below the detection limit, a value of 10 nM (half of the detection limit) was assumed. A comparison of the calculated compensation points for the ocean (χ_ocean) and melt ponds (χ_MP) are shown in Fig. 2. Also shown is the range for the nearest valid measurement (see section 2.2) of ambient NH₃(g). The NH₃(g) concentration taken during the hour of surface sampling could not be used since the ship
remained stationary for up to 12 hours while melt pond or ocean work was being conducted. Hence, the \( \text{NH}_3(g) \) measurement from several hours prior (as the ship approached the surface sampling site) had to be used. This approach should not significantly impact the analysis given that the ambient levels of \( \text{NH}_3(g) \) were observed to be fairly uniform from one hour to the next (i.e. no rapid spikes of \( \text{NH}_3(g) \) were measured). Shown in lighter yellow are the ranges of \( \text{NH}_3(g) \) observed over the entire study (~30-650 ng m\(^{-3}\)). Figure 2 clearly shows that the ambient concentrations of \( \text{NH}_3(g) \) exceed both \( \chi_{\text{ocean}} \) and \( \chi_{\text{MP}} \) by several orders of magnitude throughout the entire region. This conclusively demonstrates that during the summertime, the ocean and melt ponds are net sinks of atmospheric \( \text{NH}_3(g) \). This finding is consistent with Johnson et al. (2008) who found a tendency for downward net fluxes at higher latitudes, primarily as a result of colder sea surface temperatures. Assuming an upper limit for the ocean pH of 8.2 would increase \( \chi_{\text{ocean}} \) by less than 20%.

Figure 3 shows the magnitude of the sea-air and melt pond-air flux of \( \text{NH}_3 \). Average net downward fluxes of 1.4 ng m\(^{-2}\) s\(^{-1}\) and 1.1 ng m\(^{-2}\) s\(^{-1}\) were calculated for the open ocean and melt ponds, respectively using Eqs. (1) and (2). 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). It is unlikely that this represents a significant input of \( \text{NH}_4^+ \) into the open ocean except in cases of extremely low [\( \text{NH}_3 \)]. A simple calculation assuming a mixed layer depth of 25 m results in an increase of only ~0.3 nM d\(^{-1}\) to the ocean (assuming complete mixing and no loss pathways). However, for the much shallower melt ponds (assumed depth of 0.25 m) the same calculation yields an input of ~22 nM d\(^{-1}\). Furthermore, this does not account for atmospheric inputs from either wet deposition or dry deposition of particulate \( \text{NH}_4^+ \), and these melt ponds are cut-off from the upwelling currents in the ocean which deliver reactive N to the surface. Rates of nitrification, mineralization and \( \text{N}_2 \)-fixation in the open ocean and melt ponds would help put this atmospheric input into perspective and give insight as to whether or not it is an important process in the nitrogen cycle in these environments.

### 3.2 Sulphate Neutralization

The extent of neutralization of PM\(_{2.5}\) influences aerosol properties as discussed previously. Figure 4 depicts the relative abundances (in neq m\(^{-3}\)) of gas-phase ammonia and particulate-phase ammonium and sulphate. It is important to note that the value for sulphate is total PM\(_{2.5}\) sulphate as opposed to non-sea salt sulphate (nss-SO\(_4^{2-}\)), which is commonly reported for
marine boundary layer studies. High and variable backgrounds of Na\(^+\) from the AIM-IC prevented the calculation of nss-SO\(_4^{2-}\), hence this dataset provides an upper limit for nss-SO\(_4^{2-}\). Given the low wind speeds (< 5 m s\(^{-1}\)) that dominated the campaign, it is likely the nss-SO\(_4^{2-}\) \(\approx\) SO\(_4^{2-}\) since the contribution from sea salt to PM\(_{2.5}\) was likely small. It should also be noted that measurements of SO\(_2\), HNO\(_3\) and NO\(_3^-\) were almost always below their respective detection limits.

Particle loadings of NH\(_4^+\) and SO\(_4^{2-}\) were extremely low (typically < 5 neq m\(^{-3}\)) throughout the duration of the cruise. During the first third of the cruise (before 18 July), gas-phase NH\(_3\) was also low and neutralization (i.e. the ratio of NH\(_4^+:\)SO\(_4^{2-}\) in units of equivalents) was ambiguous due to numerous values near or below detection limit. On the other hand, after 25 July the nanoequivalents of NH\(_3(g)\) were substantially higher (NH\(_3 \approx\) NH\(_3\)) than either NH\(_4^+\) or SO\(_4^{2-}\) (i.e. NH\(_3 \approx\) NH\(_3\)), which implies a nearly neutralized sulphate aerosol. It is important to note that a nearly neutralized aerosol does not equate to an aerosol with a pH of 7 since aerosol pH is highly sensitive to liquid water content as well as the precise NH\(_4^+:\)SO\(_4^{2-}\) ratio. An aerosol with NH\(_4^+:\)SO\(_4^{2-}\) approaching 1 (with units of equivalents) can still have an acidic pH. For example, a deliquesced ammonium sulphate particle containing 20 neq m\(^{-3}\) of SO\(_4^{2-}\) and 19.98 neq m\(^{-3}\) NH\(_4^+\) at 85% RH will have a pH of ~3.1 under equilibrium conditions despite having an NH\(_4^+:\)SO\(_4^{2-}\) equivalents ratio of 0.999.

Figure 5 shows the distribution of the NH\(_4^+:\)nss-SO\(_4^{2-}\) ratio (on a per equivalent basis) measured at Alert, Nunavut (82.50 °N, 62.33 °W) as a function of month from 1996-2011. Weekly-averaged PM\(_{2.5}\) speciation measurements at Alert are made by Environment Canada and are available on-line (Environment Canada, 2014). The contribution from NO\(_3^-\) is minor and has not been included in this analysis. In warm environments volatilization of NH\(_3\)NO\(_3\) 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\(_3\)NO\(_3\). During July and August the nss-SO\(_4^{2-}\) is, on average, completely neutralized by the NH\(_4^+\) in PM\(_{2.5}\) as shown by a median neutralization ratio approaching 1 during these months. This implies there is sufficient NH\(_3(g)\) throughout the region to neutralize nss-SO\(_4^{2-}\) produced from DMS oxidation which is consistent with the measurements shown in Fig. 4. 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. Lastly, Johnson and Bell (2008)
show that a sufficiently neutralized sulphate aerosol will tend to ‘push’ gas-phase NH$_3$ into the ocean in the aerosol-gas-ocean system, also consistent with Fig. 3.

The AIM-IC and Alert measurements are both inconsistent with a previous study that used GEOS-Chem to predict a highly acidic aerosol and insignificant gas-phase ammonia (NH$_x \approx$ NH$_4^+$) throughout the summertime Arctic marine boundary layer (Breider et al., 2014). This inconsistency implies a missing process in a widely used CTM that we investigate further below.

3.3 Evidence for the Importance of Seabird Guano

Observations collected on board the Amundsen and at Alert strongly suggest a significant source of NH$_3$ in the Baffin Bay region. Decomposition of uric acid in seabird guano (excreta) has been recognized as a significant source of NH$_3$ where large colonies exist (Blackall et al., 2007; Wilson et al., 2004). However, studies measuring NH$_3$ from seabird colonies are limited due to the remoteness of most colonies and technical challenges in quantifying NH$_3$ in isolated locations (Blackall et al., 2007). The few studies that have been done have focused on colonies located in the United Kingdom (Blackall et al., 2004; Wilson et al., 2004), Antarctica (e.g. Legrand et al., 1998; Zhu et al., 2011) and remote tropical islands (Riddick et al., 2014; Schmidt et al., 2010). Recently, Riddick et al. (2012) developed a global inventory to estimate the magnitude and spatial distribution of NH$_3$(g) from seabird guano. The authors employed a bioenergetics model, first developed by Wilson et al. (2004), to calculate the NH$_3$(g) emissions (in g bird$^{-1}$ yr$^{-1}$) for 323 different seabird species. After compiling a list detailing the populations and locations of 33,225 colonies, they were able to estimate global annual emissions between 97-442 Gg NH$_3$ per year. Although this is less than 2% of total global NH$_3$(g) emissions, it can be the dominant source in remote regions where seabird populations are large and other sources are negligible.

In order to assess the impact of seabird guano on NH$_3$ across the Baffin Bay region, seabird colony NH$_3$ emissions were implemented in the GEOS-Chem model, and the impact on monthly mean surface layer NH$_3$ was examined. The NH$_3$ emissions inventory used in the standard GEOS-Chem v9-02 (and in many other CTMs) is from Bouwman et al. (1997) and does not include seabird emissions. 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. The Riddick et al. (2012, 2012b) seabird colony NH$_3$
emissions inventory (scenario 3) was added to the original inventory in GEOS-Chem following Paulot et al. (2015). Scenario 3 was chosen since this represented the midpoint between the minimum and maximum emissions of scenario 1 and 2, respectively. Close inspection of this seabird inventory revealed that some large seabird colonies in our study region were not accounted for. To investigate this, the spatial co-ordinates of northern colonies (>50 °N) in the Riddick et al. (2012) inventory were cross-referenced against colonies in the on-line Circumpolar Seabird Data Portal (Seabird Information Network, 2015). Annual emissions for large colonies in the seabird data portal were calculated in the same manner as in Riddick et al. (2012). In total, there were 42 colonies present in the seabird data portal but absent in the Riddick inventory in the region north of 50 °N. These additional emissions were added to the inventory we implemented in GEOS-Chem. These colonies totaled 7.5 Gg NH₃ year⁻¹ (approximately one quarter of the existing emissions north of 50 °N) and were primarily in Siberia and western Alaska. The Riddick et al. (2012) bioenergetics model only counts emissions that occur during breeding season and while the seabirds are at the colony. Hence, the annual emission estimates (Gg NH₃ year⁻¹) per colony were temporally allocated evenly between the 15 May to 15 September. This period is when the majority of seabirds in the Baffin Bay region are nesting (e.g. Gaston et al., 2005; Mallory and Forbes, 2007; McLaren, 1982). One limitation to this approach is that it does not account for additional temporal variations in NH₃ emissions. For instance, moisture increases the rate of uric acid degradation, and fluxes of NH₃ from guano have been observed to increase 10-fold for up to a day after rain events (Riddick et al., 2014).

Figure 6 shows the July mean output for surface layer NH₃ mixing ratio both without (Fig. 6a) and with (Fig. 6b) seabird emissions, along with the NH₃(g) measured by the AIM-IC denoted by circles in Fig. 6a. Comparing the top two panels reveals that seabird emissions make a substantial impact on modelled NH₃ levels in the boundary layer. Much better model-measurement agreement is achieved with the inclusion of the seabird colonies. Without the seabird emissions, NH₃ mixing ratios are underpredicted by several orders of magnitude. Surface NH₃ is still underpredicted in Fig. 6b (with guano NH₃ emissions) which could be the result of modelled emissions being independent of rainfall, which can substantially increase NH₃ emissions. Episodic rainfall was persistent throughout the latter half of the campaign. Other contributing factors may include: challenges in representing boundary layer mixing, uncertainties in deposition rates, comparing monthly averages (GEOS-Chem) to ambient hourly measurements, missing/underestimated bird colonies, and/or excreta from other fauna (e.g.
seals, caribou, musk-ox) absent in the updated inventory. The bottom two panels (Figs. 6c and 6d) show the influence of seabirds on the ammonium to non-sea salt sulphate ratio. Without seabirds (Fig. 6c) the ratio is less than 0.3 throughout most of the study region, which is inconsistent with the abundance of NH$_3$ relative to SO$_4^{2-}$ measured by the AIM-IC. Adding the seabird emissions (Fig. 6d) increases the ratio to above 0.7 in most grid cells along the ship track. Although the high ratio (July average is ~1) observed at Alert (denoted by the star in Figs. 6c and 6d) is underestimated in the GEOS-Chem simulation, the bias is reduced by nearly a factor of 2 (from 0.32 to 0.57) when seabird emissions are included.

Wildfires are also a source of NH$_3$ to the free troposphere and/or boundary layer. Particularly strong wildfire events were persistent in the Northwest Territories (NWT) during the study period. Blue circles in Fig. 7 show the location and average fire radiative power (representative of fire strength) of wildfires across the Arctic from July 20-26. It was constructed using data from NASA’s Fire Information Resource Management System (FIRMS) database (NASA, 2015). We used FLEXPART-WRF retro plumes to assess the importance of wildfire NH$_3$ emissions, as well as to further corroborate the influence of seabird guano.

The significant impact of seabird colonies on [NH$_3$(g)] is supported by the analysis of FLEXPART-WRF retro plumes shown in Fig. 7. Periods of low [NH$_3$(g)] (bottom panel in Fig. 7) correspond to air masses that spent at least the last 48 hours over the ocean and/or aloft above the MBL (~500 m) where NH$_3$ sources are negligible. This is clearly shown in Fig. 7a where the air mass sampled on 14 July 00:00 (UTC) spent the previous 96 hours in the MBL over Baffin Bay, consistent with low [NH$_3$(g)]. In contrast, on 26 July 00:00 (Fig. 7b) air had recently passed over seabird colonies (purple circles) surrounding Lancaster Sound as well as wildfires in the Northwest Territories (NWT) on mainland Canada (blue circles), coincident with the large increase in [NH$_3$(g)]. A similar NH$_3$(g) peak occurs on 3 August that can also be examined by using a retro plume analysis. Low NH$_3$(g) values observed on the morning of 2 August agree with Fig. 7c showing the air originating from the MBL over Baffin Bay. At 3 August 00:00 (Fig. 7d) the air had spent the last 12 hours in the boundary layer of Western Greenland where large seabird colonies exist. However, by 4 August 00:00 (Fig. 7e) the retro plume shifted such that air is now originating from primarily above the boundary layer (altitude plots not shown) leading to a decrease in NH$_3$(g). In addition from August 2-4 the ship was north of 79° N and in the Eastern Canadian Arctic, hence it is unlikely that this increase in NH$_3$ can be attributed to wildfires given how far removed this region is from wildfires in the NWT. While Fig. 7 only
highlights five examples from the study period, retro plumes throughout the entire campaign also support the hypothesis that NH$_3$(g) in the MBL originates primarily from seabird colonies (for the Eastern Canadian Arctic) with contributions from wildfires in some regions (central Canadian Arctic). All NH$_3$(g) spikes in the time series can be attributed to air that had recently passed over seabird colonies and/or wildfires, whereas low values coincide with air masses from either the open ocean or free troposphere not influenced by wildfires.

To further investigate the potential influence of wildfires on NH$_3$ in the Arctic MBL, GEOS-Chem simulations were performed using a wildfire emissions inventory for 2014 (QFED2). Simulations with/without wildfires and with/without seabirds revealed that in Lancaster Sound (along 74° N) roughly 40% and 55% of the boundary layer NH$_3$ can be attributed to seabirds and wildfires, respectively. In other words, air sampled in Lancaster Sound (20 July to 27 July) was likely influenced by wildfires in NWT in addition to seabird guano. On the other hand, north of Lancaster Sound, contributions from seabirds and wildfires to surface layer NH$_3$ were approximately 95% and 5%, respectively. Wildfires in the NWT are an important but episodic source of summertime NH$_3$ in the Canadian Arctic. This is due to periodic transport events associated with this source that is located remote to our study region. Whereas, seabird colonies are a local, and persistent source of NH$_3$ from May to September. Given the observation of consistently neutralized sulfate at Alert each summer, and the large interannual variability and episodic wildfire influence, emissions from migratory seabirds are likely to be a significant contributor to NH$_3$ abundance in the Arctic marine boundary layer.

### 3.4 Implications for N-deposition to Ecosystems

Previous studies have highlighted the important role that seabird-derived N can play in the nitrogen cycle of ecosystems adjacent to bird colonies due to large deposition rates of NH$_3$ and NH$_4^+$ (e.g. Anderson and Polis, 1999; Lindeboom, 1984). However, little attention has been paid to the effects of seabird-derived N on deposition at the regional scale. In this section, we consider the importance of seabird-derived nitrogen as an input of reactive N to Arctic ecosystems. These ecosystems tend to be N-limited during the summer and hence have a large sensitivity to N input (Shaver and Chapin III, 1980). In terrestrial ecosystems, soil N availability is a key factor in determining both plant community structure (McKane et al., 2002) and greenhouse gas emissions from soil (Stewart et al., 2012).
Nitrogen (N\textsubscript{2}) fixation via microbes is thought to be the primary N input to remote Arctic terrestrial ecosystems (e.g. Cleveland et al., 1999; Hobara et al., 2006; Stewart et al., 2014). Numerous field studies have been conducted to estimate N\textsubscript{2}-fixation rates via the acetylene reduction technique (Hardy et al., 1968). The N\textsubscript{2}-fixation rates for most terrestrial Arctic sites fall within the range of 10 to 120 mg N m\textsuperscript{-2} yr\textsuperscript{-1} (Hobara et al., 2006). However, highly variable rates (due to spatial heterogeneity of microbial populations) and assumptions in the acetylene reduction technique yield high degrees of uncertainty for N\textsubscript{2}-fixation rates (Stewart et al., 2014).

Total atmospheric N-deposition (wet and dry) in the Arctic is thought to be smaller than fixation, with typical ranges from 8 to 56 mg N m\textsuperscript{-2} yr\textsuperscript{-1} (Van Cleve and Alexander, 1981). Only a few N\textsubscript{2}-fixation studies also quantify wet deposition, with dry deposition being ignored altogether (e.g. Hobara et al., 2006). Nonetheless, in certain Arctic regions atmospheric deposition may exceed N\textsubscript{2}-fixation in soils (DeLuca et al., 2008). These processes are coupled since large inputs of NH\textsubscript{4}\textsuperscript{+} have been shown to inhibit N\textsubscript{2}-fixation in certain microbial species and lichens (Chapin and Bledsoe, 1992).

Figure 8 shows results from the GEOS-Chem simulation of total NH\textsubscript{x} (≡NH\textsubscript{3}+NH\textsubscript{4}\textsuperscript{+}) deposition (both wet and dry) for the months May to September (inclusive) both without (Fig. 8a) and with (Fig. 8b) seabird NH\textsubscript{3} emissions. The difference in total NH\textsubscript{x} deposition for birds and no birds is shown in Fig. 8c (absolute difference) and Fig. 8d (percent different). Areas near large colonies are heavily influenced by seabird guano with NH\textsubscript{x} deposition from seabirds exceeding 10 mg N m\textsuperscript{-2} yr\textsuperscript{-1}, particularly in western Greenland and near the mouth of Lancaster Sound. The majority of NH\textsubscript{x} deposition is caused by NH\textsubscript{3} as opposed to NH\textsubscript{4}\textsuperscript{+}. Most regions in Fig. 8b are on the lower end of the annual N-deposition rate of 8 to 56 mg N m\textsuperscript{-2} yr\textsuperscript{-1} suggested by Van Cleve and Alexander (1981). However, there are two important distinctions: the latter is an estimate of total N-deposition and annual input. Estimates in Fig. 8 might be more useful for comparing N-deposition to N\textsubscript{2}-fixation since it captures deposition only during the growing season, and NH\textsubscript{x} is likely the dominant form of atmospheric reactive N in the summertime Arctic boundary layer. Furthermore, Fig. 8b provides information on regions where N-deposition rates could be comparable to input from terrestrial N\textsubscript{2}-fixation (>10 mg N m\textsuperscript{-2} yr\textsuperscript{-1}) which can help inform subsequent studies exploring N-cycling in the region. According to Hobara et al. (2006), Arctic terrestrial N\textsubscript{2}-fixation only occurs from May-September (inclusive) and peaks in July, similar to migration patterns of Arctic seabirds.
Estimates of N\textsubscript{2}-fixation rates in the Arctic Ocean mixed layer are even sparser than estimates for terrestrial ecosystems. To our knowledge, only Blais et al. (2012) have measured oceanic N\textsubscript{2}-fixation in the summertime Arctic Ocean mixed layer. The authors found that open ocean N\textsubscript{2}-fixation rates averaged 0.12 nM d\textsuperscript{-1} in the upper 50 m of the water column throughout the Beaufort Sea to Baffin Bay. For the period of May to September (inclusive) this represents an input of approximately 13 mg N m\textsuperscript{-2} which is comparable to inputs we calculate from guano-derived NH\textsubscript{3} in regions close to seabird colonies as shown in Fig. 8b.

4 Conclusions

Simultaneous measurements of atmospheric and oceanic composition in the eastern Canadian Arctic revealed that the summertime Arctic Ocean and melt ponds were net sinks of NH\textsubscript{3(g)}. Concentrations of NH\textsubscript{3(g)} ranging from 30-650 ng m\textsuperscript{-3} were observed and represent the first reported measurements of NH\textsubscript{3(g)} in the Canadian Arctic. An average downward flux of 1.4 ng m\textsuperscript{-2} s\textsuperscript{-1} into the Arctic Ocean was calculated, consistent with previous studies showing that higher latitude waters are a net NH\textsubscript{3} sink (Johnson et al., 2008). Melt ponds had a smaller net downward flux (1.1 ng m\textsuperscript{-2} s\textsuperscript{-1}) as well as a slightly higher \(\chi\) as compared to the open ocean (median 2 ng m\textsuperscript{-3} versus 0.8 ng m\textsuperscript{-3}). To our knowledge, this is the first study to estimate melt pond-air NH\textsubscript{3} exchange despite the ubiquitous presence of melt ponds throughout the summertime Arctic.

On a nanoequivalent basis, NH\textsubscript{3(g)} values were significantly greater (up to an order of magnitude more) than both NH\textsubscript{4}\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{2-}. This finding was consistent with a 15-year historical dataset of weekly PM\textsubscript{2.5} composition from Alert, NU which showed that nss-SO\textsubscript{4}\textsuperscript{2-} is, on average, completely neutralized by NH\textsubscript{4}\textsuperscript{+} during July and August. These measurements imply strong regional source(s) of NH\textsubscript{3(g)} in the eastern Canadian Arctic Archipelago that are sufficient to neutralize nss-SO\textsubscript{4}\textsuperscript{2-} produced from DMS oxidation. Our surface-air flux estimates show that the Arctic Ocean and melt ponds are not responsible for NH\textsubscript{3(g)} in the marine boundary layer.

It is also noteworthy that even though these melt ponds have significantly higher [NH\textsubscript{x}] than the open ocean (average of 670 nM versus 55 nM), \(\chi\textsubscript{MP}\) is only marginally higher. More acidic pHs and slightly lower temperatures mitigate the effect of higher [NH\textsubscript{x}] on \(\chi\). Chemical transport models (CTMs) that explicitly account for bi-directional NH\textsubscript{3} exchange typically require \(\chi\) as a predefined model input (e.g. Bash et al., 2013; Wichink Kruit et al., 2012). Therefore, from a modelling standpoint, similar values of \(\chi\textsubscript{Ocean}\) and \(\chi\textsubscript{MP}\) are convenient since they can be parameterized in a similar fashion which would remove the need for CTMs to
resolve the spatial extent and temporal evolution of melt ponds to properly model surface-atmosphere NH$_3$ exchange in the summertime Arctic.

To investigate the impact of NH$_3$ emissions from seabird guano, we examined GEOS-Chem simulations both with and without seabird colony NH$_3$ emissions. The seabird NH$_3$ emission inventory developed by Riddick et al. (2012) was updated for this study to include northern colonies (>50 °N) that had been overlooked in the original inventory. Without the seabirds, GEOS-Chem underestimated NH$_3$(g) by several orders of magnitude and predicted highly acidic aerosol at the surface in July, which is in direct contrast to our measurements. The inclusion of seabird emissions provided much better agreement with NH$_3$(g) observations and yielded more neutralized aerosol throughout most of the Baffin Bay region. The importance of seabird NH$_3$ emissions is also supported by analysis of FLEXPART-WRF retro plumes throughout the study period. Air masses enriched in NH$_3$(g) had recently passed through regions with seabird colonies whereas periods of low NH$_3$(g) involved air masses originating from the open ocean or above the boundary layer. Together, these models provide strong evidence that seabird colonies are the dominant and persistent local source of NH$_3$(g) in the summertime Arctic. FLEXPART-WRF and GEOS-Chem were also used to assess the influence of wildfires on NH$_3$. Wildfires are an important but episodic source of NH$_3$ source to the Arctic due to ongoing changes in transport patterns and fire intensity. Further work should be done to examine the inter-annual influence of NH$_3$ emissions from wildfires in the NWT on other regions in the Arctic.

Deposition estimates of NH$_x$ from GEOS-Chem during the seabird nesting season (May to September) exceed 10 mg N m$^{-2}$ season$^{-1}$ in grid cells close to large seabird colonies, which is on the lower end of microbial N$_2$-fixation in Arctic tundra (Hobara et al., 2006). Hence, in some regions seabird-derived NH$_x$ could be a significant N-input to terrestrial Arctic ecosystems which are typically very N-sensitive. Estimates of NH$_3$ fluxes into the open ocean are unlikely to be an important input of reactive-N except for waters close to large seabird colonies; however, these fluxes may be important for the N-cycle in the much shallower melt ponds.

There is strong evidence that seabird colonies are likely the dominant and persistent source of NH$_3$(g) to the summertime Arctic boundary layer. Emissions appear to be significant enough to at least partially neutralize nss-SO$_4^{2-}$ throughout most of the study region, in contrast to previous model simulations that did not consider seabird colony emissions. Further research is required to better constrain the location, population, and NH$_3$ emissions of Arctic seabird colonies. It is also important to quantify meteorological effects (e.g. rainfall, wind speed) on seabird...
emissions. The NH$_3$ emissions inventory in CTMs should be updated to include seabird emissions with correct representation of the breeding season so that emissions only occur when seabirds are nesting. Summertime measurements of atmospheric NH$_x$ elsewhere in the Arctic are needed to assess whether the impacts of seabirds observed in this study (substantial NH$_3$(g), nss-SO$_4^{2-}$ neutralization, and N-deposition) are relevant to the entire Arctic.

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*with corrected calculation of skin temperature over sea ice when snow melting is occurring,
see http://www2.mmm.ucar.edu/wrf/users/wrfv3.7/updates-3.7.1.html.
Figure 1. CCGS Amundsen ship track (purple) coloured by gas-phase NH$_3$ concentrations (when valid measurements were available) measured by the AIM-IC. Invalid measurements (e.g. instrument troubleshooting, influenced by ship) are purple along the ship track. Units of ng m$^{-3}$ were chosen as a convenience for flux calculations. At STP, 100 ng m$^{-3}$ $\approx$ 130 pptv. Relevant landmarks are also labelled. Dates and arrows indicate the position of the ship at 0:00 UTC on that day.
Figure 2. Box-and-whisker plot showing the observed ranges of χ (on a log scale) for both the ocean surface (dark blue) and melt ponds (light blue). The range of NH₃(g) measured by the AIM-IC near the time of surface sampling is shown in darker yellow whereas NH₃(g) over the entire campaign is shown in lighter yellow. The box represents 25th to 75th percentile while the line within the box denotes the median. Whiskers extend to the 10th and 90th percentile.
Figure 3. Box-and-whisker plot of the estimated fluxes into the open ocean and melt ponds. The percentiles are represented in the same fashion as Fig. 2.
Figure 4. Time series of neq m\(^{-3}\) for NH\(_3(g)\) (black dots), NH\(_4^+\) in PM\(_{2.5}\) (orange trace), and SO\(_4^{2-}\) in PM\(_{2.5}\) (red trace). Interruptions in the data are a result of zero air experiments, calibrations, values below detection limit, instrument downtime, and (for gas-phase species) periods when the wind direction/speed were not conducive for ambient sampling (as explained in detail in section 2.2).
Figure 5. Box-and-whisker plot of neutralization (defined as \( \text{NH}_4^+ / 2 \times \text{nss-SO}_4^{2-} \)) for fifteen years (1996-2011) of weekly PM\(_{2.5}\) speciation measurements taken at Alert, Nunavut. The percentiles are represented in the same fashion as Fig. 2.
Figure 6. GEOS-Chem simulation of NH$_3$ mixing ratio (ppb) of the July monthly mean surface layer for (a) no seabird emissions and (b) with seabird emissions. Circles in (a) represent the ship track coloured by NH$_3$ measurements. Panels (c) and (d) show GEOS-Chem simulations for the ammonium to non-sea salt sulphate ratio during the same period for (c) no seabird emissions and (d) with seabird emissions. The star indicates the average ratio observed at Alert during July.
Figure 7. PES plots of FLEXPART-WRF seven day retroplumes from the ship’s location on (a) 14 July 00:00, (b) 26 July 00:00, (c) 2 August 00:00, (d) 3 August 00:00 and (e) 4 August 00:00. The ship track is shown in black and the ship location at the release time is indicated in red. Colors show the airmass residence time prior to arrival at the ship (PES) in seconds. The plume centroid locations at 1 and 2 days (the approximate lifetime of NH$_3$) before release are shown (numbers 1 and 2). Purple circles represent the location of bird colonies with the size of each circle indicating the magnitude of estimated NH$_3$ emissions (in Mg NH$_3$ yr$^{-1}$). Blue circles show the location of wildfires from the NASA FIRMS measurements of fire radiative power from July 20-26 (in MW). The bottom panel is a time series of NH$_3$(g) and particle-phase NH$_4^+$ and SO$_4^{2-}$ measured by the AIM-IC with arrows indicating times of retroplume initiation in the upper panels. The NASA FIRMS dataset was provided by LANCE FIRMS operated by NASA/GSFC/ESDIS with funding from NASA/HQ.
Figure 8. GEOS-Chem simulation of for total NH$_3$ deposition (in mg N m$^{-2}$ season$^{-1}$) for the months May to September (inclusive). Panel (a) does not include seabird emissions, whereas the panel (b) does. The difference in total NH$_3$ deposition between the two emissions scenarios (with birds minus without birds) is shown in panels (c) and (d) as an absolute amount and percentage increase, respectively.
## Supplemental

### Table S1. Surface ocean parameters relevant for determining surface-air NH₃ exchange

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Table S2. Melt pond parameters relevant for determining surface-air NH$_3$ exchange

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