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2 throughout this document in blue text. Sections added or significantly altered in the manuscript
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5 **Interactive comment on “Ammonia in the summertime** 6 **Arctic marine boundary layer: sources, sinks and** 7 **implications” by G. R. Wentworth et al.**

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

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11

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

19

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

22

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

25

26 As a point of interest the authors may wish to explore briefly the hypothesis presented in
27 Johnson and Bell, 2008 (<http://www.publish.csiro.au/?paper=EN08030>), which suggests that
28 away from strong local sources of ammonia, the gas phase concentration is likely to be
29 controlled by the partial pressure of ammonia over the aerosol (akin to the compensation point
30 concept applied by Wentworth et al to the ocean / melt pond surface). As level of neutralisation
31 goes up, the partial pressure (compensation point) increases. This therefore suggests that the
32 reason that NH₃ is higher in the summer not simply because of the seabird emissions but
33 additionally due to the lack of aerosol acidity to take it up, therefore ‘pushing’ it into the ocean.
34 The reverse situation was postulated in Johnson and Bell 2008 - whereby acidic sulfate
35 emissions in the remote marine boundary layer would reduce the compensation point over the
36 aerosol and lead to a consequent emission from the ocean, but the principle is basically the
37 same.

38

39 We agree with this assessment and thank the referee for pointing out the Johnson and Bell
40 (2008) study. We have clarified in the text that low sulphate loading allows seabird NH₃
41 emissions to remain in the gas-phase (i.e. “pushing” it into the ocean):

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“Lastly, Johnson and Bell (2008) show that a sufficiently neutralized sulphate aerosol will tend to ‘push’ gas-phase NH₃ 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 NH₃-to-NH₄⁺ partitioning:

“Colder SST reduces the emission potential due to increased solubility of NH₃ (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 NH₄ - could this have more of an influence?

The impact of NH₄⁺ transport from southern latitudes has little impact on NH_x in the summertime Arctic boundary layer. This is due, in part, to a polar dome that makes long-range transport to the Arctic surface layer inefficient during the summer (Stohl, 2006). In addition, most of the NH_x is gas-phase NH₃ providing further evidence that the role of NH₄⁺ transport is minor with respect to the summertime Arctic NH_x budget near the surface.

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

-why use H₂O₂ 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. H₂O₂ is used to increase the collection efficiency of SO₂ (by oxidizing it to SO₄²⁻). Previous studies that characterize the AIM-IC system have found that an acidic denuder solution is not required to achieve high collection efficiency of NH₃ (Hsu and Clair, 2015; Markovic et al., 2012). Furthermore, acidifying the denuder solution would reduce the solubility of acidic gases (e.g. HNO₃, HONO, organic acids). This has been clarified in the text:

“...dissolved in a 2 mM H₂O₂ solution (to enhance the solubility of SO₂)” (inserted in Page 29980, line 4).

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

Yes, we have corrected the text to read:

“The remaining 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 concentrtrion 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

1 fluorescence signal in seawater at high dissolved organic concentrations. Furthermore, the
2 matrix effect and the background are corrected for.

3
4 It is stated that melt pond samples were analysed within 10hrs but seawater ones within 1 hr -
5 why difference? Was this 10 hrs til inoculation or 10 hours incubation after inoculation with
6 working reagent?

7
8 There was sometimes a delay for analysis of melt pond samples due to a lack of personnel as
9 well as incubation tubes. The same operator was responsible for performing multiple analyses
10 on melt pond water. The 10 hrs was the time until inoculation – the incubation period was the
11 same as for seawater (3.5 hours).

12
13 Poteentially all such methodological details could be put into the supplementary material.

14
15 We prefer not to include all these details in the manuscript as they are readily available in
16 previous publications for both the AIM-IC (Hsu and Clair, 2015; Markovic et al., 2012) and
17 seawater NH_x method (Holmes et al., 1999). Since the focus of the manuscript is not method
18 development there would be little added value to including all these details in the text.

19
20 p29988 - discussion of Fig 3 and the fluxes is a little brief and rather unfocussed. Maybe better
21 in the discussion, expanded on a little?

22
23 The discussion has been expanded to include the following:

24
25 “Net fluxes were exclusively downwards (net deposition into the ocean and melt ponds) due to
26 the relative abundances of $\text{NH}_{3(g)}$ and $\text{NH}_4^+_{(aq)}$ in these surface pools as well as cold surface
27 temperatures as suggested by Johnson et al., (2008).” (inserted into Page 29988, line 3)

28
29 p29989 - sentence beginning 'On the other hand...' is a bit hard to follow – suggest replace
30 'nanoequivalents' with 'concentration' and move '(NH_x napprox NH_3) to after 'SO4²⁻'.

31
32 Agreed – we switched around the wording as suggested.

33
34 Also on this page - the discussion of neutralisation could do to be tightened up a bit - $\text{NH}_4:\text{SO}_4$
35 = 1 isn't 'neutralised' - given a simple system of simply H_2SO_4 and NH_4 , neutral pH should
36 be acheived at $\text{NH}_4:\text{So}_4 = 2:1$, not 1:1. However, I would argue that ph 7 always counts as
37 neutralised, whatever the $\text{NH}_4:\text{SO}_4$ ratio is? There are obviously other sources of acidity which
38 can affect pH as well as NH_4/SO_4 neutralisation.

1 Throughout the manuscript we define the $\text{NH}_4^+:\text{SO}_4^{2-}$ ratio with units of equivalents (so the
2 ratio is NH_4^+ moles to $2 \times \text{SO}_4^{2-}$ moles, such that it already accounts for the double charge of
3 sulphate). In other words, a ratio of 1 equates a fully neutralized sulphate aerosol. An aerosol
4 with $\text{NH}_4^+:\text{SO}_4^{2-}$ ratio (in equivalents) approaching 1 can still have an acidic pH. We have
5 updated the manuscript to clarify how we chose to define the ratio:

6
7 “During the first third of the cruise (before 18 July), gas-phase NH_3 was also low and
8 neutralization (i.e. the ratio $\text{NH}_4^+:\text{SO}_4^{2-}$ in units of equivalents) was ambiguous due to numerous
9 values near or below detection limit.” (Page 29988, line 26).

10
11 The concept of a particle being acidic ($\text{pH} \ll 7$) despite a $\text{NH}_4^+:\text{SO}_4^{2-}$ equivalents ratio
12 approaching 1 is also clarified:

13
14 “For example, a deliquesced ammonium sulphate particle containing 20 neq m^{-3} of SO_4^{2-} and
15 19.98 neq m^{-3} NH_4^+ at 85% RH will have a pH of ~ 3.1 under equilibrium conditions despite
16 having an $\text{NH}_4^+:\text{SO}_4^{2-}$ equivalents ratio of 0.999.” (inserted Page 29989, line 6)

17
18 Figure 1 - what does purple colour mean? (I guess it means no data) - please clarify in legend

19
20 Correct – it means periods without AIM-IC data due to: 1) instrument troubleshooting, 2)
21 invalid measurements from ship activity (validity criteria outlined on page 29981, line 11) or
22 3) NH_3 measurements below the detection limit (only 2 instances). This has been clarified in
23 the figure legend.

24 25 References

26
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4 5 **Interactive comment on “Ammonia in the summertime** 6 **Arctic marine boundary layer: sources, sinks and** 7 **implications” by G. R. Wentworth et al.**

8 **Anonymous Referee #2**

9 Received and published: 6 January 2016

10
11 This is a comprehensive paper with interesting results. Although a bit long/wordy in places, the
12 text is clear and easy to follow. I recommend publication if the comments below are addressed.

13
14 General Comments: I see no reason to present these gas and aerosol composition data using
15 mass units. Converting mass to moles would make for a more intuitive dataset and enable
16 comparison with recent publications such as Johnson et al (2008).

17
18 The main rationale behind using ng m^{-3} versus nmol m^{-3} is two-fold: 1) the flux calculations (in
19 $\text{ng m}^{-2} \text{s}^{-1}$) are more intuitive with ng m^{-3} , and 2) several publications of sea-air NH_3 exchange
20 (Asman et al., 1999; Greenaert et al., 1998) also use mass units. Furthermore, terrestrial NH_3
21 flux studies use units of $\text{ng m}^{-2} \text{s}^{-1}$ (e.g. Zhang et al., 2010) so we chose to report our fluxes in
22 these units for consistency with the broader NH_3 flux community. The conversion from mass
23 to moles is simple (divide by 17.03) such that a reader could easily convert be the two.

24
25 Inlet location: There are two issues that need to be addressed. Firstly, how far forward is the
26 inlet? The text is a little vague: “mounted to the hull near the bow of the ship”. This is
27 particularly important when it comes to choosing the wind sector to exclude/include data. If the
28 inlet is very close to the bow +/-90 degrees is probably ok. If it is further back, I’d recommend
29 a more stringent wind sector.

30
31 The inlet was about 4 m back from the bow of the ship – for reference, the length of the CCGS
32 Amundsen is 98 m. This has been clarified in the text:

33
34 “These components were contained within an aluminum inlet box that was mounted to the hull
35 near the bow of the ship (about 4 m back of the bow).” (inserted on page 29980, line 8)

36
37 Secondly, if the inlet height was only 1 m above the deck then adverse wind/wave conditions
38 could have caused substantial contamination of the signals. Sea spray generated by the ship
39 plunging into the waves tends to come right up over the bow in these conditions. I assume the

1 conditions in summer were benign but this should be stated more explicitly. In future I
2 recommend mounting the inlet higher up, above the wave spray zone!

3
4 We agree the potential for contamination by ship-generated sea spray could be an issue in
5 certain circumstances (e.g. significant waves, while breaking ice). There were several factors
6 that would mitigate this effect during the cruise: 1) relatively benign conditions (as the referee
7 pointed out), and 2) a PM_{2.5} impactor atop the inlet which removes coarse mode sea salt
8 particles generated by ship/wave action. In addition, NH_x is such a minor constituent of
9 seawater that ship-generated sea salt would not affect the NH₃ or NH₄⁺ dataset. Also, Fig. 4
10 reveals SO₄²⁻ ≈ NH₄⁺ on an equivalent basis suggesting there is negligible sea salt SO₄²⁻,
11 otherwise SO₄²⁻ would be greater than NH₄⁺.

12
13 We have briefly clarified the issue of the ship-generated sea spray in the manuscript:

14
15 “Influence from ship-generated sea spray was likely minimal due to the benign nature of the
16 summertime Arctic Ocean, in addition to the PM_{2.5} impactor designed to remove coarse
17 particles.” (inserted on page 29980, line 9)

18
19 We placed the inlet box near deck level for logistical and safety reasons. The set-up and
20 troubleshooting of the components inside the inlet box is time-consuming and finicky so is
21 much easier at deck level. Also, visual checks of the inlet box had to be performed every several
22 hours which would have been impossible (due to safety) during icebreaking, inclement weather,
23 or choppy seas had the inlet box been elevated out of arms reach. Also, the impactor was
24 swapped regularly (every few days) to prevent build-up of sea salt on its surface, although
25 visible accumulation was never observed.

26
27 Specific Comments:

28
29 Page 29976, Line 18: What does ‘area-wide nature’ mean?

30
31 It means the emissions are spread over a large area and hence more difficult to calculate or
32 estimate, relative to point sources (e.g. tailpipes, smokestacks). This has been clarified in the
33 text:

34
35 “...however, large uncertainties exist for these values due to the area-wide nature (emissions
36 spread over a large spatial extent) and poor characterization of many sources.” (inserted on page
37 29976, line 18)

38
39 Page 29981, Line 19: As far from the side of the ship or as far from the side of the melt pond?
40 Please specify.

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

3

4 “The water was sampled as far from the side of the melt pond as possible” (inserted on Page
5 29981, line 19)

6

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

12

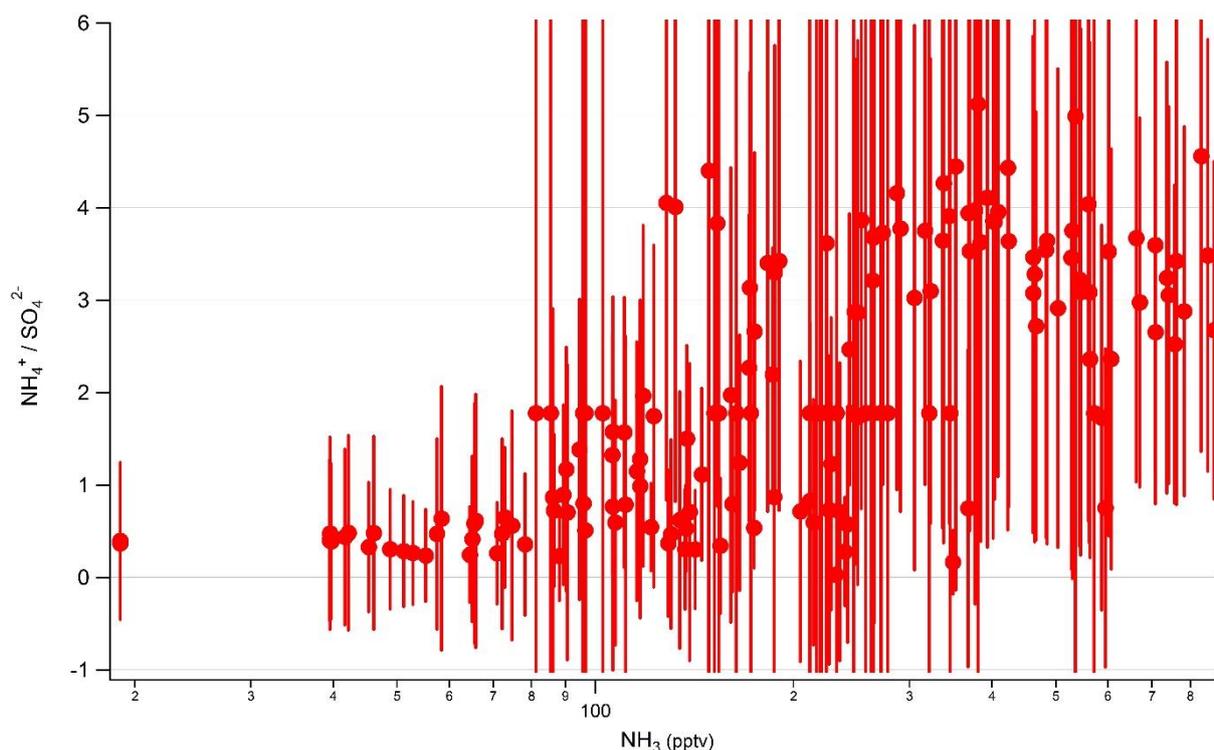
13 Since there is typically a much higher loading of NH₃ than both NH₄⁺ and SO₄²⁻, the NH₄⁺
14 concentrations should not correlate with NH₃ concentrations. This is because the sulphate is
15 already saturated with NH₄⁺ so any additional increase in NH₃ will not result in a noticeable
16 increase in NH₄⁺.

17

18 A similar trend occurs with neutralization ratio. As the ratio of NH₄⁺:SO₄²⁻ equivalents
19 approaches 1 it is not very sensitive to NH₃ concentrations. This is shown in the plot below of
20 NH₄⁺:SO₄²⁻ versus NH₃ (NOTE: this figure is a molar ratio, so the ratio approaches 2 for a fully
21 neutralized aerosol). Errors bars represent a very conservative estimate of uncertainty (± (30%
22 + detection limit)).

23

24 For the points of low NH₃ mixing ratios (<100 pptv) there is insufficient NH₃ to neutralize the
25 SO₄²⁻ (molar ratio less than 2). However, above this approximate threshold the ratio is
26 insensitive to NH₃ since the sulphate is already neutralized. We chose not to include this figure
27 in the manuscript for two reasons: 1) NH₄⁺ and SO₄²⁻ approach detection limits so uncertainties
28 regarding their ratio is large resulting in unrealistic molar ratios above two, and 2) it is
29 redundant with the analysis of Fig. 4 (since NH₄⁺ ≈ SO₄²⁻ the SO₄²⁻ is roughly neutralized).



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Figure 5: Surely it should be $2 \cdot \text{NH}_4 / \text{nssSO}_4$? This would give a neutral value of 1. I think a ratio of $\text{NH}_4 / 2 \cdot \text{nssSO}_4$ 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. $1 \text{ nmol m}^{-3} \text{ SO}_4^{2-} = 2 \text{ neq m}^{-3}$). Therefore a fully neutralized SO_4^{2-} aerosol has an equivalent ratio of $\text{NH}_4^+ : \text{SO}_4^{2-} = 1$, 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 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 $\text{PM}_{2.5}$ composition data (NH_4^+ , SO_4^{2-} , NO_3^-) of a co-located AIM-IC and Partisol $\text{PM}_{2.5}$ 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 ($\sim 0^\circ\text{C}$) 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 $\text{PM}_{2.5}$. It is possible that acidic $\text{PM}_{2.5}$ 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

1 increase the $\text{NH}_4^+:\text{SO}_4^{2-}$ on the filter such that it overestimates the average $\text{NH}_4^+:\text{SO}_4^{2-}$ ratio in
2 ambient $\text{PM}_{2.5}$. However, this would require high levels of NH_3 which is consistent with our
3 interpretation of the Hi-Vol data: that is suggests significant regional source(s) of NH_3 .

4
5 These issues of under and overestimation of NH_3 by Hi-Vol samplers has been added to the
6 text:

7
8 “In warm environments volatilization of NH_4NO_3 off of filters can cause an underestimation of
9 NH_4^+ , but this is not expected to be an issue at Alert due to cold weather and low loadings of
10 NH_4NO_3 .” (inserted Page 29989, line 11)

11
12 “However, there is no denuder upstream of the Hi-Vol filters to remove NH_3 so the observed
13 $\text{NH}_4^+:\text{SO}_4^{2-}$ ratio (Fig. 5) may be higher than for ambient $\text{PM}_{2.5}$. This effect is difficult to
14 characterize, but if it is important then it is still evidence for the abundance of NH_3 in the
15 summertime Arctic boundary layer” (inserted Page 29989, line 15)

16
17 Page 29990, Line 15: The Bouwman flux estimate uses a seawater NH_x climatology and,
18 crucially, assumes that the atmospheric NH_3 concentration is zero. This leads to an
19 overestimate of the oceanic NH_3 emissions. Using a different flux estimate would make the
20 discrepancy in NH_3 mixing ratio between the model and the data even greater than stated. It
21 would be worth including reference to the recent paper by Paulot et al (GBC, 2015), which
22 demonstrates this overestimate using different NH_3 emission schemes within the GEOS-Chem
23 model.

24
25 We agree with this assessment and have included an additional sentence further explaining the
26 recent Paulot et al. (2015) work:

27
28 “Paulot et al. (2015) recently showed the oceanic emissions from this original inventory are
29 roughly a factor of 3 too high since the initial inventory assumes atmospheric NH_3 is equal to
30 zero.” (inserted Page 29990, line 16)

31
32 Section 3.4: Implications for N-deposition. This is an interesting discussion, but it feels
33 incomplete as no attempt is made to include the particulate NH_4 deposition. The particulate
34 NH_4 contribution is likely to be from the same source (i.e. volatile gas phase NH_3 is emitted
35 from seabird colonies. Some neutralises whatever SO_4 aerosol is present, and the rest remains
36 in the gas phase).

37
38 The deposition plots in Fig. 8 represent total (wet and dry) NH_x deposition and do include NH_4^+
39 deposition. The majority of NH_x deposition results from wet/dry deposition of NH_3 ; NH_4^+
40 deposition is minor in comparison. We agree that the majority of NH_4^+ likely stems from the
41 same source as gas-phase NH_3 (as the referee points out). We have clarified the minor
42 contribution of NH_4^+ in the text:

1
2 [“The majority of NH_x deposition is caused by NH₃ as opposed to NH₄⁺.”](#) (inserted page 29994,
3 line 26)

4
5 Page 29995, Line 25: Typo – remove the word ‘a’ from between ‘slightly’ and ‘higher’

6
7 Thank you – we have removed the typo.

8
9
10 **References**

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19 [Zhang, L., Wright, L. P. and Asman, W. A. H.: Bi-directional air-surface exchange of](#)
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22
23

1 Ammonia in the summertime Arctic marine boundary layer: 2 Sources, Sinks and Implications

3
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19 Correspondence to: J. G. Murphy (jmurphy@chem.utoronto.ca)

21 Abstract

22 Continuous hourly measurements of gas-phase ammonia ($\text{NH}_{3(\text{g})}$) were taken from 13 July to 7
23 August 2014 on a research cruise throughout Baffin Bay and the eastern Canadian Arctic
24 Archipelago. Concentrations ranged from 30-650 ng m^{-3} (40-870 pptv) with the highest values
25 recorded in Lancaster Sound (74°13' N, 84°00' W). Simultaneous measurements of total
26 ammonium ($[\text{NH}_x]$), pH and temperature in the ocean and in melt ponds were used to compute
27 the compensation point (χ), which is the ambient $\text{NH}_{3(\text{g})}$ concentration at which surface-air
28 fluxes change direction. Ambient $\text{NH}_{3(\text{g})}$ was usually several orders of magnitude larger than
29 both χ_{ocean} and χ_{MP} (<0.4-10 ng m^{-3}) indicating these surface pools are net sinks of NH_3 . Flux

1 calculations estimate average net downward fluxes of 1.4 and 1.1 ng m⁻² s⁻¹ for the open ocean
2 and melt ponds, respectively. Sufficient NH_{3(g)} was present to neutralize non-sea salt sulphate
3 (nss-SO₄²⁻) in the boundary layer during most of the study. This finding was corroborated with
4 a historical dataset of PM_{2.5} composition from Alert, NU (82°30' N, 62°20' W) wherein the
5 median ratio of NH₄⁺/nss-SO₄²⁻ equivalents was greater than 0.75 in June, July and August. The
6 GEOS-Chem chemical transport model was employed to examine the impact of NH_{3(g)}
7 emissions from seabird guano on boundary-layer composition and nss-SO₄²⁻ neutralization. A
8 GEOS-Chem simulation without seabird emissions underestimated boundary layer NH_{3(g)} by
9 several orders of magnitude and yielded highly acidic aerosol. A simulation that included
10 seabird NH₃ emissions was in better agreement with observations for both NH_{3(g)}
11 concentrations and nss-SO₄²⁻ neutralization. This is strong evidence that seabird colonies are
12 significant sources of NH₃ in the summertime Arctic, and are ubiquitous enough to impact
13 atmospheric composition across the entire Baffin Bay region. Large wildfires in the Northwest
14 Territories were likely an important source of NH₃, but their influence was probably limited to
15 the Central Canadian Arctic. Implications of seabird-derived N-deposition to terrestrial and
16 aquatic ecosystems are also discussed.

17

18 **1 Introduction**

19 Ammonia (NH_{3(g)}) is the dominant alkaline gas in the atmosphere and is an important
20 component of the global nitrogen cycle. Its transport and deposition can have harmful effects
21 for N-sensitive ecosystems such as eutrophication, loss of biodiversity and soil acidification
22 (Krupa, 2003). The presence of NH_{3(g)} can impact climate by increasing rates of new particle
23 formation via stabilization of sulphuric acid clusters (Kirkby et al., 2011). Gas-phase NH₃ is
24 also able to partition to acidic fine particulate matter (PM_{2.5}) to form particulate-phase
25 ammonium (NH₄^{+(p)}), which alters various aerosol properties, such as scattering efficiency
26 (Martin et al., 2004), hygroscopicity (Petters and Kreidenweis, 2007), ice nucleating ability
27 (Abbatt et al., 2006) and heterogeneous chemistry occurring on surfaces (Fickert et al., 1999).

28 As a result, the accurate quantification of the magnitude and location of NH_{3(g)} sources is
29 important for chemical transport models (CTMs). The major anthropogenic source is
30 agriculture (fertilization and animal husbandry) with biomass burning, transport and industry
31 being minor contributors (Reis et al., 2009). Natural sources include soils, vegetation, oceans
32 and animal excreta (Sutton et al., 2013). Estimates for the annual global emissions of NH_{3(g)}

1 range from 35-54 Tg N yr⁻¹; however, large uncertainties exist for these values due to the area-
2 wide nature (emissions spread over a large spatial extent) and poor characterization of many
3 sources. In remote marine environments, the ocean is thought to be the dominant source of
4 NH_{3(g)} to the marine boundary layer and delivers an estimated 6-8 Tg N yr⁻¹ to the atmosphere
5 globally (Sutton et al., 2013). The dominant sources of oceanic NH_x (≡NH₃ + NH₄⁺) include
6 remineralisation of organic matter by bacteria and phytoplankton excretion (Carpenter et al.,
7 2012). However, NH_x is an extremely labile nutrient for microbes such that assimilation by
8 phytoplankton and bacteria prevents significant accumulation in surface waters. Nonetheless,
9 there exists a pool of dissolved ammonia (NH_{3(sw)}) available for exchange with the atmosphere.

10 In order to compute sea-air NH₃ fluxes, simultaneous measurements of both atmospheric NH_{3(g)}
11 and oceanic NH_x are required. These measurements are extremely challenging due to low
12 ambient concentrations and complications arising from making ship-based measurements (e.g.
13 proximity to human activity can cause artefacts). As a result, to our knowledge only six previous
14 studies have simultaneously quantified both [NH_{3(g)}] and oceanic [NH_x], leading to extremely
15 large uncertainties for both the direction and magnitude of global sea-air NH₃ fluxes (Asman et
16 al., 1994; Geernaert et al., 1998; Gibb et al., 1999; Johnson et al., 2008; Quinn et al., 1988,
17 1990). Johnson et al. (2008) provided the most recent dataset and summarized the previous
18 studies to show that the open ocean can be both a net source and a net sink of NH_{3(g)}, with sea
19 surface temperature (SST) being a key determinant for the direction of flux. Colder SST reduces
20 the emission potential due to increased solubility of NH₃ (because of both reduced NH_{3(aq)}
21 volatility and increased partitioning of NH_{3(aq)} to NH₄⁺(aq)); hence, at higher latitudes the open
22 ocean is more likely to act as a net sink (Johnson et al., 2008). Of the six previous studies, only
23 Johnson et al. (2008) quantified NH₃ fluxes above the Arctic Circle (66°33' N) during a summer
24 time study in the Norwegian Sea. Therefore additional measurements of sea-air NH₃ fluxes in
25 the High Arctic are invaluable for improving constraints on oceanic NH₃ emissions.

26 During the summertime, freshwater melt ponds are a ubiquitous feature on top of melting Arctic
27 sea ice and can comprise up to 80% of the sea ice surface (Lüthje et al., 2006). These melt
28 ponds form from melting sea ice and are anywhere from a few cm to over 1 m deep. They are
29 chemically distinct from the bulk ocean owing to their low salinity and physical separation from
30 the ocean mixed layer by sea ice or stratification. To our knowledge, no studies to date have
31 attempted to quantify melt pond-air NH_{3(g)} fluxes despite the abundant presence of melt ponds
32 in the summertime Arctic.

1 Quantifying sea-air and melt pond-air NH_3 exchange in the Arctic will help elucidate the role
2 these processes play as either sources or sinks in the Arctic nitrogen cycle. Many terrestrial
3 Arctic ecosystems are N-limited and highly sensitive to perturbations in N-input (Shaver and
4 Chapin III, 1980), thus Arctic soils and vegetation are unlikely to represent important sources
5 of atmospheric ammonia. Major sources at lower latitudes include agriculture, vegetation,
6 transport and industry (Reis et al., 2009; Sutton et al., 2013) but these are expected to contribute
7 minimally north of the Arctic Circle. Since the lifetime of $\text{NH}_{3(\text{g})}$ is typically less than 24 h,
8 long-range transport from lower latitudes is likely not important (Lefer et al., 1999). Substantial
9 NH_3 emissions have been measured from both seabird guano (Blackall et al., 2007) and seal
10 excreta (Theobald et al., 2006) so large colonies may be relevant point sources throughout the
11 Arctic region. Biomass burning can also inject significant quantities of NH_3 into the free
12 troposphere and/or boundary layer (Bouwman et al., 1997). Although vegetation in the high
13 Arctic is sparse, there can be large wildfires in boreal regions, and emissions may be transported
14 poleward. The potential for the ocean and melt ponds to act as sources to the atmosphere will
15 depend on the relative importance of sources and sinks within the atmosphere and the aqueous
16 systems.

17 NH_3 emission to the atmosphere can affect the extent of non-sea salt sulphate (nss-SO_4^{2-})
18 neutralization, which has implications for N-transport (Lefer et al., 1999). Therefore, it is
19 important to also consider the relative abundances of atmospheric NH_x and nss-SO_4^{2-} . The
20 dominant source of the latter in the summertime Arctic is oxidation of dimethylsulphide (DMS)
21 emitted from the Arctic Ocean (Leitch et al., 2013; Sharma et al., 1999, 2012). Measurements
22 of $\text{PM}_{2.5}$ composition in the summertime Arctic marine boundary layer are rare (e.g. Chang et
23 al., 2011; Leck et al., 2001). Previous chemical transport model (CTM) studies with GEOS-
24 Chem predict highly acidic aerosol (i.e. $\text{nss-SO}_4^{2-} \gg \text{NH}_x$) with negligible amounts of $\text{NH}_{3(\text{g})}$
25 throughout the summertime Arctic boundary layer (Breider et al., 2014).

26 The region for this study is the eastern Canadian Arctic Archipelago where ship-based
27 atmospheric ($\text{NH}_{3(\text{g})}$, $\text{NH}_4^+(\text{p})$, $\text{SO}_4^{2-}(\text{p})$) and oceanic ($[\text{NH}_x]$, pH, SST) measurements were taken
28 over a 4-week period in July and August, 2014. To our knowledge, this study presents the first
29 measurements of $\text{NH}_{3(\text{g})}$ in the Canadian Arctic. Motivated by a lack of atmospheric and oceanic
30 measurements in the region, as well as substantial uncertainties in sea-air and melt pond-air
31 NH_3 fluxes, the specific goals of this study were to:

- 1 1) Simultaneously quantify $\text{NH}_{3(g)}$ and oceanic/melt pond $[\text{NH}_x]$ to infer surface-air NH_3
- 2 fluxes
- 3 2) Assess the relative abundances of $\text{NH}_{3(g)}$, $\text{NH}_4^+_{(p)}$ and $\text{SO}_4^{2-}_{(p)}$ to determine the extent of
- 4 $\text{SO}_4^{2-}_{(p)}$ neutralization
- 5 3) Elucidate the major sources and sinks of atmospheric NH_3 throughout the summertime
- 6 Arctic marine boundary layer
- 7 4) Evaluate whether atmospheric NH_x deposition could be an important N-input to aquatic
- 8 and terrestrial Arctic ecosystems

9 **2 Materials and Methods**

10 **2.1 2014 CCGS Amundsen Cruise**

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

19 **2.2 Atmospheric Measurements**

20 Ambient levels of water-soluble ions in $\text{PM}_{2.5}$ (NH_4^+ , SO_4^{2-} , and NO_3^-) and their precursor gases
21 (NH_3 , SO_2 , and HNO_3) were measured using the Ambient Ion Monitor-Ion Chromatograph
22 (AIM-IC) system (Model 9000D, URG Corp., Chapel Hill, NC). The AIM-IC is a continuous
23 on-line system which provides simultaneous gas-phase and particle-phase measurements with
24 hourly time resolution. The system has been adapted to locate the gas and particle separation
25 and collection hardware as close as possible to the inlet sampling point (Markovic et al., 2012).
26 Ambient air is pulled through a $\text{PM}_{2.5}$ impactor to remove coarse ($>2.5 \mu\text{m}$ in diameter) particles
27 at a flow of 3 L min^{-1} . Air then enters a parallel plate wet denuder where water-soluble gases
28 are dissolved in a 2 mM H_2O_2 solution (to enhance the solubility of SO_2) which is continuously
29 flowing across the denuder membranes. The remaining $\text{PM}_{2.5}$ particles ~~with diameter larger~~
30 ~~than $2.5 \mu\text{m}$~~ have sufficient inertia to pass through the denuder into a supersaturation chamber

1 where they are collected as an aqueous solution via hygroscopic growth. These components
2 were contained within an aluminum inlet box that was mounted to the hull near the bow of the
3 ship (about 4 m back of the bow). The height of the inlet was 1 m above the deck. Influence
4 from ship-generated sea spray was likely minimal due to the benign nature of the summertime
5 Arctic Ocean, in addition to the PM_{2.5} impactor designed to remove such particles. The aqueous
6 solutions collected in the inlet box were pulled down a 22 m sample line through a conduit
7 leading to the IC systems which were housed in a laboratory below deck. Half of each ~10 mL
8 aqueous aliquot (representing 1 hour of sampling) was then separately injected onto both a
9 cation IC and anion IC for quantification of water-soluble ions.

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

17 During the campaign, three zero air overflow experiments were performed to quantify the
18 background signal of each analyte measured during AIM-IC ambient sampling. For each
19 experiment the inlet was overflowed with high purity zero air (AI 0.0 UZ-T, PraxAir, Toronto,
20 ON) at 4.5 L min^{-1} for 18 hours. The average peak area during the final 8 hours of each
21 experiment was used as a background and subtracted from each ambient measurement.
22 Detection limits were calculated by taking 3 times the standard deviation of each analyte peak
23 area during the final 8 hours of each zero air overflow. This value was then converted to either
24 a mixing ratio or mass loading assuming standard temperature and pressure (STP). Detection
25 limits for species of interest during the cruise were 29 ng m^{-3} (NH_3), 17 pptv (SO_2), 8 pptv
26 (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
27 flux calculations, NH_3 values are reported in ng m^{-3} (at STP $100 \text{ ng m}^{-3} \text{ NH}_3 \approx 130 \text{ pptv}$).

28 Standard meteorological parameters were measured using a Vaisala HMP45C212 sensor for
29 temperature, an RM Young model 61205V transducer for pressure, and an RM Young Model
30 05103 wind monitor for wind speed and direction located at the bow ship of the ship at a height
31 of 8.2 - 9.4 m above the deck. Data were averaged to 1-hour to match the time resolution of the
32 AIM-IC. In order to remove any influence from activities aboard the ship, gas-phase

1 measurements are only reported if the following conditions were met: 1) average hourly ship
2 speed > 4 knots ($\sim 7.4 \text{ km h}^{-1}$), 2) average hourly apparent wind direction $\pm 90^\circ$ of the bow, and
3 3) standard deviation of apparent wind direction < 36° . Similar cut-offs for speed and wind
4 direction have been used in previous studies of NH_3 in the marine boundary layer (e.g. Johnson
5 et al., 2008; Norman and Leck, 2005).

6 **2.3 Surface Measurements**

7 A total of 37 surface ocean and 9 melt pond samples were collected throughout the study. Melt
8 pond samples were collected directly into a cooler jug using an electrical pump fixed on a
9 telescopic arm. The water was sampled as far from the side of the melt pond as possible,
10 between 1-2 m depending on the size of the melt pond. Temperature was measured in situ with
11 a VWR high precision thermometer and total aqueous $[\text{NH}_x]$ was determined within 10 h of
12 sampling using a fluorometric technique that has been optimized for low concentrations and
13 complex matrices (Holmes et al., 1999). The method detection limit was 20 nM. Surface ocean
14 samples were obtained with a Rosette sampler equipped with GO-FLOW bottles and a CTD
15 (Seabird Electronics SBE911+) recording temperature. Total aqueous $[\text{NH}_x]$ was determined
16 as above within 1 hour of sampling. Surface water temperature along the ship's track was
17 continuously measured by a thermosalinograph (Seabird Electronics SBE 45) connected to the
18 seawater inlet. For the purposes of flux calculations, the ocean pH and salinity were assumed
19 to be 8.1 and 35 g kg^{-1} , respectively, which are representative for the region of interest
20 (Takahashi et al., 2014). These assumptions have been made previously and were not found to
21 be a major source of uncertainty when calculating sea-air NH_3 fluxes (Johnson et al., 2008).
22 The melt pond pHs were measured using a pH-meter within four hours of sampling. A three
23 point calibration of the pH probe (Orion™ Model 91-72, Thermo Scientific) was performed
24 using commercially available pH 4.01, 7.00 and 10.00 buffers. Salinity of the melt ponds were
25 determined with a WTW Cond 330i handheld conductivity meter.

26 **2.4 Flux Calculations**

27 The direction of sea-air NH_3 fluxes can be assessed by comparing ambient measurements of
28 $\text{NH}_{3(g)}$ to the atmospheric mixing ratio predicted from Henry's Law equilibrium calculations
29 using seawater $[\text{NH}_x]$ and surface temperature measurements (e.g. Asman et al., 1994; Johnson
30 et al., 2008; Quinn et al., 1988, 1996). This equilibrium NH_3 concentration signifies the ambient
31 value at which the net flux changes direction, and is known as the compensation point (denoted

1 χ). In other words, one expects a net downwards flux if ambient $\text{NH}_{3(g)}$ exceeds χ and a net
 2 upward flux if it is below χ . The magnitude of these fluxes are commonly computed using the
 3 “two-phase” model first developed by Liss and Slater (1974), which describes the sea-air
 4 transfer of gases as being controlled by molecular diffusion on either side of the interface. The
 5 transfer of NH_3 across this interface is predominantly dictated by the air-side transfer velocity,
 6 given the relatively high water solubility of NH_3 (Liss, 1983). Hence, the equation to calculate
 7 sea-air NH_3 fluxes is:

$$8 \quad F_{\text{NH}_3} = k_g \cdot (\chi - \text{NH}_{3(g)}) \cdot 17.03 \quad (1)$$

9 where F_{NH_3} is the sea-air flux of NH_3 ($\text{ng m}^{-2} \text{ s}^{-1}$), k_g is the air-side transfer velocity (m s^{-1}),
 10 $\text{NH}_{3(g)}$ is the measured ammonia concentration (nmol m^{-3}), χ is the compensation point (nmol
 11 m^{-3}), and the molecular weight of 17.03 g mol^{-1} is to convert nmol to ng . Numerous
 12 parameterizations exist for k_g with varying degrees of complexity (Johnson, 2010). Here we
 13 adopt the approach established by Duce et al. (1991):

$$14 \quad k_g = \frac{u}{770 + 45 \cdot \text{MW}^{1/3}} \quad (2)$$

15 where u is the wind speed (m s^{-1}) and MW is the molecular weight of the gas of interest (17.03
 16 for NH_3). Although simple, this parameterization has been used previously to estimate sea-air
 17 NH_3 fluxes (e.g. Johnson et al., 2008) and has been shown to be in good agreement (within 20
 18 %) with a more complex scheme, particularly at lower wind speeds (Johnson, 2010). The
 19 following equation is used to calculate χ :

$$20 \quad \chi = K_H \cdot [\text{NH}_{3(\text{sw})}] \quad (3)$$

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

$$24 \quad K_H = \frac{1}{17.93 \cdot \frac{T}{273.15} \cdot e^{(4092/T) - 9.70}} \quad (4)$$

25 where T is the surface temperature (in K). The following equation is used to relate the $\text{NH}_{3(\text{sw})}$
 26 to the concentration of total dissolved NH_x ($[\text{NH}_{x(\text{sw})}]$), which is the value actually measured by
 27 the procedure outlined in section 2.3:

$$1 \quad [NH_{3(sw)}] = \frac{[NH_{x(sw)}] \cdot K_a}{10^{-pH} + K_a} \quad (5)$$

2 where K_a is the acid dissociation constant of NH_4^+ . The pK_a ($\equiv -\log K_a$) is calculated according
3 to Bell et al. (2008), which provides an empirical correction for salinity (S , dimensionless) at a
4 given temperature (T , in $^{\circ}C$):

$$5 \quad pK_a = 10.0423 + 0.003071 \cdot S - 0.031556 \cdot T \quad (6)$$

6 Equations (2) and (4) closely follow that of Johnson et al. (2008) but are sufficiently similar to
7 analogous approaches for calculating K_H and k_g used in other sea-air NH_3 exchange studies
8 (e.g. Asman et al., 1994; Gibb et al., 1999; Quinn et al., 1992). Johnson (2004) reported that
9 fluxes calculated with these various schemes usually agree within 2 %. Melt pond-air exchange
10 was also examined using Eqs. (1) to (6).

11 **2.5 GEOS-Chem**

12 The GEOS-Chem chemical transport model (www.geos-chem.org) is used to aid in the
13 interpretation of the atmospheric measurements. We use GEOS-Chem version 9-02 at $2^{\circ} \times 2.5^{\circ}$
14 resolution globally, and with 47 vertical layers between the surface and 0.01 hPa. The
15 assimilated meteorology is taken from the NASA Global Modelling and Assimilation Office
16 (GMAO) Goddard Earth Observing System version 5.11.0 (GEOS-FP) assimilated
17 meteorology product. Boundary layer mixing uses the non-local scheme implemented by Lin
18 and McElroy (2010). Our simulations use 2014 meteorology and allow a 2-month spin-up prior
19 to the simulation.

20 The GEOS-Chem model includes a detailed oxidant-aerosol tropospheric chemistry mechanism
21 as originally described by Bey et al. (2001). Simulated aerosol species include sulphate-nitrate-
22 ammonium (Park et al., 2004; Park et al., 2006), carbonaceous aerosols (Park et al., 2003; Liao
23 et al., 2007), dust (Fairlie et al., 2007; Fairlie et al., 2010) and sea salt (Alexander et al., 2005).
24 The sulphate-nitrate-ammonium chemistry uses the ISORROPIA II thermodynamic model
25 (Fountoukis and Nenes, 2007), which partitions ammonia and nitric acid between the gas and
26 aerosol phases. For our simulations, the natural NH_3 emissions are from Bouwman et al. (1997)
27 and biomass burning emissions are from the Quick Fire Emissions Dataset (QFED2)
28 (Darmenov and da Silva, 2013), which provides daily open fire emissions at $0.1^{\circ} \times 0.1^{\circ}$
29 resolution. Anthropogenic NH_3 emissions are from Bouwman et al. (1997). The model includes

1 natural and anthropogenic sources of SO₂ (van Donkelaar et al., 2008; Fischer et al., 2011) and
2 DMS emissions based on the Nightingale (2000) formulation and oceanic DMS concentrations
3 from Lana et al. (2011). Oxidation of SO₂ occurs in clouds by reaction with H₂O₂ and O₃ and
4 in the gas phase with OH (Alexander et al., 2009) and DMS oxidation occurs by reaction with
5 OH and NO₃.

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

12 **2.6 FLEXPART-WRF**

13 FLEXPART-WRF (Brioude et al., 2013, website: flexpart.eu/wiki/FpLimitedareaWrf) is a
14 Lagrangian particle dispersion model based on FLEXPART (Stohl et al., 2005) that is driven
15 by meteorology from the Weather Research and Forecasting (WRF) Model (Skamarock et al.,
16 2005). Here we use FLEXPART-WRF run in backward mode to study the emissions source
17 regions and transport pathways influencing ship-based ammonia measurements. A WRF
18 simulation for the summer 2014 NETCARE campaign was performed using WRF 3.5.1 with
19 initial and boundary conditions provided by the operational analysis (0.25° x 0.25° resolution)
20 from European Centre for Medium-Range Weather Forecasts (ECMWF). Parameterizations
21 and options for the WRF simulations are given in Table 1. The WRF model was run from 1
22 July 2014 to 13 August 2014 and nudged to ECMWF winds, temperature, and humidity every
23 6 hours above the atmospheric boundary layer. The WRF run was evaluated using
24 meteorological measurements made onboard the Amundsen and from Polar-6 aircraft flights
25 during this period. FLEXPART-WRF was run in backward mode to produce retroplume output
26 that is proportional to the residence time of the particles in a given volume of air. Runs were
27 performed using the location of the ship, with one model run performed every 15 minutes while
28 the ship was in the model domain (13 July-13 August 2014). For each run, 100,000 particles
29 were released at the ship location (100 m extent horizontally and vertically) and the
30 FLEXPART-WRF was run backwards for 7 days prior to release. The output provides
31 retroplume information (the residence time of air prior to sampling) which is used to calculate

1 the potential emission sensitivities (PES) integrated over the seven days prior to sampling by
2 instruments aboard the Amundsen.

3 **3 Results and Discussion**

4 **3.1 Surface-Atmosphere NH₃ Fluxes**

5 Figure 1 shows the ambient NH_{3(g)} concentrations measured by the AIM-IC throughout the
6 cruise. Measured values of NH_{3(g)} range between 30-650 ng m⁻³ with the highest values
7 occurring in Lancaster Sound as the ship was steaming eastward into Baffin Bay. Only two
8 measurements of NH₃ were below the detection limit (29 ng m⁻³) throughout the entire cruise.
9 NH₃ consistently exceeded 100 ng m⁻³ during later parts of the cruise along the eastern shores
10 of Ellesmere Island and western shores of Greenland. Lower values (<100 ng m⁻³) were
11 observed at the beginning of the campaign along the eastern shores of Baffin Island.
12 Measurements of NH_{3(g)} in the marine boundary layer at northern latitudes (>50°N) are sparse;
13 however the concentrations measured in this study are within the few previously reported
14 ranges for the regions above 50 °N. Johnson et al. (2008) reported NH_{3(g)} between 20-300 ng
15 m⁻³ in the Norwegian Sea during spring and summer, but a lower range (20-90 ng m⁻³) in the
16 northern North Sea in winter. In the southern North Sea, Asman et al. (1994) measured higher
17 values (30-1500 ng m⁻³) in a study lasting from February to October.

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

26 Parameters listed in Tables S1 and S2 were input into Eqs. (3) to (6) to calculate χ for both the
27 surface ocean and melt pond samples. For samples with [NH_x] below the detection limit, a value
28 of 10 nM (half of the detection limit) was assumed. A comparison of the calculated
29 compensation points for the ocean (χ_{ocean}) and melt ponds (χ_{MP}) are shown in Fig. 2. Also shown
30 is the range for the nearest valid measurement (see section 2.2) of ambient NH_{3(g)}. The NH_{3(g)}
31 concentration taken during the hour of surface sampling could not be used since the ship

1 remained stationary for up to 12 hours while melt pond or ocean work was being conducted.
2 Hence, the $\text{NH}_{3(\text{g})}$ measurement from several hours prior (as the ship approached the surface
3 sampling site) had to be used. This approach should not significantly impact the analysis given
4 that the ambient levels of $\text{NH}_{3(\text{g})}$ were observed to be fairly uniform from one hour to the next
5 (i.e. no rapid spikes of $\text{NH}_{3(\text{g})}$ were measured). Shown in lighter yellow are the ranges of $\text{NH}_{3(\text{g})}$
6 observed over the entire study ($\sim 30\text{-}650 \text{ ng m}^{-3}$). Figure 2 clearly shows that the ambient
7 concentrations of $\text{NH}_{3(\text{g})}$ exceed both χ_{ocean} and χ_{MP} by several orders of magnitude throughout
8 the entire region. This conclusively demonstrates that during the summertime, the ocean and
9 melt ponds are net sinks of atmospheric $\text{NH}_{3(\text{g})}$. This finding is consistent with Johnson et al.
10 (2008) who found a tendency for downward net fluxes at higher latitudes, primarily as a result
11 of colder sea surface temperatures. Assuming an upper limit for the ocean pH of 8.2 would
12 increase χ_{ocean} by less than 20 %.

13 Figure 3 shows the magnitude of the sea-air and melt pond-air flux of NH_3 . Average net
14 downward fluxes of $1.4 \text{ ng m}^{-2} \text{ s}^{-1}$ and $1.1 \text{ ng m}^{-2} \text{ s}^{-1}$ were calculated for the open ocean and
15 melt ponds, respectively using Eqs. (1) and (2). Net fluxes were exclusively downwards (net
16 deposition into the ocean and melt ponds) due to the relative abundances of $\text{NH}_{3(\text{g})}$ and $\text{NH}_4^+(\text{aq})$
17 in these surface pools as well as cold surface temperatures as suggested by Johnson et al.,
18 (2008). It is unlikely that this represents a significant input of NH_4^+ into the open ocean except
19 in cases of extremely low $[\text{NH}_x]$. A simple calculation assuming a mixed layer depth of 25 m
20 results in an increase of only $\sim 0.3 \text{ nM d}^{-1}$ to the ocean (assuming complete mixing and no loss
21 pathways). However, for the much shallower melt ponds (assumed depth of 0.25 m) the same
22 calculation yields an input of $\sim 22 \text{ nM d}^{-1}$. Furthermore, this does not account for atmospheric
23 inputs from either wet deposition or dry deposition of particulate NH_4^+ , and these melt ponds
24 are cut-off from the upwelling currents in the ocean which deliver reactive N to the surface.
25 Rates of nitrification, mineralization and N_2 -fixation in the open ocean and melt ponds would
26 help put this atmospheric input into perspective and give insight as to whether or not it is an
27 important process in the nitrogen cycle in these environments.

28 3.2 Sulphate Neutralization

29 The extent of neutralization of $\text{PM}_{2.5}$ influences aerosol properties as discussed previously.
30 Figure 4 depicts the relative abundances (in neq m^{-3}) of gas-phase ammonia and particulate-
31 phase ammonium and sulphate. It is important to note that the value for sulphate is total $\text{PM}_{2.5}$
32 sulphate as opposed to non-sea salt sulphate (nss-SO_4^{2-}), which is commonly reported for

1 marine boundary layer studies. High and variable backgrounds of Na^+ from the AIM-IC
2 prevented the calculation of nss-SO_4^{2-} , hence this dataset provides an upper limit for nss-SO_4^{2-}
3 . Given the low wind speeds ($< 5 \text{ m s}^{-1}$) that dominated the campaign, it is likely the nss-SO_4^{2-}
4 $\approx \text{SO}_4^{2-}$ since the contribution from sea salt to $\text{PM}_{2.5}$ was likely small. It should also be noted
5 that measurements of SO_2 , HNO_3 and NO_3^- were almost always below their respective detection
6 limits.

7 Particle loadings of NH_4^+ and SO_4^{2-} were extremely low (typically $< 5 \text{ neq m}^{-3}$) throughout the
8 duration of the cruise. During the first third of the cruise (before 18 July), gas-phase NH_3 was
9 also low and neutralization (i.e. the ratio of $\text{NH}_4^+:\text{SO}_4^{2-}$ in units of equivalents) was ambiguous
10 due to numerous values near or below detection limit. On the other hand, after 25 July the
11 nanoequivalents of $\text{NH}_{3(\text{g})}$ were substantially higher (~~$\text{NH}_x \approx \text{NH}_3$~~) than either NH_4^+ or SO_4^{2-} (i.e.
12 $\text{NH}_x \approx \text{NH}_3$), which implies a nearly neutralized sulphate aerosol. It is important to note that a
13 nearly neutralized aerosol does not equate to an aerosol with a pH of 7 since aerosol pH is
14 highly sensitive to liquid water content as well as the precise $\text{NH}_4^+:\text{SO}_4^{2-}$ ratio. An aerosol with
15 $\text{NH}_4^+:\text{SO}_4^{2-}$ approaching 1 (with units of equivalents) can still have an acidic pH. For example,
16 a deliquesced ammonium sulphate particle containing 20 neq m^{-3} of SO_4^{2-} and 19.98 neq m^{-3}
17 NH_4^+ at 85% RH will have a pH of ~ 3.1 under equilibrium conditions despite having an
18 $\text{NH}_4^+:\text{SO}_4^{2-}$ equivalents ratio of 0.999.

19 Figure 5 shows the distribution of the $\text{NH}_4^+:\text{nss-SO}_4^{2-}$ ratio (on a per equivalent basis) measured
20 at Alert, Nunavut (82.50°N , 62.33°W) as a function of month from 1996-2011. Weekly-
21 averaged $\text{PM}_{2.5}$ speciation measurements at Alert are made by Environment Canada and are
22 available on-line (Environment Canada, 2014). The contribution from NO_3^- is minor and has
23 not been included in this analysis. In warm environments volatilization of NH_4NO_3 off of filters
24 can cause an underestimation of NH_4^+ , but this is not expected to be an issue at Alert due to
25 cold weather and low loadings of NH_4NO_3 . During July and August the nss-SO_4^{2-} is, on average,
26 completely neutralized by the NH_4^+ in $\text{PM}_{2.5}$ as shown by a median neutralization ratio
27 approaching 1 during these months. This implies there is sufficient $\text{NH}_{3(\text{g})}$ throughout the region
28 to neutralize nss-SO_4^{2-} produced from DMS oxidation which is consistent with the
29 measurements shown in Fig. 4. However, there is no denuder upstream of the Hi-Vol filters to
30 remove NH_3 so the observed $\text{NH}_4^+:\text{SO}_4^{2-}$ ratio (Fig. 5) may be higher than for ambient $\text{PM}_{2.5}$.
31 This effect is difficult to characterize, but if it is important then it is still evidence for the
32 abundance of NH_3 in the summertime Arctic boundary layer. Lastly, Johnson and Bell (2008)

1 [show that a sufficiently neutralized sulphate aerosol will tend to ‘push’ gas-phase NH₃ into the](#)
2 [ocean in the aerosol-gas-ocean system, also consistent with Fig. 3.](#)

3 The AIM-IC and Alert measurements are both inconsistent with a previous study that used
4 GEOS-Chem to predict a highly acidic aerosol and insignificant gas-phase ammonia (NH_x ≈
5 NH₄⁺) throughout the summertime Arctic marine boundary layer (Breider et al., 2014). This
6 inconsistency implies a missing process in a widely used CTM that we investigate further
7 below.

8 **3.3 Evidence for the Importance of Seabird Guano**

9 Observations collected on board the Amundsen and at Alert strongly suggest a significant
10 source of NH₃ in the Baffin Bay region. Decomposition of uric acid in seabird guano (excreta)
11 has been recognized as a significant source of NH₃ where large colonies exist (Blackall et al.,
12 2007; Wilson et al., 2004). However, studies measuring NH₃ from seabird colonies are limited
13 due to the remoteness of most colonies and technical challenges in quantifying NH₃ in isolated
14 locations (Blackall et al., 2007). The few studies that have been done have focused on colonies
15 located in the United Kingdom (Blackall et al., 2004; Wilson et al., 2004), Antarctica (e.g.
16 Legrand et al., 1998; Zhu et al., 2011) and remote tropical islands (Riddick et al., 2014; Schmidt
17 et al., 2010). Recently, Riddick et al. (2012) developed a global inventory to estimate the
18 magnitude and spatial distribution of NH_{3(g)} from seabird guano. The authors employed a
19 bioenergetics model, first developed by Wilson et al. (2004), to calculate the NH_{3(g)} emissions
20 (in g bird⁻¹ yr⁻¹) for 323 different seabird species. After compiling a list detailing the populations
21 and locations of 33,225 colonies, they were able to estimate global annual emissions between
22 97-442 Gg NH₃ per year. Although this is less than 2% of total global NH_{3(g)} emissions, it can
23 be the dominant source in remote regions where seabird populations are large and other sources
24 are negligible.

25 In order to assess the impact of seabird guano on NH₃ across the Baffin Bay region, seabird
26 colony NH₃ emissions were implemented in the GEOS-Chem model, and the impact on
27 monthly mean surface layer NH₃ was examined. The NH₃ emissions inventory used in the
28 standard GEOS-Chem v9-02 (and in many other CTMs) is from Bouwman et al. (1997) and
29 does not include seabird emissions. [Paulot et al. \(2015\) recently showed the oceanic emissions](#)
30 [from this original inventory are roughly a factor of 3 too high since the initial inventory assumes](#)
31 [atmospheric NH₃ is equal to zero.](#) The Riddick et al. (2012, 2012b) seabird colony NH₃

1 emissions inventory (scenario 3) was added to the original inventory in GEOS-Chem following
2 Paulot et al. (2015). Scenario 3 was chosen since this represented the midpoint between the
3 minimum and maximum emissions of scenario 1 and 2, respectively. Close inspection of this
4 seabird inventory revealed that some large seabird colonies in our study region were not
5 accounted for. To investigate this, the spatial co-ordinates of northern colonies ($>50^\circ\text{N}$) in the
6 Riddick et al. (2012) inventory were cross-referenced against colonies in the on-line
7 Circumpolar Seabird Data Portal (Seabird Information Network, 2015). Annual emissions for
8 large colonies in the seabird data portal were calculated in the same manner as in Riddick et al.
9 (2012). In total, there were 42 colonies present in the seabird data portal but absent in the
10 Riddick inventory in the region north of 50°N . These additional emissions were added to the
11 inventory we implemented in GEOS-Chem. These colonies totaled $7.5 \text{ Gg NH}_3 \text{ year}^{-1}$
12 (approximately one quarter of the existing emissions north of 50°N) and were primarily in
13 Siberia and western Alaska. The Riddick et al. (2012) bioenergetics model only counts
14 emissions that occur during breeding season and while the seabirds are at the colony. Hence,
15 the annual emission estimates ($\text{Gg NH}_3 \text{ year}^{-1}$) per colony were temporally allocated evenly
16 between the 15 May to 15 September. This period is when the majority of seabirds in the Baffin
17 Bay region are nesting (e.g. Gaston et al., 2005; Mallory and Forbes, 2007; McLaren, 1982).
18 One limitation to this approach is that it does not account for additional temporal variations in
19 NH_3 emissions. For instance, moisture increases the rate of uric acid degradation, and fluxes of
20 NH_3 from guano have been observed to increase 10-fold for up to a day after rain events
21 (Riddick et al., 2014).

22 Figure 6 shows the July mean output for surface layer NH_3 mixing ratio both without (Fig. 6a)
23 and with (Fig. 6b) seabird emissions, along with the $\text{NH}_{3(\text{g})}$ measured by the AIM-IC denoted
24 by circles in Fig. 6a. Comparing the top two panels reveals that seabird emissions make a
25 substantial impact on modelled NH_3 levels in the boundary layer. Much better model-
26 measurement agreement is achieved with the inclusion of the seabird colonies. Without the
27 seabird emissions, NH_3 mixing ratios are underpredicted by several orders of magnitude.
28 Surface NH_3 is still underpredicted in Fig. 6b (with guano NH_3 emissions) which could be the
29 result of modelled emissions being independent of rainfall, which can substantially increase
30 NH_3 emissions. Episodic rainfall was persistent throughout the latter half of the campaign.
31 Other contributing factors may include: challenges in representing boundary layer mixing,
32 uncertainties in deposition rates, comparing monthly averages (GEOS-Chem) to ambient hourly
33 measurements, missing/underestimated bird colonies, and/or excreta from other fauna (e.g.

1 seals, caribou, musk-ox) absent in the updated inventory. The bottom two panels (Figs. 6c and
2 6d) show the influence of seabirds on the ammonium to non-sea salt sulphate ratio. Without
3 seabirds (Fig. 6c) the ratio is less than 0.3 throughout most of the study region, which is
4 inconsistent with the abundance of NH_3 relative to SO_4^{2-} measured by the AIM-IC. Adding the
5 seabird emissions (Fig. 6d) increases the ratio to above 0.7 in most grid cells along the ship
6 track. Although the high ratio (July average is ~ 1) observed at Alert (denoted by the star in Figs.
7 6c and 6d) is underestimated in the GEOS-Chem simulation, the bias is reduced by nearly a
8 factor of 2 (from 0.32 to 0.57) when seabird emissions are included.

9 Wildfires are also a source of NH_3 to the free troposphere and/or boundary layer. Particularly
10 strong wildfire events were persistent in the Northwest Territories (NWT) during the study
11 period. Blue circles in Fig. 7 show the location and average fire radiative power (representative
12 of fire strength) of wildfires across the Arctic from July 20-26. It was constructed using data
13 from NASA's Fire Information Resource Management System (FIRMS) database (NASA,
14 2015). We used FLEXPART-WRF retro plumes to assess the importance of wildfire NH_3
15 emissions, as well as to further corroborate the influence of seabird guano.

16 The significant impact of seabird colonies on $[\text{NH}_{3(g)}]$ is supported by the analysis of
17 FLEXPART-WRF retro plumes shown in Fig. 7. Periods of low $[\text{NH}_{3(g)}]$ (bottom panel in Fig.
18 7) correspond to air masses that spent at least the last 48 hours over the ocean and/or aloft above
19 the MBL (~ 500 m) where NH_3 sources are negligible. This is clearly shown in Fig. 7a where
20 the air mass sampled on 14 July 00:00 (UTC) spent the previous 96 hours in the MBL over
21 Baffin Bay, consistent with low $[\text{NH}_{3(g)}]$. In contrast, on 26 July 00:00 (Fig. 7b) air had recently
22 passed over seabird colonies (purple circles) surrounding Lancaster Sound as well as wildfires
23 in the Northwest Territories (NWT) on mainland Canada (blue circles), coincident with the
24 large increase in $[\text{NH}_{3(g)}]$. A similar $\text{NH}_{3(g)}$ peak occurs on 3 August that can also be examined
25 by using a retro plume analysis. Low $\text{NH}_{3(g)}$ values observed on the morning of 2 August agree
26 with Fig. 7c showing the air originating from the MBL over Baffin Bay. At 3 August 00:00
27 (Fig. 7d) the air had spent the last 12 hours in the boundary layer of Western Greenland where
28 large seabird colonies exist. However, by 4 August 00:00 (Fig. 7e) the retro plume shifted such
29 that air is now originating from primarily above the boundary layer (altitude plots not shown)
30 leading to a decrease in $\text{NH}_{3(g)}$. In addition from August 2-4 the ship was north of 79° N and in
31 the Eastern Canadian Arctic, hence it is unlikely that this increase in NH_3 can be attributed to
32 wildfires given how far removed this region is from wildfires in the NWT. While Fig. 7 only

1 highlights five examples from the study period, retro plumes throughout the entire campaign
2 also support the hypothesis that $\text{NH}_{3(g)}$ in the MBL originates primarily from seabird colonies
3 (for the Eastern Canadian Arctic) with contributions from wildfires in some regions (central
4 Canadian Arctic). All $\text{NH}_{3(g)}$ spikes in the time series can be attributed to air that had recently
5 passed over seabird colonies and/or wildfires, whereas low values coincide with air masses
6 from either the open ocean or free troposphere not influenced by wildfires.

7 To further investigate the potential influence of wildfires on NH_3 in the Arctic MBL, GEOS-
8 Chem simulations were performed using a wildfire emissions inventory for 2014 (QFED2).
9 Simulations with/without wildfires and with/without seabirds revealed that in Lancaster Sound
10 (along 74°N) roughly 40% and 55% of the boundary layer NH_3 can be attributed to seabirds
11 and wildfires, respectively. In other words, air sampled in Lancaster Sound (20 July to 27 July)
12 was likely influenced by wildfires in NWT in addition to seabird guano. On the other hand,
13 north of Lancaster Sound, contributions from seabirds and wildfires to surface layer NH_3 were
14 approximately 95% and 5%, respectively. Wildfires in the NWT are an important but episodic
15 source of summertime NH_3 in the Canadian Arctic. This is due to periodic transport events
16 associated with this source that is located remote to our study region. Whereas, seabird colonies
17 are a local, and persistent source of NH_3 from May to September. Given the observation of
18 consistently neutralized sulfate at Alert each summer, and the large interannual variability and
19 episodic wildfire influence, emissions from migratory seabirds are likely to be a significant
20 contributor to NH_3 abundance in the Arctic marine boundary layer.

21 **3.4 Implications for N-deposition to Ecosystems**

22 Previous studies have highlighted the important role that seabird-derived N can play in the
23 nitrogen cycle of ecosystems adjacent to bird colonies due to large deposition rates of NH_3 and
24 NH_4^+ (e.g. Anderson and Polis, 1999; Lindeboom, 1984). However, little attention has been
25 paid to the effects of seabird-derived N on deposition at the regional scale. In this section, we
26 consider the importance of seabird-derived nitrogen as an input of reactive N to Arctic
27 ecosystems. These ecosystems tend to be N-limited during the summer and hence have a large
28 sensitivity to N input (Shaver and Chapin III, 1980). In terrestrial ecosystems, soil N availability
29 is a key factor in determining both plant community structure (McKane et al., 2002) and
30 greenhouse gas emissions from soil (Stewart et al., 2012).

1 Nitrogen (N_2) fixation via microbes is thought to be the primary N input to remote Arctic
2 terrestrial ecosystems (e.g. Cleveland et al., 1999; Hobara et al., 2006; Stewart et al., 2014).
3 Numerous field studies have been conducted to estimate N_2 -fixation rates via the acetylene
4 reduction technique (Hardy et al., 1968). The N_2 -fixation rates for most terrestrial Arctic sites
5 fall within the range of 10 to 120 mg N m⁻² yr⁻¹ (Hobara et al., 2006). However, highly variable
6 rates (due to spatial heterogeneity of microbial populations) and assumptions in the acetylene
7 reduction technique yield high degrees of uncertainty for N_2 -fixation rates (Stewart et al., 2014).
8 Total atmospheric N-deposition (wet and dry) in the Arctic is thought to be smaller than
9 fixation, with typical ranges from 8 to 56 mg N m⁻² yr⁻¹ (Van Cleve and Alexander, 1981). Only
10 a few N_2 -fixation studies also quantify wet deposition, with dry deposition being ignored
11 altogether (e.g. Hobara et al., 2006). Nonetheless, in certain Arctic regions atmospheric
12 deposition may exceed N_2 -fixation in soils (DeLuca et al., 2008). These processes are coupled
13 since large inputs of NH_4^+ have been shown to inhibit N_2 -fixation in certain microbial species
14 and lichens (Chapin and Bledsoe, 1992).

15 Figure 8 shows results from the GEOS-Chem simulation of total NH_x ($\equiv NH_3 + NH_4^+$) deposition
16 (both wet and dry) for the months May to September (inclusive) both without (Fig. 8a) and with
17 (Fig. 8b) seabird NH_3 emissions. The difference in total NH_x deposition for birds and no birds
18 is shown in Fig. 8c (absolute difference) and Fig. 8d (percent different). Areas near large
19 colonies are heavily influenced by seabird guano with NH_x deposition from seabirds exceeding
20 10 mg N m⁻² yr⁻¹, particularly in western Greenland and near the mouth of Lancaster Sound.
21 The majority of NH_x deposition is caused by NH_3 as opposed to NH_4^+ . Most regions in Fig. 8b
22 are on the lower end of the annual N-deposition rate of 8 to 56 mg N m⁻² yr⁻¹ suggested by Van
23 Cleve and Alexander (1981). However, there are two important distinctions: the latter is an
24 estimate of total N-deposition and annual input. Estimates in Fig. 8 might be more useful for
25 comparing N-deposition to N_2 -fixation since it captures deposition only during the growing
26 season, and NH_x is likely the dominant form of atmospheric reactive N in the summertime
27 Arctic boundary layer. Furthermore, Fig. 8b provides information on regions where N-
28 deposition rates could be comparable to input from terrestrial N_2 -fixation (>10 mg N m⁻² yr⁻¹)
29 which can help inform subsequent studies exploring N-cycling in the region. According to
30 Hobara et al. (2006), Arctic terrestrial N_2 -fixation only occurs from May-September (inclusive)
31 and peaks in July, similar to migration patterns of Arctic seabirds.

1 Estimates of N₂-fixation rates in the Arctic Ocean mixed layer are even sparser than estimates
2 for terrestrial ecosystems. To our knowledge, only Blais et al. (2012) have measured oceanic
3 N₂-fixation in the summertime Arctic Ocean mixed layer. The authors found that open ocean
4 N₂-fixation rates averaged 0.12 nM d⁻¹ in the upper 50 m of the water column throughout the
5 Beaufort Sea to Baffin Bay. For the period of May to September (inclusive) this represents an
6 input of approximately 13 mg N m⁻² which is comparable to inputs we calculate from guano-
7 derived NH₃ in regions close to seabird colonies as shown in Fig. 8b.

8 **4 Conclusions**

9 Simultaneous measurements of atmospheric and oceanic composition in the eastern Canadian
10 Arctic revealed that the summertime Arctic Ocean and melt ponds were net sinks of NH_{3(g)}.
11 Concentrations of NH_{3(g)} ranging from 30-650 ng m⁻³ were observed and represent the first
12 reported measurements of NH_{3(g)} in the Canadian Arctic. An average downward flux of 1.4 ng
13 m⁻² s⁻¹ into the Arctic Ocean was calculated, consistent with previous studies showing that
14 higher latitude waters are a net NH₃ sink (Johnson et al., 2008). Melt ponds had a smaller net
15 downward flux (1.1 ng m⁻² s⁻¹) as well as a slightly-a higher χ as compared to the open ocean
16 (median 2 ng m⁻³ versus 0.8 ng m⁻³). To our knowledge, this is the first study to estimate melt
17 pond-air NH₃ exchange despite the ubiquitous presence of melt ponds throughout the
18 summertime Arctic.

19 On a nanoequivalent basis, NH_{3(g)} values were significantly greater (up to an order of magnitude
20 more) than both NH₄⁺ and SO₄²⁻. This finding was consistent with a 15-year historical dataset
21 of weekly PM_{2.5} composition from Alert, NU which showed that nss-SO₄²⁻ is, on average,
22 completely neutralized by NH₄⁺ during July and August. These measurements imply strong
23 regional source(s) of NH_{3(g)} in the eastern Canadian Arctic Archipelago that are sufficient to
24 neutralize nss-SO₄²⁻ produced from DMS oxidation. Our surface-air flux estimates show that
25 the Arctic Ocean and melt ponds are not responsible for NH_{3(g)} in the marine boundary layer.

26 It is also noteworthy that even though these melt ponds have significantly higher [NH_x] than
27 the open ocean (average of 670 nM versus 55 nM), χ_{MP} is only marginally higher. More acidic
28 pHs and slightly lower temperatures mitigate the effect of higher [NH_x] on χ . Chemical
29 transport models (CTMs) that explicitly account for bi-directional NH₃ exchange typically
30 require χ as a predefined model input (e.g. Bash et al., 2013; Wichink Kruit et al., 2012).
31 Therefore, from a modelling standpoint, similar values of χ_{ocean} and χ_{MP} are convenient since
32 they can be parameterized in a similar fashion which would remove the need for CTMs to

1 resolve the spatial extent and temporal evolution of melt ponds to properly model surface-
2 atmosphere NH₃ exchange in the summertime Arctic.

3 To investigate the impact of NH₃ emissions from seabird guano, we examined GEOS-Chem
4 simulations both with and without seabird colony NH₃ emissions. The seabird NH₃ emission
5 inventory developed by Riddick et al. (2012) was updated for this study to include northern
6 colonies (>50 °N) that had been overlooked in the original inventory. Without the seabirds,
7 GEOS-Chem underestimated NH_{3(g)} by several orders of magnitude and predicted highly acidic
8 aerosol at the surface in July, which is in direct contrast to our measurements. The inclusion of
9 seabird emissions provided much better agreement with NH_{3(g)} observations and yielded more
10 neutralized aerosol throughout most of the Baffin Bay region. The importance of seabird NH₃
11 emissions is also supported by analysis of FLEXPART-WRF retro plumes throughout the study
12 period. Air masses enriched in NH_{3(g)} had recently passed through regions with seabird colonies
13 whereas periods of low NH_{3(g)} involved air masses originating from the open ocean or above
14 the boundary layer. Together, these models provide strong evidence that seabird colonies are
15 the dominant and persistent local source of NH_{3(g)} in the summertime Arctic. FLEXPART-
16 WRF and GEOS-Chem were also used to assess the influence of wildfires on NH₃. Wildfires
17 are an important but episodic source of NH₃ source to the Arctic due to ongoing changes in
18 transport patterns and fire intensity. Further work should be done to examine the inter-annual
19 influence of NH₃ emissions from wildfires in the NWT on other regions in the Arctic.

20 Deposition estimates of NH_x from GEOS-Chem during the seabird nesting season (May to
21 September) exceed 10 mg N m⁻² season⁻¹ in grid cells close to large seabird colonies, which is
22 on the lower end of microbial N₂-fixation in Arctic tundra (Hobara et al., 2006). Hence, in some
23 regions seabird-derived NH_x could be a significant N-input to terrestrial Arctic ecosystems
24 which are typically very N-sensitive. Estimates of NH₃ fluxes into the open ocean are unlikely
25 to be an important input of reactive-N except for waters close to large seabird colonies;
26 however, these fluxes may be important for the N-cycle in the much shallower melt ponds.

27 There is strong evidence that seabird colonies are likely the dominant and persistent source of
28 NH_{3(g)} to the summertime Arctic boundary layer. Emissions appear to be significant enough to
29 at least partially neutralize nss-SO₄²⁻ throughout most of the study region, in contrast to previous
30 model simulations that did not consider seabird colony emissions. Further research is required
31 to better constrain the location, population, and NH₃ emissions of Arctic seabird colonies. It is
32 also important to quantify meteorological effects (e.g. rainfall, wind speed) on seabird

1 emissions. The NH₃ emissions inventory in CTMs should be updated to include seabird
2 emissions with correct representation of the breeding season so that emissions only occur when
3 seabirds are nesting. Summertime measurements of atmospheric NH_x elsewhere in the Arctic
4 are needed to assess whether the impacts of seabirds observed in this study (substantial NH_{3(g)},
5 nss-SO₄²⁻ neutralization, and N-deposition) are relevant to the entire Arctic.

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22

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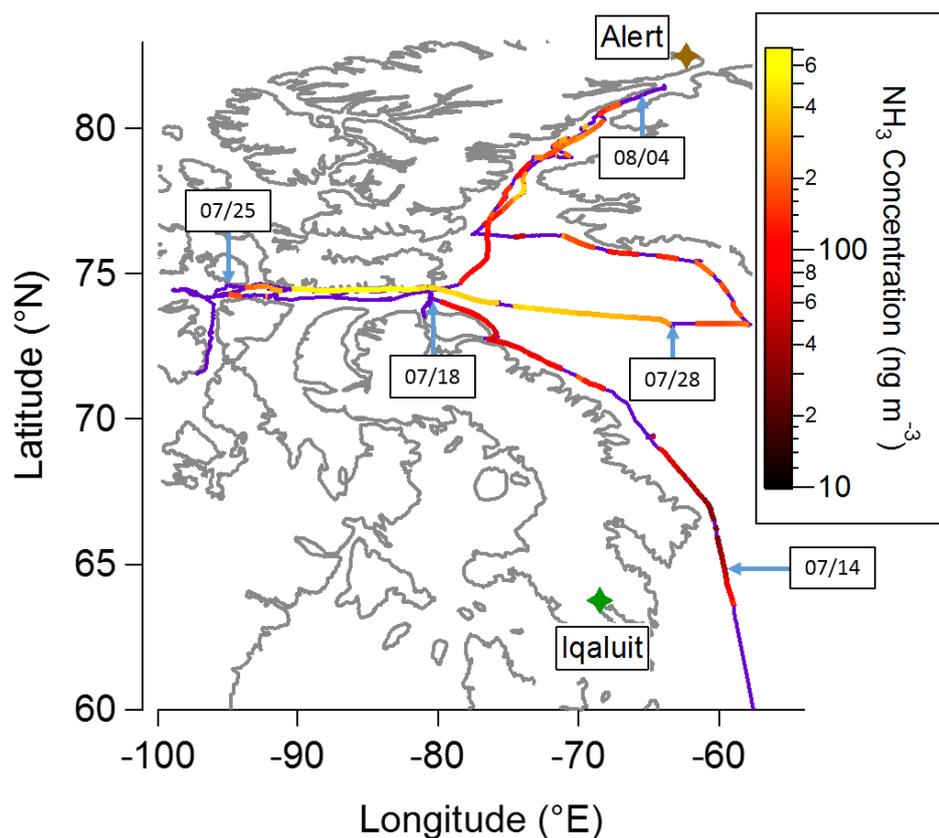
11

1 Table 1. Parameterizations and options used for the NETCARE WRF simulations

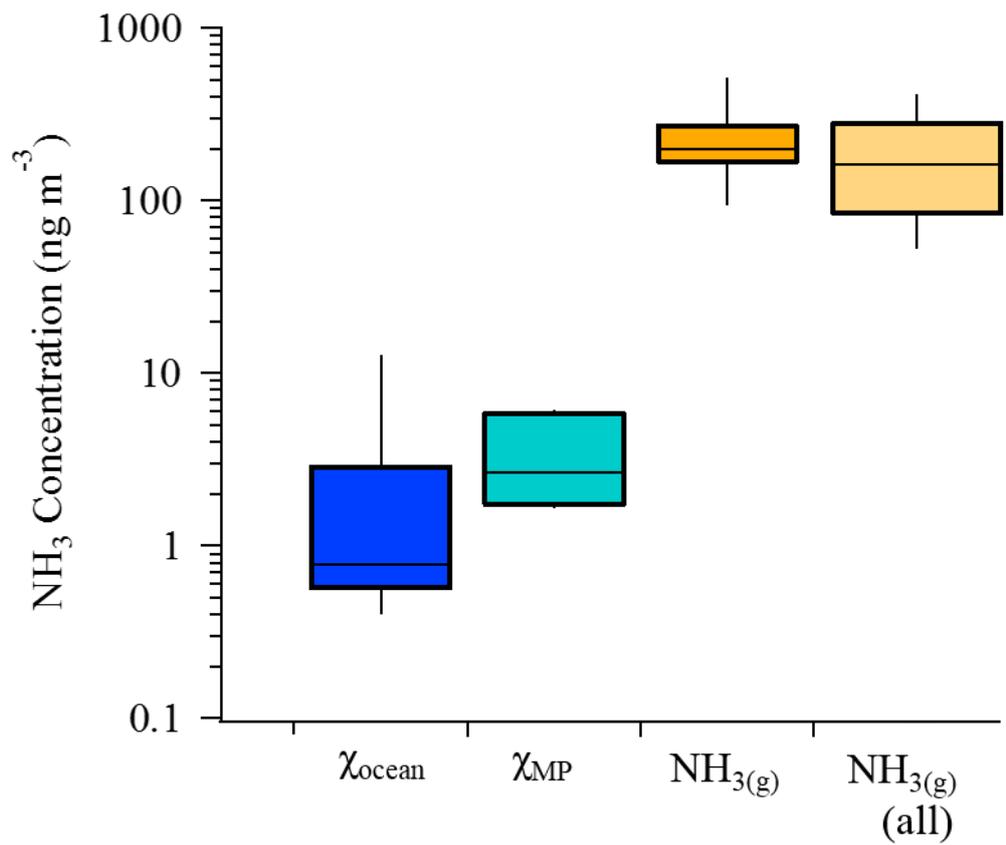
Atmospheric process	WRF option
Planetary Boundary Layer	Mellor–Yamada–Janjic Scheme (MYJ) (Janjic, 1994)
Surface layer	Monin-Obukhov Janjic Eta similarity scheme (Monin and Obukhov, 1954; Janjic, 1994, 1996, 2002)
Land surface	Unified Noah Land Surface Model (Tewari et al., 2004)*
Microphysics	WRF Single-Moment 5-class scheme (Hong, Dudhia, and Chen, 2004)
SW radiation	Goddard Shortwave Scheme (Chou and Suarez, 1994)
LW radiation	RRTMG (Iacono et al., 2008)
Cumulus parameterization	Kain–Fritsch Scheme (Kain, 2004)

2 *with corrected calculation of skin temperature over sea ice when snow melting is occurring,
 3 see <http://www2.mmm.ucar.edu/wrf/users/wrfv3.7/updates-3.7.1.html>.

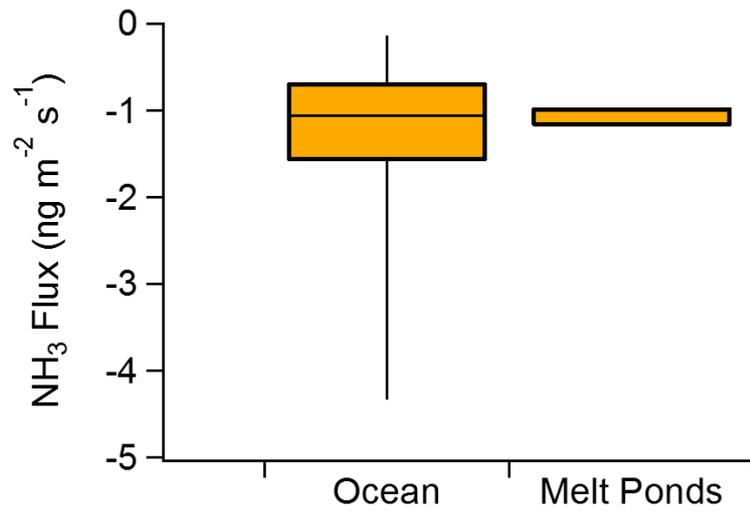
4



1
 2 Figure 1. CCGS *Amundsen* ship track (~~purple~~) coloured by gas-phase NH₃ concentrations
 3 (~~when valid measurements were available~~) measured by the AIM-IC. Invalid measurements
 4 (e.g. instrument troubleshooting, influenced by ship) are purple along the ship track. Units of
 5 ng m⁻³ were chosen as a convenience for flux calculations. At STP, 100 ng m⁻³ ≈ 130 pptv.
 6 Relevant landmarks are also labelled. Dates and arrows indicate the position of the ship at 0:00
 7 UTC on that day.
 8



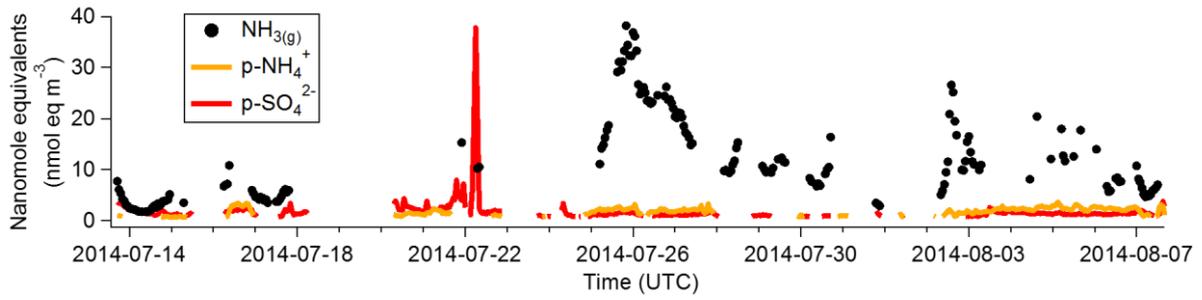
1
 2 Figure 2. Box-and-whisker plot showing the observed ranges of χ (on a log scale) for both the
 3 ocean surface (dark blue) and melt ponds (light blue). The range of $\text{NH}_3(\text{g})$ measured by the
 4 AIM-IC near the time of surface sampling is shown in darker yellow whereas $\text{NH}_3(\text{g})$ over the
 5 entire campaign is shown in lighter yellow. The box represents 25th to 75th percentile while the
 6 line within the box denotes the median. Whiskers extend to the 10th and 90th percentile.
 7



1

2 Figure 3. Box-and-whisker plot of the estimated fluxes into the open ocean and melt ponds. The
3 percentiles are represented in the same fashion as Fig. 2.

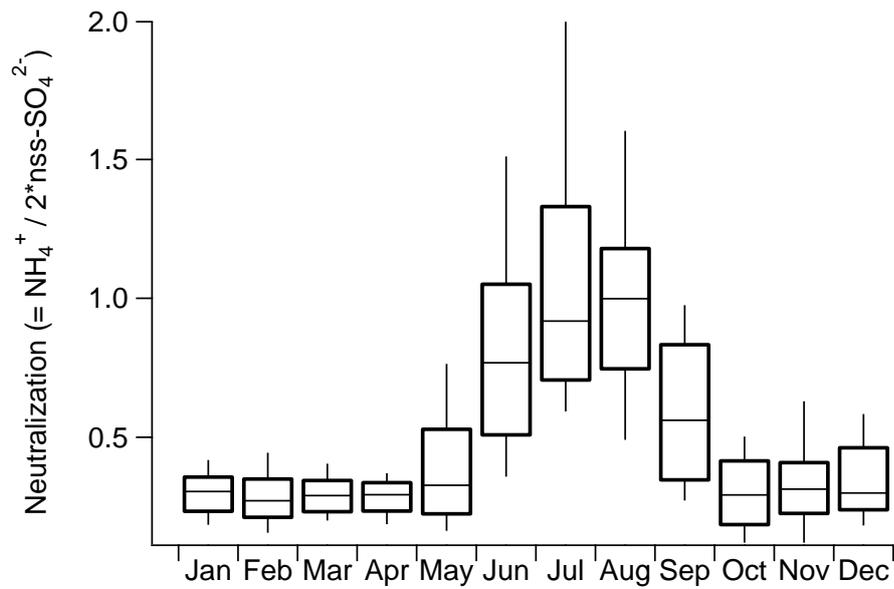
4



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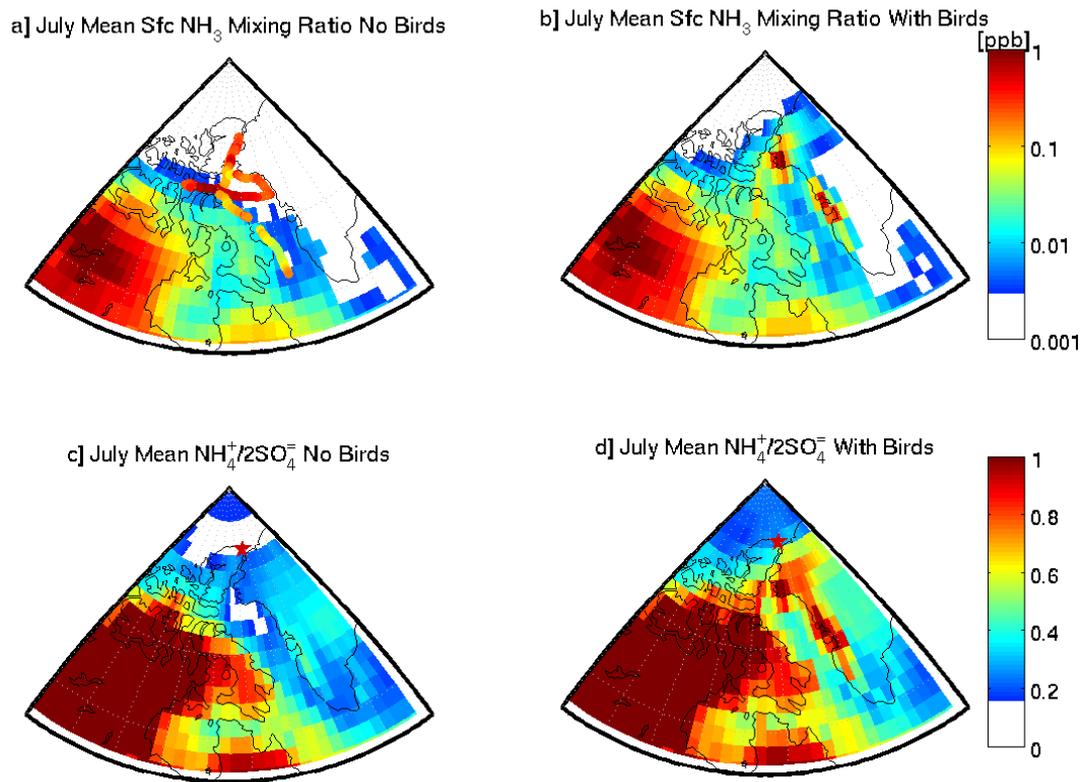
2 Figure 4. Time series of neq m^{-3} for $\text{NH}_3(\text{g})$ (black dots), NH_4^+ in $\text{PM}_{2.5}$ (orange trace), and SO_4^{2-}
 3 in $\text{PM}_{2.5}$ (red trace). Interruptions in the data are a result of zero air experiments, calibrations,
 4 values below detection limit, instrument downtime, and (for gas-phase species) periods when
 5 the wind direction/speed were not conducive for ambient sampling (as explained in detail in
 6 section 2.2).

7



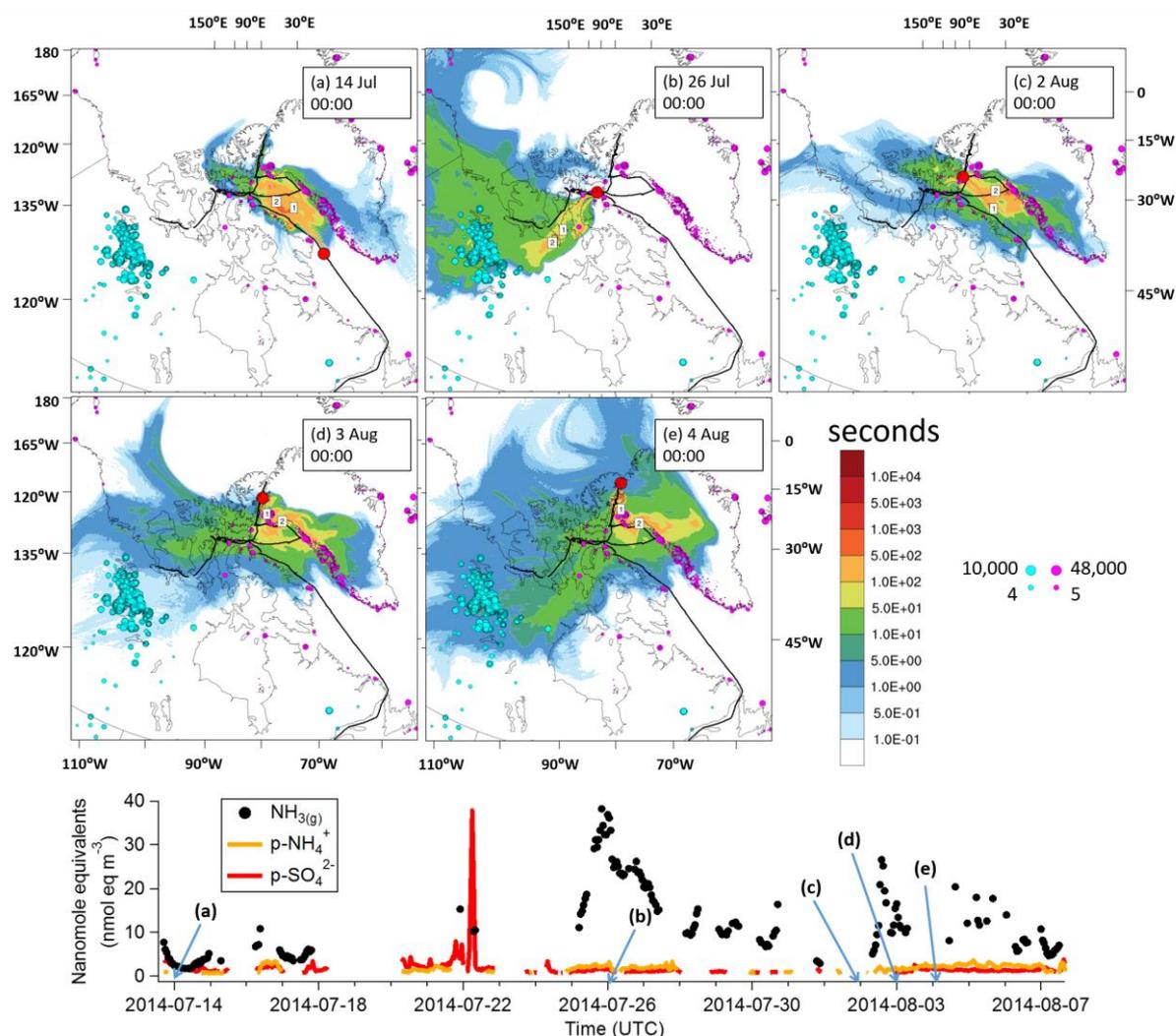
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Figure 5. Box-and-whisker plot of neutralization (defined as $\text{NH}_4^+ / 2 \cdot \text{nss-SO}_4^{2-}$) for fifteen years (1996-2011) of weekly $\text{PM}_{2.5}$ speciation measurements taken at Alert, Nunavut. The percentiles are represented in the same fashion as Fig. 2.

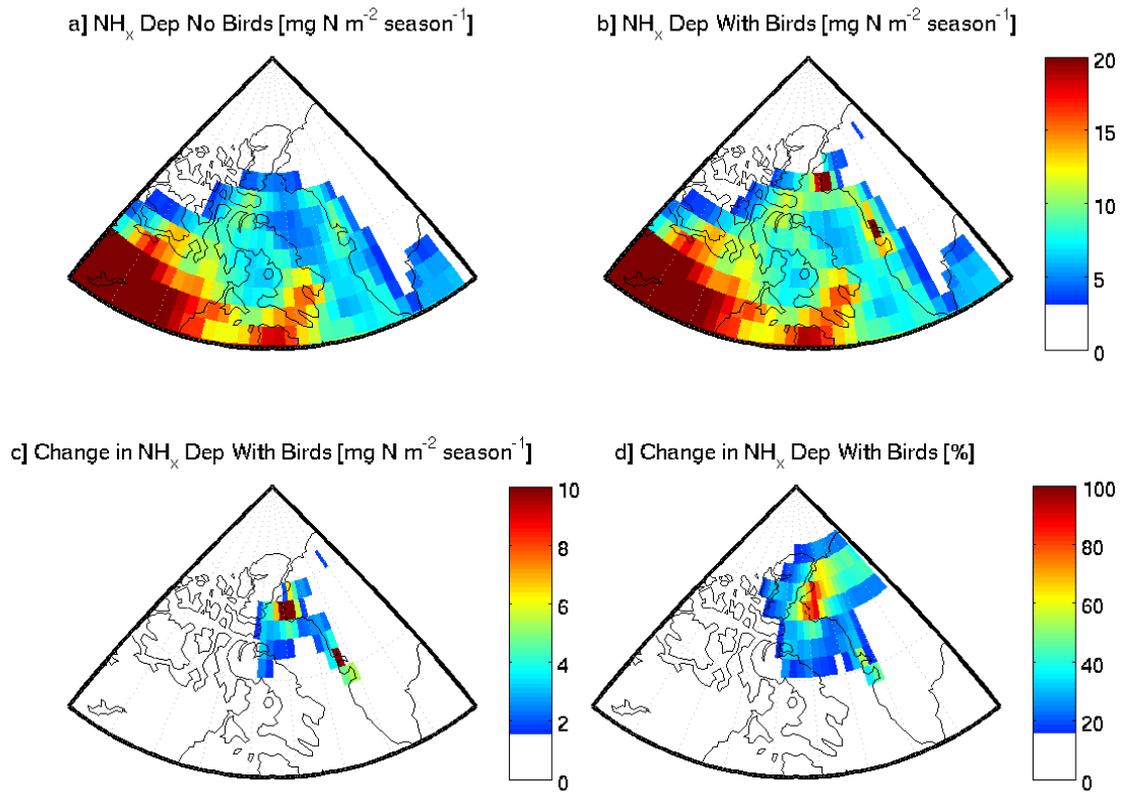


1
 2 Figure 6. GEOS-Chem simulation of NH_3 mixing ratio (ppb) of the July monthly mean surface
 3 layer for (a) no seabird emissions and (b) with seabird emissions. Circles in (a) represent the
 4 ship track coloured by NH_3 measurements. Panels (c) and (d) show GEOS-Chem simulations
 5 for the ammonium to non-sea salt sulphate ratio during the same period for (c) no seabird
 6 emissions and (d) with seabird emissions. The star indicates the average ratio observed at Alert
 7 during July.

8



1
 2 Figure 7. PES plots of FLEXPART-WRF seven day retroplumes from the ship's location on
 3 (a) 14 July 00:00, (b) 26 July 00:00, (c) 2 August 00:00, (d) 3 August 00:00 and (e) 4 August
 4 00:00. The ship track is shown in black and the ship location at the release time is indicated in
 5 red. Colors show the air mass residence time prior to arrival at the ship (PES) in seconds. The
 6 plume centroid locations at 1 and 2 days (the approximate lifetime of NH_3) before release are
 7 shown (numbers 1 and 2). Purple circles represent the location of bird colonies with the size of
 8 each circle indicating the magnitude of estimated NH_3 emissions (in $\text{Mg NH}_3 \text{ yr}^{-1}$). Blue circles
 9 show the location of wildfires from the NASA FIRMS measurements of fire radiative power
 10 from July 20-26 (in MW). The bottom panel is a time series of $\text{NH}_3(\text{g})$ and particle-phase NH_4^+
 11 and SO_4^{2-} measured by the AIM-IC with arrows indicating times of retroplume initiation in the
 12 upper panels. The NASA FIRMS dataset was provided by LANCE FIRMS operated by
 13 NASA/GSFC/ESDIS with funding from NASA/HQ.



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2 Figure 8. GEOS-Chem simulation of for total NH_x deposition (in $\text{mg N m}^{-2} \text{ season}^{-1}$) for the
 3 months May to September (inclusive). Panel (a) does not include seabird emissions, whereas
 4 the panel (b) does. The difference in total NH_x deposition between the two emissions scenarios
 5 (with birds minus without birds) is shown in panels (c) and (d) as an absolute amount and
 6 percentage increase, respectively.

7

1 **Supplemental**

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

Date and Time (UTC)	Lat (°N)	Lon (°W)	[NH _x] (nM)	SST (°C)
2014-07-15 9:12	69.3672	64.8667	< 20	2.68
2014-07-17 21:42	74.1566	80.4861	< 20	6.18
2014-07-19 13:15	74.1084	83.4386	< 20	3.58
2014-07-19 19:21	74.0991	83.4067	< 20	3.38
2014-07-20 17:08	74.2391	91.5339	< 20	-0.54
2014-07-20 19:18	74.2339	91.4947	< 20	-0.59
2014-07-22 9:32	74.3199	94.9029	< 20	-0.15
2014-07-27 15:37	73.2906	63.6075	22	2.99
2014-07-28 17:43	73.2611	57.8854	20	5.73
2014-07-29 22:26	75.4001	61.6649	< 20	5.06
2014-07-30 18:44	76.3347	71.2126	58	3.06
2014-07-30 21:42	76.3212	71.1668	49	3.18
2014-07-25 17:00	74.4525	89.2145	380	0.82
2014-07-25 19:00	74.4114	87.6705	104	3.21
2014-07-25 21:30	74.4583	85.6265	< 20	3.16
2014-07-25 23:00	74.449	84.4133	136	4.4
2014-07-16 10:30	71.5087	70.2804	< 20	5.34
2014-07-31 15:30	76.3056	73.2270	< 20	4.5
2014-08-01 1:30	76.2675	74.5992	< 20	4.32
2014-08-01 10:30	76.3137	75.7749	< 20	4.69
2014-08-01 21:40	76.3708	77.4110	< 20	2.67
2014-08-02 17:40	78.461	73.8764	294	1.84
2014-08-02 18:20	78.5946	73.5861	310	1.11
2014-08-02 19:30	78.8293	73.0194	< 20	0.84
2014-08-02 20:20	78.9863	72.5310	44	0.87
2014-08-02 20:40	79.0496	72.3455	42	0.96
2014-08-02 21:30	79.2011	71.7628	275	0.94
2014-08-02 21:40	79.2245	71.6052	176	0.96
2014-08-02 22:30	79.3809	71.1979	< 20	2.22
2014-08-02 22:40	79.401	71.0861	58	2.13
2014-08-03 16:50	81.3601	63.9560	54	-0.59
2014-08-04 6:30	80.7955	67.3011	< 20	-0.1
2014-08-04 18:10	79.9931	69.7773	< 20	0.46
2014-08-05 8:30	79.3461	71.8578	< 20	2.68
2014-08-06 1:50	79.0015	73.2046	< 20	1.99
2014-08-06 15:50	77.3259	75.7041	20	3.63
2014-08-07 12:40	74.7331	78.3273	< 20	4.5
2014-08-07 12:50	74.7019	78.3784	26	4.65

3

1 Table S2. Melt pond parameters relevant for determining surface-air NH₃ exchange

Date and Time (UTC)	Lat (°N)	Lon (°W)	[NH _x] (nM)	Temp (°C)	pH	Salinity
2014-07-18 18:00	73.5191	80.9863	706	1.86	7.2	5.2
2014-07-18 18:00	73.5191	80.9863	896	1.82	7.1	4.1
2014-07-21 2:00	74.2795	91.6322	779	0.42	6.7	1.3
2014-07-21 2:00	74.2795	91.6322	1042	0.31	6.7	0.4
2014-07-21 2:00	74.2795	91.6322	739	0.23	6.7	0.2
2014-07-21 18:00	74.2387	92.2041	1262	0.21	6.9	1.1
2014-07-21 18:00	74.2387	92.2041	642	0.21	6.9	0.9
2014-07-23 17:30	74.6033	94.9108	< 20	0.80	7.0	8.1
2014-07-23 17:30	74.6033	94.9108	< 20	0.23	7.0	8.5

2