

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

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

9 martin.johnson@uea.ac.uk

10 Received and published: 21 November 2015

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 NH<sub>3</sub> 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 NH<sub>3</sub>  
41 emissions to remain in the gas-phase (i.e. “pushing” it into the ocean):

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40

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

Specific comments/corrections:

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

The following sentence has been expanded to clarify the impact on NH<sub>3</sub>-to-NH<sub>4</sub><sup>+</sup> partitioning:

“Colder SST reduces the emission potential due to increased solubility of NH<sub>3</sub> (because of both reduced NH<sub>3(aq)</sub> volatility and increased partitioning of NH<sub>3(aq)</sub> to NH<sub>4<sup>+</sup>(aq)</sub>); 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<sub>4</sub> - could this have more of an influence?

The impact of NH<sub>4</sub><sup>+</sup> transport from southern latitudes has little impact on NH<sub>x</sub> 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<sub>x</sub> is gas-phase NH<sub>3</sub> providing further evidence that the role of NH<sub>4</sub><sup>+</sup> transport is minor with respect to the summertime Arctic NH<sub>x</sub> budget near the surface.

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

-why use H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> is used to increase the collection efficiency of SO<sub>2</sub> (by oxidizing it to SO<sub>4</sub><sup>2-</sup>). 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<sub>3</sub> (Hsu and Clair, 2015; Markovic et al., 2012). Furthermore, acidifying the denuder solution would reduce the solubility of acidic gases (e.g. HNO<sub>3</sub>, HONO, organic acids). This has been clarified in the text:

“...dissolved in a 2 mM H<sub>2</sub>O<sub>2</sub> solution (to enhance the solubility of SO<sub>2</sub>)” (inserted in Page 29980, line 4).

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41

-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<sub>2.5</sub> 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<sup>-1</sup> each (so the flow rate through each sample line is 10 mL hr<sup>-1</sup>, since each line feeds only two syringes). After one hour of sampling the syringes are automatically injected onto both a cation IC and anion IC for quantification of dissolved ions. The mole loading on each syringe is related back to an atmospheric concentration by use of a calibration curve (converting IC peak area to moles) and average air flow during sample time (to give units of mole m<sup>-3</sup>).

-Seawater/melt pond 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  $\text{NH}_x$  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 '( $\text{NH}_x$  napprox  $\text{NH}_3$ ) to after 'SO4<sup>2-</sup>'.

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  $\text{H}_2\text{SO}_4$  and  $\text{NH}_4$ , 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  $\text{NH}_4/\text{SO}_4$  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  $\text{NH}_4^+$  moles to  $2*\text{SO}_4^{2-}$  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  $\text{NH}_3$  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  $20 \text{ neq m}^{-3}$  of  $\text{SO}_4^{2-}$  and  
15  $19.98 \text{ neq m}^{-3}$   $\text{NH}_4^+$  at 85% RH will have a pH of  $\sim 3.1$  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)  $\text{NH}_3$  measurements below the detection limit (only 2 instances). This has been clarified in  
23 the figure legend.

## 24 25 References

26  
27 Holmes, R. M., Aminot, A., K erouel, R., Hooker, B. A and Peterson, B. J.: A simple and precise  
28 method for measuring ammonium in marine and freshwater ecosystems, *Can. J. Fish. Aquat.*  
29 *Sci.*, 56(10), 1801–1808, doi:10.1139/f99-128, 1999.

30 Hsu, Y.-M. and Clair, T. A.: Measurement of fine particulate matter water-soluble inorganic  
31 species and precursor gases in the Alberta Oil Sands Region using an improved  
32 semicontinuous monitor, *J. Air Waste Manage.*, 65(4), 423-435, 2015.

33 Markovic, M. Z., VandenBoer, T. C. and Murphy, J. G.: Characterization and optimization of  
34 an online system for the simultaneous measurement of atmospheric water-soluble constituents  
35 in the gas and particle phases, *J. Environ. Monit.*, 14(7), 1872, doi:10.1039/c2em00004k, 2012.

36  
37 Stohl, A.: Characteristics of atmospheric transport into the Arctic troposphere, *J. Geophys.*  
38 *Res.-Atmos.*, 111, D11306, 2006.

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

## 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  $\text{ng m}^{-3}$  versus  $\text{nmol m}^{-3}$  is two-fold: 1) the flux calculations (in  
19  $\text{ng m}^{-2} \text{s}^{-1}$ ) are more intuitive with  $\text{ng m}^{-3}$ , and 2) several publications of sea-air  $\text{NH}_3$  exchange  
20 (Asman et al., 1999; Greenaert et al., 1998) also use mass units. Furthermore, terrestrial  $\text{NH}_3$   
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  $\text{NH}_3$  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<sub>2.5</sub> impactor atop the inlet which removes coarse mode sea salt  
8 particles generated by ship/wave action. In addition, NH<sub>x</sub> is such a minor constituent of  
9 seawater that ship-generated sea salt would not affect the NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup> dataset. Also, Fig. 4  
10 reveals SO<sub>4</sub><sup>2-</sup> ≈ NH<sub>4</sub><sup>+</sup> on an equivalent basis suggesting there is negligible sea salt SO<sub>4</sub><sup>2-</sup>,  
11 otherwise SO<sub>4</sub><sup>2-</sup> would be greater than NH<sub>4</sub><sup>+</sup>.

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<sub>2.5</sub> 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 NH<sub>3</sub> vs particulate NH<sub>4</sub> and gas phase NH<sub>3</sub> vs the degree of aerosol  
9 neutralisation (NH<sub>4</sub>:SO<sub>4</sub> ratio). Assuming the analysis in Figure 5 is correct, the cruise data  
10 should follow a similar trend – i.e. higher NH<sub>4</sub> concentrations/greater aerosol neutralisation  
11 when gas phase NH<sub>3</sub> concentrations increased.

12

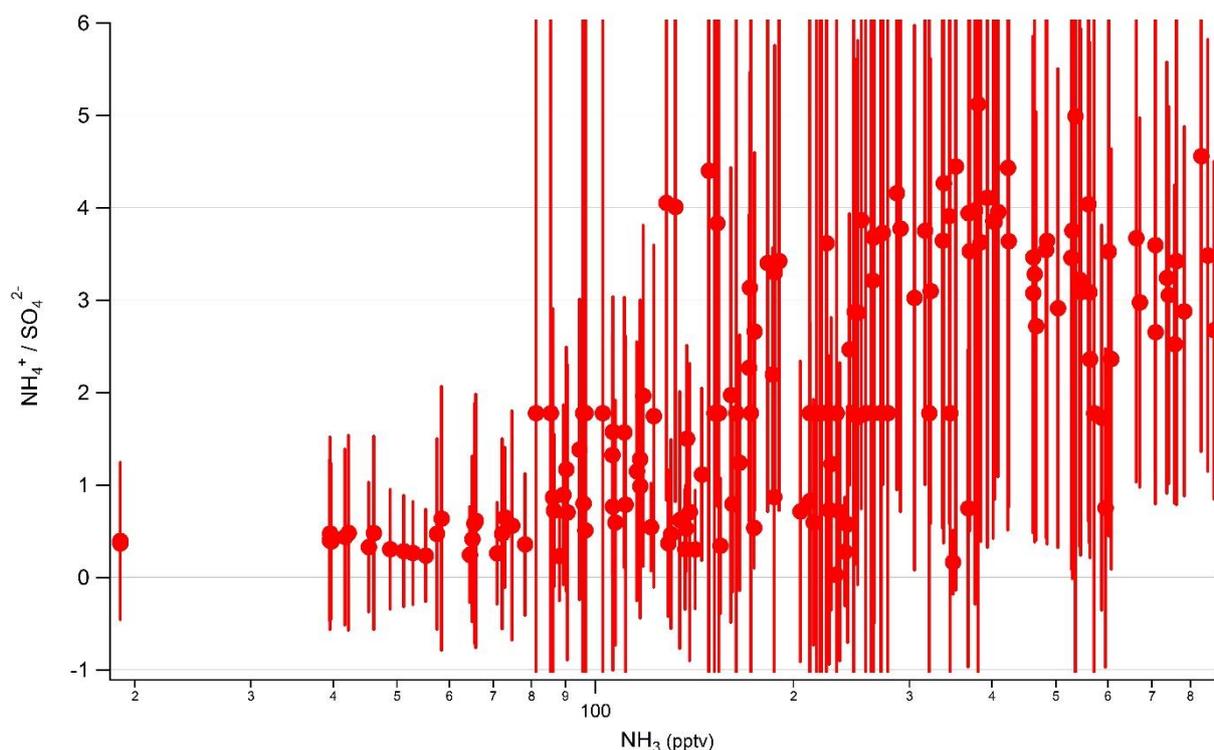
13 Since there is typically a much higher loading of NH<sub>3</sub> than both NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, the NH<sub>4</sub><sup>+</sup>  
14 concentrations should not correlate with NH<sub>3</sub> concentrations. This is because the sulphate is  
15 already saturated with NH<sub>4</sub><sup>+</sup> so any additional increase in NH<sub>3</sub> will not result in a noticeable  
16 increase in NH<sub>4</sub><sup>+</sup>.

17

18 A similar trend occurs with neutralization ratio. As the ratio of NH<sub>4</sub><sup>+</sup>:SO<sub>4</sub><sup>2-</sup> equivalents  
19 approaches 1 it is not very sensitive to NH<sub>3</sub> concentrations. This is shown in the plot below of  
20 NH<sub>4</sub><sup>+</sup>:SO<sub>4</sub><sup>2-</sup> versus NH<sub>3</sub> (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 NH<sub>3</sub> mixing ratios (<100 pptv) there is insufficient NH<sub>3</sub> to neutralize the  
25 SO<sub>4</sub><sup>2-</sup> (molar ratio less than 2). However, above this approximate threshold the ratio is  
26 insensitive to NH<sub>3</sub> since the sulphate is already neutralized. We chose not to include this figure  
27 in the manuscript for two reasons: 1) NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> 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 NH<sub>4</sub><sup>+</sup> ≈ SO<sub>4</sub><sup>2-</sup> the SO<sub>4</sub><sup>2-</sup> is roughly neutralized).



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25

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  $\text{neq m}^{-3}$ , which is the  $\text{nmol m}^{-3}$  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  $\text{SO}_4^{2-}$  aerosol has an equivalent ratio of  $\text{NH}_4^+ : \text{SO}_4^{2-} = 1$ , meaning there is 1 equivalent ( $\equiv 1$  mole) of  $\text{NH}_4^+$  for every 1 equivalent ( $\equiv 0.5$  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  $\text{NH}_3$  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 ( $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) 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  $\text{NH}_4^+$  relative to the AIM-IC due to volatilization of  $\text{NH}_4\text{NO}_3$  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  $\text{NH}_4\text{NO}_3$ .

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  $\text{NH}_3$  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  $\text{NH}_3$  which is consistent with our  
3 interpretation of the Hi-Vol data: that is suggests significant regional source(s) of  $\text{NH}_3$ .

4  
5 These issues of under and overestimation of  $\text{NH}_3$  by Hi-Vol samplers has been added to the  
6 text:

7  
8 “In warm environments volatilization of  $\text{NH}_4\text{NO}_3$  off of filters can cause an underestimation of  
9  $\text{NH}_4^+$ , but this is not expected to be an issue at Alert due to cold weather and low loadings of  
10  $\text{NH}_4\text{NO}_3$ .” (inserted Page 29989, line 11)

11  
12 “However, there is no denuder upstream of the Hi-Vol filters to remove  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_x$  climatology and,  
18 crucially, assumes that the atmospheric  $\text{NH}_3$  concentration is zero. This leads to an  
19 overestimate of the oceanic  $\text{NH}_3$  emissions. Using a different flux estimate would make the  
20 discrepancy in  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_4$  deposition. The particulate  
34  $\text{NH}_4$  contribution is likely to be from the same source (i.e. volatile gas phase  $\text{NH}_3$  is emitted  
35 from seabird colonies. Some neutralises whatever  $\text{SO}_4$  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)  $\text{NH}_x$  deposition and do include  $\text{NH}_4^+$   
39 deposition. The majority of  $\text{NH}_x$  deposition results from wet/dry deposition of  $\text{NH}_3$ ;  $\text{NH}_4^+$   
40 deposition is minor in comparison. We agree that the majority of  $\text{NH}_4^+$  likely stems from the  
41 same source as gas-phase  $\text{NH}_3$  (as the referee points out). We have clarified the minor  
42 contribution of  $\text{NH}_4^+$  in the text:

1  
2 [“The majority of NH<sub>x</sub> deposition is caused by NH<sub>3</sub> as opposed to NH<sub>4</sub><sup>+</sup>.”](#) (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**

11 [Asman, W. A. H., Harrison, R. M. and Ottley, C. J.: Estimation of the net air-sea flux of](#)  
12 [ammonia over the southern bight of the North Sea, Atmos. Environ., 28\(22\), 3647–3654,](#)  
13 [doi:10.1016/1352-2310\(94\)00192-N, 1994.](#)

14 [Geernaert, L. L. S., Geernaert, G. L., Granby, K. and Asman, W. A. H.: Fluxes of soluble](#)  
15 [gases in the marine atmosphere surface layer, Tellus, 50B, 111–127, 1998.](#)

16 [Hsu, Y.-M. and Clair, T. A.: Measurement of fine particulate matter water-soluble inorganic](#)  
17 [species and precursor gases in the Alberta Oil Sands Region using an improved](#)  
18 [semicontinuous monitor, J. Air Waste Manage., 65\(4\), 423-435, 2015.](#)

19 [Zhang, L., Wright, L. P. and Asman, W. A. H.: Bi-directional air-surface exchange of](#)  
20 [atmospheric ammonia: A review of measurements and a development of a big-leaf model for](#)  
21 [applications in regional-scale air-quality models, J. Geophys. Res., 115, D20310, 2010.](#)

22  
23

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

3  
4 G. R. Wentworth<sup>1</sup>, J. G. Murphy<sup>1</sup>, B. Croft<sup>2</sup>, R. V. Martin<sup>2</sup>, J. R. Pierce<sup>3,2</sup>, J.-S.  
5 Côté<sup>4</sup>, I. Courchesne<sup>4</sup>, J.-É. Tremblay<sup>4</sup>, J. Gagnon<sup>4</sup>, J. L. Thomas<sup>5</sup>, S. Sharma<sup>6</sup>, D.  
6 Toom-Sauntry<sup>6</sup>, A. Chivulescu<sup>6</sup>, M. Levasseur<sup>4</sup>, and J. P. D. Abbatt<sup>1</sup>

7 [1]{Department of Chemistry, University of Toronto, 80 St. George Street, M5S 3H6, Toronto,  
8 Canada}

9 [2]{Department of Physics and Atmospheric Science, Dalhousie University, 6310 Coburg  
10 Road, B3H 4R2, Halifax, Canada}

11 [3]{Department of Atmospheric Science, Colorado State University, 3915 W. Laporte Ave.,  
12 80523, Fort Collins, USA}

13 [4]{Department of Biology, Université Laval, 1045 avenue de la Médecine, G1V 0A6, Québec  
14 City, Canada}

15 [5]{Sorbonne Universités, UPMC Univ. Paris 06; Université Versailles St-Quentin;  
16 CNRS/INSU, LATMOS-IPSL, Paris, France}

17 [6]{Science and Technology Branch, Environment Canada, 4905 Dufferin Street, M3H 5T4,  
18 Toronto, Canada}

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  $\text{ng m}^{-3}$  (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 ( $\chi$ ), 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  $\chi_{\text{ocean}}$  and  $\chi_{\text{MP}}$  (<0.4-10  $\text{ng m}^{-3}$ ) indicating these surface pools are net sinks of  $\text{NH}_3$ . Flux

1 calculations estimate average net downward fluxes of 1.4 and 1.1 ng m<sup>-2</sup> s<sup>-1</sup> for the open ocean  
2 and melt ponds, respectively. Sufficient NH<sub>3(g)</sub> was present to neutralize non-sea salt sulphate  
3 (nss-SO<sub>4</sub><sup>2-</sup>) in the boundary layer during most of the study. This finding was corroborated with  
4 a historical dataset of PM<sub>2.5</sub> composition from Alert, NU (82°30' N, 62°20' W) wherein the  
5 median ratio of NH<sub>4</sub><sup>+</sup>/nss-SO<sub>4</sub><sup>2-</sup> 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<sub>3(g)</sub>  
7 emissions from seabird guano on boundary-layer composition and nss-SO<sub>4</sub><sup>2-</sup> neutralization. A  
8 GEOS-Chem simulation without seabird emissions underestimated boundary layer NH<sub>3(g)</sub> by  
9 several orders of magnitude and yielded highly acidic aerosol. A simulation that included  
10 seabird NH<sub>3</sub> emissions was in better agreement with observations for both NH<sub>3(g)</sub>  
11 concentrations and nss-SO<sub>4</sub><sup>2-</sup> neutralization. This is strong evidence that seabird colonies are  
12 significant sources of NH<sub>3</sub> 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 NH<sub>3</sub>, 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<sub>3(g)</sub>) 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<sub>3(g)</sub> can impact climate by increasing rates of new particle  
23 formation via stabilization of sulphuric acid clusters (Kirkby et al., 2011). Gas-phase NH<sub>3</sub> is  
24 also able to partition to acidic fine particulate matter (PM<sub>2.5</sub>) to form particulate-phase  
25 ammonium (NH<sub>4</sub><sup>+(p)</sup>), 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<sub>3(g)</sub> 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<sub>3(g)</sub>

1 range from 35-54 Tg N yr<sup>-1</sup>; 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<sub>3(g)</sub> to the marine boundary layer and delivers an estimated 6-8 Tg N yr<sup>-1</sup> to the atmosphere  
5 globally (Sutton et al., 2013). The dominant sources of oceanic NH<sub>x</sub> (≡NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>) include  
6 remineralisation of organic matter by bacteria and phytoplankton excretion (Carpenter et al.,  
7 2012). However, NH<sub>x</sub> 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<sub>3(sw)</sub>) available for exchange with the atmosphere.

10 In order to compute sea-air NH<sub>3</sub> fluxes, simultaneous measurements of both atmospheric NH<sub>3(g)</sub>  
11 and oceanic NH<sub>x</sub> 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<sub>3(g)</sub>] and oceanic [NH<sub>x</sub>], leading to extremely  
15 large uncertainties for both the direction and magnitude of global sea-air NH<sub>3</sub> 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<sub>3(g)</sub>, 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 NH<sub>3</sub> (because of both reduced NH<sub>3(aq)</sub>  
21 volatility and increased partitioning of NH<sub>3(aq)</sub> to NH<sub>4</sub><sup>+</sup>(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 NH<sub>3</sub> fluxes above the Arctic Circle (66°33' N) during a summer  
24 time study in the Norwegian Sea. Therefore additional measurements of sea-air NH<sub>3</sub> fluxes in  
25 the High Arctic are invaluable for improving constraints on oceanic NH<sub>3</sub> 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<sub>3(g)</sub> fluxes despite the abundant presence of melt ponds  
32 in the summertime Arctic.

1 Quantifying sea-air and melt pond-air  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  emission to the atmosphere can affect the extent of non-sea salt sulphate ( $\text{nss-SO}_4^{2-}$ )  
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  $\text{NH}_x$  and  $\text{nss-SO}_4^{2-}$ . 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  $\text{NH}_3$  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  $\text{NH}_3$
- 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  $\text{NH}_3$  throughout the summertime
- 6 Arctic marine boundary layer
- 7 4) Evaluate whether atmospheric  $\text{NH}_x$  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  $\text{PM}_{2.5}$  ( $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ ) and their precursor gases  
21 ( $\text{NH}_3$ ,  $\text{SO}_2$ , and  $\text{HNO}_3$ ) 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  $3 \text{ L min}^{-1}$ . Air then enters a parallel plate wet denuder where water-soluble gases  
28 are dissolved in a 2 mM  $\text{H}_2\text{O}_2$  solution (to enhance the solubility of  $\text{SO}_2$ ) 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<sub>2.5</sub> 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  $4.5 \text{ L min}^{-1}$  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  $29 \text{ ng m}^{-3}$  ( $\text{NH}_3$ ), 17 pptv ( $\text{SO}_2$ ), 8 pptv  
26 ( $\text{HNO}_3$ ),  $12 \text{ ng m}^{-3}$  ( $\text{NH}_4^+$ ),  $36 \text{ ng m}^{-3}$  ( $\text{SO}_4^{2-}$ ), and  $64 \text{ ng m}^{-3}$  ( $\text{NO}_3^-$ ). For the convenience of  
27 flux calculations,  $\text{NH}_3$  values are reported in  $\text{ng m}^{-3}$  (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 <  $36^\circ$ . Similar cut-offs for speed and wind  
4 direction have been used in previous studies of  $\text{NH}_3$  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  $35 \text{ g kg}^{-1}$ , 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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  concentration signifies the ambient  
31 value at which the net flux changes direction, and is known as the compensation point (denoted

1  $\chi$ ). In other words, one expects a net downwards flux if ambient  $\text{NH}_{3(g)}$  exceeds  $\chi$  and a net  
 2 upward flux if it is below  $\chi$ . 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  $\text{NH}_3$  across this interface is predominantly dictated by the air-side transfer velocity,  
 6 given the relatively high water solubility of  $\text{NH}_3$  (Liss, 1983). Hence, the equation to calculate  
 7 sea-air  $\text{NH}_3$  fluxes is:

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

9 where  $F_{\text{NH}_3}$  is the sea-air flux of  $\text{NH}_3$  ( $\text{ng m}^{-2} \text{ s}^{-1}$ ),  $k_g$  is the air-side transfer velocity ( $\text{m s}^{-1}$ ),  
 10  $\text{NH}_{3(g)}$  is the measured ammonia concentration ( $\text{nmol m}^{-3}$ ),  $\chi$  is the compensation point ( $\text{nmol}$   
 11  $\text{m}^{-3}$ ), and the molecular weight of  $17.03 \text{ g mol}^{-1}$  is to convert  $\text{nmol}$  to  $\text{ng}$ . 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 ( $\text{m s}^{-1}$ ) and  $\text{MW}$  is the molecular weight of the gas of interest (17.03  
 16 for  $\text{NH}_3$ ). Although simple, this parameterization has been used previously to estimate sea-air  
 17  $\text{NH}_3$  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  $\chi$ :

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

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 ( $\text{nmol m}^{-3}$ ). 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  $\text{NH}_x$  ( $[\text{NH}_{x(\text{sw})}]$ ), 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](http://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 SO<sub>2</sub> (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 SO<sub>2</sub> occurs in clouds by reaction with H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> and  
4 in the gas phase with OH (Alexander et al., 2009) and DMS oxidation occurs by reaction with  
5 OH and NO<sub>3</sub>.

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<sup>-1</sup> 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](http://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 NH<sub>3</sub> Fluxes**

5 Figure 1 shows the ambient NH<sub>3(g)</sub> concentrations measured by the AIM-IC throughout the  
6 cruise. Measured values of NH<sub>3(g)</sub> range between 30-650 ng m<sup>-3</sup> with the highest values  
7 occurring in Lancaster Sound as the ship was steaming eastward into Baffin Bay. Only two  
8 measurements of NH<sub>3</sub> were below the detection limit (29 ng m<sup>-3</sup>) throughout the entire cruise.  
9 NH<sub>3</sub> consistently exceeded 100 ng m<sup>-3</sup> during later parts of the cruise along the eastern shores  
10 of Ellesmere Island and western shores of Greenland. Lower values (<100 ng m<sup>-3</sup>) were  
11 observed at the beginning of the campaign along the eastern shores of Baffin Island.  
12 Measurements of NH<sub>3(g)</sub> 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<sub>3(g)</sub> between 20-300 ng  
15 m<sup>-3</sup> in the Norwegian Sea during spring and summer, but a lower range (20-90 ng m<sup>-3</sup>) 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<sup>-3</sup>) in a study lasting from February to October.

18 The relevant measurements needed to calculate  $\chi$  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<sub>x</sub>] 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  $\chi$  for both the  
27 surface ocean and melt pond samples. For samples with [NH<sub>x</sub>] 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 ( $\chi_{\text{ocean}}$ ) and melt ponds ( $\chi_{\text{MP}}$ ) are shown in Fig. 2. Also shown  
30 is the range for the nearest valid measurement (see section 2.2) of ambient NH<sub>3(g)</sub>. The NH<sub>3(g)</sub>  
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  $\chi_{\text{ocean}}$  and  $\chi_{\text{MP}}$  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  $\chi_{\text{ocean}}$  by less than 20 %.

13 Figure 3 shows the magnitude of the sea-air and melt pond-air flux of  $\text{NH}_3$ . 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  $\text{NH}_4^+$  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  $\text{NH}_4^+$ , 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  $\text{N}_2$ -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  $\text{neq m}^{-3}$ ) 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 ( $\text{nss-SO}_4^{2-}$ ), which is commonly reported for

1 marine boundary layer studies. High and variable backgrounds of  $\text{Na}^+$  from the AIM-IC  
2 prevented the calculation of  $\text{nss-SO}_4^{2-}$ , hence this dataset provides an upper limit for  $\text{nss-SO}_4^{2-}$   
3 . Given the low wind speeds ( $< 5 \text{ m s}^{-1}$ ) that dominated the campaign, it is likely the  $\text{nss-SO}_4^{2-}$   
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  $\text{SO}_2$ ,  $\text{HNO}_3$  and  $\text{NO}_3^-$  were almost always below their respective detection  
6 limits.

7 Particle loadings of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  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  $\text{NH}_3$  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  $\text{NH}_4^+$  or  $\text{SO}_4^{2-}$  (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  $20 \text{ neq m}^{-3}$  of  $\text{SO}_4^{2-}$  and  $19.98 \text{ neq m}^{-3}$   
17  $\text{NH}_4^+$  at 85% RH will have a pH of  $\sim 3.1$  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 ( $82.50^\circ \text{N}$ ,  $62.33^\circ \text{W}$ ) 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  $\text{NO}_3^-$  is minor and has  
23 not been included in this analysis. In warm environments volatilization of  $\text{NH}_4\text{NO}_3$  off of filters  
24 can cause an underestimation of  $\text{NH}_4^+$ , but this is not expected to be an issue at Alert due to  
25 cold weather and low loadings of  $\text{NH}_4\text{NO}_3$ . During July and August the  $\text{nss-SO}_4^{2-}$  is, on average,  
26 completely neutralized by the  $\text{NH}_4^+$  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  $\text{nss-SO}_4^{2-}$  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  $\text{NH}_3$  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  $\text{NH}_3$  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 NH<sub>3</sub> 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<sub>x</sub> ≈  
5 NH<sub>4</sub><sup>+</sup>) 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 NH<sub>3</sub> in the Baffin Bay region. Decomposition of uric acid in seabird guano (excreta)  
11 has been recognized as a significant source of NH<sub>3</sub> where large colonies exist (Blackall et al.,  
12 2007; Wilson et al., 2004). However, studies measuring NH<sub>3</sub> from seabird colonies are limited  
13 due to the remoteness of most colonies and technical challenges in quantifying NH<sub>3</sub> 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<sub>3(g)</sub> from seabird guano. The authors employed a  
19 bioenergetics model, first developed by Wilson et al. (2004), to calculate the NH<sub>3(g)</sub> emissions  
20 (in g bird<sup>-1</sup> yr<sup>-1</sup>) 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 NH<sub>3</sub> per year. Although this is less than 2% of total global NH<sub>3(g)</sub> 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 NH<sub>3</sub> across the Baffin Bay region, seabird  
26 colony NH<sub>3</sub> emissions were implemented in the GEOS-Chem model, and the impact on  
27 monthly mean surface layer NH<sub>3</sub> was examined. The NH<sub>3</sub> 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 NH<sub>3</sub> is equal to zero.](#) The Riddick et al. (2012, 2012b) seabird colony NH<sub>3</sub>

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  $50^{\circ}\text{N}$ . 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  $50^{\circ}\text{N}$ ) 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  $\text{NH}_3$  emissions. For instance, moisture increases the rate of uric acid degradation, and fluxes of  
20  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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,  $\text{NH}_3$  mixing ratios are underpredicted by several orders of magnitude.  
28 Surface  $\text{NH}_3$  is still underpredicted in Fig. 6b (with guano  $\text{NH}_3$  emissions) which could be the  
29 result of modelled emissions being independent of rainfall, which can substantially increase  
30  $\text{NH}_3$  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  $\text{NH}_3$  relative to  $\text{SO}_4^{2-}$  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  $\sim 1$ ) 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  $\text{NH}_3$  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  $\text{NH}_3$   
15 emissions, as well as to further corroborate the influence of seabird guano.

16 The significant impact of seabird colonies on  $[\text{NH}_{3(\text{g})}]$  is supported by the analysis of  
17 FLEXPART-WRF retro plumes shown in Fig. 7. Periods of low  $[\text{NH}_{3(\text{g})}]$  (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 ( $\sim 500$  m) where  $\text{NH}_3$  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  $[\text{NH}_{3(\text{g})}]$ . 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  $[\text{NH}_{3(\text{g})}]$ . A similar  $\text{NH}_{3(\text{g})}$  peak occurs on 3 August that can also be examined  
25 by using a retro plume analysis. Low  $\text{NH}_{3(\text{g})}$  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  $\text{NH}_{3(\text{g})}$ . In addition from August 2-4 the ship was north of  $79^\circ$  N and in  
31 the Eastern Canadian Arctic, hence it is unlikely that this increase in  $\text{NH}_3$  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  $\text{NH}_3$  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  $74^\circ \text{N}$ ) roughly 40% and 55% of the boundary layer  $\text{NH}_3$  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  $\text{NH}_3$  were  
14 approximately 95% and 5%, respectively. Wildfires in the NWT are an important but episodic  
15 source of summertime  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  and  
24  $\text{NH}_4^+$  (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<sup>-2</sup> yr<sup>-1</sup> (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<sup>-2</sup> yr<sup>-1</sup> (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<sup>-2</sup> yr<sup>-1</sup>, 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<sup>-2</sup> yr<sup>-1</sup> 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<sup>-2</sup> yr<sup>-1</sup>)  
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 N<sub>2</sub>-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 N<sub>2</sub>-fixation in the summertime Arctic Ocean mixed layer. The authors found that open ocean  
4 N<sub>2</sub>-fixation rates averaged 0.12 nM d<sup>-1</sup> 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<sup>-2</sup> which is comparable to inputs we calculate from guano-  
7 derived NH<sub>3</sub> 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<sub>3(g)</sub>.  
11 Concentrations of NH<sub>3(g)</sub> ranging from 30-650 ng m<sup>-3</sup> were observed and represent the first  
12 reported measurements of NH<sub>3(g)</sub> in the Canadian Arctic. An average downward flux of 1.4 ng  
13 m<sup>-2</sup> s<sup>-1</sup> into the Arctic Ocean was calculated, consistent with previous studies showing that  
14 higher latitude waters are a net NH<sub>3</sub> sink (Johnson et al., 2008). Melt ponds had a smaller net  
15 downward flux (1.1 ng m<sup>-2</sup> s<sup>-1</sup>) as well as a slightly ~~a~~ higher  $\chi$  as compared to the open ocean  
16 (median 2 ng m<sup>-3</sup> versus 0.8 ng m<sup>-3</sup>). To our knowledge, this is the first study to estimate melt  
17 pond-air NH<sub>3</sub> exchange despite the ubiquitous presence of melt ponds throughout the  
18 summertime Arctic.

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

26 It is also noteworthy that even though these melt ponds have significantly higher [NH<sub>x</sub>] than  
27 the open ocean (average of 670 nM versus 55 nM),  $\chi_{MP}$  is only marginally higher. More acidic  
28 pHs and slightly lower temperatures mitigate the effect of higher [NH<sub>x</sub>] on  $\chi$ . Chemical  
29 transport models (CTMs) that explicitly account for bi-directional NH<sub>3</sub> exchange typically  
30 require  $\chi$  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  $\chi_{ocean}$  and  $\chi_{MP}$  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 NH<sub>3</sub> exchange in the summertime Arctic.

3 To investigate the impact of NH<sub>3</sub> emissions from seabird guano, we examined GEOS-Chem  
4 simulations both with and without seabird colony NH<sub>3</sub> emissions. The seabird NH<sub>3</sub> 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<sub>3(g)</sub> 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<sub>3(g)</sub> observations and yielded more  
10 neutralized aerosol throughout most of the Baffin Bay region. The importance of seabird NH<sub>3</sub>  
11 emissions is also supported by analysis of FLEXPART-WRF retro plumes throughout the study  
12 period. Air masses enriched in NH<sub>3(g)</sub> had recently passed through regions with seabird colonies  
13 whereas periods of low NH<sub>3(g)</sub> 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<sub>3(g)</sub> in the summertime Arctic. FLEXPART-  
16 WRF and GEOS-Chem were also used to assess the influence of wildfires on NH<sub>3</sub>. Wildfires  
17 are an important but episodic source of NH<sub>3</sub> 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 NH<sub>3</sub> emissions from wildfires in the NWT on other regions in the Arctic.

20 Deposition estimates of NH<sub>x</sub> from GEOS-Chem during the seabird nesting season (May to  
21 September) exceed 10 mg N m<sup>-2</sup> season<sup>-1</sup> in grid cells close to large seabird colonies, which is  
22 on the lower end of microbial N<sub>2</sub>-fixation in Arctic tundra (Hobara et al., 2006). Hence, in some  
23 regions seabird-derived NH<sub>x</sub> could be a significant N-input to terrestrial Arctic ecosystems  
24 which are typically very N-sensitive. Estimates of NH<sub>3</sub> 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<sub>3(g)</sub> to the summertime Arctic boundary layer. Emissions appear to be significant enough to  
29 at least partially neutralize nss-SO<sub>4</sub><sup>2-</sup> 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 NH<sub>3</sub> emissions of Arctic seabird colonies. It is  
32 also important to quantify meteorological effects (e.g. rainfall, wind speed) on seabird

1 emissions. The NH<sub>3</sub> 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<sub>x</sub> elsewhere in the Arctic  
4 are needed to assess whether the impacts of seabirds observed in this study (substantial NH<sub>3(g)</sub>,  
5 nss-SO<sub>4</sub><sup>2-</sup> neutralization, and N-deposition) are relevant to the entire Arctic.

## 6 **Acknowledgements**

7 The authors are grateful for the hard work and dedication of the CCGS *Amundsen* crew. The  
8 authors also thank E. Mungall, A. Lee, V. Irish, H. Stark and J. J. B. Wentzell for help during  
9 mobilization, demobilization and calibration of the AIM-IC, as well as T. Papakyriakou and T.  
10 Burgers for providing meteorological data. The GEOS5-FP data used in this study/project have  
11 been provided by the Global Modeling and Assimilation Office (GMAO) at NASA Goddard  
12 Space Flight Center. The hi-volume sampler used for the Alert measurements was maintained  
13 and calibrated by D. Veber, as well as numerous other technicians and operators over the years.  
14 Acknowledgement is also extended to the crew at CFS Alert for maintaining the base year  
15 round. The fieldwork and model analysis was supported by NSERC's Climate Change and  
16 Atmospheric Research program, ArcticNet and NSERC. The QFED2 code and emissions data  
17 was provided by K. Travis and P. Kim. The NASA FIRMS data set was provided by LANCE  
18 FIRMS operated by NASA/GSFC/ESDIS with funding provided by NASA/HQ. G. R. W.  
19 acknowledges funding from the NSERC program Integrating Atmospheric Chemistry from  
20 Earth to Space (IACPES). Lastly, the authors wish to thank B. Christensen for providing  
21 logistical support throughout the project.

22

## 1 **References**

- 2 Abbatt, J. P. D., Benz, S., Cziczo, D. J., Kanji, Z., Lohmann, U. and Möhler, O.: Solid  
3 Ammonium Sulfate Aerosols as Ice Nuclei: A Pathway for Cirrus Cloud Formation, *Science*,  
4 313, 1770–1773, 2006.
- 5 Anderson, W. B. and Polis, G. A.: Nutrient fluxes from water to land : seabirds affect plant  
6 nutrient status on Gulf of California islands, *Oecologia*, 118, 324–332,  
7 doi:10.1007/s004420050733, 1999.
- 8 Asman, W. A. H., Harrison, R. M. and Ottley, C. J.: Estimation of the net air-sea flux of  
9 ammonia over the southern bight of the North Sea, *Atmos. Environ.*, 28(22), 3647–3654,  
10 doi:10.1016/1352-2310(94)00192-N, 1994.
- 11 Bash, J. O., Cooter, E. J., Dennis, R. L., Walker, J. T. and Pleim, J. E.: Evaluation of a  
12 regional air-quality model with bidirectional NH<sub>3</sub> exchange coupled to an agroecosystem  
13 model, *Biogeosciences*, 10(3), 1635–1645, doi:10.5194/bg-10-1635-2013, 2013.
- 14 Bell, T. G., Johnson, M. T., Jickells, T. D. and Liss, P. S.: Ammonia/ammonium dissociation  
15 coefficient in seawater: A significant numerical correction, *Environ. Chem.*, 5(3), 183–186,  
16 doi:10.1071/EN07032, 2008.
- 17 Blackall, T. D., Theobald, M. R., Milford, C., Hargreaves, K. J., Nemitz, E., Wilson, L. J.,  
18 Bull, J., Bacon, P. J., Hamer, K. C., Wanless, S. and Sutton, M. A.: Application of tracer ratio  
19 and inverse dispersion methods with boat-based plume measurements to estimate ammonia  
20 emissions from seabird colonies, *Water, Air, Soil Pollut. Focus*, 4(6), 279–285,  
21 doi:10.1007/s11267-004-3038-9, 2004.
- 22 Blackall, T. D., Wilson, L. J., Theobald, M. R., Milford, C., Nemitz, E., Bull, J., Bacon, P. J.,  
23 Hamer, K. C., Wanless, S. and Sutton, M. A.: Ammonia emissions from seabird colonies,  
24 *Geophys. Res. Lett.*, 34(10), 1–5, doi:10.1029/2006GL028928, 2007.
- 25 Blais, M., Tremblay, J.-É., Jungblut, A. D., Gagnon, J., Martin, M. and Lovejoy, C.: Nitrogen  
26 fixation and identification of potential diazotrophs in the Canadian Arctic, *Global*  
27 *Biogeochem. Cycles*, 26, GB3022, 2012.
- 28 Bouwman, A. F., Lee, D. S., Asman, W. A. H., Dentener, F. J., Van Der Hoek, K. W.,  
29 Olivier, J. G. J. and Tg, N.: A global high-resolution emission inventory for ammonia, *Global*  
30 *Biogeochem. Cycles*, 11(4), 561–587, 1997.
- 31 Breider, T. J., Mickley, L. J., Jacob, D. J., Wang, Q., Fisher, J. A., Chang, R. Y.-W. and  
32 Alexander, B.: Annual distributions and sources of Arctic aerosol components, aerosol optical  
33 depth, and aerosol absorption, *J. Geophys. Res. Atmos.*, 119, 4107–4124,  
34 doi:10.1002/2013JD020996, 2014.
- 35 Brioude, J., Arnold, D., Stohl, A., Cassiani, M., Morton, D., Seibert, P., Agevine, W., Evan,  
36 S., Dingwell, A., Fast, J. D., Easter, R. C., Pisso, I., Burkhardt, J., and Wotawa, G.: The  
37 Lagrangian particle dispersion model FLEXPART-WRF version 3.1., *Geosci. Model Dev.*, 6,  
38 1889–1904, doi:10.5194/gmd-6-1889-2013, 2013.

- 1 Carpenter, L. J., Archer, S. D. and Beale, R.: Ocean-atmosphere trace gas exchange, *Chem.*  
2 *Soc. Rev.*, 41, 6473–6506, doi:10.1039/c2cs35121h, 2012.
- 3 Chang, R. Y.-W., Leck, C., Graus, M., Müller, M., Paatero, J., Burkhardt, J. F., Stohl, A., Orr,  
4 L. H., Hayden, K., Li, S. M., Hansel, A., Tjernström, M., Leaitch, W. R. and Abbatt, J. P. D.:  
5 Aerosol composition and sources in the central Arctic Ocean during ASCOS, *Atmos. Chem.*  
6 *Phys.*, 11(20), 10619–10636, doi:10.5194/acp-11-10619-2011, 2011.
- 7 Chapin, D. M. and Bledsoe, C.: Nitrogen fixation in arctic plant communities, in *Arctic*  
8 *Ecosystems in a Changing Climate: An Ecophysiological Perspective*, edited by R. S. Chapin  
9 III, R. L. Jeffries, J. F. Reynolds, G. R. Shaver, and J. Svoboda, pp. 301–319, Academic  
10 Press, San Diego., 1992.
- 11 Chou, M.-D. and Suarez, M. J.: An efficient thermal infrared radiation parameterization for  
12 use in general circulation models, National Aeronautics and Space Administration, NASA  
13 Tech. Memo, 84 pp., 1994.
- 14 Cleveland, C. C., Townsend, A. R., Schimel, D. S., Fisher, H., Hedin, L. O., Perakis, S.,  
15 Latty, E. F., Fischer, C. Von, Elseroad, A. and Wasson, M. F.: Global patterns of terrestrial  
16 biological nitrogen (N<sub>2</sub>) fixation in natural ecosystems, *Global Biogeochem. Cycles*, 13(2),  
17 623–645, doi:10.1029/1999GB900014, 1999.
- 18 Darmenov, A. and da Silva, A.: The Quick Fire Emissions Dataset (QFED) – Documentation  
19 of versions 2.1, 2.2 and 2.4, NASA Technical Report Series on Global Modeling and Data  
20 Assimilation, NASA TM-2013-104606, 32, 183 pp., Draft Document (12939 kB), 2013.
- 21 DeLuca, T. H., Zackrisson, O., Gundale, M. J. and Nilsson, M.-C.: Ecosystem feedbacks and  
22 nitrogen fixation in boreal forests., *Science*, 320, 1181, doi:10.1126/science.1154836, 2008.
- 23 Duce, R. A., Liss, P. S., Merrill, J. T., Atlas, E. L., Buat-Menard, P., Hicks, B. B., Miller, J.  
24 M., Prospero, J. M., Arimoto, R., Church, T. M., Ellis, W., Galloway, J. N., Hansen, L.,  
25 Jickells, T. D., Knap, A. H., Reinhardt, K. H., Schneider, B., Soudine, A., Tokos, J. J.,  
26 Tsunogai, S., Wollast, R. and Zhou, M.: The atmospheric input of trace species to the world  
27 ocean, *Global Biogeochem. Cycles*, 5(3), 193–259, doi:10.1029/91GB01778, 1991.
- 28 Environment Canada: Canadian Aerosol Baseline Measurement (CABM) Data, [online]  
29 Available from: [http://www.ec.gc.ca/donneesnatchem-](http://www.ec.gc.ca/donneesnatchem-natchemdata/default.asp?lang=En&n=22F5B2D4-1)  
30 [natchemdata/default.asp?lang=En&n=22F5B2D4-1](http://www.ec.gc.ca/donneesnatchem-natchemdata/default.asp?lang=En&n=22F5B2D4-1) (Accessed 7 May 2015), 2014.
- 31 Fickert, S., Adams, J. W. and Crowley, J. N.: Activation of Br<sub>2</sub> and BrCl via uptake of HOBr  
32 onto aqueous salt solutions, *J. Geophys. Res.*, 104, 23719–23727, 1999.
- 33 Gaston, A. J., Gilchrist, H. G. and Hipfner, J. M.: Climate change, ice conditions and  
34 reproduction in an Arctic nesting marine bird: Brunnich’s guillemot (*Uria lomvia* L.), *J.*  
35 *Anim. Ecol.*, 74(5), 832–841, doi:10.1111/j.1365-2656.2005.00982.x, 2005.
- 36 Geernaert, L. L. S., Geernaert, G. L., Granby, K. and Asman, W. A. H.: Fluxes of soluble  
37 gases in the marine atmosphere surface layer, *Tellus*, 50B, 111–127, 1998.

- 1 Gibb, S. W., Mantoura, R. F. C. and Liss, P. S.: Ocean-atmosphere exchange and atmospheric  
2 speciation of ammonia and methylamines in the region of the NW Arabian Sea, *Global*  
3 *Biogeochem. Cycles*, 13(1), 161–178, doi:10.1029/98GB00743, 1999.
- 4 Hardy, R. W. F., Holsten, R. D., Jackson, E. K. and Burns, R. C.: The Acetylene-Ethylene  
5 Assay for N<sub>2</sub> Fixation: Laboratory and Field Evaluation, *Plant Physiol.*, 43, 1185–1207, 1968.
- 6 Hobara, S., McCalley, C., Koba, K., Giblin, A. E., Weiss, M. S., Gettel, G. M. and Shaver, G.  
7 R.: Nitrogen Fixation in Surface Soils and Vegetation in an Arctic Tundra Watershed: A Key  
8 Source of Atmospheric Nitrogen, *Arctic, Antarct. Alp. Res.*, 38(3), 363–372, 2006.
- 9 Holmes, R. M., Aminot, A., K erouel, R., Hooker, B. A and Peterson, B. J.: A simple and  
10 precise method for measuring ammonium in marine and freshwater ecosystems, *Can. J. Fish.*  
11 *Aquat. Sci.*, 56(10), 1801–1808, doi:10.1139/f99-128, 1999.
- 12 Hong, S.-Y., Dudhia, J. and Chen, S.-H.: A revised approach to ice microphysical processes  
13 for the bulk parameterization of clouds and precipitation, *Mon. Weather Rev.*, 132, 103-120,  
14 2004.
- 15 Iacono, M. J., Delamere, J. S., Mlawer, E. J., Shephard, M. W., Clough, S. A. and Collins, W.  
16 D.: Radiative forcing by long-lived greenhouse gases: Calculations with the AER radiative  
17 transfer models, *J. Geophys. Res.*, 113, D13103, 2008.
- 18 Janjic, Z. I.: The Step-Mountain Eta Coordinate Model: Further developments of the  
19 convection, viscous sublayer, and turbulence closure schemes, *Mon. Weather Rev.*, 122, 927-  
20 945, 1994.
- 21 Janjic, Z. I.: The surface layer in the NCEP eta Model, in: Eleventh conference on numerical  
22 weather prediction, Norfolk, VA, 19-23 August 1996, 354-355, 1996.
- 23 Janjic, Z. I.: Nonsingular implementation of the Mellor-Yamada Level 2.5 Scheme in the  
24 NCEP Meso model, National Centers for Environmental Prediction, Office Note No. 437, 61  
25 pp., 2002.
- 26 Johnson, M. T.: The air-sea flux of ammonia, Ph.D. thesis, University of East Anglia., 2004.
- 27 Johnson, M. T.: A numerical scheme to calculate temperature and salinity dependent air-water  
28 transfer velocities for any gas, *Ocean Sci.*, 6(4), 913–932, doi:10.5194/os-6-913-2010, 2010.
- 29 [Johnson, M. T. and Bell, T. G.: Coupling between dimethylsulphide emissions and the ocean-](#)  
30 [atmosphere exchange of ammonia, \*Environ. Chem.\*, 5, 259-267, doi:10.107/EN08030, 2008.](#)
- 31 Johnson, M. T., Liss, P. S., Bell, T. G., Lesworth, T. J., Baker, A. R., Hind, A. J., Jickells, T.  
32 D., Biswas, K. F., Woodward, E. M. S. and Gibb, S. W.: Field observations of the ocean-  
33 atmosphere exchange of ammonia: Fundamental importance of temperature as revealed by a  
34 comparison of high and low latitudes, *Global Biogeochem. Cycles*, 22(1), 1–15,  
35 doi:10.1029/2007GB003039, 2008.

- 1 Kain, J. S.: The Kain-Fritsch convective parameterization: An update, *J. Appl. Meteorol.*, 43,  
2 170-181, 2004.
- 3 Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné,  
4 S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S.,  
5 Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A.,  
6 Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud,  
7 W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E.,  
8 R., Makhmutov, V., Mathot, S., Mikkilä, J., Minginette, P., Mogo, S., Nieminen, T., Onnela,  
9 A., Pereira, P., Petäjä, T., Schnitzhofer, R., Seinfeld, J. H., Sipilä, M., Stozhkov, Y.,  
10 Stratmann, F., Tomé, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H.,  
11 Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U.  
12 and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric  
13 aerosol nucleation., *Nature*, 476, 429–433, doi:10.1038/nature10343, 2011.
- 14 Krupa, S. V.: Effects of atmospheric ammonia (NH<sub>3</sub>) on terrestrial vegetation: A review,  
15 *Environ. Pollut.*, 124(2), 179–221, doi:10.1016/S0269-7491(02)00434-7, 2003.
- 16 Leaitch, W. R., Sharma, S., Huang, L., Toom-Sauntry, D., Chivulescu, A., Macdonald, A. M.,  
17 von Salzen, K., Pierce, J. R., Bertram, A. K., Schroder, J. C., Shantz, N. C., Chang, R. Y.-W.  
18 and Norman, A.-L.: Dimethyl sulfide control of the clean summertime Arctic aerosol and  
19 cloud., *Elem. Sci. Anth.*, 1, doi:10.12952/journal.elementa.000017, 2013.
- 20 Leck, C., Nilsson, E. D., Bigg, E. K. and Bäcklin, L.: Atmospheric program on the Arctic  
21 Ocean Expedition 1996 (AOE-96): An overview of scientific goals, experimental approach,  
22 and instruments, *J. Geophys. Res.*, 106(D23), 32051–32067, doi:10.1029/2000JD900461,  
23 2001.
- 24 Lefer, B. L., Talbot, R. W. and Munger, J. W.: Nitric acid and ammonia at a rural  
25 northeastern U.S. site, *J. Geophys. Res.*, 104(D1), 1645, doi:10.1029/1998JD100016, 1999.
- 26 Legrand, M., Ducroz, F., Wagenbach, D., Mulvaney, R. and Hall, J.: Ammonium in coastal  
27 Antarctic aerosol and snow: Role of polar ocean and penguin emissions, *J. Geophys. Res.*,  
28 103, 11043–11056, 1998.
- 29 Lin, J.-T. and McElroy, M.: Impacts of boundary layer mixing on pollutant vertical profiles in  
30 the lower troposphere: Implications to satellite remote sensing, *Atmos. Environ.* 44(14),  
31 1726-1739, doi:10.1016/j.atmosenv.2010.02.09, 2010.
- 32 Lindeboom, H. J.: The Nitrogen Pathway in a Penguin Rookery, *Ecology*, 65(1), 269–277,  
33 1984.
- 34 Liss, P. S.: Gas transfer: Experiments and geochemical implications, in *Air-Sea Exchange of*  
35 *Gases and Particles*, edited by P. S. Liss and W. G. N. Slinn, pp. 241–298, Springer  
36 Netherlands., 1983.
- 37 Liss, P. S. and Slater, P. G.: Flux of Gases across the Air-Sea Interface, *Nature*, 247, 181–184,  
38 doi:10.1038/247181a0, 1974.

- 1 Lüthje, M., Feltham, D. L., Taylor, P. D. and Worster, M. G.: Modeling the summertime  
2 evolution of sea-ice melt ponds, *J. Geophys. Res. Ocean.*, 111, C02001,  
3 doi:10.1029/2004JC002818, 2006.
- 4 Mallory, M. L. and Forbes, M. R.: Does sea ice constrain the breeding schedules of high  
5 Arctic Northern Fulmars?, *Condor*, 109(4), 894–906, 2007.
- 6 Markovic, M. Z., VandenBoer, T. C. and Murphy, J. G.: Characterization and optimization of  
7 an online system for the simultaneous measurement of atmospheric water-soluble constituents  
8 in the gas and particle phases, *J. Environ. Monit.*, 14(7), 1872, doi:10.1039/c2em00004k,  
9 2012.
- 10 Martin, J., Tremblay, J.-É., Gagnon, J., Tremblay, G., Lapoussiere, A., Jose, C., Poulin, M.,  
11 Gosselin, M., Gratton, Y. and Michel, C.: Prevalence, structure and properties of subsurface  
12 chlorophyll maxima in Canadian Arctic waters, *Mar. Ecol.-Prog. Ser.*, 412, 69-84, 2010.
- 13 Martin, S. T., Hung, H.-M., Park, R. J., Jacob, D. J., Spurr, R. J. D., Chance, K. V. and Chin,  
14 M.: Effects of the physical state of tropospheric ammonium-sulfate-nitrate particles on global  
15 aerosol direct radiative forcing, *Atmos. Chem. Phys.*, 4, 183–214, 2004.
- 16 McKane, R. B., Johnson, L. C., Shaver, G. R., Nadelhoffer, K. J., Rastetter, E. B., Fry, B.,  
17 Giblin, A. E., Kielland, K., Kwiatkowski, B. L., Laundre, J. A. and Murray, G.: Resource-  
18 based niches provide a basis for plant species diversity and dominance in arctic tundra.,  
19 *Nature*, 415, 68–71, doi:10.1038/415068a, 2002.
- 20 McKee, C. M.: Biogeochemical Cycles of Ammonia and Dimehtylsulphide in the Marine  
21 Environment, Ph.D. thesis, University of East Anglia., 2001.
- 22 McLaren, P. L.: Spring migration and habitat use by seabirds in eastern Lancaster Sound and  
23 western Baffin Bay, *Arctic*, 35(1), 88–111, 1982.
- 24 Monin, A. S. and Obukhov, A. M.: Basic laws of turbulent mixing in the surface layer of the  
25 atmosphere, *Contrib. Geophys. Inst. Acad. Sci. USSR*, 151, 163-187, 1954. (in Russian)
- 26 NASA: Fire Information Resource Management System (FIRMS), [online] Available from:  
27 <https://earthdata.nasa.gov/earth-observation-data/near-real-time/firms> (Accessed 30 June  
28 2015), 2015.
- 29 Norman, M. and Leck, C.: Distribution of marine boundary layer ammonia over the Atlantic  
30 and Indian Oceans during the Aerosols99 cruise, *J. Geophys. Res.*, 110, D16302,  
31 doi:10.1029/2005JD005866, 2005.
- 32 Paulot, F., Jacob, D. J., Johnson, M. T., Bell, T. G., Baker, A. R., Keene, W. C., Lima, I. D.,  
33 Doney, S. C. and Stock, C. A.: Global oceanic emission of ammonia: Constraints from  
34 seawater and atmospheric observations, *Global Biogeochem. Cycles*, 29,  
35 doi:10.1002/2015GB005106, 2015.
- 36 Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic  
37 growth and cloud condensation nucleus activity, *Atmos. Chem. Phys.*, 7, 1961-1971, 2007.

- 1 Quinn, P. K., Charlson, R. J. and Bates, T. S.: Simultaneous observations of ammonia in the  
2 atmosphere and ocean, *Nature*, 335, 336–338, doi:10.1038/335336a0, 1988.
- 3 Quinn, P. K., Bates, T. S., Johnson, J. E., Covert, D. S. and Charlson, R. J.: Interactions  
4 between the sulfur and reduced nitrogen cycles over the central Pacific Ocean, *J. Geophys.*  
5 *Res.*, 95, 16405–16416, 1990.
- 6 Quinn, P. K., Asher, W. E. and Charlson, R. J.: Equilibria of the Marine Multiphase  
7 Ammonia System, *J. Atmos. Chem.*, 14, 11–30, 1992.
- 8 Quinn, P. K., Barrett, K. J., Dentener, F. J., Lipschultz, F. and Six, K. D.: Estimation of the  
9 air/sea exchange of ammonia for the North Atlantic Basin, *Biogeochemistry*, 35(1), 275–304,  
10 doi:10.1007/BF02179831, 1996.
- 11 Reis, S., Pinder, R. W., Zhang, M., Lijie, G. and Sutton, M. A.: Reactive nitrogen in  
12 atmospheric emission inventories, *Atmos. Chem. Phys.*, 9, 7657–7677, doi:10.5194/acp-9-  
13 7657-2009, 2009.
- 14 Riddick, S. N., Dragosits, U., Blackall, T. D., Daunt, F., Wanless, S. and Sutton, M. A.: The  
15 global distribution of ammonia emissions from seabird colonies, *Atmos. Environ.*, 55, 319–  
16 327, doi:10.1016/j.atmosenv.2012.02.052, 2012.
- 17 [Riddick, S. N., Dragosits, U., Blackall, T. D., Daunt, F., Wanless, S. and Sutton, M. A.:](https://doi.org/10.5285/c9e802b3-43c8-4b36-a3a3-8861d9da8ea9)  
18 [Global ammonia emissions from seabirds. NERC Environmental Information Data Centre.](https://doi.org/10.5285/c9e802b3-43c8-4b36-a3a3-8861d9da8ea9)  
19 [doi:10.5285/c9e802b3-43c8-4b36-a3a3-8861d9da8ea9, 2012b.](https://doi.org/10.5285/c9e802b3-43c8-4b36-a3a3-8861d9da8ea9)
- 20 Riddick, S. N., Blackall, T. D., Dragosits, U., Daunt, F., Braban, C. F., Tang, Y. S.,  
21 MacFarlane, W., Taylor, S., Wanless, S. and Sutton, M. A.: Measurement of ammonia  
22 emissions from tropical seabird colonies, *Atmos. Environ.*, 89, 35–42,  
23 doi:10.1016/j.atmosenv.2014.02.012, 2014.
- 24 Schmidt, S., Mackintosh, K., Gillett, R., Pudmenzky, A., Allen, D. E., Rennenberg, H. and  
25 Mueller, J. F.: Atmospheric concentrations of ammonia and nitrogen dioxide at a tropical  
26 coral cay with high seabird density., *J. Environ. Monit.*, 12(2), 460–465,  
27 doi:10.1039/b910922f, 2010.
- 28 Seabird Information Network: Circumpolar Seabird Data Portal, [online] Available from:  
29 [http://axiom.seabirds.net/circumpolar\\_portal.php](http://axiom.seabirds.net/circumpolar_portal.php) (Accessed 13 March 2015), 2015.
- 30 Sharma, S., Barrie, L. A., Plummer, D., McConnell, J. C., Brickell, P. C., Levasseur, M.,  
31 Gosselin, M. and Bates, T. S.: Flux estimation of oceanic dimethyl sulfide around North  
32 America, *J. Geophys. Res.*, 104, 21327–21342, 1999.
- 33 Sharma, S., Chan, E., Ishizawa, M., Toom-Saunty, D., Gong, S. L., Li, S.-M., Tarasick, D.  
34 W., Leitch, W. R., Norman, A.-L., Quinn, P. K., Bates, T. S., Levasseur, M., Barrie, L. A.  
35 and Maenhaut, W.: Influence of transport and ocean ice extent on biogenic aerosol sulfur in  
36 the Arctic atmosphere, *J. Geophys. Res.-Atmos.*, 117, D12209, doi:10.1029/2011JD017074,  
37 2012.

- 1 Shaver, G. R. and Chapin III, F. S.: Response to fertilization by various plant growth forms in  
2 an Alaskan tundra: nutrient accumulation and growth, *Ecology*, 61(3), 662–675,  
3 doi:10.2307/1937432, 1980.
- 4 Skamarock, W. C., Klemp, J. B., Dudhia, J., Gill, D. O., Barker, D. M., Wang, W. and  
5 Powers, J. G.: A description of the advanced research WRF version 2, National Center for  
6 Atmospheric Research, Technical Note, 88 pp., 2005.
- 7 Stewart, K. J., Brummell, M. E., Coxson, D. S. and Siciliano, S. D.: How is nitrogen fixation  
8 in the high arctic linked to greenhouse gas emissions?, *Plant Soil*, 362, 215–229,  
9 doi:10.1007/s11104-012-1282-8, 2012.
- 10 Stewart, K. J., Grogan, P., Coxson, D. S. and Siciliano, S. D.: Topography as a key factor  
11 driving atmospheric nitrogen exchanges in arctic terrestrial ecosystems, *Soil Biol. Biochem.*,  
12 70(3), 96–112, doi:10.1016/j.soilbio.2013.12.005, 2014.
- 13 Stohl, A., Forster, C., Frank, A., Seibert, P., and Wotawa, G.: Technical note: The Lagrangian  
14 particle dispersion model FLEXPART version 6.2, *Atmos. Chem. Phys.*, 5, 2461–2474,  
15 doi:10.5194/acp-5-2461-2005, 2005.
- 16 Sutton, M. A., Reis, S., Riddick, S. N., Dragosits, U., Nemitz, E., Theobald, M. R., Tang, Y.  
17 S., Braban, C. F., Viero, M., Dore, A. J., Mitchell, R. F., Wanless, S., Daunt, F., Fowler, D.,  
18 Blackall, T. D., Milford, C., Flechard, C. R., Loubet, B., Massad, R., Cellier, P., Personne, E.,  
19 Coheur, P. F., Clarisse, L., Van Damme, M., Ngadi, Y., Clerbaux, C., Skjøth, C. A., Geels,  
20 C., Hertel, O., Wichink Kruit, R. J., Pinder, R. W., Bash, J. O., Walker, J. T., Simpson, D.,  
21 Horváth, L., Misselbrook, T. H., Bleeker, A., Dentener, F. and de Vries, W.: Towards a  
22 climate-dependent paradigm of ammonia emission and deposition., *Phil. Trans. R. Soc. B*,  
23 368, doi:10.1098/rstb.2013.0166, 2013.
- 24 Takahashi, T., Sutherland, S. C., Chipman, D. W., Goddard, J. G. and Ho, C.: Climatological  
25 distributions of pH, pCO<sub>2</sub>, total CO<sub>2</sub>, alkalinity, and CaCO<sub>3</sub> saturation in the global surface  
26 ocean, and temporal changes at selected locations, *Mar. Chem.*, 164, 95–125,  
27 doi:10.1016/j.marchem.2014.06.004, 2014.
- 28 Tewari, M., Chen, F., Wang, W., Dudhia, J., LeMone, M. A., Mitchell, K., Ek, M., Gayno,  
29 G., Wegiel, J. and Cuenca, R. H.: Implementation and verification of the unified NOAA land  
30 surface model, 20<sup>th</sup> Conference on Weather Analysis and Forecasting/16<sup>th</sup> Conference on  
31 Numerical Weather Prediction, Seattle, WA, American Meteorological Society, 2004.
- 32 Theobald, M. R., Crittenden, P. D., Hunt, A. P., Tang, Y. S., Dragosits, U. and Sutton, M. A.:  
33 Ammonia emissions from a Cape fur seal colony, Cape Cross, Namibia, *Geophys. Res. Lett.*,  
34 33, L03812, doi:10.1029/2005GL024384, 2006.
- 35 Van Cleve, K. and Alexander, V.: Nitrogen cycling in tundra and boreal ecosystems, in  
36 *Terrestrial Nitrogen Cycles*, edited by F. E. Clark and T. Rosswall, pp. 375–404, Swedish  
37 National Research Council, Stockholm., 1981.
- 38 Wichink Kruit, R. J., Schaap, M., Sauter, F. J., Van Zanten, M. C. and Van Pul, W. A. J.:  
39 Modeling the distribution of ammonia across Europe including bi-directional surface-

1 atmosphere exchange, *Biogeosciences*, 9(12), 5261–5277, doi:10.5194/bg-9-5261-2012,  
2 2012.

3 Wilson, L. J., Bacon, P. J., Bull, J., Dragosits, U., Blackall, T. D., Dunn, T. E., Hamer, K. C.,  
4 Sutton, M. A. and Wanless, S.: Modelling the spatial distribution of ammonia emissions from  
5 seabirds in the UK, *Environ. Pollut.*, 131(2), 173–185, doi:10.1016/j.envpol.2004.02.008,  
6 2004.

7 Zhu, R., Sun, J., Liu, Y., Gong, Z. and Sun, L.: Potential ammonia emissions from penguin  
8 guano, ornithogenic soils and seal colony soils in coastal Antarctica: effects of freezing-  
9 thawing cycles and selected environmental variables, *Antarct. Sci.*, 23, 78–92,  
10 doi:10.1017/S0954102010000623, 2011.

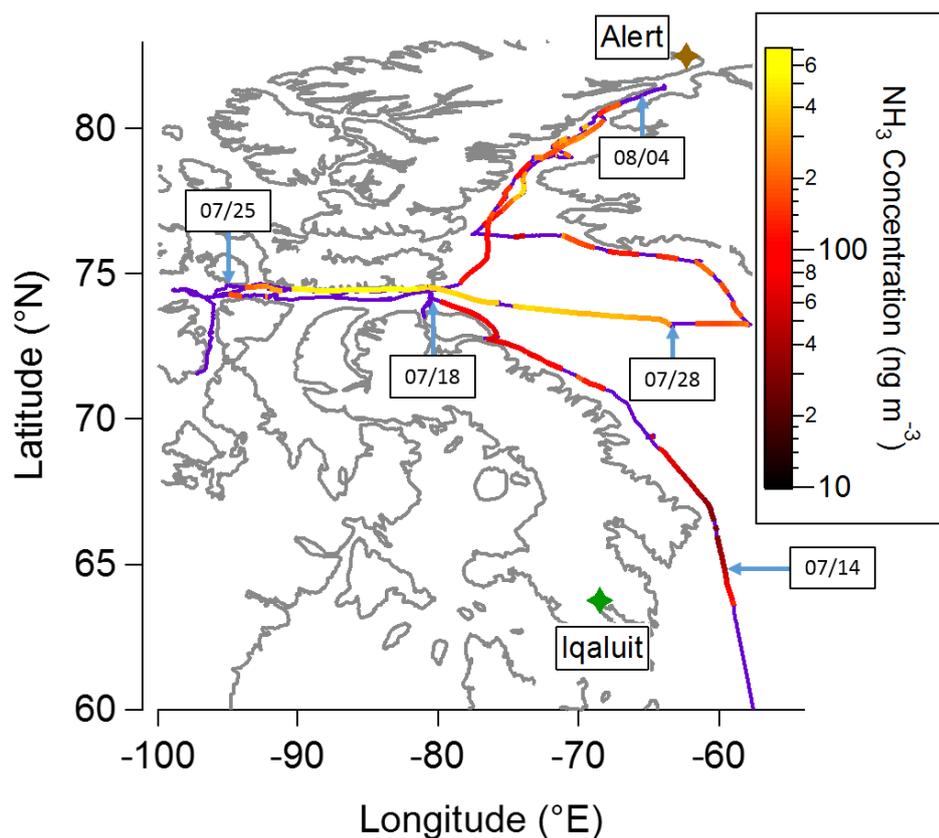
11

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

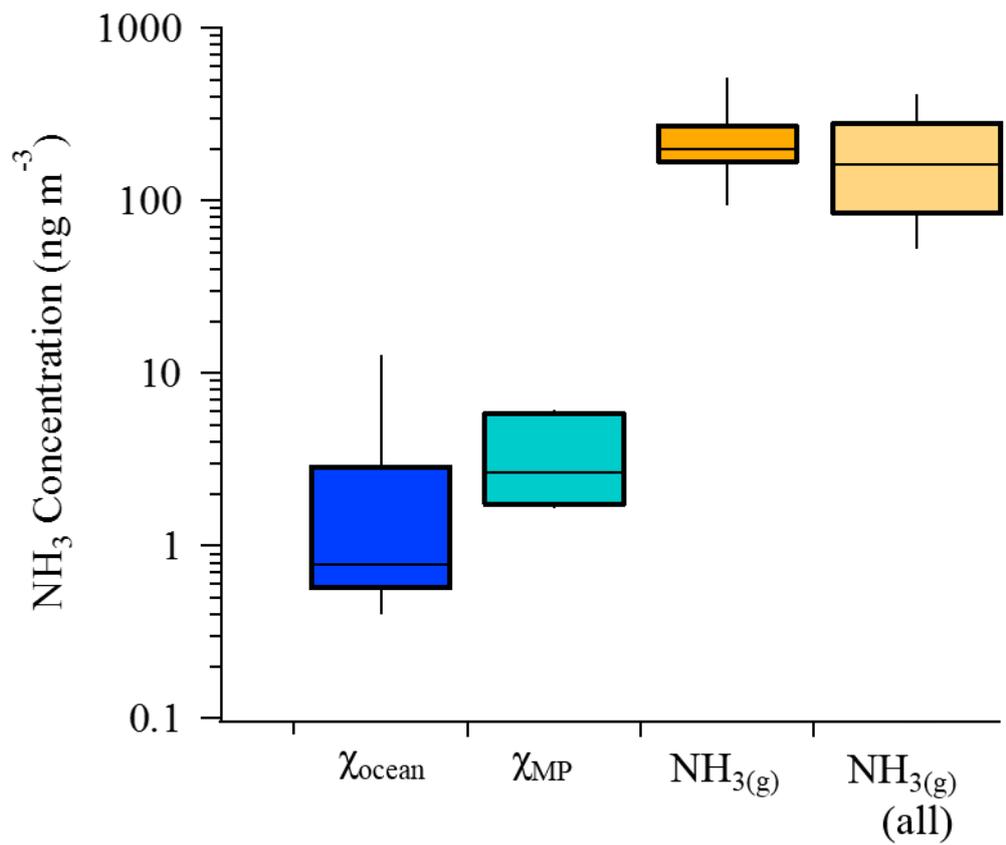
Atmospheric process	WRF option
Planetary Boundary Layer	Mellor–Yamada–Janjic Scheme (MYJ) (Janjic, 1994)
Surface layer	Monin-Obukhov Janjic Eta similarity scheme (Monin and Obukhov, 1954; Janjic, 1994, 1996, 2002)
Land surface	Unified Noah Land Surface Model (Tewari et al., 2004)*
Microphysics	WRF Single-Moment 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>.

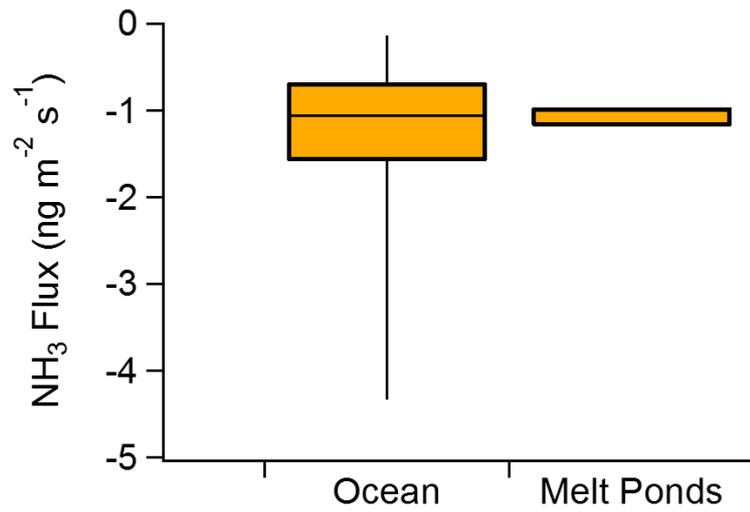
4



1  
 2 Figure 1. CCGS *Amundsen* ship track (~~purple~~) coloured by gas-phase NH<sub>3</sub> 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<sup>-3</sup> were chosen as a convenience for flux calculations. At STP, 100 ng m<sup>-3</sup> ≈ 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



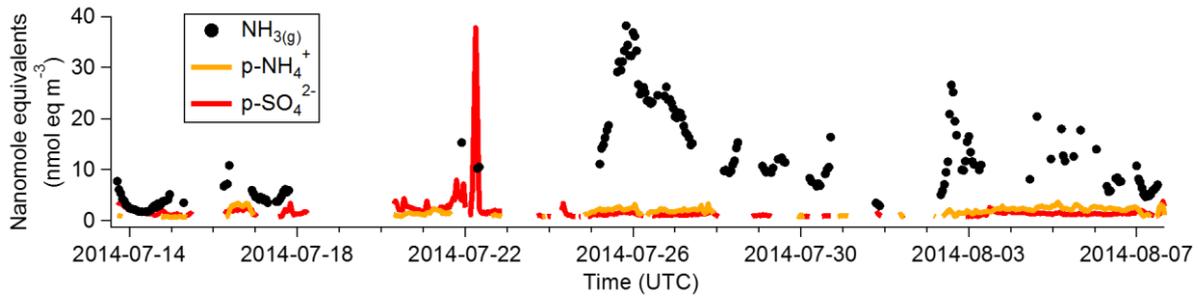
1  
 2 Figure 2. Box-and-whisker plot showing the observed ranges of  $\chi$  (on a log scale) for both the  
 3 ocean surface (dark blue) and melt ponds (light blue). The range of  $\text{NH}_3(\text{g})$  measured by the  
 4 AIM-IC near the time of surface sampling is shown in darker yellow whereas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

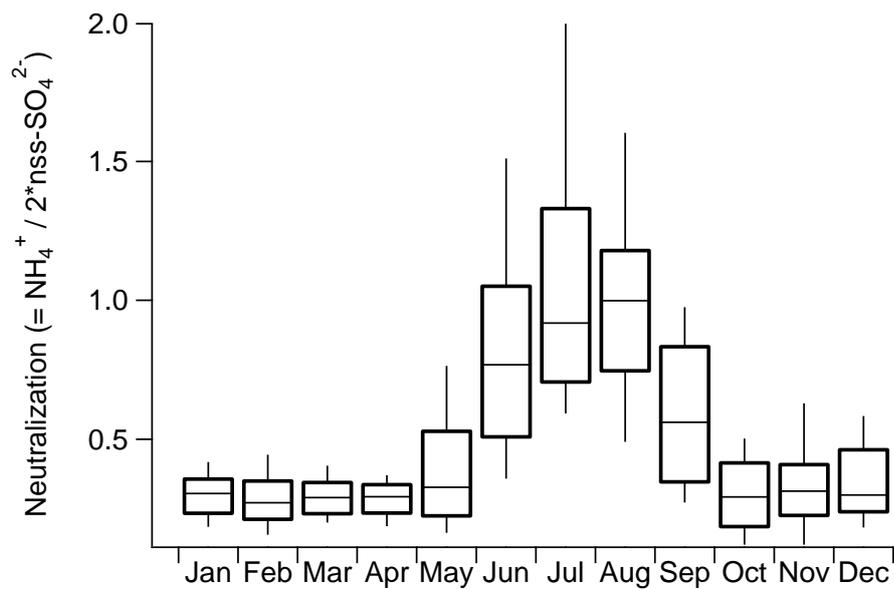
4



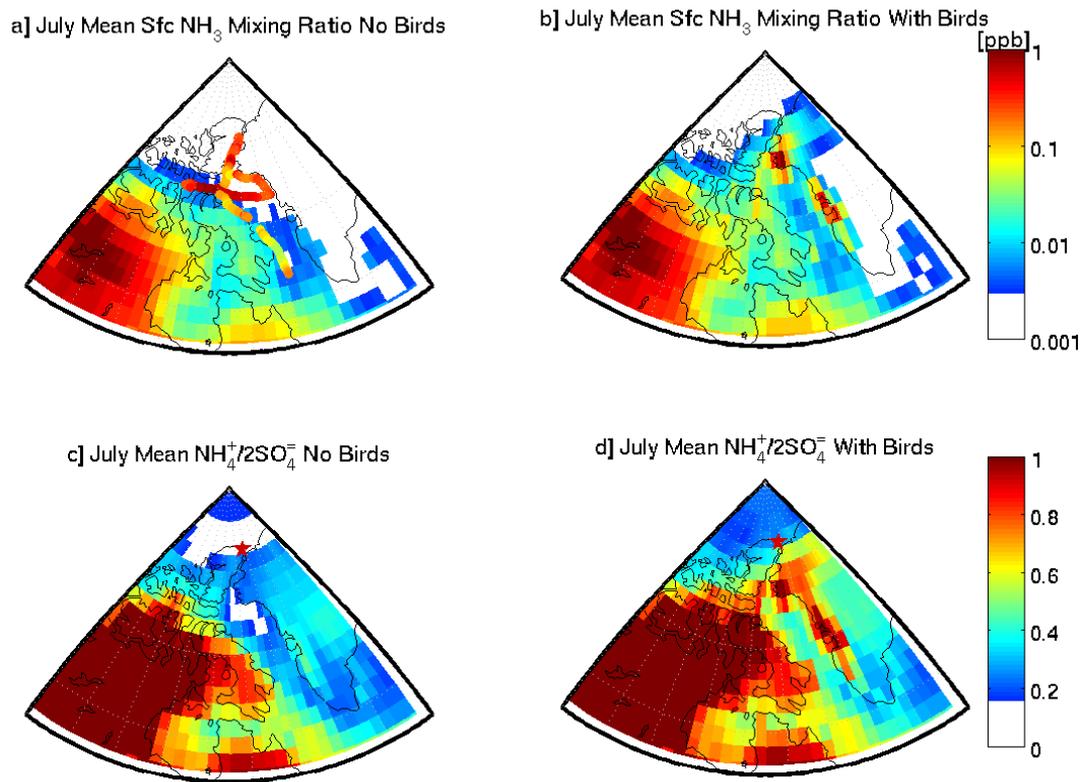
1

2 Figure 4. Time series of  $\text{neq m}^{-3}$  for  $\text{NH}_3(\text{g})$  (black dots),  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  (orange trace), and  $\text{SO}_4^{2-}$   
 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



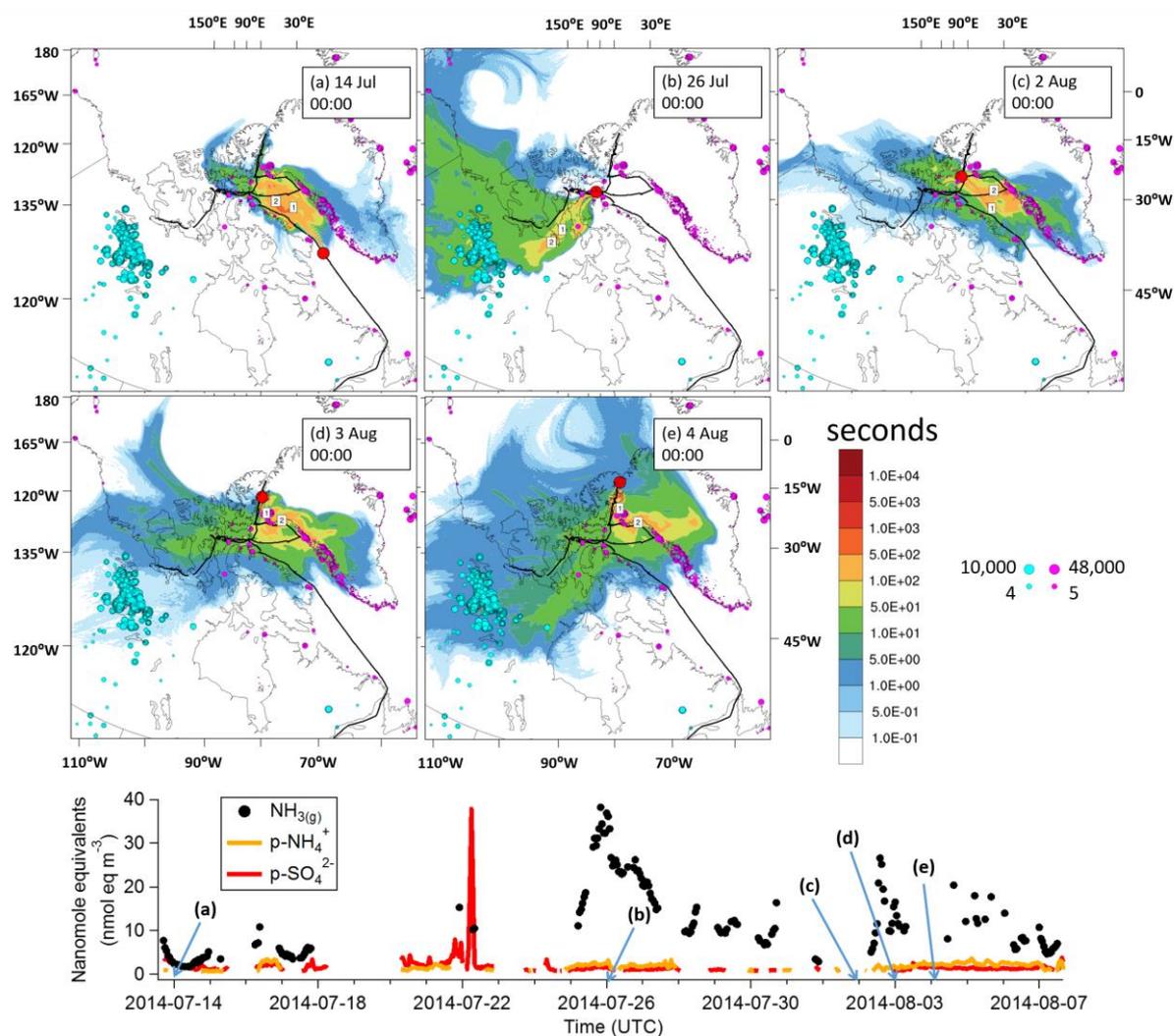
1  
 2 Figure 5. Box-and-whisker plot of neutralization (defined as  $\text{NH}_4^+ / 2 \cdot \text{nss-SO}_4^{2-}$ ) for fifteen  
 3 years (1996-2011) of weekly  $\text{PM}_{2.5}$  speciation measurements taken at Alert, Nunavut. The  
 4 percentiles are represented in the same fashion as Fig. 2.  
 5



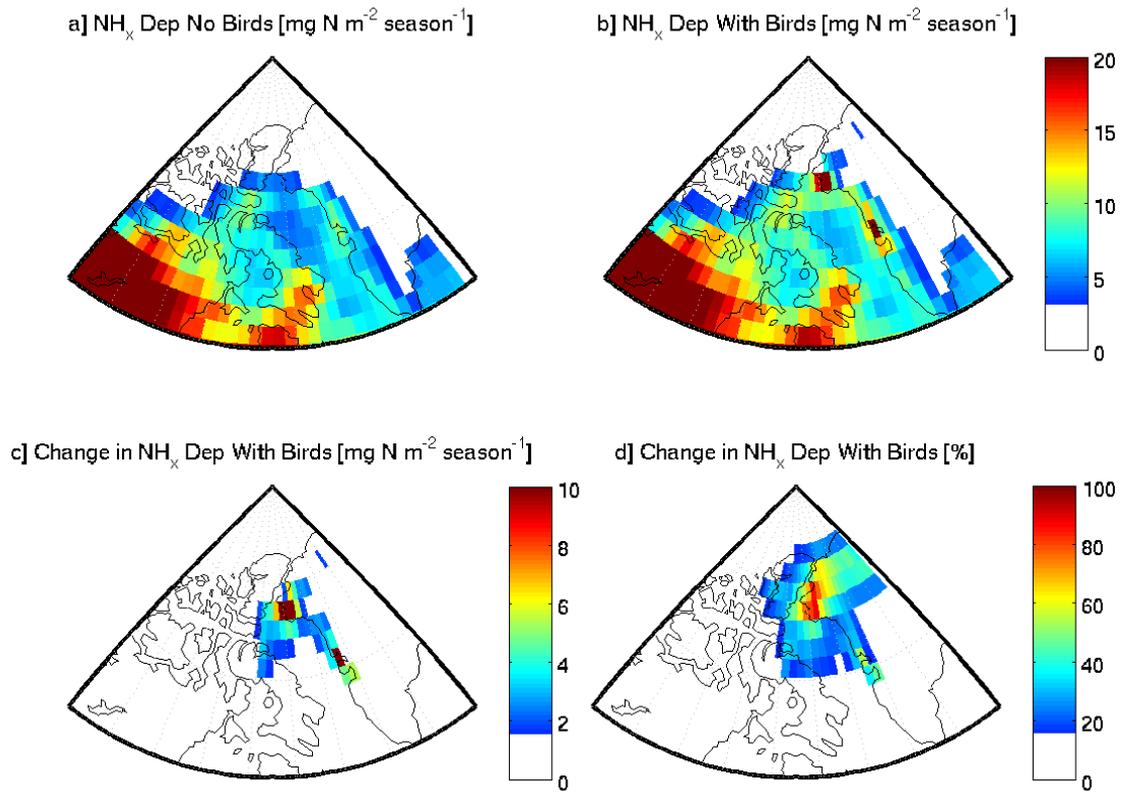
1

2 Figure 6. GEOS-Chem simulation of  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$ ) 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  $\text{NH}_3$  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  $\text{NH}_4^+$   
 11 and  $\text{SO}_4^{2-}$  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.



1

2 Figure 8. GEOS-Chem simulation of for total NH<sub>x</sub> deposition (in mg N m<sup>-2</sup> season<sup>-1</sup>) 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<sub>x</sub> 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 NH<sub>3</sub> exchange

Date and Time (UTC)	Lat (°N)	Lon (°W)	[NH <sub>x</sub> ] (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 NH<sub>3</sub> exchange

Date and Time (UTC)	Lat (°N)	Lon (°W)	[NH <sub>x</sub> ] (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