

Received: 24 September 2015 – Accepted: 13 October 2015 – Published: 2 November 2015

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

Published by Copernicus Publications on behalf of the European Geosciences Union.

ACPD

15, 29973–30016, 2015

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Continuous hourly measurements of gas-phase ammonia ($\text{NH}_{3(\text{g})}$) were taken from 13 July to 7 August 2014 on a research cruise throughout Baffin Bay and the eastern Canadian Arctic Archipelago. Concentrations ranged from 30–650 ng m^{-3} (40–870 pptv) with the highest values recorded in Lancaster Sound (74°13' N, 84°00' W). Simultaneous measurements of total ammonium ($[\text{NH}_x]$), pH and temperature in the ocean and in melt ponds were used to compute the compensation point (χ), which is the ambient $\text{NH}_{3(\text{g})}$ concentration at which surface–air fluxes change direction. Ambient $\text{NH}_{3(\text{g})}$ was usually several orders of magnitude larger than both χ_{ocean} and χ_{MP} ($< 0.4\text{--}10\text{ ng m}^{-3}$) indicating these surface pools are net sinks of NH_3 . Flux calculations estimate average net downward fluxes of 1.4 and 1.1 $\text{ng m}^{-2} \text{s}^{-1}$ for the open ocean and melt ponds, respectively. Sufficient $\text{NH}_{3(\text{g})}$ was present to neutralize non-sea salt sulphate (nss-SO_4^{2-}) in the boundary layer during most of the study. This finding was corroborated with a historical dataset of $\text{PM}_{2.5}$ composition from Alert, NU (82°30' N, 62°20' W) wherein the median ratio of $\text{NH}_4^+/\text{nss-SO}_4^{2-}$ equivalents was greater than 0.75 in June, July and August. The GEOS-Chem chemical transport model was employed to examine the impact of $\text{NH}_{3(\text{g})}$ emissions from seabird guano on boundary-layer composition and nss-SO_4^{2-} neutralization. A GEOS-Chem simulation without seabird emissions underestimated boundary layer $\text{NH}_{3(\text{g})}$ by several orders of magnitude and yielded highly acidic aerosol. A simulation that included seabird NH_3 emissions was in better agreement with observations for both $\text{NH}_{3(\text{g})}$ concentrations and nss-SO_4^{2-} neutralization. This is strong evidence that seabird colonies are significant sources of NH_3 in the summertime Arctic, and are ubiquitous enough to impact atmospheric composition across the entire Baffin Bay region. Large wildfires in the Northwest Territories were likely an important source of NH_3 , but their influence was probably limited to the Central Canadian Arctic. Implications of seabird-derived N-deposition to terrestrial and aquatic ecosystems are also discussed.

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

Ammonia ($\text{NH}_{3(\text{g})}$) is the dominant alkaline gas in the atmosphere and is an important component of the global nitrogen cycle. Its transport and deposition can have harmful effects for N-sensitive ecosystems such as eutrophication, loss of biodiversity and soil acidification (Krupa, 2003). The presence of $\text{NH}_{3(\text{g})}$ can impact climate by increasing rates of new particle formation via stabilization of sulphuric acid clusters (Kirkby et al., 2011). Gas-phase NH_3 is also able to partition to acidic fine particulate matter ($\text{PM}_{2.5}$) to form particulate-phase ammonium ($\text{NH}_{4(\text{p})}^+$), which alters various aerosol properties, such as scattering efficiency (Martin et al., 2004), hygroscopicity (Petters and Kreidenweis, 2007), ice nucleating ability (Abbatt et al., 2006) and heterogeneous chemistry occurring on surfaces (Fickert et al., 1999).

As a result, the accurate quantification of the magnitude and location of $\text{NH}_{3(\text{g})}$ sources is important for chemical transport models (CTMs). The major anthropogenic source is agriculture (fertilization and animal husbandry) with biomass burning, transport and industry being minor contributors (Reis et al., 2009). Natural sources include soils, vegetation, oceans and animal excreta (Sutton et al., 2013). Estimates for the annual global emissions of $\text{NH}_{3(\text{g})}$ range from 35–54 Tg N yr^{-1} ; however, large uncertainties exist for these values due to the area-wide nature and poor characterization of many sources. In remote marine environments, the ocean is thought to be the dominant source of $\text{NH}_{3(\text{g})}$ to the marine boundary layer and delivers an estimated 6–8 Tg N yr^{-1} to the atmosphere globally (Sutton et al., 2013). The dominant sources of oceanic NH_x ($\equiv \text{NH}_3 + \text{NH}_4^+$) include remineralisation of organic matter by bacteria and phytoplankton excretion (Carpenter et al., 2012). However, NH_x is an extremely labile nutrient for microbes such that assimilation by phytoplankton and bacteria prevents significant accumulation in surface waters. Nonetheless, there exists a pool of dissolved ammonia ($\text{NH}_{3(\text{sw})}$) available for exchange with the atmosphere.

In order to compute sea–air NH_3 fluxes, simultaneous measurements of both atmospheric $\text{NH}_{3(\text{g})}$ and oceanic NH_x are required. These measurements are extremely

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2. Assess the relative abundances of $\text{NH}_{3(\text{g})}$, $\text{NH}_{4(\text{p})}^+$ and $\text{SO}_{4(\text{p})}^{2-}$ to determine the extent of $\text{SO}_{4(\text{p})}^{2-}$ neutralization
3. Elucidate the major sources and sinks of atmospheric NH_3 throughout the summertime Arctic marine boundary layer
- 5 4. Evaluate whether atmospheric NH_x deposition could be an important N-input to aquatic and terrestrial Arctic ecosystems

2 Materials and methods

2.1 2014 CCGS *Amundsen* cruise

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

2.2 Atmospheric measurements

20 Ambient levels of water-soluble ions in $\text{PM}_{2.5}$ (NH_4^+ , SO_4^{2-} , and NO_3^-) and their precursor gases (NH_3 , SO_2 , and HNO_3) were measured using the Ambient Ion Monitor-Ion Chromatograph (AIM-IC) system (Model 9000D, URG Corp., Chapel Hill, NC). The AIM-IC is a continuous on-line system which provides simultaneous gas-phase and particle-phase measurements with hourly time resolution. The system has been adapted to locate the gas and particle separation and collection hardware as close

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ously measured by a thermosalinograph (Seabird Electronics SBE 45) connected to the seawater inlet. For the purposes of flux calculations, the ocean pH and salinity were assumed to be 8.1 and 35 g kg^{-1} , respectively, which are representative for the region of interest (Takahashi et al., 2014). These assumptions have been made previously and were not found to be a major source of uncertainty when calculating sea–air NH_3 fluxes (Johnson et al., 2008). The melt pond pHs were measured using a pH-meter within four hours of sampling. A three point calibration of the pH probe (Orion™ Model 91-72, Thermo Scientific) was performed using commercially available pH 4.01, 7.00 and 10.00 buffers. Salinity of the melt ponds were determined with a WTW Cond 330i handheld conductivity meter.

2.4 Flux calculations

The direction of sea–air NH_3 fluxes can be assessed by comparing ambient measurements of $\text{NH}_{3(\text{g})}$ to the atmospheric mixing ratio predicted from Henry’s Law equilibrium calculations using seawater $[\text{NH}_x]$ and surface temperature measurements (e.g. Asman et al., 1994; Johnson et al., 2008; Quinn et al., 1988, 1996). This equilibrium NH_3 concentration signifies the ambient value at which the net flux changes direction, and is known as the compensation point (denoted χ). In other words, one expects a net downwards flux if ambient $\text{NH}_{3(\text{g})}$ exceeds χ and a net upward flux if it is below χ . The magnitude of these fluxes are commonly computed using the “two-phase” model first developed by Liss and Slater (1974), which describes the sea–air transfer of gases as being controlled by molecular diffusion on either side of the interface. The transfer of NH_3 across this interface is predominantly dictated by the air-side transfer velocity, given the relatively high water solubility of NH_3 (Liss, 1983). Hence, the equation to calculate sea–air NH_3 fluxes is:

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

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

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

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

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

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

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

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

$$[\text{NH}_{3(\text{sw})}] = \frac{[\text{NH}_{x(\text{sw})}] \times K_a}{10^{-\text{pH}} + K_a} \quad (5)$$

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

$$\text{p}K_a = 10.0423 + 0.003071 \times S - 0.031556 \times T \quad (6)$$

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

2.5 GEOS-Chem

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

The GEOS-Chem model includes a detailed oxidant-aerosol tropospheric chemistry mechanism as originally described by Bey et al. (2001). Simulated aerosol species include sulphate-nitrate-ammonium (Park et al., 2004, 2006), carbonaceous aerosols (Park et al., 2003; Liao et al., 2007), dust (Fairlie et al., 2007, 2010) and sea salt (Alexander et al., 2005). The sulphate-nitrate-ammonium chemistry uses the ISOR-ROPIA II thermodynamic model (Fountoukis and Nenes, 2007), which partitions ammonia and nitric acid between the gas and aerosol phases. For our simulations, the natural NH_3 emissions are from Bouwman et al. (1997) and biomass burning emissions

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

3.2 Sulphate neutralization

The extent of neutralization of $\text{PM}_{2.5}$ influences aerosol properties as discussed previously. Figure 4 depicts the relative abundances (in neq m^{-3}) of gas-phase ammonia and particulate-phase ammonium and sulphate. It is important to note that the value for sulphate is total $\text{PM}_{2.5}$ sulphate as opposed to non-sea salt sulphate (nss-SO_4^{2-}), which is commonly reported for marine boundary layer studies. High and variable backgrounds of Na^+ from the AIM-IC prevented the calculation of nss-SO_4^{2-} , hence this dataset provides an upper limit for nss-SO_4^{2-} . Given the low wind speeds ($< 5 \text{ m s}^{-1}$) that dominated the campaign, it is likely the $\text{nss-SO}_4^{2-} \approx \text{SO}_4^{2-}$ since the contribution from sea salt to $\text{PM}_{2.5}$ was likely small. It should also be noted that measurements of SO_2 , HNO_3 and NO_3^- were almost always below their respective detection limits.

Particle loadings of NH_4^+ and SO_4^{2-} were extremely low (typically $< 5 \text{ neq m}^{-3}$) throughout the duration of the cruise. During the first third of the cruise (before 18 July), gas-phase NH_3 was also low and neutralization (i.e. $\text{NH}_4^+ : \text{SO}_4^{2-}$) was ambiguous due

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to numerous values near or below detection limit. On the other hand, after 25 July the nanoequivalents of $\text{NH}_{3(\text{g})}$ were substantially higher ($\text{NH}_x \approx \text{NH}_3$) than either NH_4^+ or SO_4^{2-} , which implies a nearly neutralized sulphate aerosol. It is important to note that a nearly neutralized aerosol does not equate to an aerosol with a pH of 7 since aerosol pH is highly sensitive to liquid water content as well as the precise $\text{NH}_4^+ : \text{SO}_4^{2-}$ ratio. An aerosol with $\text{NH}_4^+ : \text{SO}_4^{2-}$ approaching 1 can still have an acidic pH.

Figure 5 shows the distribution of the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio (on a per equivalent basis) measured at Alert, Nunavut (82.50 °N, 62.33 °W) as a function of month from 1996–2011. Weekly-averaged $\text{PM}_{2.5}$ speciation measurements at Alert are made by Environment Canada and are available on-line (Environment Canada, 2014). The contribution from NO_3^- is minor and has not been included in this analysis. During July and August the nss-SO_4^{2-} is, on average, completely neutralized by the NH_4^+ in $\text{PM}_{2.5}$ as shown by a median neutralization ratio approaching 1 during these months. This implies there is sufficient $\text{NH}_{3(\text{g})}$ throughout the region to neutralize nss-SO_4^{2-} produced from DMS oxidation which is consistent with the measurements shown in Fig. 4.

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

3.3 Evidence for the importance of seabird guano

Observations collected on board the *Amundsen* and at Alert strongly suggest a significant source of NH_3 in the Baffin Bay region. Decomposition of uric acid in seabird guano (excreta) has been recognized as a significant source of NH_3 where large colonies exist (Blackall et al., 2007; Wilson et al., 2004). However, studies measuring NH_3 from seabird colonies are limited due to the remoteness of most colonies and technical challenges in quantifying NH_3 in isolated locations (Blackall et al., 2007). The

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



useful for comparing N-deposition to N_2 -fixation since it captures deposition only during the growing season, and NH_x is likely the dominant form of atmospheric reactive N in the summertime Arctic boundary layer. Furthermore, Fig. 8b provides information on regions where N-deposition rates could be comparable to input from terrestrial N_2 -fixation ($> 10 \text{ mg N m}^{-2} \text{ yr}^{-1}$) which can help inform subsequent studies exploring N-cycling in the region. According to Hobara et al. (2006), Arctic terrestrial N_2 -fixation only occurs from May-September (inclusive) and peaks in July, similar to migration patterns of Arctic seabirds.

Estimates of N_2 -fixation rates in the Arctic Ocean mixed layer are even sparser than estimates for terrestrial ecosystems. To our knowledge, only Blais et al. (2012) have measured oceanic N_2 -fixation in the summertime Arctic Ocean mixed layer. The authors found that open ocean N_2 -fixation rates averaged 0.12 nM d^{-1} in the upper 50 m of the water column throughout the Beaufort Sea to Baffin Bay. For the period of May to September (inclusive) this represents an input of approximately 13 mg N m^{-2} which is comparable to inputs we calculate from guano-derived NH_3 in regions close to seabird colonies as shown in Fig. 8b.

4 Conclusions

Simultaneous measurements of atmospheric and oceanic composition in the eastern Canadian Arctic revealed that the summertime Arctic Ocean and melt ponds were net sinks of $NH_{3(g)}$. Concentrations of $NH_{3(g)}$ ranging from 30–650 ng m^{-3} were observed and represent the first reported measurements of $NH_{3(g)}$ in the Canadian Arctic. An average downward flux of $1.4 \text{ ng m}^{-2} \text{ s}^{-1}$ into the Arctic Ocean was calculated, consistent with previous studies showing that higher latitude waters are a net NH_3 sink (Johnson et al., 2008). Melt ponds had a smaller net downward flux ($1.1 \text{ ng m}^{-2} \text{ s}^{-1}$) as well as a slightly a higher χ as compared to the open ocean (median 2 vs. 0.8 ng m^{-3}). To our

knowledge, this is the first study to estimate melt pond–air NH_3 exchange despite the ubiquitous presence of melt ponds throughout the summertime Arctic.

On a nanoequivalent basis, $\text{NH}_{3(\text{g})}$ values were significantly greater (up to an order of magnitude more) than both NH_4^+ and SO_4^{2-} . This finding was consistent with a 15 year historical dataset of weekly $\text{PM}_{2.5}$ composition from Alert, NU which showed that nss- SO_4^{2-} is, on average, completely neutralized by NH_4^+ during July and August. These measurements imply strong regional source(s) of $\text{NH}_{3(\text{g})}$ in the eastern Canadian Arctic Archipelago that are sufficient to neutralize nss- SO_4^{2-} produced from DMS oxidation. Our surface–air flux estimates show that the Arctic Ocean and melt ponds are not responsible for $\text{NH}_{3(\text{g})}$ in the marine boundary layer.

It is also noteworthy that even though these melt ponds have significantly higher $[\text{NH}_x]$ than the open ocean (average of 670 vs. 55 nM), χ_{MP} is only marginally higher. More acidic pHs and slightly lower temperatures mitigate the effect of higher $[\text{NH}_x]$ on χ . Chemical transport models (CTMs) that explicitly account for bi-directional NH_3 exchange typically require χ as a predefined model input (e.g. Bash et al., 2013; Wichink Kruit et al., 2012). Therefore, from a modelling standpoint, similar values of χ_{ocean} and χ_{MP} are convenient since they can be parameterized in a similar fashion which would remove the need for CTMs to resolve the spatial extent and temporal evolution of melt ponds to properly model surface–atmosphere NH_3 exchange in the summertime Arctic.

To investigate the impact of NH_3 emissions from seabird guano, we examined GEOS-Chem simulations both with and without seabird colony NH_3 emissions. The seabird NH_3 emission inventory developed by Riddick et al. (2012) was updated for this study to include northern colonies ($> 50^\circ\text{N}$) that had been overlooked in the original inventory. Without the seabirds, GEOS-Chem underestimated $\text{NH}_{3(\text{g})}$ by several orders of magnitude and predicted highly acidic aerosol at the surface in July, which is in direct contrast to our measurements. The inclusion of seabird emissions provided much better agreement with $\text{NH}_{3(\text{g})}$ observations and yielded more neutralized aerosol throughout most of the Baffin Bay region. The importance of seabird NH_3 emissions is also supported by analysis of FLEXPART-WRF retro plumes throughout the study period. Air

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

References

- Abbatt, J. P. D., Benz, S., Cziczo, D. J., Kanji, Z., Lohmann, U., and Möhler, O.: Solid ammonium sulfate aerosols as ice nuclei: a pathway for cirrus cloud formation, *Science*, 313, 1770–1773, 2006.
- Anderson, W. B. and Polis, G. A.: Nutrient fluxes from water to land?: seabirds affect plant nutrient status on Gulf of California islands, *Oecologia*, 118, 324–332, doi:10.1007/s004420050733, 1999.
- Asman, W. A. H., Harrison, R. M., and Ottley, C. J.: Estimation of the net air–sea flux of ammonia over the southern bight of the North Sea, *Atmos. Environ.*, 28, 3647–3654, doi:10.1016/1352-2310(94)00192-N, 1994.

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

composition and sources in the central Arctic Ocean during ASCOS, *Atmos. Chem. Phys.*, 11, 10619–10636, doi:10.5194/acp-11-10619-2011, 2011.

Chapin, D. M. and Bledsoe, C.: Nitrogen fixation in arctic plant communities, in: *Arctic Ecosystems in a Changing Climate: an Ecophysiological Perspective*, edited by: Chapin III, R. S., Jeffries, R. L., Reynolds, J. F., Shaver, G. R. and Svoboda J., Academic Press, San Diego, USA, 301–319, 1992.

Chou, M.-D. and Suarez, M. J.: An efficient thermal infrared radiation parameterization for use in general circulation models, National Aeronautics and Space Administration, NASA Tech. Memo, Greenbelt, Maryland, USA, 84 pp., 1994.

Cleveland, C. C., Townsend, A. R., Schimel, D. S., Fisher, H., Howarth, R. W., Hedin, L. O., Perakis, S. S., Latty, E. F., Von Fischer, J. C., Elseroad, A., and Wasson, M. F.: Global patterns of terrestrial biological nitrogen (N_2) fixation in natural ecosystems, *Global Biogeochem. Cy.*, 13, 623–645, doi:10.1029/1999GB900014, 1999.

Darmenov, A. and da Silva, A.: The Quick Fire Emissions Dataset (QFED) – Documentation of versions 2.1, 2.2 and 2.4, NASA Technical Report Series on Global Modeling and Data Assimilation, NASA TM-2013-104606, 32, Greenbelt, Maryland, USA, 183 pp., Draft Document (12939 kB), 2013.

DeLuca, T. H., Zackrisson, O., Gundale, M. J., and Nilsson, M.-C.: Ecosystem feedbacks and nitrogen fixation in boreal forests., *Science*, 320, 1181, doi:10.1126/science.1154836, 2008.

Duce, R. A., Liss, P. S., Merrill, J. T., Atlas, E. L., Buat-Menard, P., Hicks, B. B., Miller, J. M., Prospero, J. M., Arimoto, R., Church, T. M., Ellis, W., Galloway, J. N., Hansen, L., Jickells, T. D., Knap, A. H., Reinhardt, K. H., Schneider, B., Soudine, A., Tokos, J. J., Tsunogai, S., Wollast, R., and Zhou, M.: The atmospheric input of trace species to the world ocean, *Global Biogeochem. Cy.*, 5, 193–259, doi:10.1029/91GB01778, 1991.

Environment Canada: Canadian Aerosol Baseline Measurement (CABM) data, available at: <http://www.ec.gc.ca/donneesnatchem-natchemdata/default.asp?lang=En&n=22F5B2D4-1> (last access: 7 May 2015), 2014.

Fickert, S., Adams, J. W., and Crowley, J. N.: Activation of Br_2 and $BrCl$ via uptake of HOBr onto aqueous salt solutions, *J. Geophys. Res.*, 104, 23719–23727, 1999.

Gaston, A. J., Gilchrist, H. G., and Hipfner, J. M.: Climate change, ice conditions and reproduction in an Arctic nesting marine bird: Brunnich's guillemot (*Uria lomvia* L.), *J. Anim. Ecol.*, 74, 832–841, doi:10.1111/j.1365-2656.2005.00982.x, 2005.

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Geernaert, L. L. S., Geernaert, G. L., Granby, K., and Asman, W. A. H.: Fluxes of soluble gases in the marine atmosphere surface layer, *Tellus*, 50B, 111–127, 1998.
- Gibb, S. W., Mantoura, R. F. C., and Liss, P. S.: Ocean–atmosphere exchange and atmospheric speciation of ammonia and methylamines in the region of the NW Arabian Sea, *Global Biogeochem. Cy.*, 13, 161–178, doi:10.1029/98GB00743, 1999.
- Hardy, R. W. F., Holsten, R. D., Jackson, E. K., and Burns, R. C.: The acetylene-ethylene assay for N_2 fixation: laboratory and field evaluation, *Plant Physiol.*, 43, 1185–1207, 1968.
- Hobara, S., McCalley, C., Koba, K., Giblin, A. E., Weiss, M. S., Gettel, G. M., and Shaver, G. R.: Nitrogen fixation in surface soils and vegetation in an arctic tundra watershed: a key source of atmospheric nitrogen, *Arct. Antarct. Alp. Res.*, 38, 363–372, 2006.
- Holmes, R. M., Aminot, A., K erouel, R., Hooker, B. A., and Peterson, B. J.: A simple and precise method for measuring ammonium in marine and freshwater ecosystems, *Can. J. Fish. Aquat. Sci.*, 56, 1801–1808, doi:10.1139/f99-128, 1999.
- Hong, S.-Y., Dudhia, J., and Chen, S.-H.: A revised approach to ice microphysical processes for the bulk parameterization of clouds and precipitation, *Mon. Weather Rev.*, 132, 103–120, 2004.
- Iacono, M. J., Delamere, J. S., Mlawer, E. J., Shephard, M. W., Clough, S. A., and Collins, W. D.: Radiative forcing by long-lived greenhouse gases: calculations with the AER radiative transfer models, *J. Geophys. Res.*, 113, D13103, doi:10.1029/2008JD009944, 2008.
- Janjic, Z. I.: The Step-Mountain Eta Coordinate Model: Further developments of the convection, viscous sublayer, and turbulence closure schemes, *Mon. Weather Rev.*, 122, 927–945, 1994.
- Janjic, Z. I.: The surface layer in the NCEP eta Model, in: Eleventh conference on numerical weather prediction, Norfolk, VA, USA, 19–23 August 1996, 354–355, 1996.
- Janjic, Z. I.: Nonsingular implementation of the Mellor-Yamada Level 2.5 Scheme in the NCEP Meso model, National Centers for Environmental Prediction, Office Note No. 437, Camp Springs, Maryland, USA, 61 pp., 2002.
- Johnson, M. T.: The air–sea flux of ammonia, PhD thesis, University of East Anglia, Norwich, UK, 2004.
- Johnson, M. T.: A numerical scheme to calculate temperature and salinity dependent air-water transfer velocities for any gas, *Ocean Sci.*, 6, 913–932, doi:10.5194/os-6-913-2010, 2010.
- Johnson, M. T., Liss, P. S., Bell, T. G., Lesworth, T. J., Baker, A. R., Hind, A. J., Jickells, T. D., Biswas, K. F., Woodward, E. M. S., and Gibb, S. W.: Field observations of the ocean–atmosphere exchange of ammonia: Fundamental importance of temperature as

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Liss, P. S.: Gas transfer: experiments and geochemical implications, in: Air–Sea Exchange of Gases and Particles, edited by: Liss, P. S. and Slinn, W. G. N., 241–298, Springer Netherlands, Dordrecht, the Netherlands, 1983.

Liss, P. S. and Slater, P. G.: Flux of gases across the air–sea interface, *Nature*, 247, 181–184, doi:10.1038/247181a0, 1974.

Lüthje, M., Feltham, D. L., Taylor, P. D., and Worster, M. G.: Modeling the summertime evolution of sea-ice melt ponds, *J. Geophys. Res.-Ocean*, 111, C02001, doi:10.1029/2004JC002818, 2006.

Mallory, M. L. and Forbes, M. R.: Does sea ice constrain the breeding schedules of high Arctic Northern Fulmars?, *Condor*, 109, 894–906, 2007.

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

Martin, J., Tremblay, J.-É., Gagnon, J., Tremblay, G., Lapoussiere, A., Jose, C., Poulin, M., Gosselin, M., Gratton, Y., and Michel, C.: Prevalence, structure and properties of subsurface chlorophyll maxima in Canadian Arctic waters, *Mar. Ecol.-Prog. Ser.*, 412, 69–84, 2010.

Martin, S. T., Hung, H.-M., Park, R. J., Jacob, D. J., Spurr, R. J. D., Chance, K. V., and Chin, M.: Effects of the physical state of tropospheric ammonium-sulfate-nitrate particles on global aerosol direct radiative forcing, *Atmos. Chem. Phys.*, 4, 183–214, doi:10.5194/acp-4-183-2004, 2004.

McKane, R. B., Johnson, L. C., Shaver, G. R., Nadelhoffer, K. J., Rastetter, E. B., Fry, B., Giblin, A. E., Kielland, K., Kwiatkowski, B. L., Laundre, J. A., and Murray, G.: Resource-based niches provide a basis for plant species diversity and dominance in arctic tundra., *Nature*, 415, 68–71, doi:10.1038/415068a, 2002.

McKee, C. M.: Biogeochemical Cycles of Ammonia and Dimehtylsulphide in the Marine Environment, PhD thesis, University of East Anglia, UK, 2001.

McLaren, P. L.: Spring migration and habitat use by seabirds in eastern Lancaster Sound and western Baffin Bay, *Arctic*, 35, 88–111, 1982.

Monin, A. S. and Obukhov, A. M.: Basic laws of turbulent mixing in the surface layer of the atmosphere, *Contrib. Geophys. Inst. Acad. Sci. USSR*, 151, 163–187, 1954 (in Russian).

NASA: Fire Information Resource Management System (FIRMS), available at: <https://earthdata.nasa.gov/earth-observation-data/near-real-time/firms>, last access: 30 June 2015.

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Norman, M. and Leck, C.: Distribution of marine boundary layer ammonia over the Atlantic and Indian Oceans during the Aerosols99 cruise, *J. Geophys. Res.*, 110, D16302, doi:10.1029/2005JD005866, 2005.

Paulot, F., Jacob, D. J., Johnson, M. T., Bell, T. G., Baker, A. R., Keene, W. C., Lima, I. D., Doney, S. C., and Stock, C. A.: Global oceanic emission of ammonia: constraints from seawater and atmospheric observations, *Global Biogeochem. Cy.*, 29, 1165–1178, doi:10.1002/2015GB005106, 2015.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, *Atmos. Chem. Phys.*, 7, 1961–1971, doi:10.5194/acp-7-1961-2007, 2007.

Quinn, P. K., Charlson, R. J., and Bates, T. S.: Simultaneous observations of ammonia in the atmosphere and ocean, *Nature*, 335, 336–338, doi:10.1038/335336a0, 1988.

Quinn, P. K., Bates, T. S., Johnson, J. E., Covert, D. S., and Charlson, R. J.: Interactions between the sulfur and reduced nitrogen cycles over the central Pacific Ocean, *J. Geophys. Res.*, 95, 16405–16416, 1990.

Quinn, P. K., Asher, W. E., and Charlson, R. J.: Equilibria of the Marine Multiphase Ammonia System, *J. Atmos. Chem.*, 14, 11–30, 1992.

Quinn, P. K., Barrett, K. J., Dentener, F. J., Lipschultz, F., and Six, K. D.: Estimation of the air/sea exchange of ammonia for the North Atlantic Basin, *Biogeochemistry*, 35, 275–304, doi:10.1007/BF02179831, 1996.

Reis, S., Pinder, R. W., Zhang, M., Lijie, G., and Sutton, M. A.: Reactive nitrogen in atmospheric emission inventories, *Atmos. Chem. Phys.*, 9, 7657–7677, doi:10.5194/acp-9-7657-2009, 2009.

Riddick, S. N., Dragosits, U., Blackall, T. D., Daunt, F., Wanless, S., and Sutton, M. A.: The global distribution of ammonia emissions from seabird colonies, *Atmos. Environ.*, 55, 319–327, doi:10.1016/j.atmosenv.2012.02.052, 2012.

Riddick, S. N., Blackall, T. D., Dragosits, U., Daunt, F., Braban, C. F., Tang, Y. S., MacFarlane, W., Taylor, S., Wanless, S., and Sutton, M. A.: Measurement of ammonia emissions from tropical seabird colonies, *Atmos. Environ.*, 89, 35–42, doi:10.1016/j.atmosenv.2014.02.012, 2014.

Schmidt, S., Mackintosh, K., Gillett, R., Pudmenzky, A., Allen, D. E., Rennenberg, H., and Mueller, J. F.: Atmospheric concentrations of ammonia and nitrogen dioxide at a tropical coral cay with high seabird density, *J. Environ. Monitor.*, 12, 460–465, doi:10.1039/b910922f, 2010.

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Takahashi, T., Sutherland, S. C., Chipman, D. W., Goddard, J. G., and Ho, C.: Climatological distributions of pH, $p\text{CO}_2$, total CO_2 , alkalinity, and CaCO_3 saturation in the global surface ocean, and temporal changes at selected locations, *Mar. Chem.*, 164, 95–125, doi:10.1016/j.marchem.2014.06.004, 2014.
- 5 Tewari, M., Chen, F., Wang, W., Dudhia, J., LeMone, M. A., Mitchell, K., Ek, M., Gayno, G., Wegiel, J., and Cuenca, R. H.: Implementation and verification of the unified NOAA land surface model, 20th Conference on Weather Analysis and Forecasting/16th Conference on Numerical Weather Prediction, 10–15 January 2004, Seattle, WA, American Meteorological Society, 14.2a, 2004.
- 10 Theobald, M. R., Crittenden, P. D., Hunt, A. P., Tang, Y. S., Dragosits, U., and Sutton, M. A.: Ammonia emissions from a Cape fur seal colony, Cape Cross, Namibia, *Geophys. Res. Lett.*, 33, L03812, doi:10.1029/2005GL024384, 2006.
- Van Cleve, K. and Alexander, V.: Nitrogen cycling in tundra and boreal ecosystems, in: *Terrestrial Nitrogen Cycles*, edited by: Clark, F. E. and Rosswall T., Swedish National Research Council, Stockholm, Sweden, 375–404, 1981.
- 15 Wichink Kruit, R. J., Schaap, M., Sauter, F. J., van Zanten, M. C., and van Pul, W. A. J.: Modelling the distribution of ammonia across Europe including bi-directional surface–atmosphere exchange, *Biogeosciences*, 9, 5261–5277, doi:10.5194/bg-9-5261-2012, 2012.
- Wilson, L. J., Bacon, P. J., Bull, J., Dragosits, U., Blackall, T. D., Dunn, T. E., Hamer, K. C., Sutton, M. A., and Wanless, S.: Modelling the spatial distribution of ammonia emissions from seabirds in the UK, *Environ. Pollut.*, 131, 173–185, doi:10.1016/j.envpol.2004.02.008, 2004.
- 20 Zhu, R., Sun, J., Liu, Y., Gong, Z., and Sun, L.: Potential ammonia emissions from penguin guano, ornithogenic soils and seal colony soils in coastal Antarctica: effects of freezing-thawing cycles and selected environmental variables, *Antarct. Sci.*, 23, 78–92, doi:10.1017/S0954102010000623, 2011.
- 25

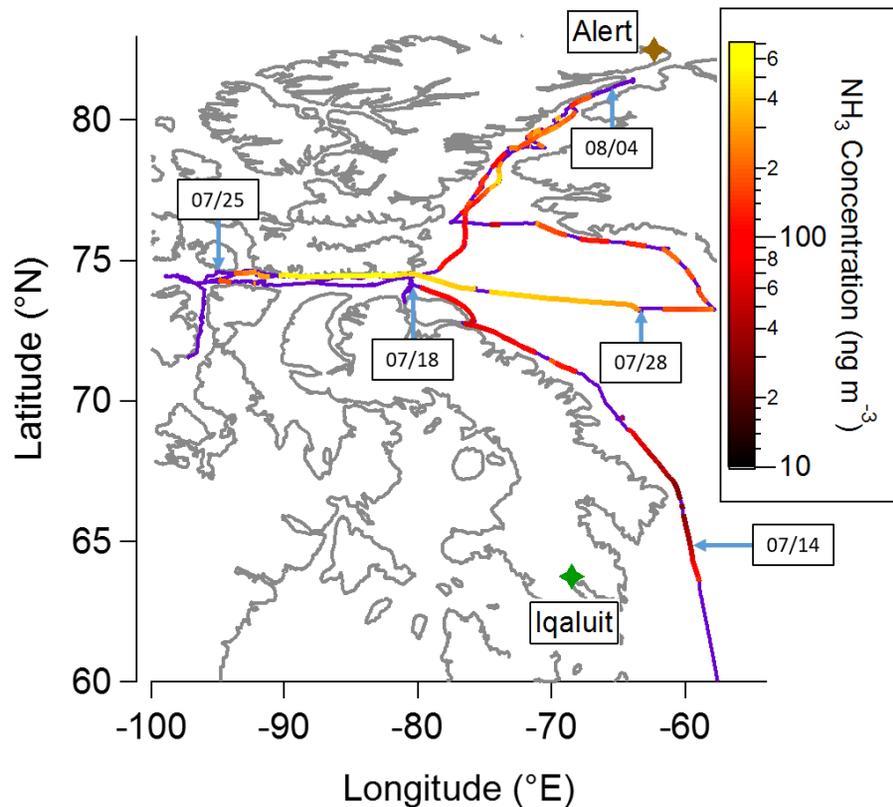


Figure 1. CCGS *Amundsen* ship track (purple) coloured by gas-phase NH_3 concentrations (when valid measurements were available) measured by the AIM-IC. Units of ng m^{-3} were chosen as a convenience for flux calculations. At STP, $100 \text{ ng m}^{-3} \approx 130 \text{ pptv}$. Relevant landmarks are also labelled. Dates and arrows indicate the position of the ship at 00:00 UTC on that day.

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



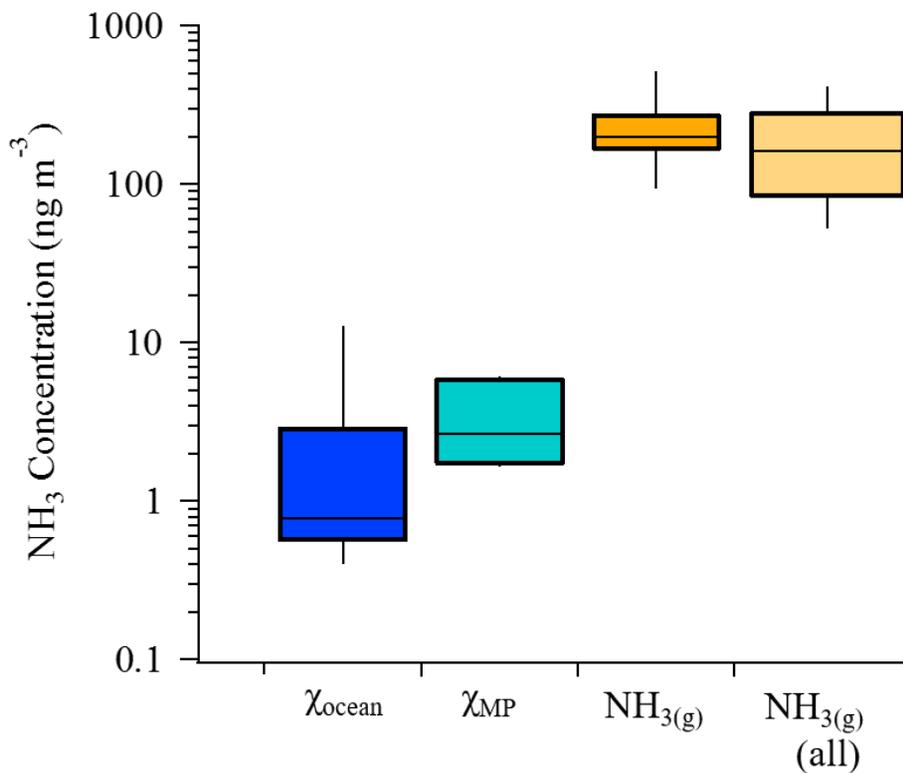


Figure 2. Box-and-whisker plot showing the observed ranges of χ (on a log scale) for both the ocean surface (dark blue) and melt ponds (light blue). The range of $\text{NH}_3(\text{g})$ measured by the AIM-IC near the time of surface sampling is shown in darker yellow whereas $\text{NH}_3(\text{g})$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

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



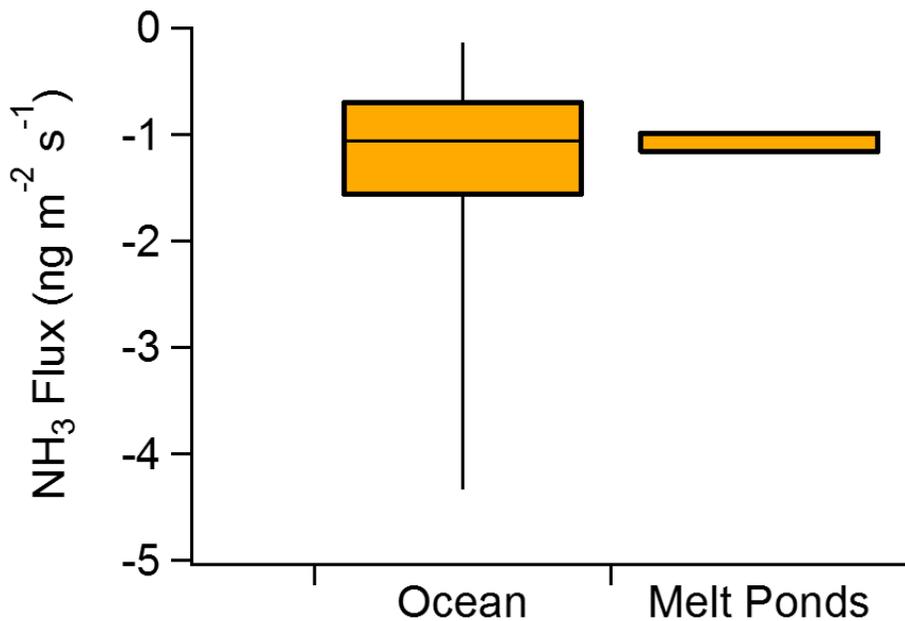


Figure 3. Box-and-whisker plot of the estimated fluxes into the open ocean and melt ponds. The percentiles are represented in the same fashion as Fig. 2.

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

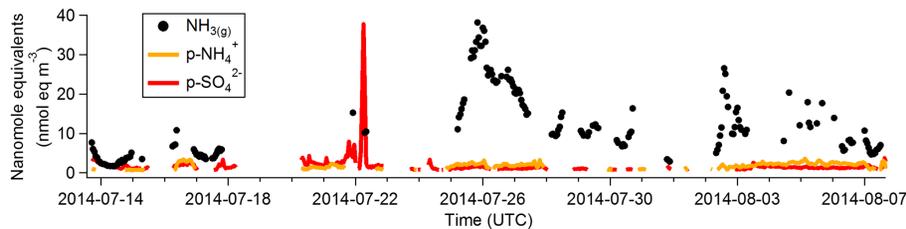


Figure 4. Time series of neq m^{-3} for $\text{NH}_3(\text{g})$ (black dots), NH_4^+ in $\text{PM}_{2.5}$ (orange trace), and SO_4^{2-} in $\text{PM}_{2.5}$ (red trace). Interruptions in the data are a result of zero air experiments, calibrations, values below detection limit, instrument downtime, and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

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

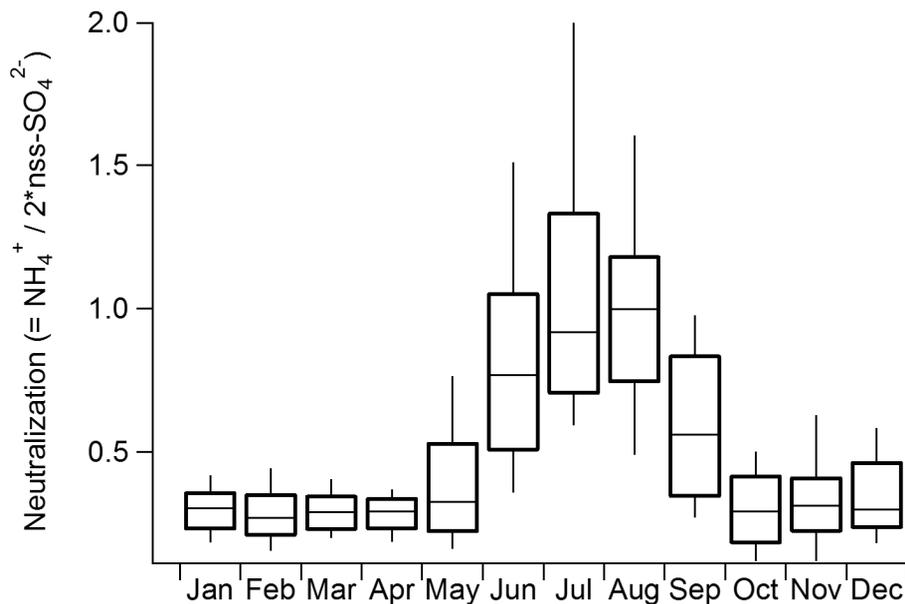


Figure 5. Box-and-whisker plot of neutralization (defined as $\text{NH}_4^+ / 2^* \text{nss-SO}_4^{2-}$) for fifteen years (1996–2011) of weekly $\text{PM}_{2.5}$ speciation measurements taken at Alert, Nunavut. The percentiles are represented in the same fashion as Fig. 2.

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

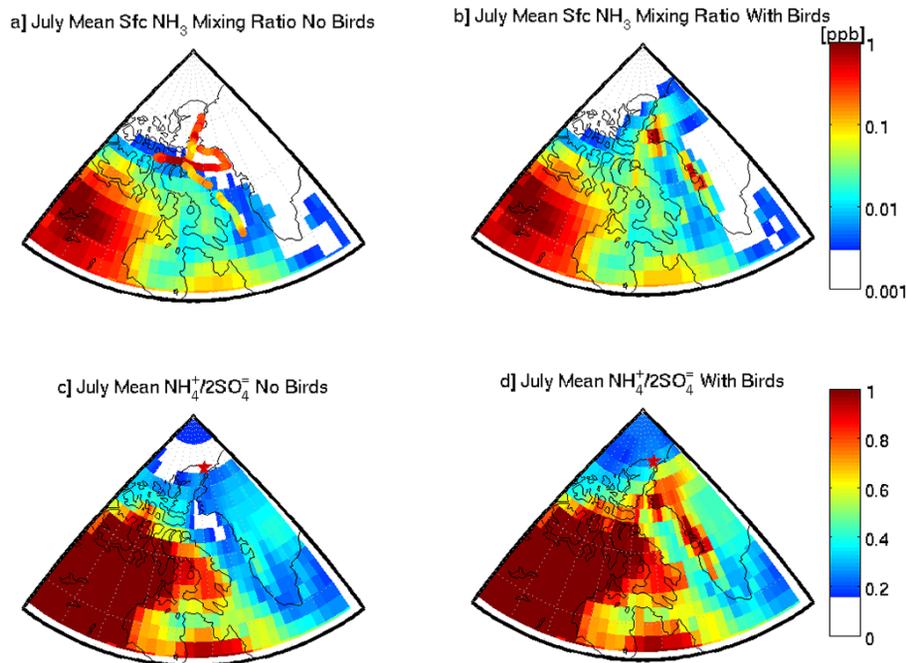
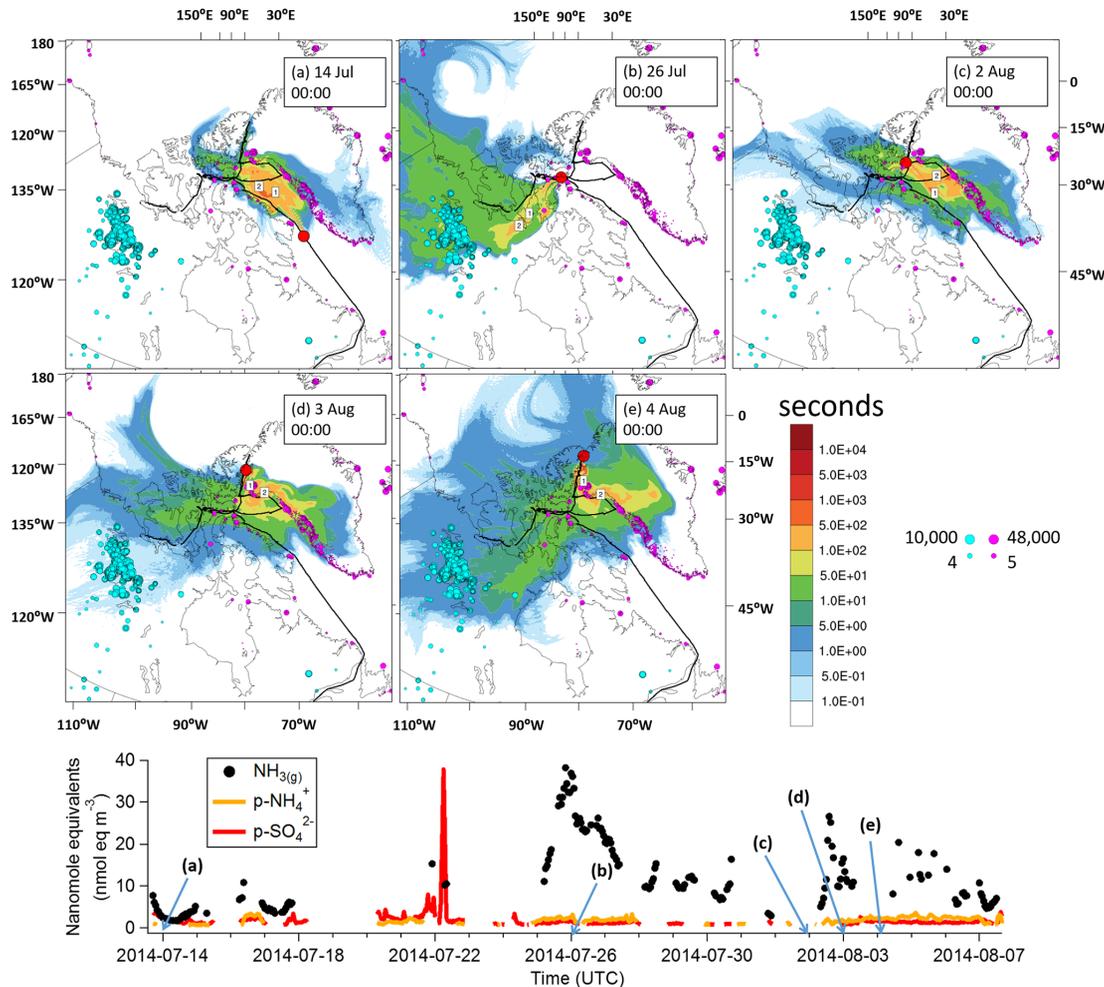


Figure 6. GEOS-Chem simulation of NH_3 mixing ratio (ppb) of the July monthly mean surface layer for (a) no seabird emissions and (b) with seabird emissions. Circles in panel (a) represent the ship track coloured by NH_3 measurements. Panels (c) and (d) show GEOS-Chem simulations for the ammonium to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

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.



Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Ammonia in the summertime Arctic marine boundary layer

G. R. Wentworth et al.

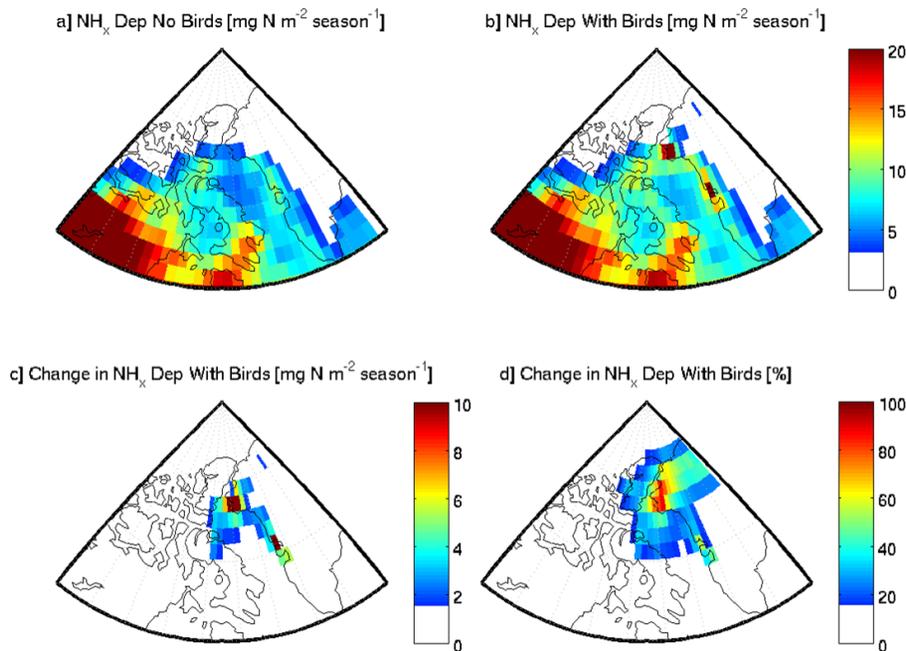


Figure 8. GEOS-Chem simulation of for total NH_x deposition (in mg N m⁻² season⁻¹) for the months May to September (inclusive). Panel (a) does not include seabird emissions, whereas panel (b) does. The difference in total NH_x deposition between the two emissions scenarios (with birds minus without birds)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

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)