Riddick, S.N.; Blackall, T.D.; Dragosits, U.; Daunt, F.; Newell, M.; Braban, C.F.; Tang, Y.S.; Schmale, J.; Hill, P.W.; Wanless, S.; Trathan, P.; Sutton, M.A. 2016. **Measurement of ammonia emissions from temperate and sub-polar seabird colonies**.

Measurement of ammonia emissions from temperate and sub-polar seabird colonies

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Key Words: Coastal nitrogen; seabirds; penguins; temperate; sub-polar; NH_3 emissions; atmospheric dispersion; inverse modelling

Abstract

The chemical breakdown of marine derived reactive nitrogen transported to the land as seabird guano represents a significant source of ammonia (NH_3) in areas far from other NH_3 sources. Measurements made at tropical and temperate seabird colonies indicate substantial NH_3 emissions, with emission rates larger than many anthropogenic point sources. However, several studies indicate that thermodynamic processes limit the amount of NH_3 emitted from guano, suggesting that the percentage of guano volatilizing as NH_3 may be considerably lower in colder climates. This study undertook high resolution temporal ammonia measurements in the field and coupled results with modelling to estimate NH_3 emissions at a temperate puffin colony and two sub-polar penguin colonies (Signy Island, South Orkney Islands and Bird Island, South Georgia) during the breeding season. These emission rates are then compared with NH_3 volatilization rates from other climates. Ammonia emissions were calculated using a Lagrangian atmospheric dispersion model, resulting in mean emissions of 5 µg m^{-2} s^{-1} at the Isle of May, 12 µg m^{-2} s^{-1} at Signy Island and 9 µg m^{-2} s^{-1} at Bird Island. The estimated percentage of total guano nitrogen volatilized was 5% on the Isle of May, 3% on Signy and 2% on Bird Island. These values are much smaller than the percentage of guano nitrogen volatilized in tropical contexts (31-65%). The study confirmed temperature, wind speed and water availability have a significant influence on the magnitude of NH_3 emissions, which has implications for reactive nitrogen in both modern remote regions and pre-industrial atmospheric composition and ecosystem interactions.

1. Introduction

Nitrogen is found in all living cells and is necessary for the growth and survival of all living things. However, nitrogen in its most abundant form, diatomic nitrogen (N_2), is a relatively un-reactive molecule and needs to be 'fixed' to become useable as reactive nitrogen (N_r) compounds. Nr includes all N forms with the exception of N_2, including ammonium and nitrate ions, gases such as nitrous oxide (N_2O), nitrogen oxides (NO_x) and ammonia (NH_3) and organic nitrogen compounds. Human activities, including the Haber-Bosch process, legume cultivation and fossil fuel combustion, are estimated to create 210 Tg of plant-useable N_r annually (Fowler et al., 2013). Reactive nitrogen added to the Earth's surface as fertilizer can wash off into the hydrosphere, volatilize to the atmosphere as NH_3 or form organic nitrogen compounds in soils. Further decomposition of oceanic, terrestrial, plant and animal N_r can produce N_2 as well as NO_x and N_2O.

Studies suggest the emission of NH_3 gas is likely to negatively impact local ecosystems causing acidification and eutrophication, which has been shown to alter local interspecies competition and biodiversity (Cape et al., 2009; Sutton et al., 2011, 2012). Currently, the biogeochemical processes following the addition of seabird derived N_r to the surface of land are not well understood. However studies have reported NH_3 emission from poultry excreta which has similar properties to seabird guano (Elliott and Collins, 1982; Harper et al., 2010) and a study of Adelie penguin colony on the Antarctic continent suggests volatilized NH_3 creates a spatial impact zone of up to 300 km^2 surrounding the colony where phosphomonoesterase activity is increased in indigenous organisms (Crittenden et al., 2014). In order to be emitted as NH_3, excreted uric acid must first be hydrolysed under microbial decomposition to produce ammonium and bicarbonate ions. Both the processes of uric acid hydrolysis and NH_3 volatilization appear to be affected by environmental conditions, including water availability and temperature (Nemitz et al., 2001; Sutton et al., 2013). Food composition and pH may also play a significant role in NH_3 emission (Elliott and Collins, 1982; Harper et al., 2010) where NH_3 emission depends on the ratio between the nitrogen and energy content of the food (Wilson et al., 2004) and the pH affects the rate at which uric acid is converted to ammonium (Elliott and Collins, 1982).

In a theoretical study on seabird N_r excretion by Riddick et al. (2012), the estimated percentage of N_r that volatilizes (P_v) ranged from 9 % in colder temperatures (average temperature during breeding season *c.* 5°C) to 100 % at colonies in higher temperatures (> 19°C). Recent measurement-based estimates showed mean P_v values of 31 to 65 % at two tropical seabird colonies estimated (Riddick et al., 2014). Additionally, some variation in P_v is expected in relation to habitat, so that birds nesting in vegetation and breeding in burrows (such as puffins), would show a lower percentage emission as NH_3 as compared with birds nesting and breeding on bare rock surfaces (Blackall et al., 2007; Riddick et al., 2012). Similarly, Zhu et al. (2011) suggest temperature is an important driver in the production of NH_3, however they also suggest temperature may not be the sole climatic variable that affects NH_3 emission.

Seabird colonies are well suited for measuring NH_3 emissions because they are generally remote from human activity, resulting in near-background NH_3 concentrations in the surrounding area. Biogeochemical processes are relatively simple because the majority of seabirds nest on rocky surfaces where excreted guano can: (1) build up on the surface; (2) decompose, converting uric acid to ammoniacal forms which are liable to volatilization, or (3) be washed into the sea. As a model system for studying the effect of climate/environment on NH_3 emissions, seabird colonies also have the advantage that they are generally not influenced by human management practices (other than those which may affect seabird numbers). In addition to this, the penguin species' annual presence in the nitrogen poor regions of the Southern Ocean supplies 858 Gg of N_r per year (~ 3 kg m^{-2}) in the form of guano to the land (Riddick et al., 2012). In agriculture terms, the average penguin colony receives 30,000 kg ha^{-1} compared with 246 kg ha^{-1} for fertilizer consumption on arable land in the UK in 2015 (Worldbank, 2015).

As a result of these features, seabird colonies offer a system that is well fitted to address the question of how NH_3 emission rates vary globally through different climatic regimes as well as develop understanding of atmosphere-ecosystem interaction in the natural world. The present study contributes to this question by providing data on NH_3 emissions from seabird guano in temperate and sub-polar conditions, for comparison with previous measurements in tropical conditions (Riddick et al., 2014). By bringing these measurements together with other published datasets, we are then able to investigate the global scale variation in NH_3 emission rates.

2. Methods and Materials

2.1 Ammonia measurements

Two methods were applied in this study to make NH_3 concentration measurements: (1) passive sampling and (2) an on-line active sampling NH_3 analysis instrument, as summarized below.

The passive samplers used (ALPHA samplers, CEH Edinburgh) consist of a 23 mm diameter sampler with a 6 mm diffusion path between a Teflon membrane and an adsorbent sampling surface (filter-paper disc impregnated with citric acid). Further details of ALPHA sampler and its system of pre- and post-sampling protective caps are provided by Tang et al. (2001). In this study, triplicate samplers were used at each sampling location and exposed for periods of 2 to 4 weeks. The samplers were attached by Velcro to an upturned plant saucer (for protection) that was fastened to a pole (The sampling heights above the ground for the different sites are described below, with further details given in Supplementary Material 7). Aluminium strips were mounted on top of each saucer to deter perching birds.

At all times, except during deployment, the ALPHA samplers were sealed in plastic containers and refrigerated. In the laboratory, the NH_3 concentration of the air at the seabird colony was determined using ammonium flow injection analysis, based on selective diffusion of NH_3 across a Teflon membrane at high pH (FLORRIA, Mechatronics, NL). Laboratory and field blanks were also analysed to ensure samples were not contaminated. In the present study, the high sensitivity ALPHA samplers were used with a Method Detection Limit (MDL) = 0.09 µg m^{-3} for two-weekly exposure on Signy Island. A description of how the MDL was calculated is given in Supplementary Material Section 1. ALPHA samplers were also deployed at Bird Island and the Isle of May for comparison with the on-line measurements.

The on-line NH_3 concentration measurements were made with an AiRRmonia gas analyser (Mechatronics, NL) on Bird Island and a Nitrolux 1000 gas analyser (Pranalytica, USA) on the Isle of May. At each site air was drawn into the instrument through 20 m PTFE tubing, to minimize NH_3 sticking the PTFE tubing was heated and insulated a full description of the online active measurement set up is given in Supplementary Material Section 3, with inlet flows of 8 l min^{-1}.

The AiRRmonia analyser (Norman et al., 2009) is based on a similar principle to the FLORRIA. In this case, atmospheric air is passed over a first Teflon membrane with a counterflow of dilute acid to allow gaseous NH_3 to transfer to aqueous ammonium in solution. Sodium hydroxide is then added to liberate molecular NH_3, which then diffuses across a second Teflon membrane into a counter flow of deionized water, with reformed ammonium then detected by conductivity. The AiRRmonia has an instrument delay time (the time taken between air sampling and instrument response) of ~ 5 minutes with 15 min averages used to assure quantitative response, with a Limit of Detection (LOD) of ~0.1 µg m^{-3} and a MDL in this context of 0.07 µg m^{-3}. The AiRRmonia measurements were recorded every minute and then the data averaged to 15 minute periods for application in the inverse dispersion model. Calibration of the AiRRmonia was carried out every five days and agreed within 5% over the periods of measurement.

The Nitrolux analyser is a photoacoustic instrument that uses absorption of NH_3 molecules from a line-tuneable CO_2 laser to measure concentration. The Nitrolux 1000, as used here, has a detection limit of ~0.1 µg m^{-3}, a MDL in this context of 0.1 µg m^{-3}, a range of 0.1 – 2000 µg m^{-3}, and measures concentrations every 45 s. The instrument delay time of the instrument is a function of temperature and relative humidity (typically 4 (3-5) minutes), allowing the data to be averaged up to 15 minute periods for application in the inverse dispersion model. The Nitrolux 1000 requires six-monthly calibrations (Cowen et al., 2004).

2.2 Field Methodology

Site 1: The Isle of May, Scotland

The Isle of May (56.19 °N, 2.56 °W) is a nesting site for many seabird species, including Common Guillemot (*Uria aalge*), Herring Gull (*Larus argentatus*), Arctic Tern (*Sterna paradisaea*), Black-legged Kittiwake (*Rissa tridactyla*) and Atlantic puffin (*Fratercula arctica*). The island is located at the entrance to the Firth of Forth in eastern Scotland (Figure 1) and has a temperate climate (average temperature of 15°C, average humidity of 80% and average wind speed of 4 m s^{-1} during the breeding season). Passive and active measurements of NH_3 concentrations and meteorological parameters were made above Atlantic puffin burrows (Figure 1). Atlantic puffins breed on vegetated slopes and amongst rocky outcrops, where they dig and nest in 1-2 m long burrows. Atlantic puffins burrow in most parts of the Isle of May with a colony total of 45,000 pairs during June and July 2009 (Harris et al., 2009), with approximately 20,000 burrows in our study area, between the Low Light and Kirk Haven (area shaded dark grey in Figure 1). Measurements were carried out from 01/07/09 to the 06/09/09 during (July) and after (August and September) the period of chick rearing, where large numbers of prospecting juvenile birds are present in addition to breeding birds.

<u>Active Sampling Campaign</u>

The Nitrolux trace gas analyser measured NH_3 concentrations on-line over the Atlantic puffin colony on the Isle of May from 30/06/09 to 23/07/09. The air inlet was positioned 1.26 m above the ground at the measurement site (labelled in Figure 1). Measurements during the Isle of May campaign were limited to daylight hours to reduce disturbance to fledging puffins by the generator. Micrometeorological parameters were measured using a Gill Windmaster Pro sonic anemometer on a mast 2.5 m above the ground. Meteorological data were collected by instruments on a mast on the highest point of the island (Figure 1). Data collected included: air temperature, relative humidity, solar radiation (all at 1 m above ground) and ground temperature was using temperature sensors on the surface. The weather station was located away from the colony to avoid interfering with birds' nesting behaviour.

<<INSERT FIGURE 1 HERE>>

Passive Sampling Campaign

Triplicate ALPHA samplers were used to measure NH_3 concentrations above the Atlantic puffin colony ("Measurement Site", as labelled in Figure 1), at a height of 1.5 m, for 4 periods of 15 days, as described in Supplementary Material Section 7A. Meteorological data were collected by a weather station positioned at the highest point of the island (Figure 1).

Site 2: Bird Island, South Georgia

Bird Island is part of South Georgia, 1000 km south-east of the Falkland Islands (Figure 2). Ammonia concentrations were measured at the 'Big Mac' Macaroni penguin (*Eudyptes chrysolophus)* colony at the western end of the island (54.0106 °S, 38.0753 °W), where 40,000 breeding pairs were present during the measurement period from 07/11/10 and 26/12/10 (D. Briggs, British Antarctic Survey, pers. comm.). Immediately to the east of the active measurement site, the 'Little Mac' colony is located (450 pairs of Macaroni penguin in a small satellite colony). The average temperature was 3°C, average relative humidity 92 % and average wind speed 5 m s^{-1} during the measurement period.

Active Sampling Campaign

On-line NH_3 concentrations were measured at Fairy Point to the south of Big Mac (Figure 2). The air inlet for the AiRRmonia analyzer was positioned at 2 m above the ground. All the instruments were housed in a tent to provide protection from the wind, precipitation, sea spray and sun. Micrometeorological parameters were measured using a Gill Windmaster Pro sonic anemometer on a mast 2.5 m above the ground. Meteorological data were collected by instruments on two masts on the highest point at Fairy Point. Data collected included: air temperature, humidity and solar radiation at 1 m above ground, and wind speed at three heights above ground (0.5 m, 1 m, and 2 m). Ground temperature was measured using a Tiny Talk data recorder placed on the ground (Supplementary Material Section 4).

<<INSERT FIGURE 2 HERE>>

Passive Sampling Campaign

Ammonia concentrations were recorded at nine locations on Bird Island using ALPHA samplers mounted at 1 m above ground (Figure 2). These were exposed in seven sampling periods of around 2 weeks from 07/11/2010 to 26/12/2010.

Site 3: Signy Island, South Orkney Islands

Signy Island is a small island in the South Orkney Islands in the Southern Ocean (Figure 3). A relatively flat area on the Gourlay Peninsula was used for passive sampling of NH_3 concentrations from 10/01/2009 to 21/02/2009 at a colony of 10,000 pairs of Adélie penguins (*Pygoscelis adeliae)* and 9,000 pairs of Chinstrap penguins (*P. antarcticum)* (60.73° S, 45.59° W). Both species breed in snow free areas and build rudimentary nests of small stones. The climate at this site represents sub-polar conditions with average temperature of 2°C, average relative humidity of 84 % and average wind speed of 5 m s^{-1} during the breeding season.

ALPHA samplers were deployed at five locations (Mast 1 – 5, Figure 3) over three separate sampling periods of 2 weeks each. Masts 1 and 2 had ALPHA samplers at 1 m and 1.5m from the ground. Mast 5 was located as far as possible from any birds to sample background NH_3 concentrations, *en route* from the base at Borge Bay to

Gourlay (Supplementary Material 3). Representative meteorological data (temperature, wind speed, relative humidity and precipitation) were obtained from the nearest weather station, the Argentinean Orcadas Base on Laurie Island, South Orkney Islands (US National Climatic Data Center (NCDC) Integrated Surface Hourly (ISH) database; NCDC, 2011).

<<INSERT FIGURE 3 HERE>>

2.3 Estimation of NH_3 Emissions

Estimates of NH_3 emissions were calculated using an inverse application of the WindTrax atmospheric dispersion model version 2.0 (Flesch et al., 1995). Given potential temporal covariance between atmospheric NH_3 concentrations and dispersion, such calculations should ideally be based on short-term measured concentrations.

For input into WindTrax, both the on-line NH_3 concentrations and meteorological data were averaged over 15 minutes to minimise any effects of turbulence while preserving variation caused by environmental or atmospheric change (Laubach et al. 2008; Flesch et al. 2009). Fifteen minute averages of wind speed (u, m s^{-1}), wind direction (WD, °), temperature (T, °C), NH_3 concentration at 2 m (X, µg m^{-3}), roughness height (z_0, cm) and the Monin-Obukhov length (L, m) were used as input to WindTrax.

For each on-line NH_3 concentration dataset, data were removed for calibration periods, any periods when the instrument was not sampling the colony due to wind direction and any periods of high atmospheric stability (wind speed, $u < 0.15$ ms^{-1}, friction velocity, $u^* < 0.1$ ms^{-1} and Monin-Obukhov Length $|L| < 2$). Each WindTrax simulation used 50,000 particle projections to back-calculate the NH_3 emission.

While the first focus of the emission calculations was on applying the on-line NH_3 concentration measurements, it is also of interest to assess how the inverse model performs when using time-integrated NH_3 concentrations, since it is not always feasible to deploy on-line NH_3 instrumentation (e.g. as at Signy Island). For this reason, we also applied the Windtrax model using two-weekly averaged NH_3 concentrations, coupled with the time-resolved estimates of atmospheric turbulence. In principle, this relaxation is expected to contribute significant errors in the resulting flux estimates. However, experience under other conditions indicates that these errors may be small when compared with other sources of error or with the difference in emission rates between sites (Riddick et al., 2014; Theobald et al., 2013). The deployment of both passive and active sampling at the Isle of May and at Bird Island allowed comparison these two approaches, providing a basis to assess confidence in the passive measurements at Signy Island, where only the passive NH_3 concentration data were available.

The comparison of estimated NH_3 emissions calculated using the passive and on-line sampling methods can also be used to provide an indicative estimate of the respective sources of error in each approach (Riddick et al., 2014). To do this, the concentrations recorded by the on-line continuous NH_3 detector are first averaged for the same periods as the passive ALPHA sampler data, and then used to estimate NH_3 fluxes using the WindTrax system. The difference in mean flux between the approach using 15 minute NH_3 concentrations and the 2-weekly averaged data from the on-line system gives an estimate of the micrometeorological error associated with low-time resolution NH_3 concentration data. By comparison, the difference in mean flux between the 2-weekly averaged data of the on-line system and the 2-weekly estimates from the ALPHA samplers gives an estimate of the chemical sampling error. This chemical sampling error can be mostly associated with the on-line system, because it only samples for part of the time (i.e. semi-continuous), as compared with the passive system, which samples continuously.

2.4 Other Uncertainties

In order to further understand the uncertainties in the emission calculation, the input variables were assessed for both field sites. The uncertainty caused by each variable was estimated using WindTrax to back-calculate the consequent change in estimated NH_3 emission. The total uncertainty was then calculated as the square root of the sum of the squares of the individual uncertainties. Further details are provided in the Supplementary Material Section 6.

3. Results

3.1 Isle of May

Active measurements and meteorological data

Measured NH_3 concentrations ranged from 0 to 105 μg m^{-3} and were found to be lower during the morning and evening than during the day (Figure 4). Ground temperature ranged from 12 to 27 °C and peaked during the early afternoon. The roughness length estimated using the ultrasonic anemometer on the Isle of May ranged from 0.1 to 13.8 cm, i.e., within the useable range of WindTrax. Ammonia emissions generally followed a diurnal pattern with low emission early in the morning (<5 μg m^{-2} s^{-1}), building to a peak in the early afternoon (10 to 25 μg m^{-2} s^{-1}), before dropping back to low values (<5 μg m^{-2} s^{-1}) in the evening (Figure 4). Overall, for the active measurements the average emission rate was 5 μg m^{-2} s^{-1}.

The uncertainty in background NH_3 concentration for the southern North Sea (0.03 - 1.49 μg m^{-3}) resulted in an emission uncertainty of 6 %. The uncertainty in the size of the NH_3 emission area (range of 0.2 – 0.3 km^2), caused by puffins moving around near their burrows during the day, resulted in an uncertainty in NH_3 emission of 10 % (Supplementary Material Section 6). Considering only these components, the overall uncertainty in the modelling of the emission estimate on the Isle of May is estimated at 12 %. A major source of uncertainty is the representatively of the NH_3 sampling, given that measurements were only made for part of the time, with the generator having to be switched off during the hours of darkness. This is addressed further in section 3.4.

<<INSERT FIGURE 4 HERE>>

Passive measurements

Ammonia concentrations decreased from a maximum of 36.1 μg m^{-3} during the first period to a minimum of 0.9 μg m^{-3} during the fourth measurement period, due to measurements being made towards the end of the breeding season. The NH_3 emission was highest during Period 1 (01/07/09 - 15/07/09), estimated at 5.1μg m^{-2} s^{-1}. By mid-July, most puffins had fledged and had left the nesting site. As a consequence, NH_3 emission decreased to 1.9, 0.4, 0.1 μg m^{-2} s^{-1} during measurement periods 2, 3 and 4, respectively (for more details see Supplementary Material Section 7A). Temperatures were broadly similar through the four sampling periods (Supplementary Material Section 7A).

The uncertainty in the estimated emission caused by the roughness length, NH_3 background and emission area were 12, 8 and 10 %, respectively (See Supplementary Material Section 6). The largest estimated uncertainty was the Monin-Obukhov length at 28%. Overall, these factors contributed a combined uncertainty of ± 38 % to the model results from the passive campaign on the Isle of May. However, this does not include the micrometeorological uncertainty associated with long-averaging periods, which is considered separately in Section 3.4.

3.2 Bird Island, South Georgia

Active measurements and meteorological data

The NH_3 concentrations measured by the AiRRmonia trace gas analyser were between 0 and 60 μg m^{-3}, with higher concentrations recorded during the daytime (Figure 5). Ground temperature ranged from 1 to 12 °C, with maximum values during the early afternoon (Figure 5). The roughness length estimated from the ultra-sonic anemometer on Bird Island ranged from 6 to 12.5 cm and was within the useable range of WindTrax. Gras (1983) estimated open water background NH_3 concentration for Antarctica, a location representative of this area, at 0.15 μg m^{-3}, which was used as the background concentration in WindTrax. The minimum and maximum NH_3 emissions from the Big Mac penguin colony during the measurement period were 0.6 μg m^{-2} s^{-1} and 52.6 μg m^{-2} s^{-1}, respectively (Figure 5). The largest emissions occurred during the daytime, associated with higher wind speeds (Figure 5), with smaller emissions at night.

The emission uncertainty caused by the uncertainty in the size of the excretion area, again caused by penguins moving around the edge of the nesting site, and NH_3 background were estimated at 27 % and 4 %, respectively (Supplementary Material Section 6). The combined uncertainty calculated for the modelled emission estimate from the Big Mac penguin colony was at ± 28 %. The additional uncertainty associated with the semi-continuous nature of the NH_3 measurements is examined in Section 3.4.

<<INSERT FIGURE 5 HERE>>

Passive measurements

Ammonia concentrations nearest the colony (3 m from the edge of Big Mac) decreased from a maximum of 34.2 μg m^{-3} during the third period (21/11/2010 to 28/11/2010) to a minimum of 11.3 μg m^{-3} during the fifth measurement period (06/12/2010 to 12/12/2010; NH_3 concentration data is presented in Supplementary Material Section 7B, full transect data to be published elsewhere (Tang et al. in prep.). The NH_3 emission, calculated with WindTrax, was highest during Period 2 (Table 1), estimated at 11.2 μg m^{-2} s^{-1} and lowest during the fifth measurement period at 3.2 μg m^{-2} s^{-1}.

The uncertainty in the estimated emissions caused by the roughness length, NH_3 background and emission area were 15, 12 and 12%, respectively (Supplementary Material Section 6). The largest estimated uncertainty was associated with micrometeorology at 35%. Overall, these amount to a combined uncertainty for the passive campaign on Bird Island of ± 42%.

3.3 Signy Island

On Signy Island the ALPHA samplers were exposed for three two-week periods (Supplementary Material Section 7C). The NH_3 concentrations at Masts 1 and 2, measured at a height of 1 m above the ground in the middle of the colony, were the highest (maximum 483 µg m^{-3}) of the different sampling locations at Signy. NH_3 concentration decreased with distance from the penguin colony to a minimum at Mast 5 (0.9 to 2.1 µg m^{-3}). The ALPHA samplers lower to the ground (1 m height) measured larger NH_3 concentration, as expected (see Supplementary Material Section 7C for details). The atmospheric conditions averaged over the measurement period were estimated as neutral, (i.e. ($L = |\infty|$) because of low ground heating and relatively high wind (Seinfeld and Pandis, 2006). The most obvious sources of aerodynamic roughness in the otherwise very flat area were the penguins (average height 60 cm) and any larger rocks (maximum height estimated at 1 m). Therefore, a roughness height of 10 cm, corresponding to an object height of 1 m (Seinfeld and Pandis, 2006), was used for modelling. The NH_3 source area was assumed to be the observed nesting area, which was 2.7 x 10^3 m^2.

The calculated NH_3 emission fluxes for the penguin colony on Signy Island were 18, 8 and 9 µg m^{-2} s^{-1} for periods1, 2 and 3, respectively. The wind was almost constantly from the north-west, which suggests that the footprint of the source sampled by each ALPHA sampler was not a very significant source of variation. The micrometeorological conditions on Signy Island could only be estimated from available data on Laurie Island, South Orkney Islands, and therefore a larger uncertainty is associated with meteorological data needed to estimate NH_3 emissions.

The difference in the NH_3 emission rates between the first and second/third measurement periods may be explained by the birds' behaviour, with colony attendance during the first measurement period being high for both Adélie and Chinstrap penguins. The lower emissions during the second and third periods may be associated with the departure of the Adélie penguins around late January.

Together, the uncertainty in roughness length and stability resulted in an uncertainty in emission of 26 % (Supplementary Material Section 6). The uncertainty associated with background concentration from Gras (1983) was 7 % and the associated uncertainty in area was estimated at ± 6 %. The combined uncertainty in modelling NH_3 emissions for Signy Island was estimated at ± 37 %, although this does not include uncertainty related to application of the time-integrated ALPHA sampling, which is addressed in Section 3.4.

3.4 Comparison of Active and Passive Sampling methods

A summary of the measurements made at the different colonies of this study is provided in Table 1. For the Isle of May, the mean fluxes from the passive and active sampling campaigns were 5.1 and 5.3, µg m^{-2} s^{-1}, respectively. The estimate of the flux from the active sampling averaged for the same period as the ALPHA measurements was 6.0 µg m^{-2} s^{-1}. The difference between the first and third of these fluxes represents the Uncertainty in Sampling Period (USP), at -1.0 µg m^{-2} s^{-1}, while the difference between the second and third of these represents the Uncertainty in chemical Sampling Method (USM), at -1.0 µg m^{-2} s^{-1}. In both cases the USP and USM amount to around +/-20% of the mean flux at Isle of May.

<<INSERT TABLE 1 HERE>>

A similar comparison of active and passive sampling at Bird Island gave a mean flux during the first period from the passive and active sampling campaigns of 11.2 and 10.3 µg m^{-2} s^{-1}, respectively. The mean fluxes during the second period from the passive and active sampling campaigns were 8.9 and 10.5 µg m^{-2} s^{-1}, respectively.

The estimate of the flux from the active sampling averaged for the first and second periods as the ALPHA measurements was 10.6 and 10.7 µg m^{-2} s^{-1}, respectively. The estimate of the flux from the active sampling averaged for the average of the two periods of the ALPHA measurements was 10.7 µg m^{-2} s^{-1}. In this case the USP amounts to around 3% of the mean measured fluxes, whereas the USM was 6% for the first period and 17% for the second period (Table 1).

In the case of Signy, only passive estimates of the flux were available, where the overall mean of the three runs was 12 µg m^{-2} s^{-1}. Although active sampling was not possible at this site, the performance comparison distinguishing USP and USM at Isle of May and Bird Island may be taken as an indication of the scale of uncertainty associated with the long sampling periods on Signy.

4. Discussion

4.1 Variation in NH_3 emissions from seabird colonies

The largest weekly average NH_3 emission measured by this study was 18 µg m^{-2} s^{-1} on Signy Island, South Orkney Islands. Higher rates of NH_3 emission (22 µg m^{-2} s^{-1}) were observed above the Brown noddy colony on Michaelmas Cay, Great Barrier Reef, Australia (Riddick et al., 2014), while Blackall et al. (2007) reported even larger emission rates equivalent to 240 µg m^{-2} s^{-1} from Atlantic gannets on the Bass Rock, Scotland. These results illustrate how NH_3 emissions from seabird colonies are considerable discrete NH_3 sources in a wide range of climates.

However, such figures tend to mask the climatic dependence of NH_3 emission, since they are also a function of nesting density, and for total colony emissions, of bird numbers, types and colony attendance, etc. It is therefore helpful to normalize the emission rates per g of bird biomass. In this case, it can be seen that NH_3 emission is much higher at the tropical colony (7.5 ± 2.6 mg NH_3-N g^{-1} bird yr^{-1}; Michaelmas Cay) than at the sub-polar Bird Island colony reported here (0.05 ± 0.01 mg NH_3-N g^{-1} bird yr^{-1}).

Another way to normalize the NH_3 emission data is to calculate the percentage of excreted nitrogen that volatilizes as NH_3 (P_v, %), as described in Supplementary Material Section 8. An excretion rate (Furness et al., 1991; Wilson et al., 2004), calculated from the adult/chick mass, nitrogen content of the food, energy content of the food, assimilation efficiency of ingested food and proportion of time spent at the colony during the breeding season has been used instead of direct measurements of guano depth up at the colony to reduce disturbance to breeding birds and minimize the risk of egg/chick abandonment. For the measurements reported here, a P_v value of 4.7 ± 0.5 % was calculated for the Atlantic puffin colony on the Isle of May, compared with 1.6 ± 0.4 % for Bird Island and 3.1 ± 1.1 % for Signy Island, respectively (percentage error in measurement and modelling; Table 1).

In Table 2 the values from the present study are compared with emission rates and estimates of P_v from other published studies. This shows the largest values of P_v at tropical colonies, such as the Brown noddy colony on Michaelmas Cay, where P_v was estimated at 65 ± 22 % (Riddick et al., 2014), and the smallest values in sub-polar conditions, with comparable values for Bird Island and Signy Island (2%, 3%, respectively) and Cape Hallet on mainland Antarctica (2%, Theobald et al., 2013). These observations are in agreement with Zhu et al. (2011) who also found that NH_3

emissions are larger under increased temperature. However, moisture limitation can also be important at high temperatures.

As Riddick et al. (2014) showed for the two tropical islands, the higher value for Michaelmas Island (67%) than for Ascension Island (32%) reflected a moisture limitation at the latter site. In this instance, of two sites with similar temperatures, it appears that the limited water availability at Ascension Island resulted in a lower rate of uric acid hydrolysis, thereby leading to lower NH_3 emissions. By contrast, the overall increase in observed P_v with increasing temperature across the sites (Table 2) may be a consequence of both increasing volatility of NH_3 and increasing rates of uric acid hydrolysis, where sufficient moisture is available, although it is not possible to distinguish these component effects from our measurements. In order to examine these drivers separately, specific process modelling is needed (Riddick, 2012; Riddick et al. in prep).

<<INSERT TABLE 2 HERE>>

It is worth noting that the measured P_v for the Atlantic puffin colony on the Isle of May (5%) is much lower than the estimate by Riddick et al. (2012) and the measurements made in similar conditions on the rocky cliffs of the Isle of May (Guillemot) and Bass Rock (Northern gannet) by Blackall et al. (2004; 2007) (16-36%). The much lower emission rate for Atlantic puffins, compared with Northern gannets and Guillemot under the same climate, may be attributed to their habitat preference as burrow nesters in grassland. This illustrates how climatic conditions are not the only factors to affect NH_3 emission. In the case of the puffins on the Isle of May case, the comparison suggests that emissions rates are about 14-31% of what would be emitted by bare-rock breeding birds under the similar temperate climatic conditions.

Excretory behaviour of Atlantic puffins varies between individual birds and can lead to variation in NH_3 emissions. The entrance chambers of most puffin burrows are free from guano, with chicks deeper in the nest excreting inside the burrow, but adults do not excrete in the burrow (M. Newell, pers. comm.). A significant fraction of the NH_3 emitted from subterranean excreta can therefore be expected to be absorbed by overlying soil and vegetation. The amount of puffin excretion on the land surface changes during the day as well as between days, puffins can be observed in large numbers across the colony, often at dusk and less so at dawn (Harris & Wanless, 2011).

In earlier modelling estimates, the presence of substantial amounts of vegetation has been estimated to reduce NH_3 by a multiplier of 0.2 (Wilson et al., 2004), while NH_3 emissions from excretion inside burrows was estimated to be 0.1 of that on bare rock. Based on the P_v values presented in Table 2, the present measurements in the Firth of Forth indicate 0.14 or 0.31 times lower emissions for Puffins (grass and burrows) compared with Northern Gannets or Guillemots, respectively (which are both bare rock breeders) which are broadly consistent with the prior model estimates.

4.2 NH_3 Emissions and environmental conditions

The NH_3 emission estimates from the on-line measurements offer the possibility to compare and interpret emission rates with environmental parameters during the course of the measurement campaigns. This is illustrated for the Isle of May and Bird Island in the present study and for Ascension Island (Riddick et al., 2014), based on a comparison of hourly emission estimates to each environmental variable (ground temperature, relative humidity, wind speed and precipitation) at each site (Supplementary Material Section 10).

The results show ground temperature is positively correlated to measured NH_3 emission at each site, representing tropical, temperate and sub-polar climates. The strongest correlation with temperature was found at the Isle of May (R=0.7; P<0.001). Conversely, the weakest correlation between ground temperature and NH_3 emissions was found for Ascension Island (R=0.2; P<0.001), which appears to have been due to the overriding importance of moisture-limitation on the temporal pattern of emissions at this site (Riddick et al., 2014). This is illustrated by a higher correlation between NH_3 emission and relative humidity (R = 0.4; P<0.001) and NH_3 emission and precipitation events (R = 0.3; P<0.001) at Ascension Island. In fact, Ascension is the only field site where there is a positive correlation between NH_3 emission and both relative humidity and precipitation, whereas relative humidity is inversely correlated to emission at the Isle of May and Bird Island. This indicates that, where there is sufficient water availability for uric acid hydrolysis (as at Bird Island and the Isle of May), excess water tends to suppress the measured NH_3 emission.

Wind speed has a positive correlation with emission at all sites, with this correlation being strongest in the sub-polar conditions of Bird Island (R = 0.9; P<0.001) and weakest in the tropical conditions of Ascension Island (R = 0.1; P=0.09). This may reflect the fact that Bird Island is the windiest site (2 - 18 m s^{-1}) with the smallest moisture limitation and temperature variation, so that turbulence is the major controller of hourly variation in NH_3 emissions. By contrast, wind speeds were lower at Ascension Island, so that the effect of varying moisture limitation largely masked the effect of wind speed.

It was assumed that the pH at each site remained constant throughout. No direct measurements of pH were taken because of access restrictions to the breeding sites and changes in pH of the guano may explain some of the variance in results. Supplementary Material Section 11 shows there is some correlation between soil pH and P_v (R^2 = 0.40, number of points = 11, p-value 0.04). Supplementary Material Section 11 also shows that there is also a negative correlation between seabirds' food energy to nitrogen ratio (R^2 = 0.61, number of points = 11, p-value 0.004). The energy to nitrogen ratio is significantly correlated to P_v, but that the response is very weak as the ratio only goes from 167 to 189, ie around 10% variation, so cannot propagate much to other estimates, and may simply reflect input uncertainty in the dataset. The sample size of species and diet is very small and further investigation is required to ensure this is not correlated solely with temperature.

4.3 Comparison of Active and Passive sampling methods

The comparison summarized in Table 1 shows that the approach of calculating time-averaged NH_3 fluxes from ALPHA samplers provided surprisingly similar estimates to those calculated from on-line sampling with 15 minute averaging. This finding is consistent with a similar comparison by Riddick et al. (2014) for tropical colonies, and by Theobald et al. (2013) for measurements on mainland Antarctica. In principle, while co-variance between NH_3 concentrations and varying atmospheric turbulence is expected to lead to significant errors, these comparisons show that the errors associated with this can be relatively modest in practice. While this finding may be a surprise to micrometeorologists, it appears to result from the fact that non-linearities associated with averaging over periods of changing atmospheric stability are relatively modest when compared with other sources of uncertainty, especially for such sites at relatively windy locations.

By calculating the flux using the on-line NH_3 sampling, but with the time resolution of the ALPHA samplers, we can also compare the chemical and meteorological sources of uncertainty. In this way, Table 1 shows that the Uncertainty associated with the Sampling Period (USP) is of comparable magnitude to the Uncertainty associated with the chemical Sampling Method (USM). This study therefore further provides support for the utility of low-cost passive sampling measurements at remote locations where it is often logistically much harder to deploy expensive active sampling methods. While such passive NH_3 flux measurements cannot replace continuous measurements for the examination of detailed (e.g. hourly) temporal controls on emissions (Supplementary Material Section 10), they may serve a useful role in gathering data over longer periods (e.g. 2-weekly measurements over several years) for comparison of seabird colonies in different climates.

5. Conclusions

The analysis shows that each of the environmental variables investigated have an influence on NH_3 emission (ground temperature, relative humidity, precipitation, wind speed). Increases in NH_3 emission caused by increases in relative humidity and rain events were only observed at the arid Ascension Island field site, where lack of moisture appeared to limit rates of uric acid hydrolysis. At other sites in colder climates, increases in precipitation result in decreased NH_3 emission, because rain events dilute available ammonium pools, while having the potential to wash uric acid and NH_3 from the surface. Ammonia emission was found to increase with wind speed especially at the cooler sites, reflecting a reduction in both aerodynamic and boundary layer resistances at higher wind speeds. Overall, the most consistent relationship is the increase in NH_3 emission with increasing ground temperature.

Future work will examine these mechanisms more explicitly using a mechanistic model (Blackall, 2004; Riddick, 2012), allowing the observed relationships between environmental conditions and NH_3 emission to be better understood, as well as providing a basis for simulating the effect of future climate change scenarios on global NH_3 emissions from seabird colonies.

Acknowledgements

This work was supported by a grant from the NERC CEH Integrating Fund and jointly carried out between the Centre for Ecology & Hydrology and King's College, London. Thanks to D. Briggs of BAS on Signy for information on meteorology and nesting penguins, and the BAS Bird Island crew for their technical and physical support (BAS CGS grant). Thanks to the CEH seabird group and other researchers on the Isle of May, especially to M. Harris, T. Alampo and D. Pickett (the last two from Scottish National Heritage). Special thanks to A. Easton and C. Murray for transport to and from the Isle of May.

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Figure 1 Left pane: Location of the Isle of May off the coast of Scotland, UK (56.19 °N, 2.56 °W). Right pane: Details of the Isle of May showing the Atlantic Puffin study colony, meteorological station and the site for on-line campaign measurements of ammonia concentration.

Figure 2 Top left pane: Location of measurement site on South Georgia (54.01 °S, 38.08 °W). Bottom left pane: Location of Bird Island in relation to South Georgia. Right pane: North western Bird Island indicating locations of Big Mac Macaroni penguin colony being studied, location of passive samplers and the site of the active ammonia concentration measurements, at Fairy Point.

Figure 3 Top left pane: Location of measurement site on South Orkney Island (60.73 °S, 45.59 °W). Bottom Left pane: Location of Signy Island relative to the South Orkney Islands. Right pane: Details of south-eastern Signy Island showing the ammonia sampling locations (ALPHA masts) in relation to the studied nesting area of Adélie and Chinstrap penguin nests on the Gourlay Peninsula of Signy Island.

Figure 4. Time-course of measured ammonia concentrations (top), calculated NH_3 emissions (bottom) for the active sampling campaign on the Isle of May, Scotland July 2009.

Figure 5 Time-course of measured ammonia concentrations (top), calculated NH_3 emissions (bottom) for the active sampling campaign on Bird Island, South Georgia, November & December 2010.

Table 1 Comparison of active and passive sampling. Summary of seabird colony NH_3 emissions estimated from temperate and sub-polar measurement campaigns. P_v is the percentage of excreted nitrogen that volatilizes as NH_3, Ground T is the ground temperature, USP represents the uncertainty in the flux attributable to the choice of sample averaging period and USM represents the uncertainty in the flux caused by the choice of sampling method (see notes below). Colony M indicates Isle of May, colony B indicates Big Mac on Bird Island and colony S indicates Signy Island.

Table 2 Summary of seabird colony NH_3 emissions estimated from measurement campaigns at the field sites in this study as compared with other recent measurements. Column P_v describes the percentage of seabird excreted nitrogen that volatilizes as NH_3.

		Passive				On-line measurement								
Colony	Measurement Period	$[NH_3]$ ($\mu g\ m^{-3}$)	Av. Flux NH_3 ($\mu g\ m^{-2}\ s^{-1}$) (Flux a.)	Uncertainty in flux ± ($\mu g\ m^{-2}\ s^{-1}$)	P_v (%)	Av. Flux NH_3 ($\mu g\ m^{-2}\ s^{-1}$) (Flux b.)	Uncertainty in flux ± ($\mu g\ m^{-2}\ s^{-1}$)	P_v (%)	Av. $[NH_3]$ ($\mu g\ m^{-3}$)	Flux using Av. $[NH_3]$ ($\mu g\ m^{-2}\ s^{-1}$) (Flux c.)	Uncertainty in flux ± ($\mu g\ m^{-2}\ s^{-1}$)	P_v (%)	USP ($\mu g\ m^{-2}\ s^{-1}$)	USM ($\mu g\ m^{-2}\ s^{-1}$)
M	1	36[1]	5.1	1.9	5	5.3	0.6	5	41[4]	6.0	2.0	6	-1.0	-1.0
M	2	16[1]	1.9	0.7	2									
M	3	3[1]	0.4	0.2	2									
M	4	1[1]	0.1	0.1	0									
B	1	13[2]	3.6	1.5	1									
B	2	36[2]	11.2	4.7	3	10.3	2.9	2	9[5]	10.6	2.9	3	-0.3	0.6
B	3	34[2]	8.9	3.7	2	10.5	2.9	2	9[5]	10.7	2.9	3	-0.2	-1.8
B	4	16[2]	4.4	1.8	1									
B	5	11[2]	3.5	1.5	1									
B	6	16[2]	4.3	1.8	1									
B	7	29[2]	9.2	3.9	2									
S	1	290[3]	18.2	6.1	3									
S	2	171[3]	7.9	2.7	3									
S	3	339[3]	9.0	3.1	3									

[1] Ammonia concentrations measured in the middle of the colony (Passive Measurement site, Isle of May) and 1.5 m from the ground

[2] Ammonia concentrations measured at 3 m from the edge of the colony (Mast 1, Bird Island) and 1 m from the ground

[3] Ammonia concentrations measured in the middle of the colony (Mast 1, Signy Island) and 1 m from the ground

[4] Ammonia concentrations measured in the middle of the colony (Active Measurement site, Isle of May) and 1.26 m from the ground

[5] Ammonia concentrations measured at 300 m from the edge of the colony (Active Measurement site, Bird Island) and 2 m from the ground

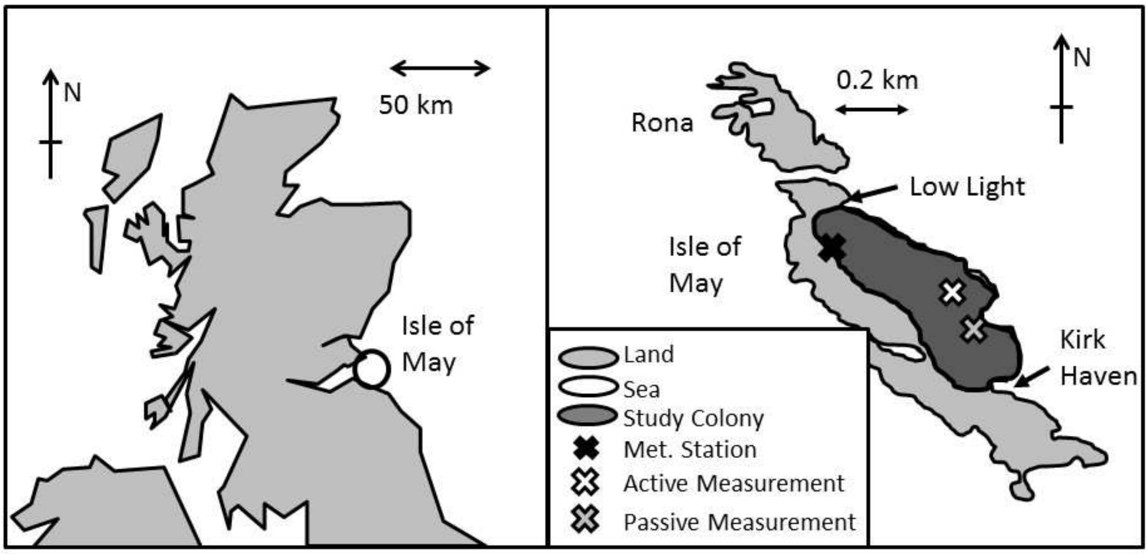
Notes:

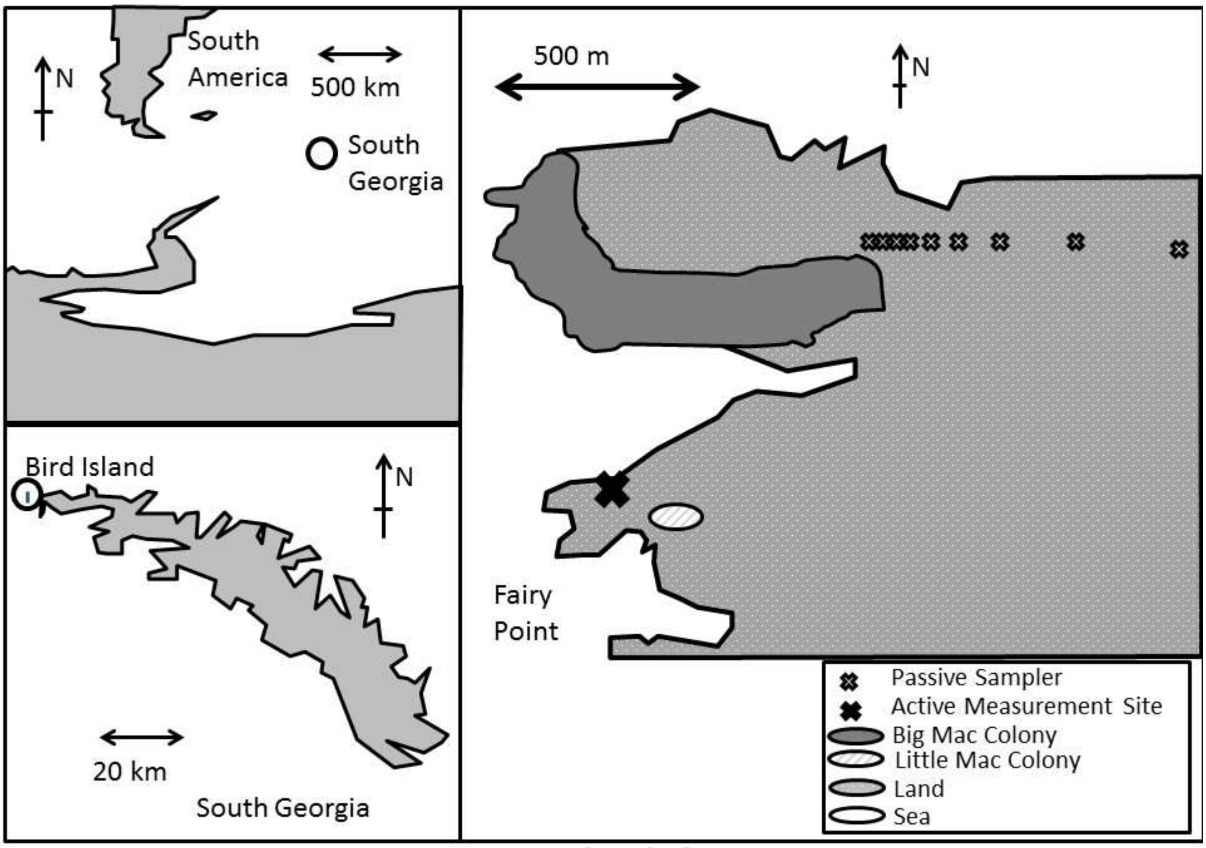
- Flux a. Flux calculated as the mean (+/- uncertainty) of hourly flux estimates based on hourly meteorology and time-integrated NH_3 concentrations from passive sampling
- Flux b. Flux calculated as the mean (+/-uncertainty) of available hourly flux estimates derived from application of the on-line hourly NH_3 measurements with hourly meteorology.
- Flux c. Flux calculated as the mean (+/-uncertainty) of flux estimates calculated from the on-line NH_3 measurements based on block averaging the NH_3 concentrations to the same extended sampling periods as used for the passive sampling.

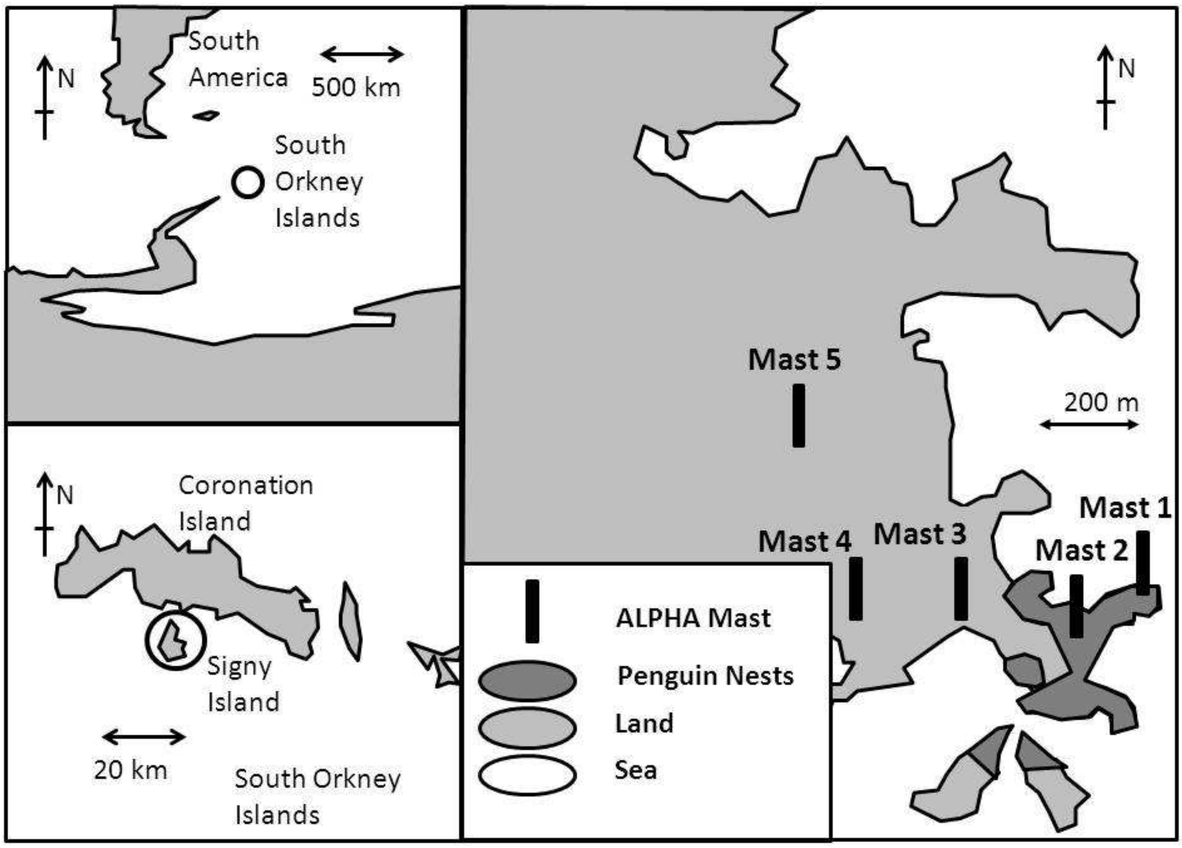
USP is calculated as flux b minus flux c, and estimates the uncertainty in flux a and c due to using time-integrated NH_3 sampling instead of continuous hourly NH_3 concentrations. USM is calculated as flux a minus flux c, and estimates the uncertainty in flux b and c due to incomplete sampling when using the on-line measurement system.

Colony	Average T (°C)	Breeding pairs of seabirds	Bird species measured	Calculated NH_3 emission (µg m-2 s-1)	P_v (%)	*Source*
Isle of May (Scotland)[#]	14	41,000	Atlantic puffin	5	5	This study
Signy Island (South Orkney)	2	19,000	Adélie and Chinstrap penguins	12	3	This study
Bird Island (South Georgia)[#]	3	40,000	Macaronic penguin	9	3	This study
Mullet Island (California, USA)	32	4,000[a]	Double-crested Cormorant	58[a]	22[a]	Tratt et al. (2014)
Ascension Island (Atlantic)	30	1,00,000	Sooty tern	19	32	Riddick et al. (2014)
Michaelmas Island (Australia)	30	10,000	Sooty tern	22	67	Riddick et al. (2014)
Cape Hallet (Antarctica)	-1	39,000	Adélie penguin	2	2	Theobald et al. (2013)
Isle of May cliffs (Scotland)	14	2,00,000	Guillemot	3	16	Blackall et al. (2007)
Bass Rock (Scotland)	17	44,000	Northern gannet	240	36	Blackall et al. (2007)
Amanda Bay, Antarctica	4		Emperor penguin		12	Zhu et al. (2011)
Gardener Island, Antarctica	4		Adélie penguin		1	Zhu et al. (2011)

[a] Estimates based on data in Tratt et al. (2014) and data from Riddick et al. (2012).
\# mean of the estimates from active and passive sampling (Table 1).


N
50 km
Isle of
May
0.2 km
N
Rona
Low Light
Isle of
May
Kirk
Haven
Land
Sea
Study Colony
Met. Station
Active Measurement
Passive Measurement


South
America
500 km
N
South
Georgia
Bird Island
N
20 km
South Georgia
500 m
N
Fairy
Point
Passive Sampler
Active Measurement Site
Big Mac Colony
Little Mac Colony
Land
Sea


South
America
500 km
N
South
Orkney
Islands
N
Coronation
Island
Signy
Island
20 km
South Orkney
Islands
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Mast 5
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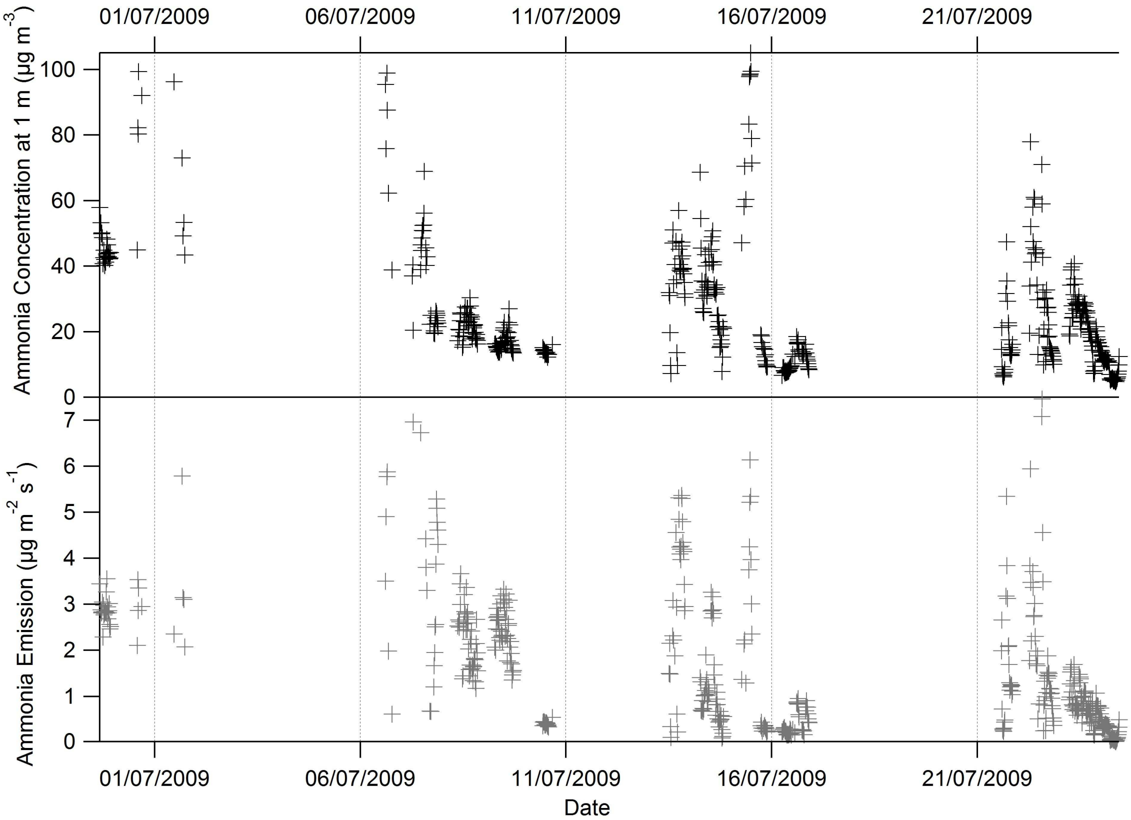
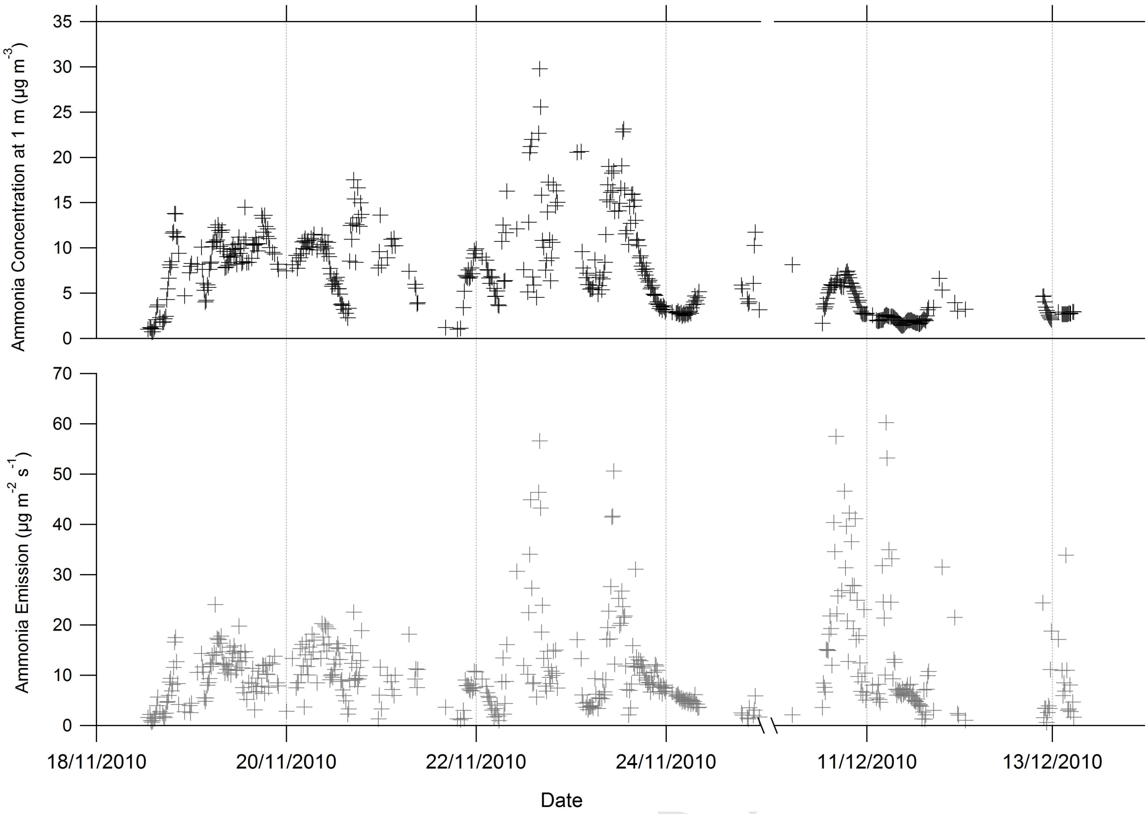
Mast 1
Mast 4
Mast 3
Mast 2
ALPHA Mast
Penguin Nests
Land
Sea



01/07/2009
06/07/2009
11/07/2009
16/07/2009
21/07/2009
Ammonia Concentration at 1 m (µg m-3)
100
80
60
40
20
0
Ammonia Emission (µg m-2 s-1)
7
6
5
4
3
2
1
0
Date



Ammonia Concentration at 1 m (µg m-3)
35
30
25
20
15
10
5
0
Ammonia Emission (µg m-2 s-1)
70
60
50
40
30
20
10
0
18/11/2010
20/11/2010
22/11/2010
24/11/2010
11/12/2010
13/12/2010
Date

>The effect of meteorology on NH_3 fluxes from temperate and sub-polar seabird colonies is measured. >The percentage of excreted nitrogen that volatilized was 3% at sub-polar penguin colonies. > The percentage of guano nitrogen volatilized in temperate and sub-polar environments is much smaller than in tropical contexts. > Confirms that temperature has a significant influence on the magnitude of NH_3 emissions.