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Measurement of ammonia emissions from tropical seabird colonies.

Measurement of ammonia emissions from tropical seabird colonies

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Abstract

The excreta (guano) of seabirds at their breeding colonies represents a notable source of ammonia (NH_3) emission to the atmosphere, with effects on surrounding ecosystems through nitrogen compounds being thereby transported from sea to land. Previous measurements in temperate UK conditions quantified emission hotspots and allowed preliminary global upscaling. However, thermodynamic processes and water availability limit NH_3 formation from guano, which suggests that the proportion of excreted nitrogen that volatilizes as NH_3 may potentially be higher at tropical seabird colonies than similar colonies in temperate or sub-polar regions. To investigate such differences, we measured NH_3 concentrations and environmental conditions at two tropical seabird colonies during the breeding season: a colony of 20,000 tern *spp*. and noddies on Michaelmas Cay, Great Barrier Reef, and a colony of 200,000 Sooty terns on Ascension Island, Atlantic Ocean. At both sites time-integrated NH_3 concentrations and meteorological parameters were measured. In addition, at Ascension Island, semi-continuous hourly NH_3 concentrations and micrometeorological parameters were measured throughout the campaign. Ammonia emissions, quantified using a backwards Lagrangian atmospheric dispersion model, were estimated at 21.8 μg m^{-2} s^{-1} and 18.9 μg m^{-2} s^{-1} from Michaelmas Cay and Ascension Island, respectively. High temporal resolution NH_3 data at Ascension Island estimated peak hourly emissions up to 377 μg NH_3 m^2 s^{-1}. The estimated percentage fraction of total guano nitrogen volatilized was 67% at Michaelmas Cay and 32% at Ascension Island, with the larger value at the former site attributed to higher water availability. These values are much larger than published data for sub-polar locations, pointing to a substantial climatic dependence on emission of atmospheric NH_3 from seabird colonies.

1. Introduction

Seabird colonies represent major point sources of ammonia (NH_3) emissions to the atmosphere. Seabirds are globally distributed; therefore the NH_3 emissions occur in a wide range of climatic environments. The high nitrogen (N) diet of seabirds is almost exclusively marine-derived (Phillips et al., 1999) and excretal N mainly occurs in the form of uric acid. Through bacterial hydrolysis, the reaction product NH_3 is formed

(Wright, 1995) which is liable to volatilize to the atmosphere, disperse and be deposited to terrestrial ecosystems. The result is that seabird-derived NH_3 provides a vector for transfer of marine N back to land (Blackall et al., 2008).

The majority of seabird colonies are found in remote coastal areas (e.g. Wilson et al. 2004). Due to their isolation from anthropogenic reactive nitrogen (N_r) sources, several studies suggest that seabird colonies are the most important pathway for plant nutrient supply within these ecosystems (Lindeboom, 1984; Hop et al., 2002). Schmidt et al. (2010) made measurements of NH_3 concentrations and enzyme assays at a tropical coral cay with large bird colonies, and the results showed that the dominant source of vegetation N was foliar NH_3 uptake.

In naturally low-N terrestrial ecosystems, even relatively small inputs of N from seabirds have been shown to cause increases in plant productivity that would not have normally been observed in already nutrient rich environments (Ellis, 2005). Even though N is essential for plant growth, excess NH_3 can negatively affect tolerance to drought or frost and resistance to disease and insects in plants, and/or lead to long term changes in plant species composition, with nitrophilic plants out-competing species adapted to low-N environments (Cape et al., 2009; Sutton et al., 2011).

Ammonia emission data from seabird populations in contrasting weather conditions have not been previously reported and emission dynamics coupled to changes in weather are not well understood. Blackall et al. (2004, 2007) measured NH_3 concentrations downwind of UK (temperate weather conditions) seabird populations (T ~ 15°C during the breeding season) and reported the percentage of seabird-N volatilized as NH_3 (P_v) =33%. Environmental factors may have a significant impact on P_v, for example recent measurements by Theobald et al. (2013) suggest only 2% NH_3 volatilization of excreted penguin guano on mainland Antarctica.

The decomposition of uric acid to NH_3 is temperature dependent (Elliott and Collins, 1982), with decomposition increasing as temperature increases. Based on a scenario that P_v is highly thermodynamically dependent, Riddick et al. (2012) modelled P_v normalized to the measurements of Blackall et al. (2007) and reaching ~ 100% at tropical seabird colonies where the average temperature during the breeding season is >19°C. Several studies support the incorporation of thermodynamic dependences into land-atmosphere ecosystem exchange models for NH_3 (e.g. Nemitz et al., 2001; Flechard et al., 2013). However, few studies have verified the extent of thermodynamic dependence.

In this work we present results from land-based measurements of NH_3 concentrations and local meteorology at two seabird colonies in the tropics and use inverse-modelling to calculate the colony NH_3 emissions and hence calculate P_v for each system. Continuous NH_3 measurement data combined with micrometeorological measurement data were available for a four week campaign at Ascension Island (Atlantic Ocean), which was then matched temporally by passive NH_3 measurements throughout the campaign. Comparison of the high-resolution NH_3 concentrations (15 minute) and micrometeorology measurements made on Ascension Island with parallel passive sampling measurements allowed the influence of sampling strategy to be assessed at Ascension. Secondly, the comparison of the passive sampling measurements at Ascension Island and Michaelmas Cay (Great Barrier Reef) allowed the influence of weather and local environment to be assessed.

2. Methods and Materials

2.1 Ammonia measurements

Ammonia concentration measurements were conducted using two methods: 1) time-integrated sampling (weekly to monthly) with passive diffusion samplers continuously sampling, and 2) continuous on-line ammonia analysis using a trace gas analyser. In the present study, the high sensitivity ALPHA (Adapted Low-cost Passive High Absorption) samplers were used with a MDL = 0.04 µg m^{-3} for monthly exposure (Michaelmas Cay) and MDL = 0.19 µg m^{-3} for weekly exposure (Ascension Island). A description of how the MDL was calculated is given in Supplementary Material Section 8.

Passive samplers have been widely used (e.g. Tang et al., 2001; Schmidt et al. 2010, Puchalski et al. 2011, Vogt et al. 2013) and performed well in a recent inter-comparison study of different passive samplers (Puchalski et al. 2011), though performance is dependent on the method variant and the details of its implementation (Sutton et al., 2001). In this study ALPHA samplers (Tang et al., 2001), were deployed in each field campaign in triplicate for the periods detailed below. They were attached with Velcro underneath shelters (upturned plant saucer) fixed on posts at measured heights above ground (as detailed in Section 2.2). To prevent false readings from contamination, spikes were mounted on top to deter bird perching and any disturbed samplers were not analysed. The samplers were stored in sealed plastic containers before and after exposure and, where possible, kept refrigerated. Citric acid coated filter papers from the samplers were extracted in 3 ml deionised water, and analysed for NH_4^+ by flow injection analysis with conductivity detection (FLORRIA, Mechatronics, NL). Laboratory blanks were subtracted from samples and field blanks were used to check for contamination.

On-line continuous ammonia concentration measurements were made with an AiRRmonia gas analyser (Mechatronics, NL). The AiRRmonia analyser comprises a membrane sampler for quantitative sampling of gas-phase ammonia. After diffusion through the membrane, the ammonia is absorbed in a sampling solution which is pumped continuously. Ammonium ions pass through into a detector block *via* diffusion through an ion selective membrane. The ion concentration is measured with a conductivity detector. The AiRRmonia was housed in a weather-proof box and sampled air at 1 $l.min^{-1}$ with a time resolution of ~15-20 minutes, dependent on relative humidity (RH). The instrument was operated with a heated Teflon inlet tube to prevent condensation and ensure a complete flow of NH_3 through the tubing. Measurements were recorded every minute and the data then averaged for 15 minute periods. The AiRRmonia has a LOD of ~0.1 µg m^{-3}, a MDL in this context of 0.07 µg m^{-3} and has previously been used to measure NH_3 emissions in agricultural field experiments (Norman et al. 2009). Calibration was carried out in the field every five days and showed good stability over the periods of measurement.

2.2 Field methodology

Site 1: Michaelmas Cay

Michaelmas Cay (16.60°S, 145.97°E) is a vegetated island cay within the Great Barrier Reef World Heritage Area off the east coast of Cairns, Australia. The Queensland Parks and Wildlife Service – Marine Parks (QPWS) conducted routine monthly bird counts. Measurements for this period indicate 20,000 seabirds breed on the island, including 3,000 Sooty terns (*Onychoprion fuscatus*), 9,000 Common noddies (*Anous stolidus*) and 1,500 Lesser-crested terns (*Thalasseus bengalensis*).

The island is hot and wet, with average air temperatures of 28°C and an average RH of 85%, as measured at Green Island, 10 km to the south (16.75°S, 145.97°E).

A passive NH_3 sampling campaign was conducted on Michaelmas Cay between November 2009 and January 2010. Four masts were set up with ALPHA samplers approximately 1 m above ground (Figure 1), with masts 1, 2 and 3 over the colony (Supplementary Material Section 1). It was intended that mast 4 should measure lower NH_3 concentrations (with no nesting birds present and located upwind relative to the prevailing wind direction). However, as this mast was <100 m from the bird colonies, NH_3 concentrations were still expected to be higher than background for an oceanic environment (e.g. NH_3 concentration of 0.01 µg m^{-3}; Quinn et al., 1990). Sampling period 1 ran from 05/11/09 to 10/12/09 and sampling period 2 from 10/12/09 to 06/01/10.

<<INSERT FIGURE 1>>

Ground temperature was measured using a Tinytag Talk 2 sensor (Gemini Data Loggers, UK). The sensor was attached to the mast on the surface of the sand to give a proxy of the surface temperature and recorded the temperature every three hours. Wind speed, wind direction, RH and precipitation for the measurement period were obtained from the meteorological station on Green Island, 10 km south of Michaelmas Cay. This represents the best meteorological data available for use in this study, as setting up an unattended meteorological station was discouraged due to the potential for interference by human visitors.

Site 2: Ascension Island

Ascension Island (7.99 °S, 14.39 °W) is a small volcanic island in the Atlantic Ocean. Ammonia concentrations and local meteorology were measured at the Sooty tern colony on the Wideawake Fairs in Mars Bay (Supplementary Material Section 2). *Circa* 100,000 pairs of Sooty tern were present during the measurements (N. Fowler, Conservation Department, Ascension Island, pers. comm.). The campaign used both continuous AiRRmonia and time-integrated ALPHA NH_3 measurements and was carried out between 22/05/2010 and 07/06/2010. The weather on Ascension Island is hot and dry with average air temperature during the breeding season at 2 m of 27°C, average humidity of 72% and average wind speed of 5 m s^{-1} during the measurement period (meteorological data courtesy of the Met Office, Wideawake Airfield, Ascension Island).

ALPHA samplers were deployed and exposed for three periods: Period 1 (20/05/2010 - 27/05/2010), Period 2 (27/05/2010 - 02/06/2010) and Period 3 (02/06/2010 - 09/06/2010). During Periods 1 and 2, samplers were deployed at 4 locations (Figure 2). Two extra samplers were added during Period 3 to provide more points on the concentration gradient away from the bird colony in the prevailing wind direction (Figure 2). In the first measurement period ALPHA samplers were located on Masts 3, 4 and 5, the second period on Masts 1, 2 and 3 and in the third period ALPHAs were attached to all masts The arrangements of the masts were changed between measurement periods to ensure NH_3 concentrations > LOD of the ALPHA samplers were measured. On all masts ALPHA samplers measured at 1.5 m above ground. This height was chosen to avoid contamination from the ground, also it was not too high to change the samplers. Background NH_3 concentrations were measured using ALPHA samplers 200 m upwind of the source area, which should provide an indicative regional background, such as that measured by Norman and Leck (2005) at 0.36 μg m^{-3} for the central Atlantic Ocean.

<<INSERT FIGURE 2>>

The continuous AiRRmonia (NH_3) measurements were made at a site downwind from the colony (labelled Met Station in Figure 2). The AiRRmonia was co-located with the meteorological measurement instrumentation. The sampling point was at a height of 2 m, with an inlet length of 10 m from inlet to detector. Due to the relatively high ambient temperatures and a heated inlet line, surface effects, though present, were minimised. The ammonia signal was corrected for transit through the inlet line and the inlet response to variations in ammonia concentrations was estimated to be short relative to the instrument response.

Meteorological measurements were made with standard met station equipment and a sonic anemometer as detailed in Supplementary Material Section 3. The spatial location of instruments and Sooty tern colony edge were mapped using a Garmin Etrex GPS (Garmin, Olathe, Kansas, USA), with an estimated accuracy of ± 1.4 m of true position in open sky settings (Wing et al., 2005).

2.2 Calculation of NH_3 Emissions

At both field sites the WindTrax atmospheric dispersion model (Flesch et al., 1995) was used to calculate the NH_3 emission fluxes. On Ascension Island, where continuous NH_3 data were available from the AiRRmonia measurements, both the NH_3 concentration and meteorological data were averaged over 15 minutes. This time period was used to match both the response time of the AiRRmonia and the time resolution recommended to minimise variability caused by turbulence, while including variation caused by environmental or atmospheric change (Laubach et al. 2008).

Data were filtered for: calibration periods, periods when the measurement location was not downwind of the colony and for periods of strong atmospheric stability ($u < 0.15$ ms^{-1}, $u^* < 0.1$ ms^{-1} and $|L| < 2$). Each simulation was run in WindTrax using 50,000 particle projections to back-calculate the NH_3 emission. Data input to WindTrax were 15 minute averages of: background NH_3 concentrations (X_b, μg m^{-3}), 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). Emission estimates using the time-integrated version of the active sampling data in WindTrax used the same method as for the active sampling data

For both Ascension Island and Michaelmas Cay, the time-integrated passive NH_3 measurements were combined with the meteorological data to provide long-term estimates using the inverse dispersion model. In this way, an estimate of the uncertainties associated with the application of the inverse dispersion model when using time integrated passive sampling was assessed.

2.3 Uncertainties

In order to 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 simulations to back-calculate the change in NH_3 emission. The total uncertainty was then calculated as the square root of the sum of the individual uncertainties squared.

Michaelmas

The surface roughness length was estimated at 1 cm, with an uncertainty range 0.01 - 15 cm. Given the island conditions of high ground temperature and clear skies, the atmospheric stability condition was assumed to be very unstable (Monin-Obukhov Length (L) = -10 m) and the variability in L was taken as: L_{max} = 100 m to L_{min} = -5 m. The NH_3 source area was assumed to be any part of the island that the birds were likely excrete on. The minimum this could have been was 6,000 m^2 but the best estimate used was 10,000 m^2.

Ascension

The Monin-Obukhov length was estimated at -14.8 m using sonic anemometer data and ranged from 30 m to -5 m. The background NH_3 concentration was measured at 0.1 µg m^{-3} with uncertainty ranging from 0.02 µg m^{-3} to 0.44 µg m^{-3} (Johnson, 1994). The NH_3 source area was taken as any part of the island that the birds were likely to have excreted on, with a best estimate of 80,000 m^2 and uncertainty range from 90,000 m^2 to 70,000 m^2.

3. Results

3.1 Michaelmas Cay

The NH_3 concentrations measured at Michaelmas Cay during both sampling periods range between 35 – 72 µg m^{-3} downwind of the colony (Supplementary Material Section 5). The upwind "background" level of 1.6 – 3.9 µg m^{-3} is clearly impacted to some extent by the bird emissions and also somewhat higher than one would expect for a marine background, for example when compared with a minimum of 0.01 µg m^{-3} measured in the region (Quinn et al., 1990). The higher background may be caused by nearby seabirds (< 100m from bird colonies) or emissions from the three regularly visiting tourist vessels.

During the sampling periods local winds predominately came from the south east. This may place the sampling equipment downwind of the colony on occasion. Higher concentrations were measured at Masts 1 and 2 than at Mast 3. Low wind direction variability means that the source footprint sampled by ALPHA samplers was very near to being constant for the two measurement periods (Supplementary Material Section 5).

Scenarios were run in WindTrax to reflect variability in roughness length, which propagates a ± 15% uncertainty in the NH_3 emission flux. Varying L *(*L_{max} = 100 m to L_{min} = -5 m) resulted in ± 29% modelled NH_3 emissions. The uncertainty in estimated NH_3 emissions due to source area was ±13%. Using the data of Quinn et al. (1990), background NH_3 has minimal effect on the modelled emissions (±2%).

The using the time-integrated passive NH_3 measurement, the WindTrax modelling results show an average NH_3 emission flux of 21 µg NH_3 m^{-2} s^{-1} during Period 1 and 22 µg NH_3 m^{-2} s^{-1} during Period 2, respectively, from the colony on Michaelmas Cay (as summarized below in Table 1). There is a remarkable similarity between the measurement periods, where 23% lower NH_3 concentrations in period 1, compared with period 2, were offset by higher wind speed, leading to only 5% lower NH_3 emissions. The overall uncertainty, on Michaelmas Cay using passive samplers, is estimated to be ± 35%, leading to an ammonia emission flux for the two periods of 21 ± 8 and 22 ± 8 µg NH_3 m^{-2} s^{-1}, respectively. Additional uncertainties related to the use of time-averaged NH_3 concentrations are addressed in Section 4 below.

3.2 Ascension Island

a) Passive Sampling Campaign Measurements

On Ascension Island the ALPHA samplers were exposed for 3 periods; the concentration and meteorological measurements are summarised in Supplementary Material Section 6. Upwind background concentrations were 0.1 µg m^{-3} for all three periods. Ammonia concentrations decreased with distance away from the colony, particularly evident during Period 3 when the 5-point transect was used. The lowest concentrations were recorded during the second period and the highest during the third period. During the measurement period, the average atmosphere conditions were unstable, with the average Monin-Obukhov length equal to -15 m, ranging from 30 m to -5 m.

Based on the time-integrated passive NH_3 measurements, the calculated NH_3 emission fluxes for the three periods of the campaign were 18, 5 and 29 µg m^{-2} s^{-1}, respectively (Table 1). The overall uncertainty of the NH_3 emission estimate made using passive samplers on Ascension Island was estimated at ± 24%, with the largest uncertainties being area estimation and atmospheric conditions contributing 7 and 23%, respectively (estimated using Method described in Section 2.3). The intra-period variability was much larger at ~70%. These values are compared with the continuous estimates in Section 4.

<<INSERT TABLE 1>>

b) Continuous Sampling Campaign Measurements

Concentrations of NH_3 were measured for 21 days and values over the range < 0.1 (limit of detection) - 230 µg m^{-3} were observed (Figure 3 Upper panel). There was a strong diurnal cycle observable in the concentrations measured, with larger values during the day and smaller values at night. This corresponds to a very strong diurnal temperature cycle as demonstrated by the ground temperature measurements (Figure 3 middle panel). Two large peaks in NH_3 concentrations were observed at 0600 on 25/05/10 and at 0800 on 06/06/10, corresponding to periods immediately after large rain events. There are five other peaks observable in the concentration time series and the reason for them is currently unknown.

<<INSERT FIGURE 3>>

The calculated ammonia emissions similarly show a strong diurnal pattern, with values increasing to a maximum during the hottest part of the day and decreasing to almost zero during the night (Figure 3). Ammonia emissions were largest after the rain event on the 6/6/10, with a maximum emission of 377 µg NH_3 m^2 s^{-1}. In periods with no rain NH_3 emissions were relatively small. The uncertainty in meteorological parameters and measurements were significantly lower in the active measurements. The key sources of error, as described above in Section 2.3 on passive sampling results, were the background NH_3 concentrations and nesting area which resulted in an overall emission uncertainty of ± 12%.

Averaging for each hour of the day (Figure 4) shows the diurnal pattern with a high variability. An early afternoon maximum is seen (1300 - 1500) and night-time minimum (0000-0600). By integrating the average diurnal emission, as shown in Figure 4, the daily average NH_3 emission for this campaign was estimated at 1.6 g NH_3 m^{-2} day^{-1} (or 19 µg m^{-2} s^{-1}). The largest uncertainties and variability occurred during daytime emissions while the night-time variability was uniformly very low.

<<INSERT FIGURE 4>>

4. Discussion

4.1 Comparison of passive time-integrated and continuous sampling campaigns

Since making continuous measurements of NH_3 concentrations in remote locations is operationally much more challenging than making time-integrated passive measurements, the comparison of the two approaches for use in emission calculations is of high practical interest. In particular, using time averaged concentrations introduces additional errors associated with changing meteorological conditions, so that, subject to reliable NH_3 measurement, the continuous approach should be considered as the reference. Overall, the modelled NH_3 emission estimated using active and passive methods are very similar (Table 1), with the differences between chemical sampling strategies being smaller than the differences between sampling averaging periods. This is summarized in the last two columns of Table 1 which compare the Uncertainty associated with Sampling Period (USP) with the Uncertainty associated with Sampling Method (USM). These values are based on first making an additional estimate of the flux, based on averaging the NH3 concentration data from the continuous on-line system to the same periods as for the passive NH3 measurement (flux c). In this way, the difference between the continuous fluxes based on hourly data (flux a) and flux c represents USP, whereas the difference between the time integrated passive estimates (flux a) and flux c represents USM. The relative differences between flux a and flux b for the three periods on Ascension were: -18%, -44% and +4% (mean difference for the campaign: -12%). Thus, despite the additional errors induced by this practical simplification, passive sampling was found to generate valuable data when resources are not available for an active sampling campaign.

One reason why such close agreement was obtained between the different measurement strategies may be because most of the emissions from this source were associated with warm daytime unstable conditions, while cool nocturnal conditions were always associated with low emissions (Figure 2). In this way, errors associated with transition between meteorological conditions turned out to be relatively small in practice.

The similarity between the time-averaged emissions from active and passive sampling for all measurement periods shows that much of variability between the high resolution active sampling and the passive emissions are caused by differences in averaging period. Not only was the uncertainty of emission estimates resulting from the active campaign smaller, but the high resolution data collected by active sampling allowed for the observations of diurnal variations in NH_3 emission, showing the response of emission processes to dry and wet periods. Even though the active measurement method provides a great deal of data on NH_3 emission from seabird guano, it provides considerable logistical challenges, as the instruments are difficult to transport and require a power source. The passive campaigns are much more suited to measuring NH_3 concentrations at remote seabird colonies, especially if the objective is not to analyse processes in detail, but to estimate long-term or annual variations in NH_3 emission, similar to the study by Blackall et al. (2008). The advantages and disadvantages of the active and passive methods are shown in more detail in Supplementary Material Section 7.

4.2 Weather conditions and environmental dependence of NH_3 emissions from seabird colonies

In order to understand the magnitude of NH_3 emissions and their effects on the environment, both the weather conditions and local environment are important. The present study estimated P_v ranging from 64% to 66% on Michaelmas Cay and from 9% to 51% on Ascension Island (Table 1). According to the empirical temperature relationship investigated by Riddick et al. (2012), the P_v on both islands should be similar, given the similar surface temperature. Similarly, both islands are characterized by a ground environment with sandy/rocky surfaces and little vegetation, so that it is unlikely that substrate characteristics can explain the differences between the two sites.

The differences between the measured values of P_v can more easily be explained by the effect of rain events on ammonia emissions from the surface. During a rain event, water falling onto the relatively dry guano promotes bacterial hydrolysis of uric acid which is necessary for NH_3 emission to occur. On Michaelmas Cay, there were frequent rain events during the experiment, with average rainfall of around 4 mm day^{-1}, while on Ascension Island there were only two significant rain events during the measurement campaign, with an average rainfall of 1 mm day^{-1}. Both of the rain events on Ascension were followed by a significant increase in atmospheric NH_3 concentrations, consistent with increased uric acid hydrolysis following these events, with subsequent warm drying conditions promoting emissions (Figure 3). This was shown by much higher emissions during Periods 1 and 3, which had rain events, whereas Period 2 was rain free (Table 1).

While the larger precipitation rate at Michaelmas Cay allowed more rapid uric acid hydrolysis and larger P_v than at Ascension Island, it remains unclear whether even more rainfall at Michaelmas Cay would have further increased P_v. In principle, an optimum rate of water supply can be envisaged that will maximize NH_3 emissions: with too little water, uric acid hydrolysis becomes the limiting factor, while very wet conditions may promote N run-off, leaching and other loss processes (Blackall et al., 2008). In addition, wash-off by high tides may also deplete guano N pools at the colony. These factors imply that the initial temperature dependence estimated by Riddick et al. (2012) tends to overestimate NH_3 emissions in warm conditions, and that it is unlikely that P_v =100% would occur frequently in real situations.

To assess these interactions of NH_3 emission with temperature, water availability and other losses more fully, the application of process-based modelling is required (Riddick, 2012; Sutton et al., 2013), which is the subject of on-going analysis, as well as measurements of emission rates in contrasting, sub-polar climates where major seabird colonies are located (Riddick, 2012). However, comparison of the present study with the published emission rates of Blackall et al. (2007) for temperate conditions already shows some differences. Blackall et al. (2007) estimated average P_v at ~32% for bare rock breeders (Atlantic Gannet *Morus bassanus*, Bass Rock, Scotland), which is almost identical to the average P_v measured here for Ascension Island (31%). This suggests that the warmer conditions at Ascension (promoting increased P_v) were substantially offset by water limitation. By contrast, at Michaelmas Cay, with less water limitation, warmer conditions than Scotland allowed a much larger fraction of the excreted guano N to volatilize as NH_3 (65%). By comparison, in sub-polar contexts, with temperatures around 0°C, Riddick (2012) estimated much smaller P_v (< 5%), highlighting the substantial sensitivity to weather of volatilization-based NH_3 emissions (Sutton et al., 2013).These model estimates are supported by the recent Antarctic measurement results of Theobald et al. (2013), showing how P_v appears to be much smaller under cold conditions.

5. Conclusions

In the analysis of both the continuous and passive measurement strategies, micrometeorological data and NH_3 concentrations were applied in an inverse Lagrangian dispersion model (WindTrax). In principle, non-stationarity leads to errors associated with long averaging periods, when calculating trace gas emissions in this way. By contrast, active, continuous measurements of NH_3 concentrations are operationally very challenging to conduct at remote locations. Our comparison of active and passive sampling strategies addressed this and showed that, in practice, the NH_3 emissions estimated at Ascension Island by both active and passive NH_3 concentration measurements were very similar. This provides some confidence in the higher estimated rate of volatilization at the Michaelmas Cay site, with this higher value attributed to higher water availability at this site.

The main advantage of high-resolution ammonia data is that it allows further understanding of the underlying processes in formation and subsequent NH_3 emission and how these processes are affected by climatic conditions such as temperature, precipitation, wind speed and relative humidity. Measured diurnal variations in NH_3 emissions emphasize the role that ground temperature plays, as emissions follow diurnal variation in ground temperature. The observations suggest NH_3 emissions were water-limited on Ascension, with higher water availability at Michaelmas Cay allowing larger P_v, despite similar temperatures at both sites.

The NH_3 concentrations measured on Ascension Island are similar to previous studies elsewhere. Based on passive sampling methods, maximum NH_3 weekly concentrations of 83 µg m^{-3} were recorded at the Isle of May seabird colony that experience temperate weather conditions (Blackall et al., 2008), compared with 72 µg m^{-3} at Ascension Island. In addition, the 15 minute continuous data at Ascension Island showed maximum peak concentrations of up 230 µg m^{-3} at 100 m from the bird colony, as measured on the 06/06/10. These maximum NH_3 concentrations in air indicate potentially toxic environments near seabird colonies, and further studies are required to understand the impact of seabird nitrogen on local plant life.

The data presented in this paper give the first micrometeorological measurement-based NH_3 emission flux calculations for seabird colonies in tropical regions. The NH_3 emission measured on Michaelmas Cay showed that tropical seabird colonies can be significant sources of NH_3 emissions in remote areas. The largest tropical bird colonies are on Pacific Islands and remote islands in the Indian and Atlantic oceans, where bird colonies thrive in the absence of natural predators or anthropogenic disturbance. It is estimated that there are 116 tropical seabird colonies larger than the colony of 20,000 individual birds on Michaelmas Cay (Riddick et al., 2012). This study shows how seabird colonies create ammonia 'hotspots' that could affect the growth and structure of the local ecosystem, such as downwind dry shrub land on Ascension, as has been shown for many other N-limited ecosystems (Cape et al., 2009; Sutton et al., 2011). Of the several environmental factors affecting the rate of emission, ground temperature and water availability were found to be the most important, given similar temperature regimes.

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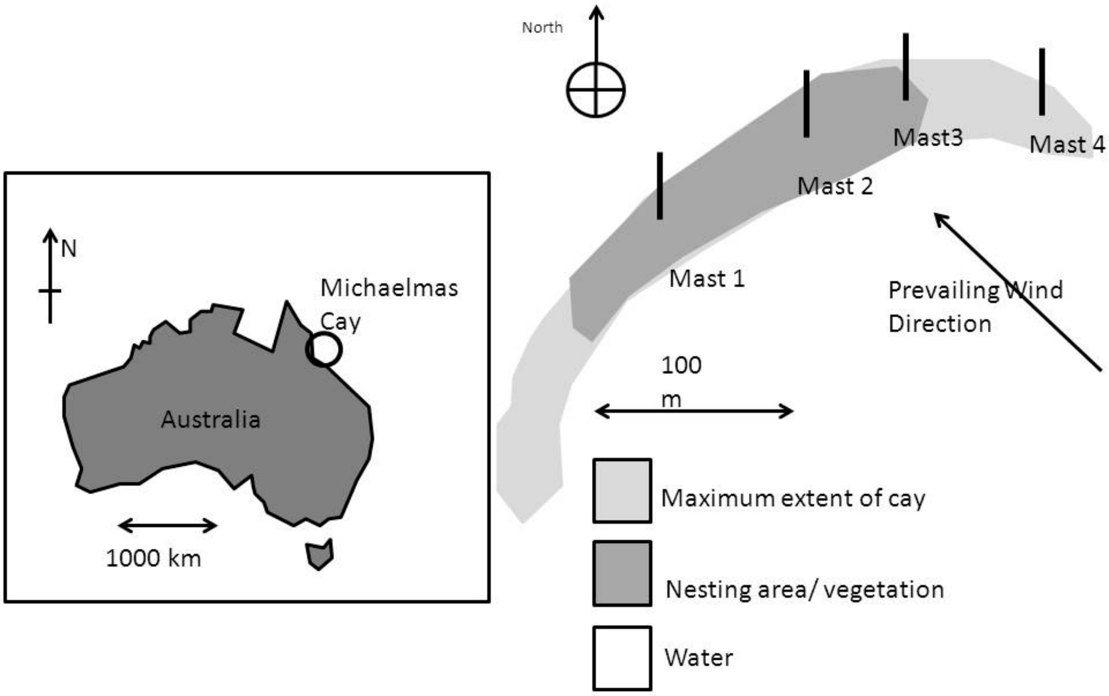

Figure 1 Location of ALPHA samplers on Michaelmas Cay. The birds nest on both vegetation and sand. Map courtesy of Queensland Parks and Wildlife Service, Cairns, Australia.

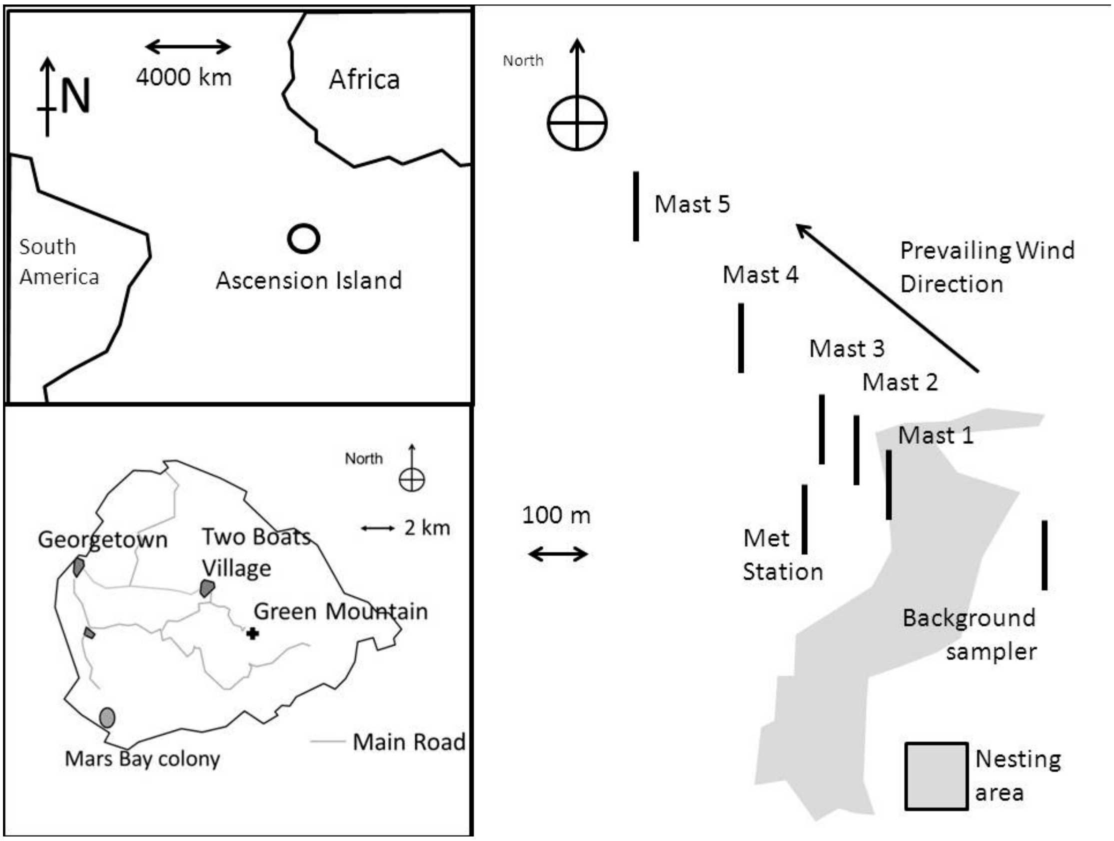

Figure 2 Arrangement of ALPHA samplers used to measure the NH_3 concentration at Mars Bay on Ascension Island. The "Source Area" indicates the extent of the Sooty terns' nest site.

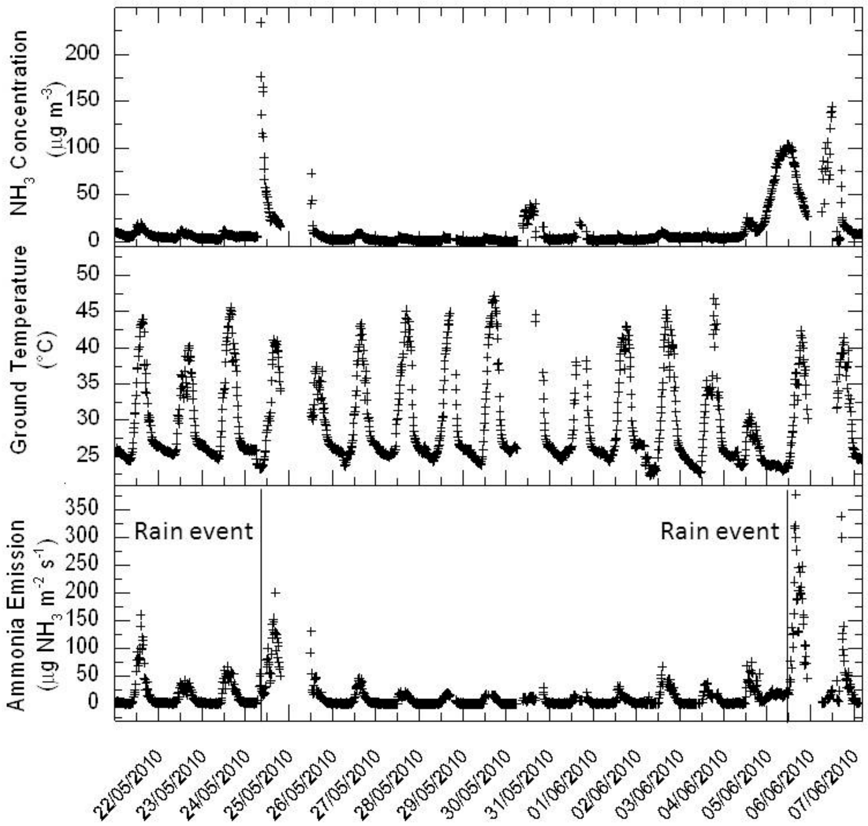

Figure 3 Time series of NH_3 concentration, wind speed, ground temperature and roughness length measured at Mars Bay, Ascension Island, 22/05/10 to 10/06/10. These data were used as input to the WindTrax model for estimating NH_3 emissions from the seabird colony, shown at the bottom. Some data gaps are due to calibration (21/05/10, 29/05/10 and 02/06/10). Also data gaps on 25/05/10 to 26/05/10 and 06/06/10 to 07/06/10 were periods where the instrument was not working.

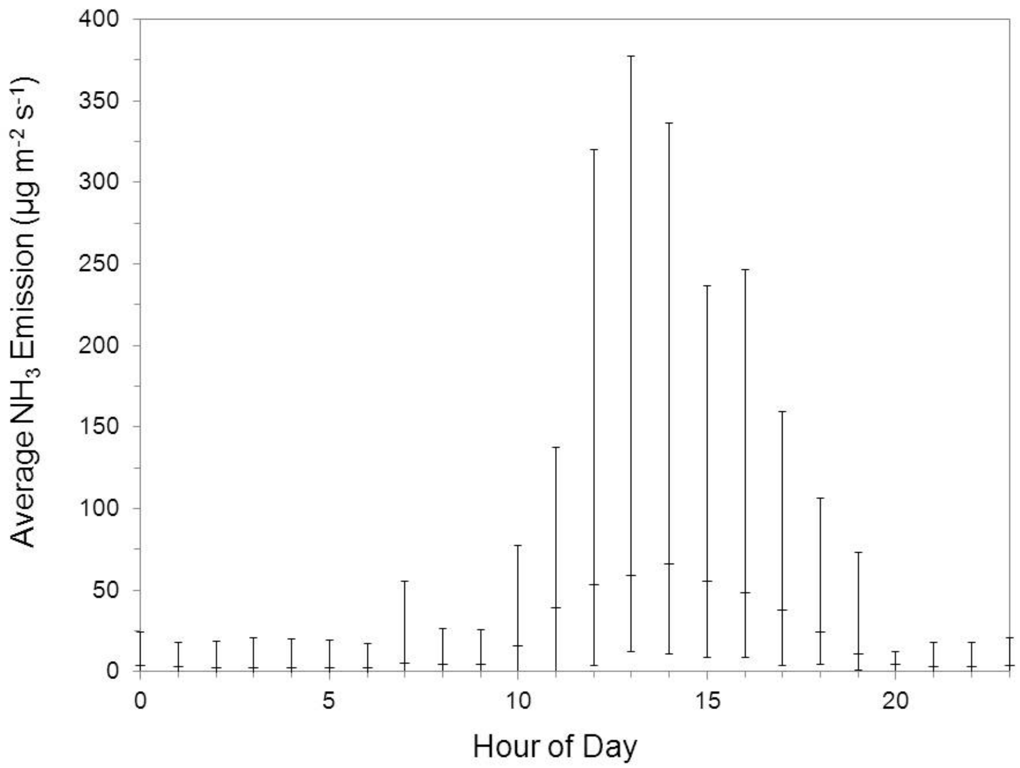

Figure 4 Average diurnal pattern of NH_3 emissions derived from WindTrax emission calculations for the Sooty Tern colony at Mars Bay, Ascension Island. This campaign estimated an average daily NH_3 emission of 18.9 µg m^{-2} s^{-1} for the period 22/05/10 and 10/06/10. The error bars show the variability in hourly emissions by representing the maximum and minimum NH_3 emissions for these hours for the duration of the campaign.

				Passive		On-line measurement						
Colony	Measurement Period	Ground T(°C)	Rain (mm)	Av. Flux NH_3 ($\mu g\ m^{-2}\ s^{-1}$) (Flux a.)	P_v (%)	Av. Flux NH_3 ($\mu g\ m^{-2}\ s^{-1}$) (Flux b.)	P_v (%)	Av. [NH_3] ($\mu g\ m^{-3}$)	Flux using Av. [NH_3] ($\mu g\ m^{-2}\ s^{-1}$) (Flux c.)	P_v (%)	USP ($\mu g\ m^{-2}\ s^{-1}$)	US ($\mu g\ m^{-2}\ s^{-1}$)
1	1	30	5	21 ± 8	64							
1	2	32	106	22 ± 8	66							
2	1	30	5	18 ± 4	32	22 ± 3	37	13	20 ± 5	34	2	-2
2	2	30	0	5 ± 1	9	9 ± 1	16	2	3 ± 1	5	6	2
2	3	29	16	29 ± 7	51	28 ± 3	48	19	26 ± 6	45	2	3

Table 1 Summary of seabird colony NH_3 emissions estimated from topical measurement campaigns. P_v is the percentage of excreted nitrogen that volatilizes, 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 1 indicates Michaelmas Cay and colony 2 indicates Ascension Island.

Supplementary Material Section 1

Tern and noddies' nesting area in the vegetation on Michaelmas Cay (photograph courtesy of W. MacFarlane).

Supplementary Material Section 2

Sooty terns nesting at the Mars Bay colony (photograph S. Riddick).

Supplementary Material Section 3

Meteorological variables measured and derived during Ascension Island field campaign (* indicates derived variable)

Variable	Instrument	Make	Units	Height (m)
Ground temperature	Tinytag Talk 2	Gemini Data Loggers, UK	°C	0
Rainfall	SBS500	Campbell Scientific, UK	mm	0
Air temperature	HMP45C Probe	Campbell Scientific, UK	°C	0.75
Relative Humidity	HMP45C Probe	Campbell Scientific, UK	%	0.75
Irradiance	SP Lite	Kipp & Zonen, NL	$W m^{-2}$	0.75
Air pressure	CS100	Campbell Scientific, UK	Pa	0.75
Wind direction	Wind Sentry Vane	RM Young, USA	°	2
Wind speed	3-cup anemometers	RM Young, USA	$m s^{-1}$	2
3D wind speed vectors	Windmaster Pro	Gill Instruments, UK	$m s^{-1}$	2.5
Sonic temperature	Windmaster Pro	Gill Instruments, UK	°C	2.5
Monin-Obukhov length*	Windmaster Pro	Gill Instruments, UK	m	2.5
Friction velocity*	Windmaster Pro	Gill Instruments, UK	$m s^{-1}$	2.5
Roughness length*	Windmaster Pro	Gill Instruments, UK	m	2.5

Supplementary Material Section 4

Calculation of percentage of nitrogen volatilized (P_v)

The percentage of nitrogen volatilized (P_v) was calculated from the total nitrogen excreted at the colony during the measurement period and the total nitrogen volatilized as NH_3. The total nitrogen excreted (N, g N bird^{-1} year^{-1}) is calculated using the bioenergetics model developed by Wilson et al. (2004) from bird specific data (Equation 1) and assumes that seabirds excrete N at a constant rate while at the colony. Bird specific data include; the adult mass (M, g bird^{-1}), nitrogen content of the food (F_{Nc}, g N g^{-1} wet mass), energy content of the food (F_{Ec}, kJ g^{-1} wet mass), assimilation efficiency of ingested food (A_{eff} , kJ [energy obtained] kJ^{-1} [energy in food]), length of the breeding season ($t_{breeding}$, days), proportion of time spent at the colony during the breeding season (f_{tc}). All values used in this study are taken from Riddick et al. (2012).

$$N = \frac{9.2 M^{0.774}}{F_{Ec} A_{eff}} F_{Nc} t_{breeding} f_{tc} \qquad \text{Equation 1}$$

Supplementary Material Section 5

Mean NH_3 concentrations (μg m^{-3}) measured by ALPHA samplers on Michaelmas Cay during sampling periods and meteorological measurements used for modelling. The NH_3 concentrations show the mean (S.D.) of the three replicates measured by the ALPHA samplers at each site.

Variable measure	Period 1	Period 2
Date of deployment	5/11/2009	10/12/2009
Date of retrieval	10/12/2009	6/1/2010
Mast 1 NH_3 concentration (μg m^{-3})	55.3 (0.05)	70.7 (0.54)
Mast 2 NH_3 concentration (μg m^{-3})	54.7 (1.36)	71.7 (0.06)
Mast 3 NH_3 concentration (μg m^{-3})	37.7 (2.64)	35.4 (1.36)
Mast 4 NH_3 concentration (μg m^{-3})	1.6 (0.04)	3.9 (0.02)
Ground temperature (°C)**	29.7	32
Wind Speed (m s^{-1})*	6.7	5.3
Wind Direction (° to North)*	135 (28.9)	130 (64.5)
Total precipitation (mm m^{-2})*	155	106
Roughness length (m)	0.01	0.01
Monin-Obukhov length, *L*, (m)	-10	-10

* NCDC (2011);
** directly measured

Supplementary Material Section 6

Mean NH_3 concentration (µg m^{-3}) measured by the ALPHA samplers deployed on Ascension Island during the campaign and meteorological measurements. The NH_3 concentrations show the mean (S.D.) of the three replicates measured by the ALPHA samplers at each site.

Variable measure	Period 1	Period 2	Period 3
Date of deployment	20/05	27/05	02/06
Date of retrieval	27/05	02/06	09/06
Mast 1 NH_3 concentration (µg m^{-3})	N/A	4.8 (0.58)	26.3 (0.18)
Mast 2 NH_3 concentration (µg m^{-3})	N/A	2.4 (0.03)	13.4 (0.09)
Mast 3 NH_3 concentration (µg m^{-3})	4.0 (0.08)	1.8 (0.03)	9.7 (0.01)
Mast 4 NH_3 concentration (µg m^{-3})	2.2 (0.02)	N/A	3.6 (0.02)
Mast 5 NH_3 concentration (µg m^{-3})	1.6 (0.08)	N/A	2.1 (0.10)
Background NH_3 concentration (µg m^{-3})	0.1 (0.01)	0.1 (0.01)	0.1 (0.02)
Ground temperature (°C)	30	30	28.8
Wind Speed (m s^{-1})	5.1	4.9	4.7
Wind Direction (°)	132	132	110
Total precipitation (mm)	5	0	16
Roughness length (m)	6.6	6.7	8.4
Monin-Obukhov length, *L*, (m)	-12.7	-11.4	-21

Supplementary Material Section 7

Advantages and disadvantages of the active and passive sampling approach to estimate ammonia emissions from seabird colonies.

Method	Active	Passive
Advantages	1. Decreased uncertainty in the modelled meteorology when combining with continuous NH_3 concentrations. 2. Gives higher time resolution estimates of emissions for comparison with process models.	1. Operationally simpler to combine real time meteorology with time integrated NH_3 concentrations. 2. Can be implemented with much lower costs and using remote site operators, while allowing measurements at multiple locations.
Disadvantages.	1. Operationally much more challenging, including requirement for trained personnel to visit field site regularly to maintain semi-continuous NH_3 measurements. 2. Capital and personnel costs are much higher. 3. Significant electricity requirements for continuous NH_3 analyzers. 4. Gaps in data during instrument down-time and calibration.	1. Additional errors associated with averaging across changing meteorological conditions. 2. Only gives time averaged concentrations, according to sampling periods chosen.

Supplementary Material Section 8

The method detection limit (MDL) was calculated to the standards presented by the U.S. Environmental Protection Agency (EPA, 2011). The MDL was calculated using the following relationship:

$$MDL = T_{(n=1,1-\alpha=0.99)} x\ SD$$

Where $T_{(n=1,1-\alpha=0.99)}$ is the t-value for the 99% confidence level and a standard deviation estimate with n - 1 degrees of freedom. The standard deviation (*SD*) is calculated from the number of blank samples (*n*) measured during each measurement campaign.