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

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HIGHLIGHTS

- 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.
- 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.

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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 $\mu g\ m^{-2}\ s^{-1}$ at the Isle of May, 12 $\mu g\ m^{-2}\ s^{-1}$ at Signy Island and 9 $\mu g\ m^{-2}\ s^{-1}$ 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 unreactive molecule and needs to be 'fixed' to become useable as

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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., 2015). 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 31–65% at two tropical seabird colonies (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 subpolar 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 2–4 weeks. The samplers were attached by Velcro to an upturned plant saucer (for protection) that was fastened to a pole (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 min 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