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High temporal resolution modelling of environmentally-dependent seabird ammonia emissions: Description and testing of the GUANO model

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HIGHLIGHTS

- A dynamic mass-flow model to simulate variation in NH_3 emissions from seabird guano.
- Model output validated against measurements from colonies across a range of climates.
- Model output captures observed dependence of NH_3 emission on environmental variables.
- This model can be a starting point to model NH_3 emissions from other sources.

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ABSTRACT

Many studies in recent years have highlighted the ecological implications of adding reactive nitrogen (N_r) to terrestrial ecosystems. Seabird colonies represent a situation with concentrated sources of N_r, through excreted and accumulated guano, often occurring in otherwise nutrient-poor areas. To date, there has been little attention given to modelling N flows in this context, and particularly to quantifying the relationship between ammonia (NH_3) emissions and meteorology. This paper presents a dynamic mass-flow model (GUANO) that simulates temporal variations in NH_3 emissions from seabird guano. While the focus is on NH_3 emissions, the model necessarily also treats the interaction with wash-off as far as this affects NH_3. The model is validated using NH_3 emissions measurements from seabird colonies across a range of climates, from sub-polar to tropical. In simulations for hourly time-resolved data, the model is able to capture the observed dependence of NH_3 emission on environmental variables. With temperature and wind speed having the greatest effects on emission for the cases considered. In comparison with empirical data, the percentage of excreted nitrogen that volatilizes as NH_3 is found to range from 2% to 67% (based on measurements), with the GUANO model providing a range of 2%–82%. The model provides a tool that can be used to investigate the meteorological dependence of NH_3 emissions from seabird guano and provides a starting point to refine models of NH_3 emissions from other sources.

1. Introduction

Reactive nitrogen (N_r) has been used to improve crop growth for the last 8000 years (Bogaard et al., 2013). However, N_r used as either manure or synthetic fertilizer has increased globally from approximately 21 Tg N yr^{-1} in 1850 to 185 Tg N yr^{-1} in 2000 (Potter et al., 2010). The consequences of applying N_r to a surface depend on the climatic conditions, the properties of the substrate and the surrounding vegetation. Reactive nitrogen can either run off during rain events, become part of the surrounding ecosystem

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(immobilized in the soil or absorbed by plants) or volatilize as nitrogen-based gas: ammonia (NH_3), nitrous oxide (N_2O), nitrogen oxides (NO_x) or nitrogen (N_2). The rate of formation and volatilization of NH_3 from N_r is highly temperature dependent (Sutton et al., 2013; Riddick et al., 2012, 2014) and NH_3 emission has been linked with acidification and eutrophication close to the emissions site (Sutton et al., 2012) and changes in radiative forcing globally (Adams et al., 2001).

The largest seabird colonies are found in remote areas far from human interaction (Riddick et al., 2012). At such locations seabird nitrogen excreta is the dominant source of N_r making seabird colonies ideal “natural laboratories” to investigate biogeochemical processes and the resulting impact of N_r pathways on plants and animals. Studies have shown that seabirds are significant sources of NH_3 (Wilson et al., 2004; Blackall et al., 2007; Zhu et al., 2011; Riddick et al., 2014, 2016) and have a large spatial impact in both the Arctic (Wentworth et al., 2015) and Antarctic (Theobald et al., 2013, Crittenden et al., 2015. Changes in atmospheric composition across the entire Baffin Bay region were attributed to seabird NH_3 (Wentworth et al., 2015), while a study of Adelie penguin colony on the Antarctic continent suggested that volatilized NH_3 creates a spatial impact zone of up to 300 km^2 surrounding the colony where phosphomonoesterase activity is increased in lichen populations (Crittenden et al., 2015).

Given the local and global importance of NH_3 emissions, two main methods have been used to estimate NH_3 emissions from N_r sources, which are broadly described as empirically derived emission factors and process-based models. The former use empirical data to integrate the effects of meteorology into a single value (‘emission factor’) that can be used, for example, to estimate emission of a particular animal species. Alternatively, the emission can be estimated based on a percentage of N_r that volatilizes as NH_3, e.g. on average 21% of N in manure volatilizes as NH_3 in industrialized countries (Bouwman et al., 2002).

Process-based models attempt to replicate the effects of meteorology on the formation of NH_3 from an N_r source. NH_3 volatilization has been shown to increase at both high temperatures and high wind speeds (Demmers et al., 1998; Sommer and Christensen, 1991), while rain events may cause NH_3 emissions to drop to almost zero, as illustrated by Sommer and Olesen (2000) for liquid manure spreading in Denmark. Most recent models calculate NH_3 fluxes using Henry's Law, i.e. the dissociation reactions of ammonium and NH_3 in solution is used to calculate the NH_3 gas on the surface, with the flux estimated using a resistance-based approach (e.g. Sutton et al., 1998; Cooter et al., 2010; Massad et al., 2010; Flechard et al., 2013). For instance, Cooter et al. (2010) used a process-based model to predict measured diurnal variation and daily means of NH_3 emissions from agricultural soils.

Even though Henry's Law has been used to calculate NH_3 emissions from N_r sources, these models have not been explicitly validated with high resolution empirical measurements from a range of meteorological conditions. For example, Massad et al. (2010) reviewed existing measurements to compile a comprehensive dataset and derived generalized parameterizations for a range of fertilizers and ecosystems to be used in large-scale chemical transport and earth system models. Flechard et al. (2013) synthesized data from a range of studies to generate consistent parameterizations that can be used to calculate NH_3 emissions on the regional and global scale. Cooter et al. (2010) used their model to calculate NH_3 emissions at the field scale and compared their model output to fertilizer application at a site in North Carolina, USA.

In an initial approach to modelling NH_3 emissions from seabirds, only the bioenergetics part of the GUANO model was used, linked to empirical estimates of the percentage volatilized (Wilson et al., 2004; Blackall et al., 2007). This approach provided an adequate description of the spatial differences in NH_3 emissions on a regional and country scale. However, it meant that there was a high uncertainty in the estimates in the extrapolations to a global scale by Blackall et al. (2007).

A first approach to address this uncertainty was provided by Riddick et al. (2012) who used an empirical temperature correction, with uncertainty ranges of estimates based on a) no temperature dependence and b) full solubility dependence according to the thermodynamics of Henry's Law and ammonium dissociation. If, like Blackall et al. (2007), they ignored the possible effect of temperature, then they found total global NH_3 emissions from seabirds of 442 Gg NH_3 year^{-1} (where penguins contributed 83%, due to improved bird statistics). By contrast, if NH_3 emissions were proportional to the thermodynamic effect of temperature, they found total global NH_3 emission from seabirds to be only 97 Gg NH_3 year^{-1} (where penguins contributed 63%). According to a mid-range estimate of the temperature dependence, they estimated 270 Gg NH_3 year^{-1} (with 80% from penguins). Penguins were thus estimated to be the main source of NH_3 emissions from seabird colonies globally under all three scenarios, while this clearly shows the importance of addressing the temperature dependence of emissions.

The main limitation of Riddick et al. (2012) was the wide uncertainty range of their estimates and the need to constrain these by measurements, ideally using a process-based approach. A first application of the GUANO model reported by Sutton et al. (2013) to different sites globally showed that the main measured differences in the percentage of excreted guano that volatilizes as NH_3 in relation to temperature could be reproduced.

This paper describes the GUANO model (Generation of emissions from Uric Acid Nitrogen Outputs), a dynamic mass-flow process-based model developed to simulate NH_3 losses from seabird colonies. The model incorporates the main environmental factors affecting the volatilization process, allowing calculation of NH_3 emissions from seabird-derived N_r on an hourly basis and upscaling to consider the effects of different meteorological conditions. The NH_3 emissions simulated by the model are compared with NH_3 emission estimates based on concentration measurements and turbulent exchange parameters from a climatically diverse set of seabird colonies. We use this comparison to investigate how NH_3 emissions from seabirds vary with changing environmental conditions.

2. Methods and materials

2.1. Outline of the GUANO model

The GUANO model is designed to predict temporal variations in the formation of NH_3 from a source of seabird-derived uric acid (Fig. 1). The model calculates NH_3 emissions from a seabird colony using environmental variables and colony-specific data as input. Temperature, relative humidity, precipitation and wind speed are considered to have the greatest effect on NH_3 formation and emission (Groot Koerkamp, 1994; Cooter et al., 2010; Massad et al., 2010; Flechard et al., 2013). The main elements of the model are described here, with additional details given in Supplementary Material Section 1.

The pathways taken by nitrogen following excretion as uric acid can be summarised in four steps (Fig. 1). Excreted guano forms uric acid (UA) that decomposes to form total ammoniacal nitrogen (TAN), which then partitions to form gaseous NH_3. Other pathways include wash-off of guano, UA and TAN from the surface at any stage during rain events. It should be noted that the loss of nitrogen due to plant uptake and immobilization, and other gaseous