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

S.N. Riddick a, b, c, *, T.D. Blackall b, U. Dragosits a, Y.S. Tang a, A. Moring a, e, F. Daunta a, S. Wanless a, K.C. Hamer d, M.A. Sutton a

a Centre for Ecology & Hydrology Edinburgh, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK
b Department of Geography, King’s College London, Strand, London, WC2R 2LS, UK
c Department of Civil and Environmental Engineering, Princeton University, Princeton, 08540, USA
d School of Biology, University of Leeds, Leeds, LS2 9JT, UK
e School of Geosciences, University of Edinburgh, EH9 3FE, UK

HIGHLIGHTS

• A dynamic mass-flow model to simulate variation in NH₃ emissions from seabird guano.
• Model output validated against measurements from colonies across a range of climates.
• Model output captures observed dependence of NH₃ emission on environmental variables.
• This model can be a starting point to model NH₃ emissions from other sources.

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ABSTRACT

Many studies in recent years have highlighted the ecological implications of adding reactive nitrogen (N₅) to terrestrial ecosystems. Seabird colonies represent a situation with concentrated sources of N₅ 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 (NH₃) emissions and meteorology. This paper presents a dynamic mass-flow model (GUANO) that simulates temporal variations in NH₃ emissions from seabird guano. While the focus is on NH₃ emissions, the model necessarily also treats the interaction with wash-off as far as this affects NH₃. The model is validated using NH₃ 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 NH₃ 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 NH₃ 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 NH₃ emissions from seabird guano and provides a starting point to refine models of NH₃ emissions from other sources. © 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Reactive nitrogen (N₅) has been used to improve crop growth for the last 8000 years (Bogaard et al., 2013). However, N₅ 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 N₅ 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...
can be estimated based on a percentage of $N_\text{r}$ that volatilizes as emission of a particular animal species. Alternatively, the emission orology on the formation of NH$_3$ from an $N_\text{r}$ source. NH$_3$ volatili-
et al., 2013). For instance, Cooter et al. (2010) used a process-
t based model to predict measured diurnal variation and daily
-fl NH$_3$ in solution is used to calculate the NH$_3$ gas on the surface, with
spatial impact zone of up to 300 km$^2$ surrounding the colony where
transport and earth system models. Flechard et al. (2013)synthe-
-izations that can be used to calculate NH$_3$ emissions on the
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 $N_\text{r}$ on an hourly basis and upsampling 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 ammonical 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
emissions, have not been included in the model since these are considered to take place on a slower time scale than NH₃ emissions. The following steps are included in the model:

1. Nitrogen-rich guano, in the form of UA, is excreted onto the surface by seabirds at the colony. The amount of guano varies depending on the mass and behaviour of the nesting species (e.g. Wilson et al., 2004). At each time-step (tₙ), the UA budget (QUA, g m⁻²) is calculated from the total nitrogen excreted (Fₑ, g m⁻² hour⁻¹), the TAN produced per hour (FTAN, g m⁻² hour⁻¹) and the uric acid nitrogen washed off by the rain (FW(UA), g m⁻² hour⁻¹), where N is the hour of the year (Equation (1)).

\[
Q_{UA}(t_{n+1}) = Q_{UA}(t_n) + F_e - F_{TAN} - F_{W(UA)}
\]  

(1)

2. Uric acid is converted to TAN, with the conversion rate depending on climatic conditions and the pH of the surface (Elliott and Collins, 1982, Elzing and Monteny, 1997; Groot Koerkamp et al., 1998). At each time step the TAN budget (Q_{TAN}, g m⁻²) is calculated from the TAN produced per hour from UA (F_{TAN}, g m⁻² hour⁻¹), the amount of NH₃ emitted (F_{NH₃}, g m⁻² hour⁻¹) and the TAN washed off by the rain (FW(TAN), g m⁻² hour⁻¹), where N is the hour of the year (Equation (2)).

\[
Q_{TAN}(t_{n+1}) = Q_{TAN}(t_n) + F_{TAN} - F_{NH₃} - F_{W(TAN)}
\]  

(2)

3. TAN partitions between NH₄ and NH₃ on the surface, with the position of the equilibrium depending on the pH and the temperature (T, K) of the surface (Equation (3)). A function, \( T = \frac{[NH₄]^+/[H^+]]}{[NH₃]} \), is used to describe the equilibrium at the surface (Nemitz et al., 2000) such that the gaseous concentration of NH₃ at the surface (X₃) is:

\[
X_3 = \frac{161500}{T} \exp \left( \frac{-10378}{T} \right) T
\]  

(3)

The TAN concentration is a function of the water content of the guano. The water budget (Q_{H₂O}, kg m⁻²) is calculated (Equation (4)) from the flux of water contained in excreted guano (F_{H₂O}(g/ℓ), kg m⁻² hour⁻¹), rain events (F_{H₂O}(pptn), kg m⁻² hour⁻¹), water run-off (F_{H₂O}(ro), kg m⁻² hour⁻¹) and evaporation (F_{H₂O}(evap), kg m⁻² hour⁻¹). Each of the parameters in Equation (4) is further described in the Supplementary Material Section 1.

\[
Q_{H₂O}(t_{n+1}) = Q_{H₂O}(t_n) + F_{H₂O}(g) + F_{H₂O}(pptn) - F_{H₂O}(ro) - F_{H₂O}(evap)
\]  

(4)

4. NH₃ on the surface volatilizes to the atmosphere, with the rate of volatilization (Equation (5)) depending on the NH₃ concentration difference between the surface (X₃) and the atmosphere (Xₐ), the aerodynamic and boundary layer resistances (Rₐ and Rₐ) (Sutton et al., 1993; Nemitz et al., 2001) estimating the effect of NH₃ reabsorption by the substrate and any overlying vegetation using an empirical habitat factor (F_{hab}). A habitat factor was used here in preference to a more process based description involving the bi-directional exchange of NH₃ from vegetation because of the complexity of the mix of nesting types. The values of the habitat factors used are described in Section 2.2.3.

\[
NH₃\text{ emission} = \frac{X_3 - X_a}{R_a + R_b} F_{hab}
\]  

(5)

2.2. Model input data

Site-specific NH₃ emissions were calculated for five seabird colonies in a range climate zones: Tropical: Michaelmas Cay on the Great Barrier Reef (16.60° S, 145.97° E) and Ascension Island in the South Atlantic (7.99° S, 14.39° W), Temperate: the Isle of May in Scotland (56.19° N, 2.56° W) and Sub-Polar: Signy Island in the South Orkney Islands (60.72° S, 45.60° W) and Bird Island in South Georgia (54.0° S, 38.05° W).

2.2.1. Meteorological input data

To run the GUANO model, meteorological data are required for periods before, during and after the measurement campaigns. Continuous monitoring of the weather was conducted in-situ only on the Isle of May. For the other colonies, meteorological data (wind speed, ground temperature, relative humidity and rainfall) were collected during short term campaigns, with data beyond these periods obtained from the nearest meteorological station (Table 1).

2.2.2. Seabird colony data

The site-specific seabird data that have the greatest effect on the NH₃ emission, as identified by Wilson et al. (2004), were collated from field observations and the literature: nest density and duration of the breeding season, adult mass, proportion of time spent at the colony (see Table 1 also Riddick et al., 2012). The estimated total nitrogen excreted at a colony is based on the assumption that adult seabirds excrete N at a constant rate while at the colony and away from it.

2.2.3. Habitat factors

Habitat factors (F_{hab}) are used in Equation (5) to account for NH₃ immobilized by the nesting substrate or recaptured by the overlying canopy and are listed in Table 1A in the Supplementary Material Section 1. This reflects a base value for bare rock of 1, where no NH₃ is immobilized or recaptured, which is then reduced as a correction factor, to parameterise the effect of nesting behaviour of the birds. Following Wilson et al. (2004) and the
measurements of Riddick et al. (2012), habitat factors for birds that build nests on bare rock is taken as 1, while for those that nest on sand is taken as 0.67. For those bird species that nest on vegetation or use a nest, \( F_{hab} \) is 0.20 and birds excreting in burrows have a \( F_{hab} \) value of 0.

Penguins on Bird Island and Signy Island nest on bare rock (\( F_{hab} = 1 \)), while the birds on Michaelmas Cay and Ascension Island nest on sand (\( F_{hab} = 0.67 \)). On the Isle of May, adult penguins make burrows, but excrete outside, while their young excrete in burrows. Where adult penguins excrete depends on the time of day and climatic conditions: at dawn and dusk, large numbers of penguins can be seen on exposed rocks across the colony, and this also happens when it is warm and sunny. For the remainder of the time, penguins excrete on the soil outside their burrow. To accommodate variations in this assumption, the \( F_{hab} \) value for adult penguins was changed from vegetation only (0.2 as estimated by Wilson et al., 2004) to an \( F_{hab} \) value between rock and vegetation of 0.60 (average of 1 and 0.20). For puffin chicks, data suggest that these only excrete inside the burrows and leave the colony as soon as they leave the nest (Harris and Wanless, 2011). Puffin chicks are therefore not thought to contribute to seabird NH\(_3\) emission at the colony, with any emissions inside the burrows being absorbed by the soil inside the burrow, therefore \( F_{hab} \) for chicks is here set at 0.

### Table 1

| Colony           | Target Species          | Population (Pairs) | Measure-ment strategy | \( Av \) T | \( Av \) RH | \( Av \) WS | \( D_{ref} \) (km) | \( F_{hab} \) | Adult Mass (g) | Nest Density \( D \) (m\(^2\)) | Breeding season \( D \) (days) | FC N excretion rate \( F_e \) (g m\(^{-2}\) hr\(^{-1}\)) | Average Measured NH\(_3\) Emission (µg m\(^{-2}\) s\(^{-1}\)) |
|------------------|-------------------------|--------------------|-----------------------|----------|----------|----------|-----------------|----------|----------------|-----------------------------|-----------------------------|-----------------------------|--------------------------------|
| Ascension Island | Sooty tern              | 100,000            | Active                | 27       | 72       | 5        | 2               | 0.67     | 190            | 1.26                        | 122                         | 0.60                        | 14.39                          |
| Isle of May      | Atlantic puffin         | 20,000             | Active                | 15       | 80       | 4        | 1               | 0.60     | 410            | 1.27                        | 152                         | 0.30                        | 5.00                           |
| Bird Island      | Macaroni penguin       | 40,000             | Active                | 3        | 92       | 5        | 5               | 1.00    | 680            | 0.85                        | 213                         | 0.60                        | 12.90                          |
| Michaelmas Cay   | Common noddy           | 12,000             | Passive               | 28       | 85       | 5        | 17              | 0.67    | 200            | 1.70                        | 122                         | 0.60                        | 22.30                          |
| Signy Island     | Adelie and Chinstrap penguin | 19,000          | Passive               | 2       | 84       | 5        | 50              | 1.00    | 1450           | 0.63                        | 274                         | 0.60                        | 9.00                           |

\(^{a}\) Riddick et al. (2014).
\(^{b}\) Riddick et al. (2016).

The GUANO model was coded in Microsoft Excel. For each seabird colony the GUANO model uses meteorological and bird data to calculate the hourly NH\(_3\) emission (g NH\(_3\) m\(^{-2}\) h\(^{-1}\)). The annual NH\(_3\) emission is calculated as the sum of hourly emissions. The model runs were initialized with zero UA, TAN and water in the budgets starting at least 24 months before the assessment period for comparison with the emission estimates based on concentration measurements and turbulent exchange parameters.

#### 2.3. Model validation

The model setup and parametrization was set based on theoretical considerations and on available data to parametrize the model. In principle, the model setup was independent of measured validation data, according to the parameters considered. In the case of substrate pH and roughness length runs were based on a constant value, while TAN and Guano run off were based on a fixed percentage per mm of rain. The habitat factors were based on prior studies drawing on Blackall (2004), Wilson et al. (2004) and Blackall et al. (2007). The only parameter which was tuned according to measurements was \( F_{hab} \) at the Atlantic Puffin site on the Isle of May, Scotland. By contrast, the model tests in comparison with measurements at Mars Bay, Ascension Island, at Bird Island, South Atlantic, at Michaelmas Cay, Great Barrier Reef, at Signy Island, South Atlantic were made without tuning any other model parameters and therefore represent fully independent tests of the model in a wide range of climatic conditions.

#### 2.3.1. Measured NH\(_3\) emissions for comparison with the model

Two methods were employed to conduct NH\(_3\) concentration emission estimates based on concentration measurements and turbulent exchange parameters, which were used to quantify NH\(_3\) emissions, as reported in detail by Riddick et al. (2014): (1) passive sampling and (2) active on-line NH\(_3\) analysis instrument. For the passive sampler measurements (ALPHA samplers, CEH Edinburgh, Tang et al., 2001), triplicate samplers were used at each sampling location and exposed for periods of 2–4 weeks to measure an average concentration for the exposure period. The time-averaged NH\(_3\) concentration data were then used with the WindTrax inverse dispersion model version 2.0 to calculate the emission (Flesch et al., 1995; Riddick et al., 2014).
Active on-line NH$_3$ concentration measurements were made by Riddick et al. (2014, 2016) with an AiRMonia gas analyser (Mechatronics, NL) on Bird Island and Ascension Island and a Nitrolux 1 000 gas analyser (Pranalytica, USA) on the Isle of May. The NH$_3$ concentration data were averaged to 15-min data and used as input to the WindTrax in an inverse model to calculate the emission. The calculation of the NH$_3$ emissions used as validation at each of the sites are the result of five separate field campaigns and are described in full in Riddick et al. (2014) for Michaelmas Cay and Ascension Island and Riddick et al. (2016) for Signy Island, the Isle of May and Bird Island (locations of the five fieldwork sites are presented in Supplementary Material Section 2).

As a result of the method employed at Michaelmas Cay and Signy Island (passive sampling only), hourly resolved measured NH$_3$ fluxes were not available at these sites (Riddick et al., 2014, 2016). However, at Ascension Island (Riddick et al., 2014) and the Isle of May (Riddick et al., 2016), both passive (time integrated) measurements and the continuous measurements, were made allowing comparison between the two approaches. In both cases, close agreement was found between the passive (time-integrated) and active (time resolved) sampling methods, the uncertainty in chemical sampling method was ±20% and ±12% of the mean flux at the Isle of May and Ascension, respectively (Riddick et al., 2016).

Calculation of a third estimate in each case (time-integrated based on concentration measurements and turbulent exchange measurements) were made allowing comparison between the two approaches. In both cases, close agreement was found between the passive (time-integrated) and active (time resolved) sampling methods, the uncertainty in chemical sampling method was ±20% and ±12% of the mean flux at the Isle of May and Ascension, respectively (Riddick et al., 2016).

Calculation of a third estimate in each case (time-integrated based on the semi-continuous active sampling data) allowed it to be shown that the meteorological uncertainties associated with long measurement periods (for the passive, time-integrated measurements) were of similar magnitude to the uncertainties between the two different chemical sampling methods.

### 2.4. Comparison modelled emissions to those estimated through measurement

The GUANO model simulations were validated with emission estimates based on concentration measurements and turbulent exchange parameters from the five field sites. To assess the fit of the model, the hourly measured emissions were plotted against the hourly modelled NH$_3$ emissions, with the slope, intercept and determination coefficient (R$^2$) of the linear regression calculated. Time-averaged modelled emissions are also presented and compared against matched time-averaged emission estimates based on concentration measurements and turbulent exchange parameters to show that the model, not only captures the hourly emissions, but also is consistent with measurements over a period of time.

In addition, the mean NH$_3$ emission for each colony was calculated (in $\mu$g m$^{-2}$ s$^{-1}$) from the hourly emissions. The percentage of nitrogen volatilized ($P_v$) was calculated from the total nitrogen excreted at each colony during the measurement period and the total nitrogen estimated to be volatilized as NH$_3$ over the same period.

### 2.5. NH$_3$ emission and meteorology

To investigate the effects of meteorology, the slope, intercept and R$^2$ between modelled NH$_3$ emission and each variable was calculated. The coefficient of determination is used to assess the size of the effect each environmental variable (ground temperature, wind speed, relative humidity and precipitation) has on the modelled NH$_3$ emission so that the key drivers of emission at each measurement site can be identified.

### 2.6. Sensitivity analysis

A sensitivity study was performed on the GUANO model to determine the most significant model parameters in relation to the model output. The following model parameters were investigated with realistic variations in each input parameter: $z_0$ (m), fraction of UA converted to TAN per day, percentage nitrogen wash-off (% mm$^{-1}$ rain), percentage non-nitrogen wash-off (% mm$^{-1}$ rain), pH, habitat factors ($P_{hub}$), boundary layer Stanton number ($B$), temperature ($T$, °C), relative humidity ($RH$, %), wind speed ($U$, m s$^{-1}$), precipitation ($P$, mm m$^{-2}$ hr$^{-1}$), net solar radiation ($R_n$, W m$^{-2}$), pH and background NH$_3$ concentration ($\mu$g m$^{-3}$). The sensitivity of the NH$_3$ emissions to each input parameter was tested using the GUANO model application to the Atlantic puffin colony on the Isle of May. The application of the GUANO model at Isle of May was used in the sensitivity analysis because this temperate site could best respond to positive and negative changes in environmental conditions in a global context.

### 3. Results

#### 3.1. Model output and validation with empirical data

##### 3.1.1. Mars Bay, Ascension Island: sooty tern colony

The NH$_3$ emissions calculated by the GUANO model for Ascension Island show a strong diurnal pattern, with the peak emissions corresponding to the hottest, most turbulent and windiest part of the day. The maximum measured emission during the study period was 370 $\mu$g NH$_3$ m$^{-2}$ s$^{-1}$ (Fig. 2). The NH$_3$ emissions calculated by the GUANO model for Ascension Island are in close agreement to those derived from field measurements (Table 3; Supplementary Material Section 2 Fig. SM 2.1), with a linear regression slope of 1.07, intercept of -1.20 $\mu$g m$^{-2}$ s$^{-1}$ and $R^2 = 0.94$. The average modelled NH$_3$ emission for Ascension Island during the measurement period was 22.3 $\mu$g NH$_3$ m$^{-2}$ s$^{-1}$, the average measured NH$_3$ emission on Ascension was 22.3 $\mu$g NH$_3$ m$^{-2}$ s$^{-1}$ and the average modelled NH$_3$ emission for periods when measurement data available was 19.8 $\mu$g NH$_3$ m$^{-2}$ s$^{-1}$. The most notable features of the modelled and measured NH$_3$ emission is the strong dependence on temperature and moisture availability (with higher emissions after rain events on 25 May and 6–7 June), with the TAN budget almost fully depleted before then end of each day. This implies that the NH$_3$ emission rate is tightly coupled to the TAN production rate at this site (Supplementary Material Section 3 Fig. SM 3.1; Supplementary Material Section 4 Fig. SM 4.1, $R^2$ value = 0.98). At this site, aerodynamic and boundary layer resistance has little effect, as the TAN produced is all quickly lost through NH$_3$ emissions. Ammonia emission is thus hydrolysis-limited for the test period at this site, with the performance of the GUANO model therefore depending almost entirely on its parametrization the urea hydrolysis rate.

##### 3.1.2. Isle of May, scotland: Atlantic puffin colony

The modelled emissions were lower for the Isle of May puffin colony than Ascension Island (Sooty tern), but showed a similar diurnal pattern [Fig. 3], with high emissions in the day (maximum of 25 $\mu$g m$^{-2}$ s$^{-1}$ during the afternoon) and negligible emissions at night. When compared with the emission estimates based on concentration measurements and turbulent exchange parameters, the hourly NH$_3$ emissions modelled by the GUANO model were underestimated, with a linear regression slope of 0.13, intercept of 5.7 $\mu$g m$^{-2}$ s$^{-1}$ and $R^2$ of 0.13 (Table 3; Supplementary Material Section 2 Fig. SM 2.2). The poorest fit occurred on 1st July 2009, where the model overestimated the measured NH$_3$ emission during the early hours of the morning. This was associated with a period of low-wind speed and stable conditions, which could also reflect uncertainties in the measurement estimate at this time. During the period of 29 June to 2 July the measured emissions were...
Fig. 2. Comparison between measured and modelled NH$_3$ emissions for the Sooty tern colony at Mars Bay, Ascension Island (22nd May to 10th June 2010). Top panel: Rain, ground temperature, relative humidity and wind speed (measured values). Middle panel: Guano water and TAN (modelled values). Bottom Panel: Measured and modelled NH$_3$ emissions. The $F_{nhb}$ value used in the GUANO model was 0.67 (based on a sand substrate). All values are hourly; tick marks on the x-axis indicate midnight.

Fig. 3. Comparison between measured and modelled NH$_3$ emissions for the Isle of May, Scotland (5th to 26th July 2009). Top panel: Rain, ground temperature, relative humidity and wind speed (measured values). Middle panel: Guano water and TAN (modelled values). Bottom Panel: Measured and modelled NH$_3$ emission. The $F_{nhb}$ value used in the GUANO model was 0.64 (based on a soil/rock substrate). All values are hourly; tick marks on the x-axis indicate midnight.
much smaller than model and this may correspond to a period of foggy weather where NH₃ could have dissolved in the fog and few puffins were seen around the colony, which may explain why the measured emissions were much smaller than the modelled emissions, which did not take account of this meteorological interaction.

The average modelled NH₃ emission for the Isle of May during the measurement period was 7.7 μg NH₃ m⁻² s⁻¹, the average measured NH₃ emission on the Isle of May was 6.9 μg NH₃ m⁻² s⁻¹ and the average modelled NH₃ emission for periods when measurement data available was 9.3 μg NH₃ m⁻² s⁻¹. At this site the TAN budget fluctuates greatly, with hourly modelled and measured emissions correlated with the TAN budget (Supplementary Material Section 3 Fig. SM 3.2, R² = 0.05. In contrast to Ascension Island, however, TAN did not deplete to near zero each evening, indicating that daily NH₃ emission is only partially limited by TAN production over the previous 24 h.

3.1.3. Bird Island, South Atlantic: macaroni penguin colony ‘Big Mac’

Compared with the other seabird colonies considered in this study, a diurnal pattern was much less noticeable for both modelled and measured NH₃ emissions from the Macaroni penguin colony on Bird Island (Fig. 4). The maximum NH₃ emission simulated by the GUANO model from the colony was 53 μg NH₃ m⁻² s⁻¹ at 0500 on 11th December 2010. Contrary to the other sites, there was also little correlation between the emission rate and ground temperature, which was associated with small variation in ground temperature (3–8 °C range) during the measurement period. Instead, at this site the periods of lowest NH₃ emissions (below 10 μg NH₃ m⁻² s⁻¹) were observed during periods of lower wind speed, with maximum emissions during periods of high wind speed, linked to a substantial range of wind speed during the measurement period (0.3–12 m s⁻¹). The GUANO model simulations reproduced the measured NH₃ emissions well, with a linear regression slope of 1.09, and intercept of −1.32 μg m⁻² s⁻¹ and R² = 0.86 (Table 3; Supplementary Material Section 2 Fig. SM 2.3). Modelled emissions from the Big Mac colony are mostly between 0 and 20 μg m⁻² s⁻¹. The average modelled NH₃ emission for Bird Island during the measurement period is 13.4 μg NH₃ m⁻² s⁻¹, the average measured NH₃ emission on Bird Island was 12.3 μg NH₃ m⁻² s⁻¹ and the average modelled NH₃ emission for periods when measurement data available was 12.4 μg NH₃ m⁻² s⁻¹.

At this site, the modelled TAN budget can be seen from Fig. 4 to show negligible fluctuation on a daily time scale, contrary to Ascension Island and the Isle of May (Supplementary Material Section 4), while showing a slight increase over the first period and first decrease then increase over the second period. At the same time this site has much larger amounts of available TAN at the surface than these other sites, at 2–3 g m⁻². With relatively modest temperature fluctuations during the measurement period, at this site, the variation in NH₃ emission rate can therefore be seen to be primarily limited by the mass transfer process itself, as affected by wind speed and surface temperature. Supplementary Material Section 3 Fig. SM 3.3 shows that there is still a significant correlation between simulated TAN production and NH₃ emission (R² = 0.29), the relationship is less than at the temperate and tropical sites.

The TAN production rate at Bird Island (0–0.15 g m⁻² hr⁻¹) is more similar to the Isle of May (0–0.4 g m⁻² hr⁻¹) than Ascension Island (0–0.1 g m⁻² hr⁻¹) (Supplementary Material Section 3 Figs. SM 3.1, SM 3.2 and SM 3.3). This suggests that, while temperature does not affect the daily variation, the overall magnitude of NH₃ emission is still largely controlled by TAN hydrolysis rate. i.e. hydrolysis rate controls the overall rate of emission while meteorology controls the short-term variation in NH₃ emission.

3.1.4. Michaelmas Cay, Great Barrier Reef: common noddy colony

The NH₃ emissions simulated by the GUANO model for Michaelmas Cay show a strong diurnal pattern, with maximum

Fig. 4. Comparison of measured and modelled NH₃ emissions from the Big Mac Macaroni penguin colony, Bird Island, South Georgia (18/11/2010 to 13/12/2010). Top panel: Rain, ground temperature, relative humidity and wind speed (measured values). Middle panel: Guano water and TAN (modelled values). Bottom panel: Measured and modelled NH₃ emission. The Fₘₜₜ value used in the GUANO model was 1 (based on a rock substrate). All values are hourly; tick marks on the x-axis indicate midnight.
emissions during the day reaching nearly 500 μg m\(^{-2}\) s\(^{-1}\) which drop to an emission during the night of between 1 and 10 μg m\(^{-2}\) s\(^{-1}\). The average NH\(_3\) emission measured using passive samplers for two periods of four weeks during November and December (Riddick et al., 2014) are very similar to the emissions simulated by the GUANO model when averaged over the same periods (Fig. 5A and Table 2). The NH\(_3\) emissions measured during the field campaign are 25.9 μg NH\(_3\) m\(^{-2}\) s\(^{-1}\). Both measured and modelled emission showed an increase from November to December. The average NH\(_3\) emission predicted by the GUANO model is 27.5 μg NH\(_3\) m\(^{-2}\) s\(^{-1}\) for November and December 2009.

The modelled TAN budget showed a high level of temporal structure, combining both substantial diurnal variations (indicating some limitation according to the TAN production rate) and some variation due to mass transfer limitations under the control of temperature and other environmental variables (see Supplementary Material Section 3 Fig. SM 3.4, where simulated TAN production rate and simulated NH\(_3\) emission are found to be correlated with \(R^2 = 0.91\)).

3.1.5. Signy Island, South Atlantic: chinstrap penguin colony
As with the tropical and temperate regions, but in contrast to

![Graph](image-url)
the other sub-polar colony at Bird Island, NH$_3$ emissions simulated for Signy by the GUANO model were strongly diurnal (Fig. 5B). This can be explained by the more regular diurnal variation in temperature (typically 4–6 °C diurnal change) than at Bird Island (Fig. 4).

The Signy colony is used by both Adélie and Chinstrap penguins for the first measurement period. During the second period, the Adélie penguins gradually left the colony and only Chinstrap penguins were present for the third period. The NH$_3$ emissions at Signy Island are the highest for the first period, reaching a maximum of 50.0 μg NH$_3$ m$^{-2}$ s$^{-1}$. The average NH$_3$ emission predicted by the GUANO model for the penguin colony during the whole measurement period was 10.7 μg NH$_3$ m$^{-2}$ s$^{-1}$. This is similar to the NH$_3$ emissions measured during the field campaign of 9.0 μg NH$_3$ m$^{-2}$ s$^{-1}$ (Table 2).

The simulated TAN budget for the penguin colony at Signy Island shows negligible diurnal variation, but rather a steady increase during the study period from 30 to 55 g m$^{-2}$ (Fig. 5). Overall, there was only a weak correlation between simulated TAN production and simulated NH$_3$ emission (Supplementary Material Section 3 Fig. SM 3.5). The reason for the smooth trend in TAN budget at the surface (Fig. 5b) is that the NH$_3$ emissions and run off during the response, where Michaelmas Cay had a higher measured percent-volatilization ($P_v = 67\%$) as compared with Ascension Island ($P_v = 52\%$) even though the sites had similar average temperature (Tables 1 and 3). This may be reflective of more moisture limitation to uric acid hydrolysis at Ascension Island. This difference is supported by the GUANO model simulation which also estimated a higher value of $P_v$ for Michaelmas Cay (82%) than for Ascension Island (37%), reflecting the generally higher simulated guano water content at Michaelmas Cay than at Ascension Island (Figs. 5A and 2).

### Table 2
Comparison between measured NH$_3$ emissions and NH$_4$ emissions simulated using the GUANO model for Michaelmas Cay, Great Barrier Reef, Australia during Period 1 (5/11/2009 to 10/12/2009) & Period 2 (10/12/2009 to 6/1/2010) and Signy Island during Period 1 (10/01/09–25/01/09), Period 2 (25/01/09–08/02/09) and Period 3 (08/02/09–21/02/09). Measured values from Riddick et al. (2014, 2016).

| Colony         | NH$_3$ emission (μg NH$_3$ m$^{-2}$ s$^{-1}$) | $P_v$ (%) | $R^2$ between hourly modelled NH$_3$ emission and meteorological variable | Comparison of hourly modelled to hourly measured emissions |
|----------------|---------------------------------------------|-----------|---------------------------------------------------------------------------|----------------------------------------------------------|
| Ascension Island | 30.2                                       | 21.5      | 0.11 0.01 0.01 0.03 0.94 1.07 – 1.2                                      | 67.0                                                     |
| Isle of May     | 5.0                                        | 3.2       | 0.39 0.04 0.06 0.01 0.94 1.07 – 1.2                                      | 5.5                                                      |
| Bird Island     | 12.9                                       | 12.7      | 0.39 0.04 0.59 0.01 0.94 1.07 – 1.2                                      | 1.6                                                      |
| Michaelmas Cay  | 22.3                                       | 27.5      | 0.18 0.04 0.01 0.01 0.94 1.07 – 1.2                                      | 20.9                                                     |
| Signy Island    | 9.0                                        | 10.7      | 0.38 0.03 0.22 0.01 0.94 1.07 – 1.2                                      | 0.11                                                     |

*This is defined as the average percentage of TAN produced in a day that volatilizes as NH$_3$. 

The next strongest driver of NH$_3$ emission is wind speed, with an average $R^2$ of 0.18 (range 0.01–0.59), with the highest correlation on Bird Island ($R^2 = 0.59$) where there was a wide range of wind speeds and small differences in temperature. Relative humidity and precipitation were not found to be strong climatic drivers of NH$_3$ emission, with $R^2$ values ranging from 0.01 to 0.04. This is not to say that these factors are unimportant, as the response of both modelled and measured NH$_3$ emission to precipitation at Ascension Island showed (Fig. 2). Precipitation and relatively humidity are fundamental controls on TAN formation from UA and influences NH$_3$ emission on a longer time scale than variation in temperature and wind speed which directly affects the hourly variation in NH$_3$ emissions.

3.2. NH$_3$ emissions and environmental conditions

Considering the simulated estimates from the GUANO model at each site, the strongest meteorological driver of NH$_3$ emission was found to be ground temperature for all sites except for Bird Island, average $R^2$ of 0.29 (range 0.11–0.39) (Table 3). As ground temperature increases, the rate of bacterial decomposition of uric acid nitrogen to form TAN (Equation (2)) increases and, coupled with an increased volatility of NH$_3$ (Equation (3)), results in increased NH$_3$ emission.

### Table 3
Comparison between measured NH$_3$ emissions and NH$_4$ emission simulated using the GUANO model for the measurement periods at different study sites. $P_v$ is the percentage of TAN simulated as NH$_3$. Determination coefficients ($R^2$) are shown for modelled emissions based on hourly data between modelled NH$_3$ emission and each climate variable and for the comparison of modelled and measured emissions (value after each $R^2$ in brackets shows + or – interaction). The mean modelled % of available TAN emitted was calculated from the total emission and the total duration of the measurement period. The climate variables $T_g$ represents Ground Temperature, $RH$ is relative humidity, $WS$ is wind speed and $P$ is precipitation. For Michaelmas Cay and Signy Island, denoted by $^a$, the values are a time-weighted mean of the measurement and model values shown in Table 2.

| Colony        | Measured | GUANO Model | Measured | GUANO Model | $T_g$ | $RH$ | $WS$ | $P$ | $R^2$ | Slope Intercept (μg m$^{-2}$ s$^{-1}$) | Modelled mean % of available TAN emitted as NH$_3$ in a day $^a$ |
|---------------|----------|-------------|----------|-------------|------|-----|-----|-----|------|--------------------------------------|--------------------------------------------------|
| Ascension Island | 30.2      | 21.5        | 51.9     | 37.0        | 0.11 | 0.01| 0.01| 0.03| 0.94 1.07 – 1.2 | 67.0                                              |
| Isle of May    | 5.0       | 3.2         | 4.7      | 2.8         | 0.39 | 0.04| 0.06| 0.01| 0.94 1.07 – 1.2 | 5.5                                               |
| Bird Island    | 12.9      | 12.7        | 1.8      | 1.7         | 0.39 | 0.04| 0.59| 0.01| 0.94 1.07 – 1.2 | 1.6                                               |
| Michaelmas Cay | 22.3      | 27.5        | 66.8     | 82.4        | 0.18 | 0.04| 0.01| 0.01| 0.94 1.07 – 1.2 | 20.9                                              |
| Signy Island $^a$ | 9.0       | 10.7        | 2.4      | 2.9         | 0.38 | 0.03| 0.22| 0.01| 0.94 1.07 – 1.2 | 0.11                                              |
3.3. Sensitivity analysis

A sensitivity analysis of the GUANO model is shown in Table 4 for each input variable selected. The estimated NH₃ emissions were most sensitive to changes in environmental variables, with highest sensitivity to ground temperature which varied by +59.9% to −36.8% for changes of +10% and −10%, respectively. The NH₃ emissions calculated by the GUANO model had the smallest response to changes in micrometeorological constants used to calculate the flux, i.e. surface roughness, boundary layer Stanton number and background NH₃ concentration.

Of the constants used, the GUANO model is most sensitive the substrate pH. The model uses a substrate pH equal to the pH of guano, estimated at 8.5 (hydron concentration: \([H^+] = 3.2E-9\) by Blackall (2004), and changes in-pH from pH 7 (\([H^+] = 1E-7\) to pH 10 (\([H^+] = 1E-10\)) result in 73% and −22% effect on NH₃ emission, respectively. The sensitivity in the model to pH is caused by the function, which is used to describe the equilibrium of the concentrations of the TAN and hydrogen ions on the surface (Equation SM18), and is directly proportional to the gaseous concentration of NH₃ at the surface (Equation (3)). We recognize that this is a source of uncertainty in the model, however the value used in the GUANO model for substrate pH is currently the best available.

The sensitivity of the modelled emission to changing environmental conditions can be seen in Supplementary Material Section 6, where in all cases the NH₃ emission increases with ground temperature and in all cases emissions is the same at 25 °C. Wind speed has the next biggest effect as NH₃ emission increases with wind speed at low temperatures. Precipitation also affects emission as higher rainfall results in lower emission at low temperatures. Relative humidity has relatively little effect on emission, but higher humidity results in lower emission.

4. Discussion

4.1. General discussion

This paper presents and describes the GUANO model, the first dynamic mass-flow process-based model developed to simulate NH₃ losses from seabird guano, which is here validated against NH₃ emissions measured at seabird colonies representative of a range of climates around the world. Comparison with NH₃ emission estimates based on measurements of NH₃ concentration and turbulent exchange parameters (Riddick et al., 2014, 2016) shows that the model is able to reproduce the magnitude and temporal variation of NH₃ emissions for a broad range of nesting habitats and climatic conditions. The GUANO model has been structured to simulate hourly NH₃ emission, using nitrogen excretion rates, temperature, relative humidity, wind speed and precipitation. This choice of time resolution, however, is purely a matter of model implementation and the model has the flexibility to allow for this to be changed. However, the advantage of calculating hourly emission estimates is that the GUANO model is able to discriminate the main effects of varying environmental conditions including diurnal variability. In this way, a clearer picture emerges of the main controls on NH₃ emissions from seabird colonies.

The model parametrization was based primarily on well-established existing principles and measured terms. Elements such as the turbulent and laminar boundary layer resistances have been widely used in other models, where the main uncertainty concerns the setting of the surface roughness length. Here we used an estimate based on observational data (Riddick et al., 2014, 2016) and Seinfeld and Pandis (2006) to set the roughness length at 0.1 m. The emission itself is driven by the concentration difference between atmospheric NH₃ concentrations and the surface NH₃ concentration. However, as the former is very small, the key uncertainty is the surface NH₃ concentration. The first challenge is to simulate the rate of uric acid hydrolysis, for which we used a parametrization unchanged from Elliott and Collins (1982), based on measurements from a poultry house context. The fact that this delivers good agreement with observed fluxes in a context where NH₃ emission is limited almost entirely by UA hydrolysis rate (Ascension Island), provides strong support for the parametrization of Elliott and Collins (1982). The other major uncertainties in the model concern surface pH, the habitat factor and the extent of wash-off. For the surface pH use of a prior measurement estimate from Blackall (2004) for all modelling sites shows that a fixed value of pH 8.5 is sufficient for the model application. The \(F_{hab}\) could be considered as a model tuning parameter, however, this would only apply for sites not on bare rock (for which \(F_{hab} = 1\)). The reduction

| Factor | Type | Base value for all model runs (and range tested) | Source of base value | % Change in NH₃ emissions |
|--------|------|-------------------------------------------------|---------------------|--------------------------|
|        |      |                                                 |                     | High Value | Low Value |
| Surface roughness height (\(z_o\), m) | C | 0.1 (0.01–0.5) | Seinfeld and Pandis (2006); Riddick et al. (2014, 2016) | +70 | −56 |
| UA conversion to TAN (% day⁻¹ at pH 5, T = 35 °C) | C | 0.83 (±10%) | Elliott and Collins (1982) | −9.42 | 9.30 |
| Nitrogen wash off (% mm⁻¹ rain) | C | 1 (±10%) | Blackall (2004) | 8.19 | −7.12 |
| Non-Nitrogen Wash off (% mm⁻¹ rain) | C | 0.5 (±10%) | Blackall (2004) | −0.15 | +0.17 |
| Boundary layer Stanton number (B) | C | 5 (±10%) | Sutton et al. (1993) | +0.04 | −0.04 |
| Habitat Factor (\(F_{hab}\)) | C | 0.60 (0.2–1) | Wilson et al. (2004) | −70 | +49 |
| Substrate pH | C | 8.5 (7–9) | Riddick et al. (2012); Blackall (2004) | +73 | −22 |
| Background NH₃ concentration (µg m⁻³) | C | 0.1 (±10%) | Sutton et al. (2003) | −0.02 | +0.01 |
| Ground Temperature (°C) | V | 20° (±10%) | Measured | −36.8 | +59.9 |
| Relative Humidity (RH, %) | V | 84% (±10%) | Measured | −13.0 | +6.7 |
| Wind Speed (Uf, m s⁻¹) | V | 4.3° (±10%) | Measured | −11.0 | +12.9 |
| Precipitation (P, mm m⁻² hr⁻¹) | V | 0.17° (±10%) | Measured | +20.7 | −11.8 |
| Net solar radiation (\(R_n\), W m⁻²) | V | 82.6° (±10%) | Measured | −2.1 | +1.2 |
factors used in this study were in fact based on prior estimates from Wilson et al. (2004) with the only changes for this study being at the Atlantic puffin site on the Isle of May where \( F_{\text{HNO}} \) was taken as an average of rock and vegetation nesters to reflect the variability of the bird’s behaviour. For the wash off factors, constant relationship for all sites was used of 1 and 0.5% mm\(^{-1}\) rain for nitrogen and non-nitrogen, respectively. While this is an extremely simple approach, its value was based on Blackall (2004) and thus set as a prior value rather than being used to fit the measurements. Overall, therefore, it can be seen that while the performance of the model runs is sensitive to the model parametrization, the parameter choices were largely based on prior estimates independently from the outcome of the measurements.

The comparison of the GUANO model output with NH3 emission estimates based on concentration measurements and turbulent exchange parameters at a range of sites showed the GUANO model is able to reasonably model the NH3 emissions in different climate regions (Table 3), while giving better agreement with observations than any single environmental variable. Hourly measurements at the different field sites had \( R^2 \) values between model and measurements of between 0.5 and 0.9 (Table 3), while \( R^2 \) values with other environmental variables were generally lower.

The model-measurement comparison also illustrates how the different primary controls on NH3 emissions at the different sites. Sufficient water is needed for uric acid hydrolysis (as shown at Ascension Island), while excess water dilutes the TAN solution and is associated with increased TAN run off (Bird Island). The combined outcome of these effects is that increases in relative humidity or rain events only increase simulated NH3 emissions at arid sites such as Ascension Island (Fig. 2).

The NH3 emissions simulated by the GUANO model increased with wind speed at all sites because vertical transport and turbulent mixing of NH3 increases as aerodynamic and boundary layer resistances decrease. However, wind speed was only the major driver of NH3 emission variations at a windy site with little variation in ground temperature (Bird Island). At the other sites, ground temperature was the major driver in temporal differences of NH3 emission. Temperature is significant for two reasons: (1) it affects the rate at which uric acid converts to NH3 and (2) it affects the potential for volatilization of NH3 from the surface.

Understanding the processes behind the measured fluxes is greatly helped by considering changes in the TAN budget of the surface (Supplementary Materials Section 5) and the accumulation of TAN varied greatly between sites. The most extreme variation was found for the simulated TAN budget at Ascension Island, where rapid NH3 emission was reflected in almost complete loss of available TAN every evening. Under these circumstances, NH3 emission is primarily controlled by the uric acid hydrolysis rate, as almost all the TAN produced (unless washed-off in rain) is immediately volatilized (Fig. 2; Supplementary Material Section 2 Fig. SM 2.1). A contrasting situation was found in the simulations for Bird Island and Signy Island, where TAN production (urea hydrolysis) is much slower than at the warm sites, average TAN Production is 0.10, 0.19 and 0.06 g m\(^{-2}\) hr\(^{-1}\) for Ascension Island, the Isle of May and Bird Island, respectively. Intermediate behaviour in the TAN budget was found at the Isle of May and Michaelmas Cay, with large diurnal variations, but still substantial night time values. At Michaelmas Cay, a large-scale structure in the TAN budget, varying over daily to weekly timescales was the effect of rain events on the available UA and TAN on the surface.

### 4.2. Process-based versus empirical approaches

On a breeding season time-scale, temperature was shown to be the most influential meteorological variable, where NH3 emission rate increases with increased temperature. Importantly this effect, which was identified empirically by Sutton et al. (2013) is here explained for the first time using a dynamic modelling approach comparing globally contrasting sites. This study therefore provides a substantial advance on initial empirical studies calculating NH3 emissions from seabirds (Wilson et al., 2004; Blackall et al., 2007), which were used to calculate NH3 emissions on a regional and country scale to Riddick et al. (2012).

The main limitation of the empirical approach of Riddick et al. (2012) was the wide uncertainty ranges related to the temperature effect and the need to constrain these by measurements, ideally using a process based approach. This is now addressed here. The GUANO model is able to explain the major differences between field sites, and the way that different variables contribute, including temperature, moisture availability and wind speed, as the most important drivers. A first application of the GUANO model reported by Sutton et al. (2013) to different sites globally showed that it was able to reproduce the main measured differences in the percentage of excreted guano that volatilizes as NH3 in relation to temperature.

The major source of uncertainty is the value for pH used in the GUANO model. Even though the same value was used at the five colonies reported in this paper, the emission estimates calculated by the GUANO model was in good agreement with emission estimates based on concentration measurements and turbulent exchange parameters. This could suggest that the biogeochemical evolution of TAN from UA and subsequent formation of NH3 happens independently of the substrate so that the pH of the underlying strata is less important. This is illustrated by the sensitivity analysis where a \( \pm 10\% \) alteration of substrate pH should equate to a sensitivity on instantaneous NH3 emission potential of +605%, −86% (i.e. +/− factor of 7). The fact that the model outcome gave a net sensitivity on simulated NH3 emissions for the Isle of May of only +73%−22% illustrates that the amount of available TAN appears to constrain the total amount emitted and that more acid pH reduces urea hydrolysis rate (Equation SM5).

#### 4.3. NH3 emissions globally

The performance of the GUANO model is illustrated for the five colony emission estimates calculated by the GUANO model shown as the NH3 emission normalized in relation to the seabird mass (Fig. 6). The GUANO model emissions are in good agreement to emission estimates based on concentration measurements and turbulent exchange parameters when they are presented with matching emissions calculated from in-situ measurements by Riddick et al. (2014, 2016) and combined with measured emissions from other sites. The additional colonies represent rock nesters on the Isle of May (Blackall et al., 2007), a cold, dry Adélie penguin colony on Antarctica (Theobald et al., 2013) and a hot dry Double-crested cormorant colony on Mullet Island, California (Tratt et al., 2013). The consistency of the observed and model estimates shows that the GUANO model could be used to calculate NH3 emissions from seabird colonies in a wide range of meteorological conditions. The GUANO model captures the large effect of NH3 emission in response to temperature and can simulate the main differences between meteorology where emission rates per unit bird body mass vary across climates by more than an order of magnitude.

It is anticipated that NH3 emissions from seabird colonies could change in a variety of ways when global climate change forecasts are considered. Changes to food supplies and changes in sea-level are both highlighted as drivers of future seabird population changes (Forcada et al., 2006; Trathan et al., 2007; Brierley, 2008). This, coupled with anticipated temperature increases in many parts of the Southern Ocean and the Antarctic Continent (Denvil, 2005),
Fig. 6. Measured amount of excreted N, that is volatilized as NH3 as a function of mean temperature during different field campaigns as compared with estimates of the GUANO model. The line shows the best fit of the measured data (NH3 (µg g⁻¹ bird⁻¹ s⁻¹) = 0.0014e⁰·¹⁰⁹⁷; R² = 0.96). The field site codes are: C.H., Cape Hallett, Antarctica; S.I., Signy Island; B.I., Bird Island, South Georgia; I.M., Isle of May, Scotland, (b) – burrows, (c) - cliffs; B.R., Bass Rock, Scotland; M.C., Michaelmas Cay, Australia; A.I., Ascension Island; M.I., Mullet Island, California.

potentially present a very different N landscape, associated with substantially increased NH3 emissions. Through the GUANO model we now have a quantitative tool to assess such changes in N partitioning which could be used to better forecast future changes to these remote nutrient-poor ecosystems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2017.04.020.

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