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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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- 1 High temporal resolution modelling of environmentally-dependent
- 2 seabird ammonia emissions: description and testing of the GUANO
- 3 **Model**
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14 Abstract

15 Many studies in recent years have highlighted the ecological implications of adding reactive nitrogen (N_r) to terrestrial ecosystems. Seabird colonies represent a situation 16 17 with concentrated sources of Nr, through excreted and accumulated guano, often 18 occurring in otherwise nutrient-poor areas. To date, there has been little attention 19 given to modelling N flows in this context, and particularly to quantifying the 20 relationship between ammonia (NH₃) emissions and meteorology. This paper presents 21 a dynamic mass-flow model (GUANO) that simulates temporal variations in NH₃ 22 emissions from seabird guano. While the focus is on NH₃ emissions, the model 23 necessarily also treats the interaction with wash-off as far as this affects NH₃. The 24 model is validated using NH₃ emissions measurements from seabird colonies across a 25 range of climates, from sub-polar to tropical. In simulations for hourly time-resolved 26 data, the model is able to capture the observed dependence of NH₃ emission on 27 environmental variables. With temperature and wind speed having the greatest effects 28 on emission for the cases considered. In comparison with empirical data, the 29 percentage of excreted nitrogen that volatilizes as NH₃ is found to range from 2% to 30 67% (based on measurements), with the GUANO model providing a range of 2% to 31 82%. The model provides a tool that can be used to investigate the meteorological 32 dependence of NH₃ emissions from seabird guano and provides a starting point to 33 refine models of NH₃ emissions from other sources.

34 **1. Introduction**

35 Reactive nitrogen (N_r) has been used to improve crop growth for the last 8,000 years (Bogaard et al., 2013). However, N_r used as either manure or synthetic fertilizer has 36 37 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 38 39 climatic conditions, the properties of the substrate and the surrounding vegetation. 40 Reactive nitrogen can either run off during rain events, become part of the 41 surrounding ecosystem (immobilized in the soil or absorbed by plants) or volatilize as 42 nitrogen-based gas: ammonia (NH₃), nitrous oxide (N₂O), nitrogen oxides (NO_x) or 43 nitrogen (N₂). The rate of formation and volatilization of NH₃ from N_r is highly 44 temperature dependent (Sutton et al., 2013; Riddick et al., 2012; 2014) and NH₃ 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).

48 The largest seabird colonies are found in remote areas far from human interaction 49 (Riddick et al., 2012). At such locations seabird nitrogen excreta is the dominant 50 source of Nr making seabird colonies ideal "natural laboratories" to investigate biogeochemical processes and the resulting impact of Nr pathways on plants and 51 animals. Studies have shown that seabirds are significant sources of NH₃ (Wilson et 52 53 al. 2004, Blackall et al. 2007, Zhu et al., 2011; Riddick et al., 2014; 2016) and have a 54 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 55 56 across the entire Baffin Bay region were attributed to seabird NH₃ (Wentworth et al., 57 2015), while a study of Adelie penguin colony on the Antarctic continent suggested that volatilized NH₃ creates a spatial impact zone of up to 300 km² surrounding the 58 59 colony where phosphomonoesterase activity is increased in lichen populations (Crittenden et al., 2015). 60

61 Given the local and global importance of NH₃ emissions, two main methods have 62 been used to estimate NH₃ emissions from N_r sources, which are broadly described as empirically derived emission factors and process-based models. 63 The former use 64 empirical data to integrate the effects of meteorology into a single value ('emission 65 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 66 67 volatilizes as NH₃, e.g. on average 21 % of N in manure volatilizes as NH₃ in 68 industrialized countries (Bouwman et al., 2002).

69 Process-based models attempt to replicate the effects of meteorology on the formation of NH₃ from an N_r source. NH₃ volatilization has been shown to increase at both high 70 71 temperatures and high wind speeds (Demmers et al., 1998; Sommer & Christensen, 72 1991), while rain events may cause NH₃ emissions to drop to almost zero, as 73 illustrated by Sommer & Olesen (2000) for liquid manure spreading in Denmark. 74 Most recent models calculate NH₃ fluxes using Henry's Law, i.e. the dissociation 75 reactions of ammonium and NH₃ in solution is used to calculate the NH₃ gas on the 76 surface, with the flux estimated using a resistance-based approach (e.g. Sutton et al., 77 1998; Cooter et al., 2010; Massad et al., 2010; Flechard et al., 2013). For instance, 78 Cooter et al. (2010) used a process-based model to predict measured diurnal variation 79 and daily means of NH₃ emissions from agricultural soils.

80 Even though Henry's Law has been used to calculate NH_3 emissions from N_r sources, 81 these models have not been explicitly validated with high resolution empirical 82 measurements from a range of meteorological conditions. For example, Massad et al. 83 (2010) reviewed existing measurements to compile a comprehensive dataset and 84 derived generalized parameterizations for a range of fertilizers and ecosystems to be 85 used in large-scale chemical transport and earth system models. Flechard et al. (2013) 86 synthesized data from a range of studies to generate consistent parameterizations that 87 can be used to calculate NH₃ emissions on the regional and global scale. Cooter et al. (2010) used their model to calculate NH₃ emissions at the field scale and compared 88 89 their model output to fertilizer application at a site in North Carolina, USA.

90 In an initial approach to modelling NH_3 emissions from seabirds, only the 91 bioenergetics part of the GUANO model was used, linked to empirical estimates of

92 the percentage volatilized (Wilson et al. 2004, Blackall et al., 2007). This approach 93 provided an adequate description of the spatial differences in NH_3 emissions on a 94 regional and country scale. However, it meant that there was a high uncertainty in the 95 estimates in the extrapolations to a global scale by Blackall et al. (2007).

96 A first approach to address this uncertainty was provided by Riddick et al. (2012) who 97 used an empirical temperature correction, with uncertainty ranges of estimates based 98 on a) no temperature dependence and b) full solubility dependence according to the 99 thermodynamics of Henry's Law and ammonium dissociation. If, like Blackall et al. 100 (2007), they ignored the possible effect of temperature, then they found total global NH₃ emissions from seabirds of 442 Gg NH₃ year⁻¹ (where penguins contributed 83%, 101 102 due to improved bird statistics). By contrast, if NH₃ emissions were proportional to 103 the thermodynamic effect of temperature, they found total global NH₃ emission from seabirds to be only 97 Gg NH₃ year⁻¹ (where penguins contributed 63%). According 104 to a mid-range estimate of the temperature dependence, they estimated 270 Gg NH₃ 105 106 year⁻¹ (with 80% from penguins). Penguins were thus estimated to be the main source 107 of NH₃ emissions from seabird colonies globally under all three scenarios, while this 108 clearly shows the importance of addressing the temperature dependence of emissions.

109 The main limitation of Riddick et al. (2012) was the wide uncertainty range of their 110 estimates and the need to constrain these by measurements, ideally using a process-111 based approach. A first application of the GUANO model reported by Sutton et al. 112 (2013) to different sites globally showed that the main measured differences in the 113 percentage of excreted guano that volatilizes as NH_3 in relation to temperature could 114 be reproduced.

115 This paper describes the GUANO model (Generation of emissions from Uric Acid 116 Nitrogen Outputs), a dynamic mass-flow process-based model developed to simulate 117 NH₃ losses from seabird colonies. The model incorporates the main environmental 118 factors affecting the volatilization process, allowing calculation of NH₃ emissions 119 from seabird-derived N_r on an hourly basis and upscaling to consider the effects of 120 different meteorological conditions. The NH₃ emissions simulated by the model are 121 compared with NH₃ emission estimates based on concentration measurements and 122 turbulent exchange parameters from a climatically diverse set of seabird colonies. We 123 use this comparison to investigate how NH₃ emissions from seabirds vary with 124 changing environmental conditions.

125 **2. Methods and Materials**

126 **2.1 Outline of the GUANO model**

127 The GUANO model is designed to predict temporal variations in the formation of 128 NH₃ from a source of seabird-derived uric acid (Figure 1). The model calculates NH₃ 129 emissions from a seabird colony using environmental variables and colony-specific 130 data as input. Temperature, relative humidity, precipitation and wind speed are 131 considered to have the greatest effect on NH₃ formation and emission (Groot 132 Koerkamp, 1994; Cooter et al., 2010; Massad et al., 2010; Flechard et al., 2013). The 133 main elements of the model are described here, with additional details given in 134 Supplementary Material Section 1.

135 <</Insert Figure 1 Here>>

136 The pathways taken by nitrogen following excretion as uric acid can be summarised 137 in four steps (Figure 1). Excreted guano forms uric acid (UA) that decomposes to 138 form total ammoniacal nitrogen (TAN), which then partitions to form gaseous NH₃. 139 Other pathways include wash-off of guano, UA and TAN from the surface at any 140 stage during rain events. It should be noted that the loss of nitrogen due to plant 141 uptake and immobilization, and other gaseous emissions, have not been included in 142 the model since these are considered to take place on a slower time scale than NH_3 143 emissions. The following steps are included in the model:

144 1. Nitrogen-rich guano, in the form of UA, is excreted onto the surface by seabirds at 145 the colony. The amount of guano varies depending on the mass and behaviour of 146 the nesting species (e.g. Wilson et al. 2004). At each time-step (t_N) , the UA budget 147 $(Q_{UA}, g m^{-2})$ is calculated from the total nitrogen excreted $(F_e, g m^{-2} hour^{-1})$, the 148 TAN produced per hour $(F_{TAN}, g m^{-2} hour^{-1})$ and the Uric acid nitrogen washed off 149 by the rain $(F_{w(UA)}, g m^{-2} hour^{-1})$, where N is the hour of the year (Equation 1).

152

$$Q_{UA}(t_{N+1}) = Q_{UA}(t_N) + F_e - F_{TAN} - F_{w(UA)}$$

153 2. Uric acid is converted to TAN, with the conversion rate depending on climatic 154 conditions and the pH of the surface (Elliot and Collins, 1982, Elzing and 155 Monteny, 1997; Groot Koerkamp et al., 1998). At each time step the TAN budget 156 $(Q_{TAN}, g m^{-2})$ is calculated from the TAN produced per hour from UA $(F_{TAN}, g m^{-2}$ 157 hour⁻¹), the amount of NH₃ emitted $(F_{NH3}, g m^{-2} hour^{-1})$ and the TAN washed off 158 by the rain $(F_{w(TAN)}, g m^{-2} hour^{-1})$, where *N* is the hour of the year (Equation 2).

160
$$Q_{TAN}(t_{N+1}) = Q_{TAN}(t_N) + F_{TAN} - F_{NH3} - F_{w(TAN)}$$
(2)
161 (2)

- 162 3. TAN partitions between NH_4^+ and NH_3 on the surface, with the position of the 163 equilibrium depending on the pH and the temperature (*T*, K) of the surface 164 (Equation 3). A function, $\Gamma = [NH_4^+]/[H^+]$, is used to describe the equilibrium at 165 the surface (Nemitz et al., 2000) such that the gaseous concentration of NH_3 at the 166 surface (*X_c*) is:
- 167

$$X_c = \frac{161500}{T} exp\left(\frac{-10378}{T}\right) \Gamma$$
(3)

170 The TAN concentration is a function of the water content of the guano. The water 171 budget $(Q_{H_20}, \text{ kg m}^{-2})$ is calculated (Equation 4) from the flux of water contained 172 in excreted guano $(F_{H_20}(g)(g), \text{ kg m}^{-2} \text{ hr}^{-1})$, rain events $(F_{H_20}(pptn), \text{ kg m}^{-2} \text{ hr}^{-1})$, 173 water run-off $(F_{H_20}(ro), \text{ kg m}^{-2} \text{ hr}^{-1})$ and evaporation $(F_{H_20}(evap), \text{ kg m}^{-2} \text{ hr}^{-1})$. 174 Each of the parameters in Equation 4 is further described in the Supplementary 175 Material Section 1.

176

177
$$Q_{H_2O}(t_{N+1}) = Q_{H_2O}(t_N) + F_{H_2O}(g) + F_{H_2O}(pptn) - F_{H_2O}(ro) - F_{H_2O}(evap)$$
(4)
178

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 (X_c) and the atmosphere (X_a) , the aerodynamic and boundary layer resistances $(R_a$ and R_b) (Sutton et al., 1993; Nemitz et al., 2001) estimating the effect of NH₃

(1)

183 reabsorption by the substrate and any overlying vegetation using an empirical 184 habitat factor (F_{hab}). A habitat factor was used here in preference to a more 185 process based description involving the bi-directional exchange of NH₃ from 186 vegetation because of the complexity of the mix of nesting types. The values of the 187 habitat factors used are described in Section 2.2.3.

 $NH_3 \ emission = \frac{X_c - X_a}{R_a + R_b} F_{hab}$

190

191**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).

198 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).

205 <</Insert Table 1 Here>>

206 2.2.2 Seabird colony data

The site-specific seabird data that have the greatest effect on the NH_3 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.

213 2.2.3 Habitat Factors

Habitat factors (F_{hab}) are used in Equation 5 to account for NH₃ immobilized by the 214 215 nesting substrate or recaptured by the overlying canopy and are listed in Table 1.1 in 216 the Supplementary Material Section 1. This reflects a base value for bare rock of 1, 217 where no NH₃ is immobilized or recaptured, which is then reduced as a correction 218 factor, to parameterise the effect of nesting behaviour of the birds. Following Wilson 219 et al. (2004) and the measurements of Riddick (2012), habitat factors for birds that 220 build nests on bare rock is taken as 1, while for those that nest on sand is taken as 221 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. 222

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 puffins make burrows, but excrete outside, while their young excrete in burrows. Where adult puffins excrete depends on the time of day and climatic

(5)

227 conditions: at dawn and dusk, large numbers of puffins can be seen on exposed rocks 228 across the colony, and this also happens when it is warm and sunny. For the 229 remainder of the time, puffins excrete on the soil outside their burrow. To 230 accommodate variations in this assumption, the F_{hab} value for adult puffins was 231 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, 232 233 data suggest that these only excrete inside the burrows and leave the colony as soon as 234 they leave the nest (Harris & Wanless, 2011). Puffin chicks are therefore not thought 235 to contribute to seabird NH₃ emission at the colony, with any emissions inside the 236 burrows being absorbed by the soil inside the burrow, therefore F_{hab} for chicks is here 237 set at 0.

238 **2.2.4 Other model inputs and implementation.**

239 Constant values are used in the model to describe the surface roughness length (z_0) 240 and the boundary layer Stanton number (B) to calculate the turbulent atmospheric 241 resistance (R_a) and the quasi-laminar boundary layer resistance (R_b) (Supplementary 242 Material Section 1, equations SM21 and SM25). Constant values of 0.1 m and 5 were 243 used in the model, and also varied as part of the model sensitivity analysis (Section 244 2.5). Based on reference Elliot & Collins (1982), the base-rate (at pH 9 and 35°C) for the fraction of UA converted to TAN was 0.83 % day⁻¹ (Supplementary Material 245 246 Section 1). The pH of the guano within the model was set at 8.5, this value was based on measurements of Blackall (2004). Factors for wash-off under rain were assumed 247 to be 1 and 0.5 % mm⁻¹ rain for nitrogen and non-nitrogen, respectively (See 248 249 Supplementary Material Section 1). Finally, based on data for remote marine 250 environments (e.g., Sutton et al., 2003), background NH₃ concentration was assumed 251 to be 0.1 μ g m⁻³.

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.

259

260 2.3 Model validation

261 The model setup and parametrization was set based on theoretical considerations and on available data to parametrize the model. In principle, the model set up was 262 263 independent of measured validation data, according to the parameters considered. In 264 the case of substrate pH and roughness length runs were based on a constant value, 265 while TAN and Guano run off were based on a fixed percentage per mm of rain. The 266 habitat factors were based on prior studies drawing on Blackall (2004), Wilson et al. 267 (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 268 269 contrast, the model tests in comparison with measurements at Mars Bay, Ascension 270 Island, at Bird Island, South Atlantic, at Michaelmas Cay, Great Barrier Reef, at 271 Signy Island, South Atlantic were made without tuning any other model parameters

272 and therefore represent fully independent tests of the model in a wide range of 273 climatic conditions.

274 2.3.1 Measured NH₃ emissions for comparison with the model

275 Two methods were employed to conduct NH₃ concentration emission estimates based 276 on concentration measurements and turbulent exchange parameters, which were used 277 to quantify NH_3 emissions, as reported in detail by Riddick et al. (2014): (1) passive 278 sampling and (2) active on-line NH₃ analysis instrument. For the passive sampler 279 measurements (ALPHA samplers, CEH Edinburgh, Tang et al., 2001), triplicate 280 samplers were used at each sampling location and exposed for periods of 2 to 4 weeks 281 to measure an average concentration for the exposure period. The time-averaged NH_3 282 concentration data were then used with the WindTrax inverse dispersion model 283 version 2.0 to calculate the emission (Flesch et al., 1995; Riddick et al. 2014).

284 Active on-line NH₃ concentration measurements were made by Riddick et al. (2014, 285 2016) with an AiRRmonia gas analyser (Mechatronics, NL) on Bird Island and 286 Ascension Island and a Nitrolux 1000 gas analyser (Pranalytica, USA) on the Isle of 287 May. The NH₃ concentration data were averaged to 15-minute data and used as input 288 to the WindTrax in an inverse model to calculate the emission. The calculation of the NH₃ emissions used as validation at each of the sites are the result of five separate 289 290 field campaigns and are described in full in Riddick et al. (2014) for Michaelmas Cay 291 and Ascension Island and Riddick et al. (2016) for Signy Island, the Isle of May and 292 Bird Island (locations of the five fieldwork sites are presented in Supplementary 293 Material Section 2).

294 As a result of the method employed at Michaelmas Cay and Signy Island (passive 295 sampling only), hourly resolved measured NH_3 fluxes were not available at these sites 296 (Riddick et al., 2014; 2016). However, at Ascension Island (Riddick et al. 2014) and 297 the Isle of May (Riddick et al., 2016), both passive (time integrated) measurements 298 and the continuous measurements, were made allowing comparison between the two 299 approaches. In both cases, close agreement was found between the passive (time-300 integrated) and active (time resolved) sampling methods, the uncertainty in chemical 301 sampling method was \pm 20% and \pm 12% of the mean flux at the Isle of May and Ascension, respectively (Riddick et al. (2016). Calculation of a third estimate in each 302 303 case (time-integrated based on the semi-continuous active sampling data) allowed it to 304 be shown that the meteorological uncertainties associated with long measurement periods (for the passive, time-integrated measurements) were of similar magnitude to 305 306 the uncertainties between the two different chemical sampling methods.

307 2.3.2 Comparison modelled emissions to those estimated through measurement

308 The GUANO model simulations were validated with emission estimates based on concentration measurements and turbulent exchange parameters from the five field 309 310 sites. To assess the fit of the model, the hourly measured emissions were plotted against the hourly modelled NH₃ emissions, with the slope, intercept and 311 determination coefficient (R^2) of the linear regression calculated. Time-averaged 312 313 modelled emissions are also presented and compared against matched time-averaged 314 emission estimates based on concentration measurements and turbulent exchange parameters to show that the model, not only captures the hourly emissions, but also is 315 consistent with measurements over a period of time. 316

In addition, the mean NH₃ emission for each colony was calculated (in $\mu g m^{-2} s^{-1}$) from the hourly emissions. The percentage of nitrogen volatilized (P_{ν}) was calculated from the total nitrogen excreted at each colony during the measurement period and the total nitrogen estimated to be volatilized as NH₃ over the same period.

321 2.4 NH₃ emission and meteorology

To investigate the effects of meteorology, the slope, intercept and R^2 between modelled NH₃ 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 NH₃ emission so that the key drivers of emission at each measurement site can be identified.

328 2.5 Sensitivity Analysis

A sensitivity study was performed on the GUANO model to determine the most 329 330 significant model parameters in relation to the model output. The following model 331 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⁻¹ 332 333 rain), percentage non-nitrogen wash-off (% mm⁻¹ rain), pH, habitat factors (F_{hab}), boundary layer Stanton number (B), temperature (T, °C), relative humidity (RH, %), 334 wind speed (U, m s⁻¹), precipitation (P, mm m⁻² hr⁻¹), net solar radiation (Rn, W m⁻²), 335 pH and background NH_3 concentration ($\mu g m^{-3}$). The sensitivity of the NH_3 emissions 336 to each input parameter was tested using the GUANO model application to the 337 338 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 339 340 respond to positive and negative changes in environmental conditions in a global 341 context.

342

343 3. Results

344 **3.1 Model output and validation with empirical data**

345 3.1.1 Mars Bay, Ascension Island: Sooty Tern Colony

346 The NH₃ emissions calculated by the GUANO model for Ascension Island show a 347 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 348 study period was 370 μ g NH₃ m⁻² s⁻¹ (Figure 2). The NH₃ emissions calculated by 349 350 the GUANO model for Ascension Island are in close agreement to those derived from field measurements (Table 3; Supplementary Material Section 2 Figure SM 2.1), with 351 a linear regression slope of 1.07, intercept of -1.20 μ g m⁻² s⁻¹ and R² = 0.94. The 352 average modelled NH₃ emission for Ascension Island during the measurement period 353 was 22.3 μ g NH₃ m⁻² s⁻¹, the average measured NH₃ emission on Ascension was 22.3 μ g NH₃ m⁻² s⁻¹ and the average modelled NH₃ emission for periods when 354 355 356 measurement data available was 19.8 μ g NH₃ m⁻² s⁻¹. The most notable features of the modelled and measured NH₃ emission is the strong dependence on temperature 357 and moisture availability (with higher emissions after rain events on 25 May and 6-7 358 359 June), with the TAN budget almost fully depleted before then end of each day. This 360 implies that the NH₃ emission rate is tightly coupled to the TAN production rate at this site (Supplementary Material Section 3 Figure SM 3.1; Supplementary Material 361

362 Section 4 Figure SM 4.1, R^2 value = 0.98). At this site, aerodynamic and boundary 363 layer resistance has little effect, as the TAN produced is all quickly lost through NH₃ 364 emissions. Ammonia emission is thus hydrolysis-limited for the test period at this site, 365 with the performance of the GUANO model therefore depending almost entirely on 366 its parametrization the urea hydrolysis rate.

367 <</Insert Figure 2 Here>>

368 3.1.2 Isle of May, Scotland: Atlantic puffin Colony

369 The modelled emissions were lower for the Isle of May puffin colony than Ascension Island (Sooty tern), but showed a similar diurnal pattern (Figure 3), with high 370 emissions in the day (maximum of 25 μ g m⁻² s⁻¹ during the afternoon) and negligible 371 372 emissions at night. When compared with the emission estimates based on 373 concentration measurements and turbulent exchange parameters, the hourly NH₃ 374 emissions modelled by the GUANO model were underestimated, with a linear regression slope of 0.13, intercept of 5.7 ug m⁻² s⁻¹ and R² of 0.13 (Table 3; 375 376 Supplementary Material Section 2 Figure SM 2.2). The poorest fit occurred on 1th 377 July 2009, where the model overestimated the measured NH₃ emission during the 378 early hours of the morning. This was associated with a period of low-wind speed and 379 stable conditions, which could also reflect uncertainties in the measurement estimate 380 at this time. During the period of 29 June to 2 July the measured emissions were 381 much smaller than model and this may correspond to a period of foggy weather where 382 NH₃ could have dissolved in the fog and few puffins were seen around the colony, 383 which may explain why the measured emissions were much smaller than the modelled 384 emissions, which did not take account of this meteorological interaction with the 385 ammonia gas, local bird behaviour and movements.

386 The average modelled NH₃ emission for the Isle of May during the measurement period was 7.7 μ g NH₃ m⁻² s⁻¹, the average measured NH₃ emission on the Isle of May 387 was 6.9 μ g NH₃ m⁻² s⁻¹ and the average modelled NH₃ emission for periods when 388 measurement data available was 9.3 μ g NH₃ m⁻² s⁻¹. At this site the TAN budget 389 fluctuates greatly, with hourly modelled and measured emissions correlated with the 390 TAN budget (Supplementary Material Section 3 Figure SM 3.2, $R^2 = 0.05$. In contrast 391 392 to Ascension Island, however, TAN did not deplete to near zero each evening, 393 indicating that daily NH₃ emission is only partially limited by TAN production over 394 the previous 24 hours.

395

396 <<Insert Figure 3 Here>>

397 3.1.3 Bird Island, South Atlantic: Macaroni Penguin Colony 'Big Mac'

398 Compared with the other seabird colonies considered in this study, a diurnal pattern 399 was much less noticeable for both modelled and measured NH₃ emissions from the Macaroni penguin colony on Bird Island (Figure 4). The maximum NH₃ emission 400 simulated by the GUANO model from the colony was 53 μ g NH₃ m⁻² s⁻¹ at 0500 on 401 11th December 2010. Contrary to the other sites, there was also little correlation 402 between the emission rate and ground temperature, which was associated with small 403 variation in ground temperature (3 - 8 °C range) during the measurement period. 404 Instead, at this site the periods of lowest NH₃ emissions (below 10 μ g NH₃ m⁻² s⁻¹) 405 406 were observed during periods of lower wind speed, with maximum emissions during

407 periods of high wind speed, linked to a substantial range of wind speed during the 408 measurement period (0.3 to 12 m s^{-1}). The GUANO model simulations reproduced the measured NH₃ emissions well, with a linear regression slope of 1.09, and intercept 409 of -1.32 μ g m⁻² s⁻¹ and R² = 0.86 (Table 3; Supplementary Material Section 2 Figure 410 SM 2.3). Modelled emissions from the Big Mac colony are mostly between 0 and 20 411 412 μg m⁻² s⁻¹. The average modelled NH₃ emission for Bird Island during the measurement period is 13.4 μ g NH₃ m⁻² s⁻¹, the average measured NH₃ emission on Bird Island was 12.3 μ g NH₃ m⁻² s⁻¹ and the average modelled NH₃ emission for 413 414 periods when measurement data available was 12.4 μ g NH₃ m⁻² s⁻¹. 415

416 At this site, the modelled TAN budget can be seen from Figure 4 to show negligible 417 fluctuation on a daily time scale, contrary to Ascension Island and the Isle of May 418 (Supplementary Material Section 4), while showing a slight increase over the first 419 period and first decrease then increase over the second period. At the same time this 420 site has much larger amounts of available TAN at the surface than these other sites, at 421 $2-3 \text{ g m}^{-2}$. With relatively modest temperature fluctuations during the measurement period, at this site, the variation in NH₃ emission rate can therefore be seen to be 422 423 primarily limited by the mass transfer process itself, as affected by wind speed and 424 surface temperature. Supplementary Material Section 3 Figure SM 3.3 shows that 425 there is still a significant correlation between simulated TAN production and NH₃ 426 emission ($R^2 = 0.29$), the relationship is less than at the temperate and tropical sites.

427 The TAN production rate at Bird Island $(0 - 0.15 \text{ g m}^{-2} \text{ hr}^{-1})$ is more similar to the Isle 428 of May $(0 - 0.4 \text{ g m}^{-2} \text{ hr}^{-1})$ than Ascension Island $(0 - 0.1 \text{ g m}^{-2} \text{ hr}^{-1})$ (Supplementary 429 Material Section 3 Figures SM 3.1, SM 3.2 and SM 3.3). This suggests that, while 430 temperature does not affect the daily variation, the overall magnitude of NH₃ emission 431 is still largely controlled by TAN hydrolysis rate. i.e. hydrolysis rate controls the 432 overall rate of emission while meteorology controls the short-term variation in NH₃ 433 emission.

434 <</Insert Figure 4 Here>>

435 3.1.4 Michaelmas Cay, Great Barrier Reef: Common noddy colony

- 436 The NH₃ emissions simulated by the GUANO model for Michaelmas Cay show a strong diurnal pattern, with maximum emissions during the day reaching nearly 500 437 $\mu g m^{-2} s^{-1}$ which drop to an emission during the night of between 1 and 10 $\mu g m^{-2} s^{-1}$. 438 The average NH₃ emission measured using passive samplers for two periods of four 439 440 weeks during November and December (Riddick et al., 2014) are very similar to the 441 emissions simulated by the GUANO model when averaged over the same periods 442 (Figure 5A and Table 2). The NH₃ emissions measured during the field campaign are 25.9 μ g NH₃ m⁻² s⁻¹. Both measured and modelled emission showed an increase from 443 444 November to December. The average NH₃ emission predicted by the GUANO model is 27.5 μ g NH₃ m⁻² s⁻¹ for November and December 2009. 445
- 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 Figure SM 3.4, where simulated TAN production rate and simulated NH₃ emission are found to be correlated with $R^2 = 0.91$).
- 452 <</Insert Figure 5 Here>>

453 <</Insert Table 2 Here>>

454 **3.1.5 Signy Island, South Atlantic: Chinstrap penguin Colony**

455 As with the tropical and temperate regions, but in contrast to the other sub-polar 456 colony at Bird Island, NH_3 emissions simulated for Signy by the GUANO model were 457 strongly diurnal (Figure 5B). This can be explained by the more regular diurnal 458 variation in temperature (typically 4-6° C diurnal change) than at Bird Island (Figure 459 4).

460 The Signy Island colony is used by both Adélie and Chinstrap penguins for the first 461 measurement period. During the second period, the Adélie penguins gradually left the 462 colony and only Chinstrap penguins were present for the third period. The NH₃ 463 emissions at Signy Island are the highest for the first period, reaching a maximum of 464 50.0 μ g NH₃ m⁻² s⁻¹. The average NH₃ emission predicted by the GUANO model for the penguin colony during the whole measurement period was 10.7 μ g NH₃ m⁻² s⁻¹. 465 This is similar to the NH₃ emissions measured during the field campaign of 9.0 μ g 466 467 $NH_3 m^{-2} s^{-1}$ (Table 2).

The simulated TAN budget for the penguin colony at Signy Island shows negligible 468 469 diurnal variation, but rather a steady increase through the study period from 30 to 55 g m^{-2} (Figure 5). Overall, there was only a weak correlation between simulated TAN 470 production and simulated NH₃ emission (Supplementary Material Section 3 Figure 471 472 SM 3.5). The reason for the smooth trend in TAN budget at the surface (Figure 5b) is 473 that the NH₃ emissions and run off during the study period represent only small 474 fraction of the TAN produced (Supplementary Material Section 4 Figure SM 4.5). 475 The values of the TAN budget at Signy Island are much higher than the other sites 476 because of the lower temperatures that allow TAN to accumulate rather than 477 volatilize.

478

479 **3.2 NH₃ Emissions and environmental conditions**

480 Considering the simulated estimates from the GUANO model at each site, the 481 strongest meteorological driver of NH₃ emission was found to be ground temperature 482 for all sites except for Bird Island, average R^2 of 0.29 (range 0.11 - 0.39) (Table 3). 483 As ground temperature increases, the rate of bacterial decomposition of uric acid 484 nitrogen to form TAN (Equation 2) increases and, coupled with an increased volatility 485 of NH₃ (Equation 3), results in increased NH₃ emission.

The next strongest driver of NH₃ emission is wind speed, with an average R^2 of 0.18 486 487 (range 0.01 - 0.59), with the highest correlation on Bird Island ($R^2 = 0.59$) where there 488 was a wide range of wind speeds and small differences in temperature. Relative 489 humidity and precipitation were not found to be strong climatic drivers of NH₃ emission, with R^2 values ranging from 0.01 to 0.04. This is not to say that these 490 491 factors are unimportant, as the response of both modelled and measured NH₃ emission 492 to precipitation at Ascension Island showed (Figure 2). Precipitation and relatively 493 humidity are fundamental controls on TAN formation from UA and influences NH₃ 494 emission on a longer time scale than variation in temperature and wind speed which 495 directly affects the hourly variation in NH₃ emissions.

496 The importance of moisture availability which is absorbed by guano may be more 497 easily seen in the measured long-term response, where Michaelmas Cay had a higher 498 measured percentage volatilization ($P_v = 67\%$) as compared with Ascension Island (P_v 499 = 52%) even though the sites had similar average temperature (Tables 1 and 3). This 500 may be reflective of more moisture limitation to uric acid hydrolysis at Ascension 501 Island. This difference is supported by the GUANO model simulation which also 502 estimated a higher value of P_v for Michaelmas Cay (82%) than for Ascension Island 503 (37%), reflecting the generally higher simulated guano water content at Michaelmas 504 Cay than at Ascension Island (Figures 5A and 2).

505 <<**Insert Table 3 Here**>>

506 **3.5 Sensitivity analysis**

507 A sensitivity analysis of the GUANO model is shown in Table 4 for each input 508 variable selected. The estimated NH_3 emissions were most sensitive to changes in 509 environmental variables, with highest sensitivity to ground temperature which varied 510 by +59.9 % to -36.8 % for changes of +10% and -10%, respectively. The NH_3 511 emissions calculated by the GUANO model had the smallest response to changes in 512 micrometeorological constants used to calculate the flux, i.e. surface roughness, 513 boundary layer Stanton number and background NH_3 concentration.

514 Of the constants used, the GUANO model is most sensitive the substrate pH. The 515 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 ($[H^+]$ 516 517 = 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 Γ function, which is 518 519 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 520 521 concentration of NH_3 at the surface (Equation 3). We recognize that this is a source 522 of uncertainty in the model, however the value used in the GUANO model for 523 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 NH_3 emission increases with ground temperature and in all cases emissions is the same at 25 °C. Wind speed has the next biggest effect as NH_3 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.

531

532 4 Discussion

533 4.1 General Discussion

534 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 535 536 here validated against NH₃ emissions measured at seabird colonies representative of a range of climates around the world. Comparison with NH₃ emission estimates based 537 on measurements of NH₃ concentration and turbulent exchange parameters (Riddick 538 539 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 540 541 The GUANO model has been structured to simulate hourly NH₃ conditions. 542 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.

549 The model parametrization was based primarily on well-established existing principles and measured terms. Elements such as the turbulent and laminar boundary 550 551 layer resistances have been widely used in other models, where the main uncertainty 552 concerns the setting of the surface roughness length. Here we used an estimate based 553 on observational data (Riddick et al. 2014; 2016) and Seinfeld and Pandis (2006) to 554 set the roughness length at 0.1 m. The emission itself is driven by the concentration 555 difference between atmospheric NH₃ concentrations and the surface NH₃ 556 concentration. However, as the former is very small, the key uncertainty is the surface 557 NH₃ concentration. The first challenge is to simulate the rate of uric acid hydrolysis, 558 for which we used a parametrization unchanged from Elliot and Collins (1982), based 559 on measurements from a poultry house context. The fact that this delivers good 560 agreement with observed fluxes in a context where NH₃ emission is limited almost 561 entirely by UA hydrolysis rate (Ascension Island), provides strong support for the 562 parametrization of Elliot and Collins (1982). The other major uncertainties in the 563 model concern surface pH, the habitat factor and the extent of wash-off. For the 564 surface pH use of a prior measurement estimate from Blackall (2004) for all 565 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 566 would only apply for sites not on bare rock (for which $F_{hab} = 1$). The reduction factors 567 568 used in this study were in fact based on prior estimates from Wilson et al. (2004) with 569 the only changes for this study being at the Atlantic puffin site on the Isle of May 570 where F_{hab} 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 571 all sites was used of 1 and 0.5 % mm⁻¹ rain for nitrogen and non-nitrogen, 572 respectively. While this is an extremely simple approach, its value was based on 573 574 Blackall (2004) and thus set as a prior value rather than being used to fit the 575 measurements. Overall, therefore, it can be seen that while the performance of the 576 model runs is sensitive to the model parametrization, the parameter choices were 577 largely based on prior estimates independently from the outcome of the 578 measurements.

The comparison of the GUANO model output with NH_3 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 NH_3 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.

586 The model-measurement comparison also illustrates how the different primary 587 controls on NH_3 emissions at the different sites. Sufficient water is needed for uric 588 acid hydrolysis (as shown at Ascension Island), while excess water dilutes the TAN 589 solution and is associated with increased TAN run off (Bird Island). The combined

590 outcome of these effects is that increases in relative humidity or rain events only 591 increase simulated NH₃ emissions at arid sites such as Ascension Island (Figure 2).

592 The NH₃ emissions simulated by the GUANO model increased with wind speed at all 593 sites because vertical transport and turbulent mixing of NH₃ increases as aerodynamic 594 and boundary layer resistances decrease. However, wind speed was only the major 595 driver of NH₃ emission variations at a windy site with little variation in ground 596 temperature (Bird Island). At the other sites, ground temperature was the major driver 597 in temporal differences of NH₃ emission. Temperature is significant for two reasons: 598 (1) it affects the rate at which uric acid converts to NH_3 and (2) it affects the potential 599 for volatilization of NH₃ from the surface.

600 Understanding the processes behind the measured fluxes is greatly helped by 601 considering changes in the TAN budget of the surface (Supplementary Materials 602 Section 5) and the accumulation of TAN varied greatly between sites. The most 603 extreme variation was found for the simulated TAN budget at Ascension Island, 604 where rapid NH₃ emission was reflected in almost complete loss of available TAN 605 every evening. Under these circumstances, NH_3 emission is primarily controlled by 606 the uric acid hydrolysis rate, as almost all the TAN produced (unless washed-off in 607 rain) is immediately volatilized (Figure 2; Supplementary Material Section 2 Figure 608 SM 2.1). A contrasting situation was found in the simulations for Bird Island and 609 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 610 611 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 612 613 variations, but still substantial night time values. At Michaelmas Cay, a large-scale 614 structure in the TAN budget, varying over daily to weekly timescales was the effect of 615 rain events on the available UA and TAN on the surface.

616

617 **4.2 Process-based versus empirical approaches**

618 On a breeding season time-scale, temperature was shown to be the most influential 619 meteorological variable, where NH₃ emission rate increases with increased 620 temperature. Importantly this effect, which was identified empirically by Sutton et al. 621 (2013) is here explained for the first time using a dynamic modelling approach 622 comparing globally contrasting sites. This study therefore provides a substantial 623 advance on initial empirical studies calculating NH₃ emissions from seabirds (Wilson 624 et al. 2004; Blackall et al., 2007), which were used to calculate NH_3 emissions on a regional and country scale to Riddick et al. (2012). 625

626 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 627 628 measurements, ideally using a process based approach. This is now addressed here. 629 The GUANO model is able to explain the major differences between field sites, and 630 the way that different variables contribute, including temperature, moisture 631 availability and wind speed, as the most important drivers. A first application of the 632 GUANO model reported by Sutton et al. (2013) to different sites globally showed that 633 it was able to reproduce the main measured differences in the percentage of excreted guano that volatilizes as NH₃ in relation to temperature. 634

635 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 636 emission estimates calculated by the GUANO model was in good agreement with 637 638 emission estimates based on concentration measurements and turbulent exchange 639 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 640 641 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 642 643 instantaneous NH₃ emission potential of +605%, -86% (i.e. +/- factor of 7). The fact 644 that the model outcome gave a net sensitivity on simulated NH₃ emissions for the Isle 645 of May of only +73%, -22% illustrates that the amount of available TAN appears to 646 constrain the total amount emitted and that more acid pH reduces urea hydrolysis rate 647 (Equation SM5).

648

649 **4.3 NH₃ emissions globally**

650 The performance of the GUANO model is illustrated for the five colony emission 651 estimates calculated by the GUANO model shown as the NH₃ emission normalized in relation to the seabird mass (Figure 6). The GUANO model emissions are in good 652 653 agreement to emission estimates based on concentration measurements and turbulent exchange parameters when they are presented with matching emissions calculated 654 from in-situ measurements by Riddick et al. (2014; 2016) and combined with 655 656 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 657 658 Antarctica (Theobald et al., 2013) and a hot dry Double-crested cormorant colony on 659 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 660 emissions from seabird colonies in a wide range of meteorological conditions. The 661 GUANO model captures the large effect of NH₃ emission in response to temperature 662 and can simulate the main differences between meteorology where emission rates per 663 664 unit bird body mass vary across climates by more than an order of magnitude.

665 <<Insert Figure 6 Here>>

666 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 667 and changes in sea-level are both highlighted as drivers of future seabird population 668 669 changes (Forcada et al., 2006; Trathan et al., 2007; Brierly, 2008). This, coupled with anticipated temperature increases in many parts of the Southern Ocean and the 670 Antarctic Continent (Denvil, 2005), potentially present a very different N_r landscape, 671 associated with substantially increased NH₃ emissions. Through the GUANO model 672 673 we now have a quantitative tool to assess such changes in Nr partitioning which could be used to better forecast future changes to these remote nutrient-poor ecosystems. 674

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- 832

Table 1 Data used in the GUANO model. D_{met} is the distance from meteorological stations to each colony. F_{hab} values describe the fraction NH₃ that is captured by the substrate and overlying vegetation (Supplementary Material Section 1, Table SM1.1). Site-specific seabird data input to the GUANO model were collated from field observation (nest density and duration of breeding season (*D*)) and from the literature (adult mass, fraction of time at colony (*FC*), see Riddick et al., 2012). The nitrogen excretion rate at colony (*F_e*) is calculated using Equation 1 in this study.

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Table 2 Comparison between the measured NH_3 emissions and NH_3 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).

847

Table 3 Comparison between measured NH₃ emissions and NH₃ emission simulated

849 using the GUANO model for the measurement periods at different study sites. P_v is 850 the percentage of N volatilized as NH₃. Determination coefficients (R^2) are shown for 851 modelled emissions based on hourly data between modelled NH₃ emission and each 852 climate variable and for the comparison of modelled and measured emissions (value 853 after each R^2 in brackets shows + or – interaction). The mean modelled % of 854 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

858 measurement and model values shown in Table 2.

859

Table 4 Sensitivity analysis of total modelled NH₃ emission for the Isle of May (28/06/10 to 23/07/10) using the GUANO model. C indicates a constant and V indicates a variable. For the meteorological variables, each hourly value used for ground temperature, relative humidity, wind speed, precipitation and net solar radiation is varied by $\pm 10\%$.⁺ the average value for each meteorological variable from 28/06/10 to 23/07/10 is given.[×] denotes F_{hab} for the Isle of May, other F_{hab} values are given in Table 1.1 in Supplementary Material Section 1.

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Figure 1 Schematic of the GUANO model. Pathways taken by nitrogen following
excretion as uric acid (after Blackall, 2004 modified). The numbers illustrate an
example where the total mass of excreta (M) is made from 0.6 M of water, 0.21 M of
uric acid and 0.19 M of non-N guano. TAN is Total Ammoniacal Nitrogen.

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Figure 2 Comparison between measured and modelled NH₃ emissions for the Sooty tern colony at Mars Bay, Ascension Island (22^{nd} May to 10^{th} 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 NH₃ emissions. The *F*_{hab} 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.

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Figure 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_{hab} 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.

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Figure 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:

895 Measured and modelled NH_3 emission. The F_{hab} value used in the GUANO model 896 was 1 (based on a rock substrate). All values are hourly; tick marks on the x-axis 897 indicate midnight.

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Figure 5 Comparison between monthly time-integrated measured NH₃ emission with modelled hourly NH₃ emissions and monthly-mean modelled emissions for A. Michaelmas Cay, Great Barrier Reef, Australia (5/11/2009 to 1/1/2010) and B. Signy Island (10/01/09 to 21/02/09). Measured ground temperature (°C) and modelled TAN amount (g m⁻²) are shown for comparison. Tick marks on the x-axis indicate midnight. The F_{hab} values were 0.67 (sand) and 1 (rock) for Michaelmas Cay and Signy Island, respectively.

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907 Figure 6 Measured amount of excreted N_r that is volatilized as NH_3 as a function of 908 mean temperature during different field campaigns as compared with estimates of the 909 GUANO model. The line shows the best fit of the measured data (NH_3 (µg g (bird)⁻¹

910 s^{-1} = 0.0014 $e^{0.1099T}$; R² = 0.96). The field site codes are: C.H., Cape Hallett,

- 911 Antarctica; S.I., Signy Island; B.I., Bird Island, South Georgia; I.M., Isle of May,
- 912 Scotland, (b) burrows, (c) cliffs; B.R., Bass Rock, Scotland; M.C., Michaelmas

913 Cay, Australia; A.I., Ascension Island; M.I., Mullet Island, California.

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Colony	Target Species	Population (Pairs)	Measure- ment	Av <i>T</i> (°C)	Av RH	Av WS (m s ⁻¹)	D _{met} (km)	F_{hab}	Adult Mass	Nest Density (m ⁻²)	Breeding season	FC	N excretion rate	Average Measured
			strategy		(%)				(g)	(1117)	(days)		$(g m^{-2} hr^{-1})$	Emission
										<u> </u>				(µg m ² s ²)
Ascension Island	Sooty tern	100,000	Active	27	72	5	2	0.67	190	1.26	122	0.6	0.14	30.2^{a}
7.99 °S, 14.39 °W								~						
Isle of Mav	Atlantic puffin	20.000	Active	15	80	4	1	0.60	410	1.27	152	0.3	0.13	5.0 ^b
56.19 °N. 2.56 °W														
Bird Island	Macaroni penguin	40.000	Active	3	92	5	5	1.00	4680	0.85	213	0.6	1.13	12.9 ^b
54 01 °S 38 08 °W	in a constant pengan	.0,000	1100110	U	/_	U				0.00	-10	0.0	1110	
Michaelmas Cav	Common noddy	12 000	Passive	28	85	5	17	0.67	200	1 70	122	0.6	0.20	22 3 ^a
16.60° S 145.07° E	Common noddy	12,000	1 455170	20	05	5		0.07	200	1.70	122	0.0	0.20	22.5
10.00 S, 145.97 E		10.000				_								a ab
Signy Island	Adélie and	19,000	Passive	2	84	5	50	1.00	4150	0.63	274	0.6	0.79	9.0°
60.73° S, 45.58° W	Chinstrap penguin													

^aRiddick et al. (2014) ^bRiddick et al. (2016) CERTER M

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	Michaelmas	Michaelmas	Signy	Signy	Signy
	Period 1	Period 2	Period	Period	Period
			1	2	3
Measured emission	21.3	22.2	18.2	7.9	9.0
$(\mu g NH_3 m^{-2} s^{-1})$					
GUANO Model emission (µg	25.1	29.9	16.7	9.7	10.7
$NH_3 m^{-2} s^{-1}$)					
Difference between measured and	15.0	25.8	-8.3	22.9	18.4
modelled (%)					

4 Pk 18.2 7.9 16.7 9.7 -8.3 22.9 1.

	$\frac{\rm NH_3\ emission}{(\mu g\ m^{-2}\ s^{-1})}$		P _v (%)		R^2 between hourly modelled NH ₃ emission and meteorological variable				Comparison of hourly modelled to hourly measured emissions			
Colony	Measured	GUANO Model	Measured	GUANO Model	T_g	RH	WS	P	R^2	Slope	Intercept $(\mu g m^{-2} s^{-1})$	Modelled mean % of available TAN emitted as NH_3 in a day ^x
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 (+)	0.13	0.13	5.7	5.5
Bird Island	12.9	12.7	1.8	1.7	0.39 (+)	0.04 (-)	0.59 (+)	0.01 (+)	0.86	1.09	-1.3	1.6
Michaelmas Cav ^a	22.3	27.5	66.8	82.4	0.18 (+)	0.04 (-)	0.01 (+)	0.01 (-)				20.9
Signy Island ^a	9.0	10.7	2.4	2.9	0.38 (+)	0.03 (-)	0.22 (+)	0.01 (+)				0.11

^X, this is defined as the average percentage of TAN produced in a day that volatilizes as NH₃

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Factor	Туре	Base	value for all model runs	Source of base value	% Change in NH ₃ emission		
		(and r	ange tested)	6	High Value	Low Value	
Surface roughness height (z_0 , m)	С	0.1	(0.01 – 0.5)	Seinfeld and Pandis (2006)	+70	-56	
	G	0.00	(100()	Riddick et al. (2014; 2016)	0.40	0.00	
UA conversion to TAN (% day ⁻¹ at pH 9, $T = 35$ °C)	С	0.83	(±10%)	Elliot and Collins (1982)	-9.42	9.30	
Nitrogen wash off (% mm ⁻¹ rain)	С	1	(±10%)	Blackall (2004)	8.19	-7.12	
Non-Nitrogen Wash off (% mm ⁻¹ rain)	С	0.5	(±10%)	Blackall (2004)	-0.15	+0.17	
Boundary layer Stanton number (B)	С	5	(±10%)	Sutton et al. (1993)	+0.04	-0.04	
Habitat Factor $(F_{hab})^{x}$	С	0.60	(0.2 – 1)	Wilson et al. (2004) Riddick (2012)	-70	+49	
Substrate pH	С	8.5	(7 – 9)	Blackall (2004)	+73	-22	
Background NH ₃ concentration ($\mu g m^{-3}$)	С	0.1	(±10%)	Sutton et al. (2003)	-0.02	+0.01	
Ground Temperature $(T, °C)$	V	20^+	(±10%)	Measured	-36.8	+59.9	
Relative Humidity (<i>RH</i> , %)	V	84+	(±10%)	Measured	-13.0	+6.7	
Wind Speed $(U, m s^{-1})$	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 , Wm ⁻²)	V	82.6^{+}	(±10%)	Measured	-2.1	+1.2	

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> 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 NH $_3$ emission on environmental variables

>This model can be a starting point to model NH₃ emissions from other sources