Biogeosciences

Discussions

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Supplement of

A process-based model for ammonia emission from urine patches, GAG (Generation of Ammonia from Grazing): description, validation and sensitivity analysis

A. Móring et al.

Correspondence to: A. Móring (a.moring@sms.ed.ac.uk)

1 # Supplementary material

2

3 **S1. Parametrization of R_a, R_b, R_{bg} and R_{sto}**

4 The value of R_a (sm^{-1}) is dependent on the stability of atmosphere. An unstable stratification –

5 when perturbing an air parcel it ascends from its initial position – favours smaller R_a, whilst a

6 stable one – when the perturbed air parcel returns to its initial position – favours larger R_a.

7 Atmospheric stability can be determined based on the measurements of the sensible heat flux

8 (H, J m^{2}s^{-1}); for H>0, the stratification is unstable, while for H<0, it is stable. The following

9 parametrization of R_a was used (following Garland (1977)):

$$R_a(z_w) = \frac{u}{u_*^2} \qquad \text{if } H<0, \tag{S1}$$

$$R_a(z_w) = \frac{u}{u_*^2} - \frac{\Psi_H\left(\frac{z_w - d}{L}\right) - \Psi_M\left(\frac{z_w - d}{L}\right)}{k u_*} \qquad \text{if } H>0, \tag{S2}$$

10 where u is the wind speed measured at z_w (m) height above ground, u_* (m s^{-1}) is the friction

11 velocity, Ψ_H and Ψ_M are the stability functions for heat and momentum flux, respectively, L

12 (m) is the Monin-Obukhov length, d is the displacement height of the vegetation, and k is the

13 Karman constant (see its value together with all the model constants used in the parametrization

14 of the compensation point model in Table S1).

15 In the case of stable conditions, we parametrized Ψ_H and Ψ_M following Webb (1970):

$$\Psi_H = \Psi_M = \frac{-5(z_w - d)}{L}, \tag{S3}$$

16 and for unstable conditions we applied the approach of Paulson (1970):

$$\Psi_M = \ln\left(\frac{1+x}{2}\right)^2 + \ln\left(\frac{1+x^2}{2}\right) - 2\arctan x + \frac{\pi}{2}, \tag{S4}$$

$$\Psi_H = 2\ln\left(\frac{1+x^2}{2}\right), \tag{S5}$$

17 where:

$$x = \left(1 - 16\frac{z_w - d}{L}\right)^{\frac{1}{4}}$$

(S6)

1   L and u_* can be obtained from measurements, but in the absence of these, parametrization
2   should be used. Eq. (S7) expresses u_*, with z_0 (m) roughness length. L was derived following
3   Eq. (S8), where T (K) is the temperature at 2 m above ground, ρ (kg m^{-3}) is air density, c_p is the
4   specific heat capacity of dry air, and g is the acceleration of gravity. As the two parameters (L
5   and u_*) depend on each other, we applied iteration to calculate both.

$$u_* = \frac{ku}{\ln\left(\frac{z_w - d}{z_0}\right) - \Psi_M\left(\frac{z_w - d}{L}\right)}$$

(S7)

$$L = -\frac{Tu_*^3\rho c_p}{kgH}$$

(S8)

6   The values of ρ can be calculated as a function of atmospheric pressure (p, Pa) and virtual
7   temperature (T_v, K):

$$\rho = \frac{p}{RT_v},$$

(S9)

8   where R is the gas constant and T_v as a function of specific humidity (q) (for actual vapour
9   pressure (e_a, Pa) see (S21)) :

$$T_v = \frac{T}{1 + 0.608q},$$

(S10)

10 where

$$q = \frac{0.622e_a}{p - 0.378e_a}.$$

(S11)

11 Based on Nemitz et al. (2001) for R_b, we used the formula of Owen and Thomson (1963),
12 where Re is the Reynolds number ($R_e = u_* z_0 \nu^{-1}$, with ν as kinematic viscosity) and Sc is the
13 Schmidt number (Sc= νD_g^{-1}, with D_g as the diffusivity of ammonia in air):

$$R_b = 1.45 \times Re^{0.24} Sc^{0.8} u_*^{-1}.$$

(S12)

14

1 Nemitz et al. (2001) applied a parametrization for R_{bg} (s m^{-1}) for oilseed rape. Based on this R_{bg}

2 can be expressed as (Schuepp, 1977):

$$R_{bg} = \frac{\dfrac{\nu}{D_g} - \ln\left(\dfrac{\delta_0}{z_l}\right)}{ku_{*g}},$$

(S13)

3 where δ_0 (m) is the height where eddy and molecular diffusivity are the same in magnitude and

4 z_l (m) is the height of the top of logarithmic wind profile (assumed to be 0.1 m as for oilseed

5 rape). According to Schuepp (1977), δ_0 (Eq. (S14)) is a function of friction velocity at ground

6 level in the canopy (u_{*g}, sm^{-1}), which can be derived from the wind speed (Eq. (S15) as an

7 approximation for oilseed rape by Nemitz et al. (2001)).

$$\delta_0 = \frac{\nu}{ku_{*g}}$$

(S14)

$$u_{*g} = \frac{1.68 \times u}{20}$$

(S15)

8 In the parametrization of R_{sto} the components g_{light}, g_{temp} and g_{VPD} were derived following

9 Emberson et al. (2000). Whilst g_{light} (Eq. (S16)) is expressed as a function of photosynthetically

10 active radiation (PAR, µmol m^2 s^{-1}), g_{temp} (Eq.(S17)) and g_{VPD} (Eq.(S18)) takes into account air

11 temperature (^{0}C) and vapour pressure deficit (VPD, kPa), respectively. The latter is defined

12 (Eq.(S19)) as the difference between saturated (e_s (kPa), Eq. (S20)) and actual vapour pressure

13 (e_a (kPa), Eq. (S21)).

$$g_{light} = 1 - \exp\left(-\alpha_{PAR} \times PAR\right)$$

(S16)

$$g_{temp} = 1 - \left(\frac{T - T_{opt}}{T_{opt} - T_{min}}\right)^2$$

(S17)

$$g_{VPD} = \min\left\{1, \left(\frac{(1 - g_{min})(VPD_{min} - VPD)}{VPD_{min} - VPD_{max}} + g_{min}\right)\right\}$$

(S18)

$$VPD = e_s - e_a$$

(S19)

$$e_s = 0.6108 \times \exp\left(\frac{17.27 \times T}{T + 237.3}\right)$$

(S20)

$$e_a = e_s \frac{RH}{100} \tag{S21}$$

1   Table S1. Constants used in the parametrization of the 2LCCPM.

Model constants	Value
For R_a and R_b	
k (Karman constant)	0.41
d (displacement height)[M]	0.189 m
z_0 (surface roughness)[M]	0.039 m
ν (kinematic viscosity)	1.56×10^{-5} m^2 s^{-1}
D_g (diffusivity of NH$_3$ in air)	2.28×10^{-5}
R (gas constant)	287 J kg^{-1} K^{-1}
g (acceleration of gravity)	9.81 m s^{-2}
c_p (heat capacity)	1005 J kg^{-1} K^{-1}
For R_{ac} and R_{bg}	
α [M]	65.24
z_l (height of the top of logarithmic wind profile)[N]	0.1 m
For R_w and R_{sto}	
$R_{w(min)}$ (minimal cuticular resistance)[H]	1 s m^{-1}
a [H]	0.074
$\frac{D_{O_3}}{D_{NH_3}}$ (ratio of diffusivity of O$_3$ and NH$_3$)[S]	$\frac{1}{1.6}$
LAI (leaf area index)[M]	3.5 m^2 m^{-2}
g_{max} (maximal stomatal conductance)[S]	270 mmol O$_3$ m^{-2}
g_{pot} (effect of phenological change on stomatal conductane)[S]	1
g_{min} (minimal stomatal conductance)[E]	0.1
α_{PAR} [E]	0.009 (μmol m^2 s^{-1})$^{-1}$
T_{opt} (temperature for optimal stomatal conducatnce)[E]	26 ºC
T_{min} (temperature for minimal stomatal conductance)[E]	12 ºC
VPD_{min} (VPD for minimal stomatal conductance)[E]	3 kPa
VPD_{max} (VPD for maximal stomatal conductance)[E]	1.3 kPa
For Γ_{sto}	

T[M]	2.88 days

1   [M]Massad et al., 2010, for summer grassland (values are available also for the other seasons)

2   [N]Nemitz et al., 2001, for oilseed rape

3   [H]Horváth et al., 2005, for summer, semi-natural grassland (values are available also for the

4   other seasons)

5   [S]Sutton et al., 2013, for grassland

6   [E]Emberson et al., 2000, for grassland

1 **S2. Chemical reactions in the GAG model and their equilibrium coefficients**

2 Table S2. Chemical equations – indicated by R0-5 - simulated within the model, (where applicable) their equilibrium coefficient according to

3 definition (K for dissociation and H for dissolution) and the coefficients expressed as the function of soil temperature (T_{soil} (K)) and their references.

4

Chemical equation	Equilibrium coefficient	Equilibrium coefficient as a function of temperature		Reference
R0: $CO(NH_2)_2 + 2H_2O + H^+ \rightarrow 2NH_4^+ + HCO_3^-$	-	-	-	
R1: $NH_4^+ \Leftrightarrow NH_{3(aq)} + H^+$	$K(NH_4^+) = \dfrac{[NH_{3(aq)}][H^+]}{[NH_4^+]}$	$K(NH_4^+) = 5.67 \times 10^{-10} \exp\left(-6286\left(\dfrac{1}{T_{soil}} - \dfrac{1}{298.15}\right)\right)$		Bates and Pinching, 1949
R2: $HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$	$K(HCO_3^-) = \dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$	$\lg(K(X)) = -\left(\left(\dfrac{a}{T_{soil}}\right) + (b \times T_{soil}) - c\right)$	a= 2902.39 b=0.02379 c=6.4980	Harned and Scholes, 1941
R3: $H_2CO_3 \Leftrightarrow HCO_3^- + H^+$	$K(H_2CO_3) = \dfrac{[HCO_3^-][H^+]}{[H_2CO_3]}$		a=3404.71 b=0.032786 c=14.8435	Harned and Davis, 1943
R4: $NH_{3(aq)} \Leftrightarrow NH_{3(g)}$	$H(NH_{3(g)}) = \dfrac{[NH_{3(g)}]}{[NH_{3(aq)}]}$	$H(NH_{3(g)}) = 56 \times \exp\left(4092 \times \left(\dfrac{1}{T_{soil}} - \dfrac{1}{298.15}\right)\right) \times c_{con}$		Dasgupta and Dong, 1986
R5: $H_2CO_3 \Leftrightarrow CO_{2(g)}$	$H(CO_{2(g)}) = \dfrac{[CO_{2(g)}]}{[H_2CO_3]}$	$H(CO_{2(g)}) = 0.034 \times \exp\left(2400 \times \left(\dfrac{1}{T_{soil}} - \dfrac{1}{298.15}\right)\right) \times c_{con}$		Wilhelm et al., 1977
		(where $c_{con} = \left(\dfrac{0.001}{8.314} \times \dfrac{1.013 \times 10^5}{T_{soil}}\right)^{-1}$ is the conversion from atm (mol dm^{-3})$^{-1}$ to (mol dm^{-3}) (mol dm^{-3})$^{-1}$)		

S3. Constants used in the soil evaporation calculation

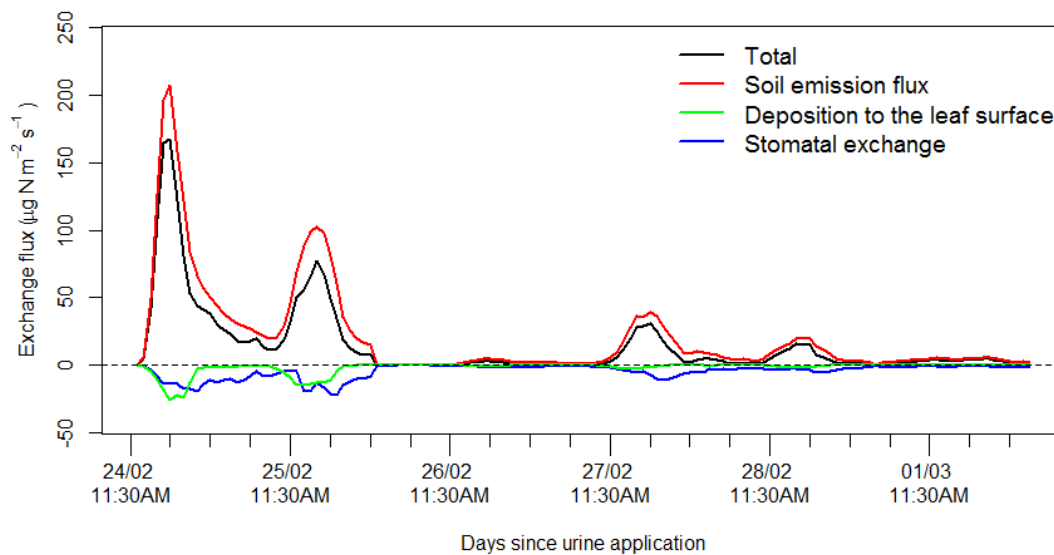Table S3. Constants used in the parametrization of soil evaporation.

Constants	Value
h^M (canopy height)	0.3 m
$K_{cb}(Tab)^A$ (coefficient)	0.7
$\Delta z_E{}^A$ (thickness of evaporation layer)	0.125 m

[M] recommended by Massad et al. (2010) for grass

[A] recommended by Allen et al. (1998) (for extensively grazed pasture)

S4. NH₃ fluxes simulated by the GAG model

Figure S1. NH₃ fluxes simulated by the GAG model: Total NH₃ (F_t), soil emission flux (F_g), deposition to the leaf surface (F_w) and the stomatal exchange (F_{sto})

## S5. Model experiment for a possible restart of urea hydrolysis after the rain event

To test the model for a possible restart of urea hydrolysis after the rain event, we assumed that 10% of the urine (0.1 litre, containing 1.5 g of urea N) was intercepted on the vegetation. From there due to the dry and warm weather conditions (according to the meteorological data in Fig. 10, on the first day of the experiment relative humidity was particularly low and air temperature

1 relatively high compared to the following days) the liquid content might evaporate quickly

2 leaving behind dry urea, which could be washed into the soil by precipitation. With this

3 assumption, allowing the hydrolysis to restart in the soil, the model gives a better representation

4 for the peaks in NH_3 emission (Fig. 10d) on the following three days. In addition, a peak in both

5 soil pH and TAN budget (Fig. S2 (a)-(b)) appears in the model results after the rain event,

6 similarly to the observed values of soil pH and NHx-N, respectively.

7
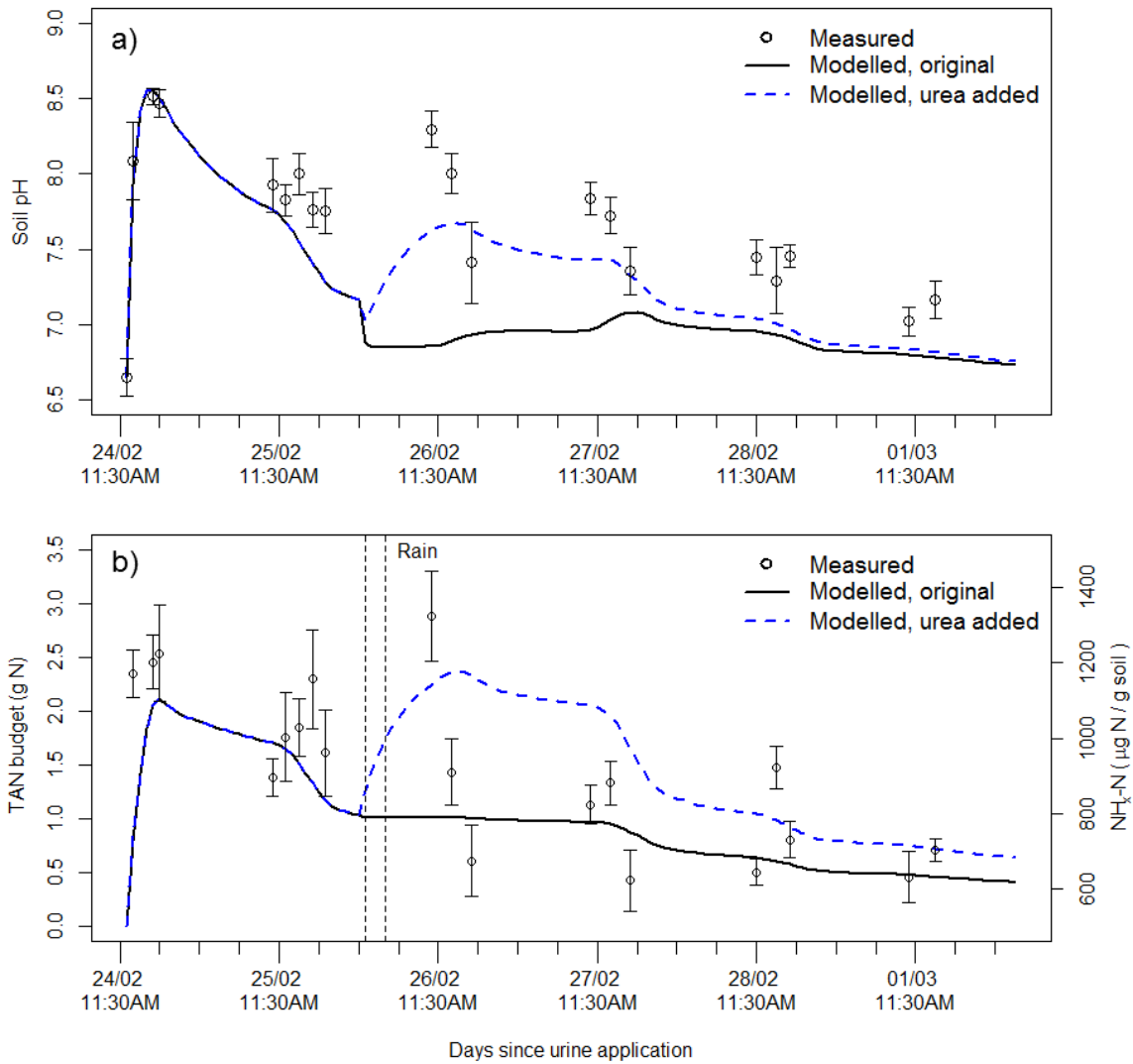
8 Figure S2. Results for soil pH (a) and TAN budget (b) from the model experiment when an

9 assumed 1.5 g of urea was added in the beginning of the rain event.

10

1   **S6. Investigation of model sensitivity to the timing of the rain event**

2   To test the model sensitivity to the timing of the rain event, we assumed the exact same hourly

3   precipitation sums and modified only the starting time of the rain event. In Fig. S3 (a) we show

4   how the timing of the rain event affects the NH_3 emission, with up to a 6% reduction or 2%

5   increase in total NH_3 emission. If it starts raining close to the time of the urine application, the

6   larger R_{soil} reduces the total emission by supressing the first peak of emission (see Fig. S3 (b),

7   time step t_3).
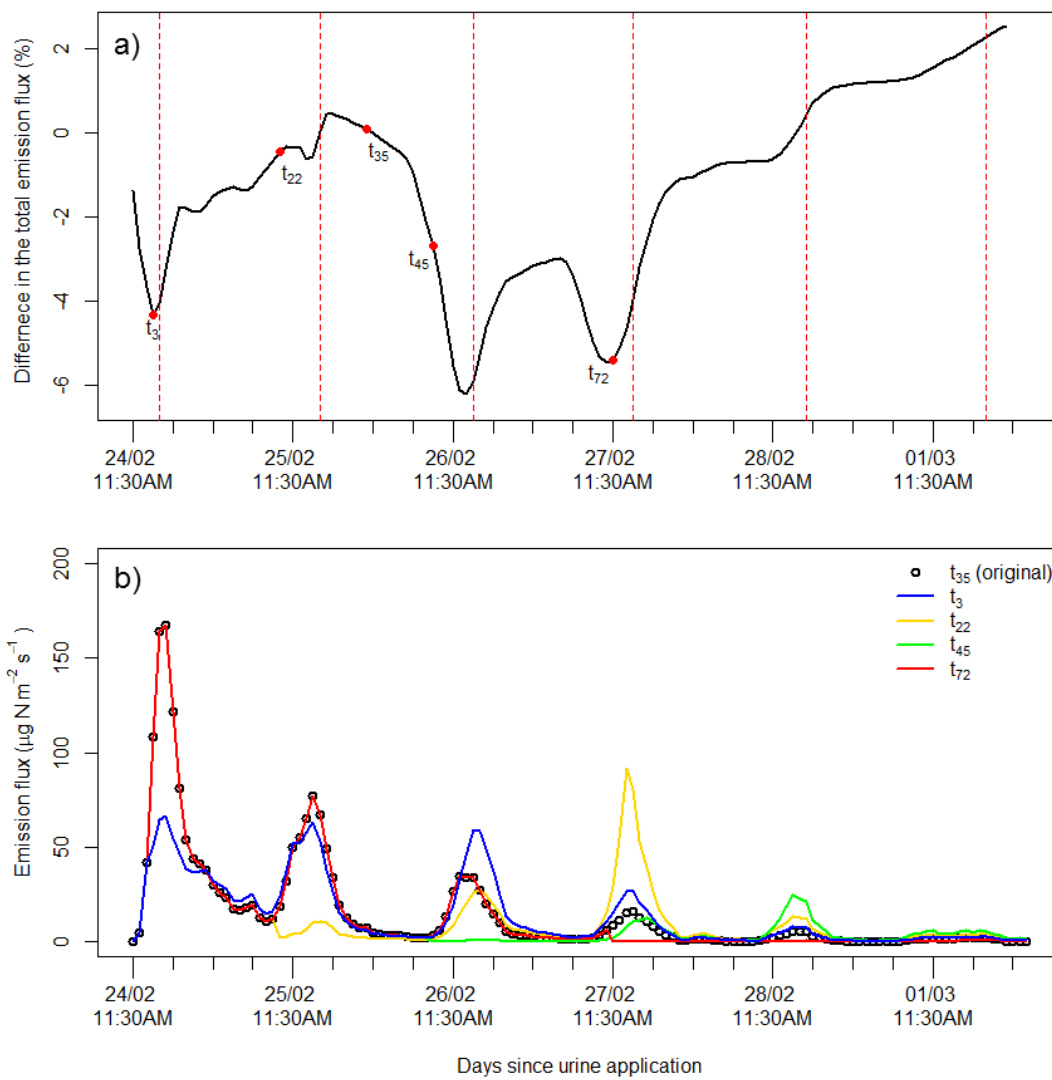
8

9   Figure S3. (a): The total ammonia emission over the period for a given starting time of the rain

10   event. Dashed red lines indicate the time of the daily maxima of soil temperature. (b): Hourly

11   ammonia emission for the time steps indicated on panel (a) with red dots.

12

Further local minima occur in the total emission two and three days after urine application, when the rain event is close to the daily maxima of soil temperature which is when the daily peak of NH_3 emission is expected. In these cases also the increased soil resistance inhibits volatilization. For example, in the 45th time step (Fig. S3 (b)) the third peak of emission disappeared. If we move the rain event after the daily maximum of soil temperature, the prevented peak appears (not shown here) and at the same time increase of the total NH_3 emission can be observed.

Nevertheless, if precipitation gets into the soil, when there is still enough TAN available for volatilization apparently, the "trapped" TAN is emitted later on, as the soil resistance declines due to evaporation. This will lead to a less low minimum in total emission. An example can be seen for this phenomenon on Fig. S3 (b), when it started raining in the 22nd time step, supressing the second NH_3 emission peak but enhancing the forth peak two days later, when the soil dried out.

On the other hand, if precipitation occurs several days after the deposition of the urine patch (e.g. four or five days after urine application) total emission does not decline. This is because, after the third day the increased soil resistance prevents all the emissions after rainfall until the end of the period (Fig. S3 (b), t_{72}). The reason for that is in this last period only a small amount of TAN is remaining in the soil, which is not able to overcome the effect of the soil resistance. Later, as the rain event passes the daily maximum temperatures, emission peaks appear, leading to an increase in total emission.

S7. References

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