Evaluation of ammonia air-surface exchange at the field scale: Improvement of soil and stomatal emission potential parameterizations

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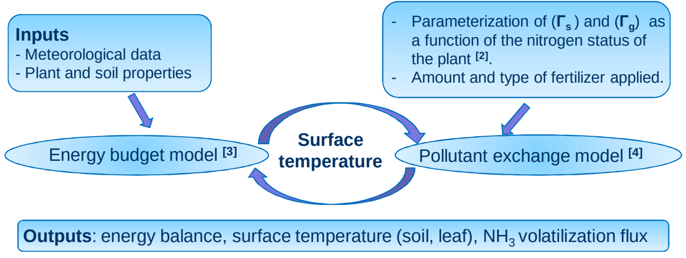
Context & Objective

Agriculture is the main source of atmospheric emissions of ammonia (NH_3). The impact of NH_3 emissions on air quality is of concern in the U.S. due to adverse effects on human health and the environment. Measurements of air-surface fluxes are important for understanding the transport and fate of NH_3 in the atmosphere. However, such measurements do not reflect individual NH_3 source and sink processes. To overcome these limitations and to understand the complex interactions between agronomic and environmental conditions, the use of a modelling approach is necessary. The compensation point, which characterizes the potential to emit or adsorb NH_3, is calculated using the emission potential. The emission potential for the vegetation (**Γ_s**) and ground layer (**Γ_g**) are given by the NH_3 gas concentrations at equilibrium with the ammonium (NH_4^+) concentration in the apoplastic fluid or soil solution. Measurements of **Γ_s** and **Γ_g** are laborious and scare; therefore, existing values are mainly estimated indirectly on the basis of experimental results or adjusted to fit experimental findings.

The primary objective of this study is to improve parameterizations of Γ_s and Γ_g emission potentials used in bi-directional NH_3 air-surface exchange models.

Materials and Methods

❖SURFATM-NH_3[1]



Inputs
- Meteorological data
- Plant and soil properties

- Parameterization of (**Γ_s**) and (**Γ_g**) as a function of the nitrogen status of the plant [2].
- Amount and type of fertilizer applied.

Energy budget model [3]

Surface temperature

Pollutant exchange model [4]

Outputs: energy balance, surface temperature (soil, leaf), NH_3 volatilization flux

❖ Parameterization of vegetation and soil emission potentials Γ_s and Γ_g[2]

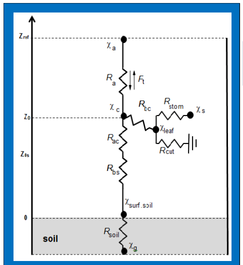


Fig.1: Resistive Scheme for NH_3 exchange model.
R_a, R_{ac}, R_{bc}, R_{stom}, R_{cut}, R_{bs} and **R_{soil}** are respectively aerodynamic resistance above the canopy, aerodynamic resistance inside the canopy, canopy boundary layer resistance, stomatal resistance, cuticular resistance, soil boundary layer resistance and soil resistance; **χ_a , χ_c, χ_s $\chi_{surf.soil}$** and **χ_g** refer to atmospheric NH_3 concentration, canopy NH_3 compensation point, stomatal compensation point, NH_3 concentration on the soil surface and the ground layer compensation point.

- **Volatilization flux of NH_3 (F_t)**

$$F_t = -\frac{1}{R_a}\left(\chi_a - \chi_c\right) \quad \text{with} \quad \chi_c = f\left(\chi_a, \chi_s, \chi_g, R_a, R_{ac}, R_{bs}, R_{bc}, R_{stom}, R_{cut}, R_{soil}\right)$$

- **Stomatal compensation point (χ_s)**

$$\chi_s = K_d \times K_H \times \exp\left(\frac{\Delta H_d^0 + \Delta H_H^0}{R} \times \left(\frac{1}{298.15} - \frac{1}{T_s}\right)\right) \times \Gamma_s$$

- **Ground layer compensation point (χ_g)**

$$\chi_g = K_d \times K_H \times \exp\left(\frac{\Delta H_d^0 + \Delta H_H^0}{R} \times \left(\frac{1}{298.15} - \frac{1}{T_g}\right)\right) \times \Gamma_g$$

- **Parameterization of Γ_s**

$$\Gamma_s = \Gamma_{s(\max)} \times \exp^{(-t/\tau)}$$

$$\Gamma_{s(\max)} = 12.3 \times N_{app} + 20.3$$

- **Parameterization of Γ_g**

$$\Gamma_g = \Gamma_{g(\max)} \times \exp^{(-t/\tau)}$$

$$\Gamma_{g(\max)} = \frac{N_{app}/(\theta_s \times M_N \times l_s \times h_m)}{10^{-pH}}$$

T_s and **T_g** refer to leaf temperature and soil temperature, **K_d** the dissociation constant for acid-base dissociation NH_4^+/NH_3, **K_H** the Henry constant, **ΔH_d^0** and **ΔH_H^0** are the free enthalpies of acid-base dissociation and volatilization, **R** is the perfect gas constant **τ** is the e-folding time constant of the decay, and **t** is the time in days, **N_{app}** is the amount of fertilizer applied, **M_N** is the molar mass of nitrogen, **l_s** is the soil layer where fertilizer is applied, **h_m** is to convert ha to m^2, and **pH** is the pH of the soil solution after fertilizer application.

❖ Parameterization of the inhibitor effect [5]

$$F_{t'} = \alpha_{inhibitor} \times F_t \quad \text{with} \quad \alpha_{inhibitor} = 0.0166 \times \exp(0.6031 \times t)$$

$F_{t'}$ is the volatilization flux of NH_3 taking into account the inhibitor effect , **$\sigma_{inhibitor}$** is the parameter describing the effect of the inhibitor during the 7 days after fertilization and **t** is the time in days.

❖Dataset for model validation[6]

- NH_3 fluxes were measured from May 9 to July 31, 2014.
- Fertilizer: Urea Ammonium Nitrate with Urease inhibitor applied on May 6, 2014 (DOY 126).
- NH_3 fluxes were continuously monitored and averaged over 30 min with the Flux-gradient method in a corn field at the Energy Farm, University of Illinois at Urbana-Champaign, IL.

Results

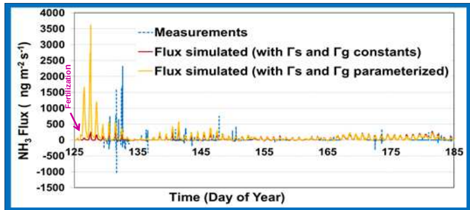


Fig.2: Comparison of measured and modeled volatilization flux of NH_3 simulated with constants values of Γ_s and Γ_g and including the parameterization of Γ_s and Γ_g.

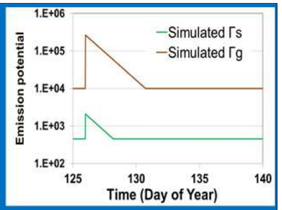


Fig.3: Evolution of the simulated Γ_s and Γ_g as a function of time.

- Measurement data could be divided in two periods: (i) **A** DOY 129-133: high fluxes following NH_3 fertilization with a volatilization peak of 2300 ng m^2 s^{-1} on DOY 132, and (i) **B** DOY 134-185: drastic decrease in emissions with small NH_3 fluxes.
- Simulations with **Γ_s = 800** and **Γ_g = 5000**[7]: underestimation of the high fluxes following fertilization.
- Simulations including the parameterization of **Γ_s** and **Γ_g** : High fluxes immediately after the fertilization and underestimation of the measured volatilization peak.
- Simulated **Γ_g** was roughly a hundred times larger than **Γ_s** .
- **Γ_g** increased the day of the fertilization to reach 2.7 x 10^5 then decreased to 1 x 10^4 on DOY 130..

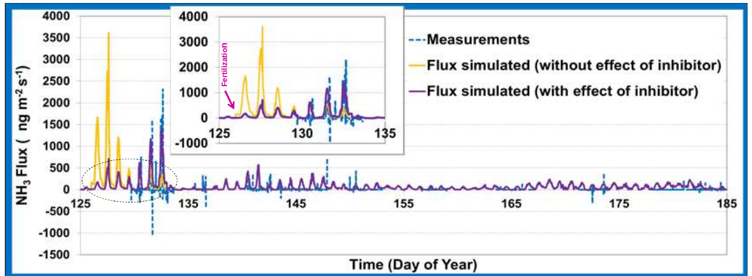


Fig.4: Comparison of measured and modeled volatilization flux of NH_3 simulated without and with the effect of inhibitor.

- Simulations including the parameterization of **Γ_s** and **Γ_g** and the effect of the inhibitor yield results closer to measurements: satisfactory simulations of the high fluxes and the volatilization peak measured 7 days after fertilization.

Discussion

❖NH_3 fluxes

- The temporal pattern of NH_3 fluxes during **period A** is associated with the fertilizer characteristics and the urease inhibitor properties.
- During **period B** the dynamic of the fluxes was related more to canopy dynamics (i.e. rapid growth and development) than fertilizer and the urease inhibitor effects.

❖Simulated Γ_s and Γ_g

- The operational parameterization of **Γ_s** and **Γ_g** as a function of the N status of the plant allows a good simulation of the dynamic and the order of magnitude of **Γ_s** and **Γ_g**.
- The **Γ_g** is much higher than **Γ_s** because it reflects the emission from the fertilizer itself.
- The maximum **Γ_g** simulated by the model (2.7 x 10^5) presents an order of magnitude close to the **Γ_g** measured by Walker et al. (2013) **[8]** in a fertilized corn field (2.5 x 10^5).

❖ Effect of Urease inhibitor

- Urease inhibitor had a considerable effect on the rate and extent of NH_3 volatilization: it reduced NH_3 volatilization and delayed the time of the maximum rate of loss.

Conclusion and Perspectives

- The SURFATM-NH_3 model satisfactorily simulates the NH_3 fluxes by implementing the operational parameterization of **Γ_s** and **Γ_g** and by taking into account the effect of the urease inhibitor.
- The new parameterization of **Γ_s** and **Γ_g** needs to be validated with other datasets using other types of fertilizers.
- The effect of the urease inhibitor need to be more closely examined in order to parameterize it in a mechanistic way.

References

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