Modeling ammonia volatilization over Chinese croplands

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Abstract
Ammonia (NH_3) released to the atmosphere leads to a cascade of impacts on the environment, yet estimation of NH_3 volatilization from cropland soils (V_{NH3}) in a broad spatial scale is still quite uncertain in China. This mainly stems from non-linear relationships between V_{NH3} and relevant factors. Based on 495 site-years of measurements at 78 sites across Chinese croplands, we developed a nonlinear Bayesian Tree Regression model to determine how environmental factors modulate the local derivative of V_{NH3} to nitrogen application rates (N_{rate}) (VR, %). V_{NH3}-N_{rate} relationship was non-linear. VR of upland soils and paddy soils depended primarily on local water input and N_{rate}, respectively. Our model demonstrated good reproductions of V_{NH3} compared to previous models, i.e., more than 91% of the observed VR variance at sites in China and 79% of those at validation sites outside China. The observed spatial pattern of V_{NH3} in China agreed well with satellite-based estimates of NH_3 column concentrations. The average VRs in China derived from our model were 14.8 ± 2.9% and 11.8 ± 2.0% for upland soils and paddy soils, respectively. The estimated annual NH_3 emission in China (3.96 ±0.76 $TgNH_3 \cdot yr^{-1}$) was 40% greater than that based on the IPCC Tier 1 guideline.

Key Words
Ammonia volatilization, atmospheric ammonia, cropping system

Introduction
Ammonia (NH_3) volatilization has doubled globally since 1860 and may double again by 2050. Fertilizer use, as the secondary contributor to NH_3 emissions after livestock production, accounts for more than 30% of anthropogenic NH_3 volatilization. Uncertainties in the estimates of NH3 emissions from cropland are as large as 50%. Apart from lack of high-resolution statistics on fertilizer use, differences in climate and agricultural practices are essential when upscaling site-scale NH_3 fluxes to regional, national or continental budgets. Recent field experiments indicate that the responses of NH3 emissions (VNH$_3$) from cropland to N application rate (N_{rate}) are quadratic or exponential, rather than linear, as assumed by the Intergovernmental Panel on Climate Change (IPCC Tier 1) guidelines. Here, we characterize the nonlinearity and variability of the response of V_{NH3} to Nrate (including synthetic fertilizers, manure, and crop residues) and environmental factors (hereafter x_k) across Chinese croplands, using a synthesis of NH_3 flux measurements from field trials.

Methods
Nonlinear model
We collected 195 V_{NH3} measurements (209 for upland soils and 286 for paddy rice) started from 1990 over Chinese cropland from 90 peer-reviewed publications, which is 2-fold larger than those used in previous studies. Thirteen factors (i.e., N application rate, fertilizer type, crop type, water input, mean air temperature, soil organic carbon content, soil pH, soil clay content, bulk density, soil nitrogen content, cation exchange capacity, sample frequency) were considered as potential predictors in the model. Due to lack of information about fertilization methods and tillage practices in the surveyed literature, those factors were not considered in the following analysis. A nonlinear model of V_{NH3}, Peking University NH_3 model (PKU-NH_3), was then calibrated by the Bayesian Recursive Regression Tree algorithm version 2.0 (BRRT v2) to estimate VR and V_{NH3} for Chinese cropland in 2008 and to assess how x_k modulate VRs. The results of the PKU-NH_3 model are then compared with those of widely used linear models based on country- or regional-scale VR values for predictive accuracy of VR and V_{NH3} at observation sites. The upscaling power of the PKU-NH_3 model is also checked through validation using independent atmospheric observations.

Results

Model performance

We calibrated the PKU-NH_3 model using site data in China for predicting the response of V_{NH3} to N_{rate}. The relevant predictors for both the sub-equation division and the regularized regression are N_{rate}, water input and clay content for upland soils, and N_{rate}, water input, and Temp for paddy soils. Figure 1A–1D show that PKU-NH_3 model with nine variables (including intercept) is able to explain 93% and 91% of the variances for upland and paddy soils, respectively. The RMSEs of the simulated VRs were only 1.6% for upland soils and 2.5% for paddy soils, indicating a low bias in the models. Yet PKU-NH_3 model significantly underestimates a few VRs. For example, one and three other larger discrepancies between simulated results and observations (blue circles in Figures 1A and 1B), for upland and paddy soils, respectively, are attributed to the fact that our models do not account for the effects of fertilizer type.

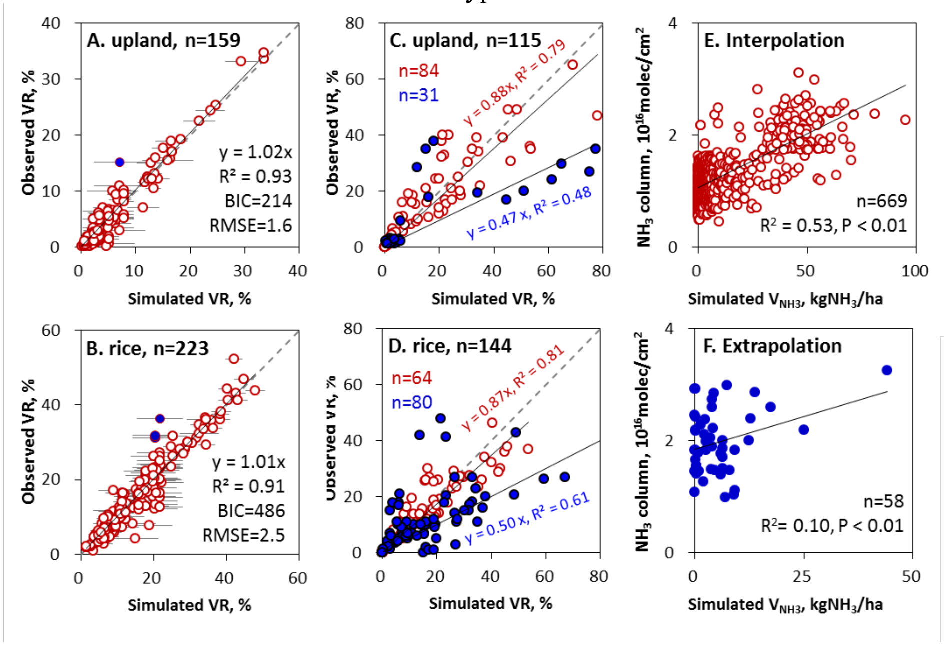

Figure 1. Calibration and validation of VR and V_{NH3}. Panels A or B: calibration of VRs of all site-years from China, panels C or D: validation of ΔVRs of all site-years from outside of China, panels E or F: validation of V_{NH3} from the annual average total columns of NH_3 in 2008 retrieved from IASI satellite observations. The full dataset is illustrated as red open circles, while significant underestimations and sites or pixels subject to extrapolation are represented as blue solid circles. All error bars for simulated VRs are one SE. The observation number (n), slope, R^2, BIC, and RMSE are indicated in the insets of each panel.

NH_3 patterns

The average VR values were 14.8 ± 2.9% and 11.8 ± 2.0% for upland and paddy soils, respectively, and the corresponding V_{NH3} of 3.96 ± 0.76 Tg $NH_3 \cdot yr^{-1}$ (1σ), split into 3.36 ± 0.66 Tg $NH_3 \cdot yr^{-1}$ for upland soils and 0.60 ± 0.10 Tg $NH_3 \cdot yr^{-1}$ for paddy soils. Figure 2A shows that VR from the PKU-NH_3 model varies across China. The average VR over the North China Plain and Southern China are ~38% and ~29%, respectively, which are 4~5 times greater than over western China (7.5%). The highest VR values are found in Guanzhong Plain and Lianghu Plain, where most of the cereals produced. The spatial distribution of V_{NH3} (Figure 2B) is similar to that of the VRs (Figure 2A), but hotspots of V_{NH3} (>100 kg$NH_3 \cdot ha^{-1}$) are amplified in high-VR regions and become smoother spatial distributions in the North China Plain, Northeast Plain and Sichuan Basin (Figure 2B).

To test the mapping of emission patterns over China, we also validated our estimates with IASI satellite observations. The IASI NH_3 total columns reflect the aggregated effects of the NH_3 emissions from arable soils and manure management. The comparison between IASI NH_3 total columns and the sum of two dominating sources is desirable, however, the emissions from manure management is difficult to be accurately estimated, owing to the lacks of wide survey on management options or considerable observations on NH_3 emission rate for each option in China. We found that county-scale V_{NH3} from arable soils is well correlated with annual amounts of manure in each of province, except for Ningxia, Xinjiang, and Fujian. Such spatial consistency implies the synergy between V_{NH3} and the emissions from manure management across most of China. Therefore, we believe that it is acceptable to compare V_{NH3} with IASI satellite observations directly for validating the predictability of PKU-NH_3 model. The result of the regions subject to interpolation is consistent with the annual average total columns of NH_3, where correlation coefficient R^2 is 0.53 ($P < 0.01$; Figure 2E). Although this result cannot prove the accuracy in the magnitude of V_{NH3}, it still provides additional validation for the PKU-NH_3 model in capturing the spatial details of NH_3 emissions.

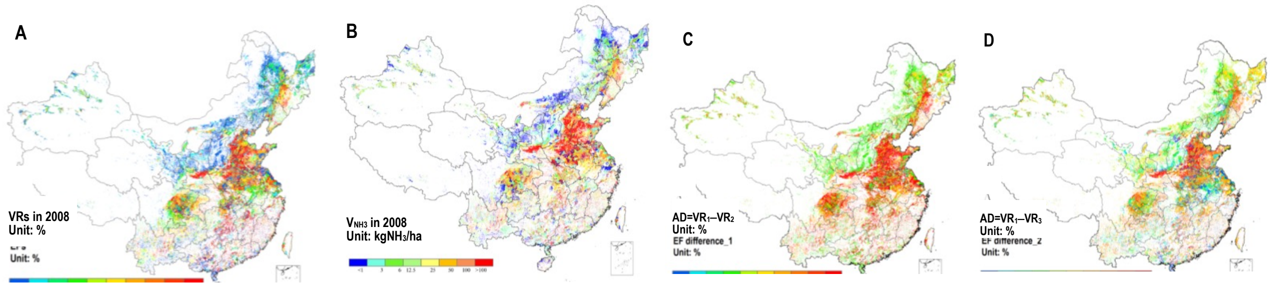

Figure 2. 1-km spatial patterns of VRs and V_{NH3}, differences with other VR models. Panel A: VRs in 2008, panel B: V_{NH3} in 2008, panel C: difference between PKU-NH_3 model and M2, panel D: difference between PKU-NH_3 model and M3.

Determinants and their effects on VRs. Water input and N_{rate} were found to be the most important determinant controlling VR for upland and paddy soils, respectively (Figures 3A and 3B). Water input can explain 78% of the spatial variation of VR for upland soils, while N_{rate} account 52% for paddy soils. Nitrogen addition provides the source of total NH_x availability (i.e., TAN = NH_3-N + NH_4^+-N) in soils, and water input probably exerts a control on VR by triggering the volatilization of NH_3. Soil clay content and Temp are ranked second in x_k next to water input as determinants controlling VR for upland and paddy soils, respectively, explaining 6% and 18% of the variance in VRs accordingly.

For the marginal effect of water input (Figures 3C and 3D), the VR of upland soils decreases from 13% to 5% until water input approaches ~1,100 mm, followed by a linear growth to 15% at ~2,000 mm and then a decline (Figure 3C). Similarly, the VR of paddy rice declines rapidly from 20% to 4.3% until reaching the amount of ~1,200 mm, but it rises abruptly to ~25% at ~1,300 mm, and finally decreases slowly to 20%. Although these complex response curves were rarely detected in the manipulation experiments, they may be interpreted by water-induced soil N dynamics and regional differences in rice cropping systems. First, limited rain or irrigation events (P+I < 1,000 mm) immediately provide a solvent to increase the dissolution of TAN as well as the chance of absorption by soil colloids, leading to the decline in NH_3 volatilization rate. Excessive water input (P+I > 2,000 mm) may also enhance the infiltration of TAN to the rooting zone or the surface flow of TAN to rivers, which altogether decreases the fraction of soil TAN lost as NH_3. On the contrary, VR increases when water input approaches a range between 1,000 and 2,000 mm, where such precipitation events or irrigation occurs at least in the North China Plain and Sichuan Basin. Possible interpretation is that the influences of other relevant factors may be hidden behind such marginal effect of water input on VR. Therefore, more analysis by using process-based model is required to simulate the effects of rainfall regime on NH_3 volatilization, which is an additional step that can be taken in the future. Second, two piecewise linear curves for paddy rice (Figure 3D), roughly divided at 1,200 mm, suggest two separate response functions for 'Northern' and 'Southern' China. Figure 3D indicates that VR is larger in the regions where P+I over 1200 mm than those where P+I less than 1200 mm. Single rice cropping systems exist in both Northern and Southern China, but double rice cropping systems only occur in wetter and warmer Southern China, where they require more water input. Additionally, agricultural water management for paddy rice in Southern China is dominated by the flooding-midseason drainage-frequent water logging with intermittent irrigation, which also increases the fraction of fertilizers and soil TAN lost as leaching or runoff. Potential of V_{NH3}, therefore, may be declined from paddy soils accordingly.

For the effect of soil clay content for upland soils, the VR can be described as a single optimum function of clay content (Figure 3E). VR grows rapidly with clay content, starting at 4% and reaching a peak of 14% at Clay of 10%, before slowly falling in the range of 10%~50% (Figure 3E). This trend is understandable based on the physical mechanism between soil water retention and clay content, as the higher the soil clay content, the higher the water retention capacity. Another possible explanation is that increasing soil clay content leads to a decrease of water conductivity, which restricts the vertical transfer of nitrogen. Thus, an increase in clay content may strengthen the occurrence probability of the hydrolysis of urea and other fertilizers. However, when clay content exceeds a threshold (e.g., 14%), the excessive water content of agricultural soils would enhance the dissolution and absorption of TAN, ultimately leading to lower VRs of NH_3.

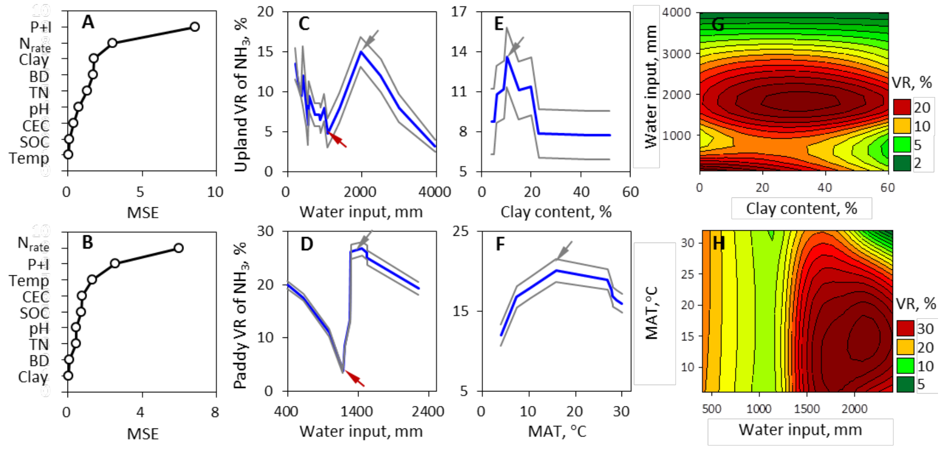

Figure 3. Functional dependence of VR upon main environmental determinants. Rank of factors contributing to VR of upland soils (A) and paddy soils (B). The meanings of abbreviations are explained in Data sets sub-section. VR is calculated for the same reference N_{rate} of 212 kg N·ha^{-1} being the mean value of the observations used for model calibration. Maximum thresholds of temperature, precipitation and clay content are indicated by gray arrows, while their minimum thresholds are indicated by red arrows. The uncertainty range (±SEM) is indicated in Panels C – F by gray lines.

For the effect of temperature on VR for paddy rice (Figure 3F), it is important to find a substantial sensitivity across the range of 4~30 °C, which was also observed in previous control experiments (Figure 3D). The VR of NH_3 rises only moderately from 12% to 20% at Temp ≈ 16 °C, followed by a slow decline to 16% at Temp ≈ 30 °C. This result indicates that the VR would be stimulated by Temp because both the hydrolysis rate and the NH_3 transfer from the liquid to the atmosphere can increase with the growth of temperature. The lag phase after fertilizer application would then be shorter and the initial loss rate of NH_3 would be greater at high soil temperatures. However, NH_3 volatilization may not be affected significantly by changes in temperature when over the optimum level (e.g., 16 °C). Volatilization could continue for a long period even at low soil temperature, resulting in an overall small temperature sensitivity of VR for paddy rice.

We also represented joint effects of the two most important determinants on VRs for each crop category. For upland soils (Figure 3G), water input of ~2,000 mm in combination with clay content of ~30% stimulates NH_3 losses significantly up to ~22%, likely because the release of TAN from fertilizers evolves sufficiently but TAN leaching or runoff appears to be moderate. For paddy rice (Figure 3H), moderate Temp (~15°C) and high water input (~2,100 mm) appear to drive up the NH_3 volatilization, leading to the highest VR (38%). Such responses were occasionally observed in field or laboratory studies.

Conclusion and remarks

PKU-NH3 is reliable in capturing nonlinear response of VR and V_{NH3}. Water input can explain 78% of the spatial variation of VR for upland soils, while N_{rate} account 52% for paddy soils. More importantly, join sensitivity of ≥2 factors could be a useful reference for both control experiments and process-based model. China's NH3 emissions are estimated greatly larger than previous results or that based on IPCC default. Spatial pattern and temporal trends of emissions from both China and globe need to be re-estimated using our model in future, and NH3 mitigation protocol could be refined and effective when considering the spatially-differential sensitivity to fertilizer reductions.

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