# Modeling ammonia volatilization over Chinese croplands

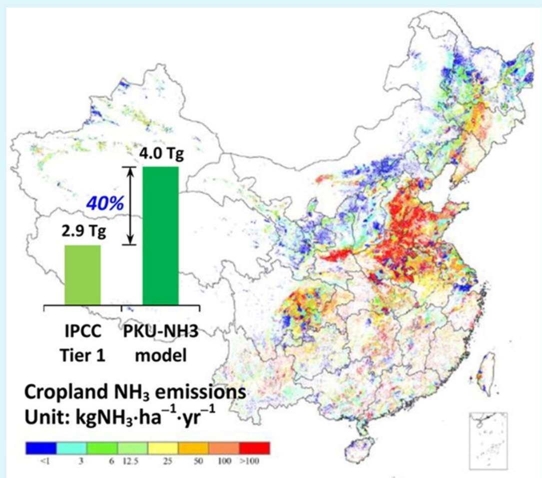

Ziyin Shang[1], Feng Zhou[1], Shuoshuo Gao [1], Yan Bo[1], Philippe Ciais [2], Kentaro Hayashi[3], James Galloway [4], Dong-Gill Kim [5], Changliang Yang [6], Shiyu Li [6], Bin Liu [6]

1 Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing, 100871,P.R. China
2 Laboratoire des Sciences du Climat et de l'Environnement, CEA CNRS UVSQ, 91191 Gif-sur-Yvette, France
3 Carbon and Nutrient Cycles Division, National Institute for Agro-Environmental Sciences, Kannondai, Tsukuba, Ibaraki 305-8604, Japan
Corresponding author: Ziyin Shang (Email: zyshang@pku.edu.cn) Feng Zhou (Email: zhouf@pku.edu.cn)
4 Environmental Sciences Department, University of Virginia, Charlottesville, Virginia 22904, USA
5 Wondo Genet College of Forestry and Natural Resources, Hawassa University, PO. Box 128, Shashemene, Ethiopia
6 Research Institute of Engineering Technology, Yunnan University, Kunming, 650091, P.R. China



## 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


## 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.

## DATA & METHODS

### 1) Piecewise models

We propose piecewise quadratic models to account for the shape and heterogeneity of $V_{NH3}$:

$$V_{NH3\,l} = \Delta VR_l(x_k) \times N_{rate}^2 + VR^0_l(x_k) \times N_{rate} + V^0_l(x_k)$$

$$VR_l(x_k) = \Delta VR_l(x_k) \times N_{rate} + VR^0_l(x_k)$$

$$\Delta VR_l(x_k) = \sum(\alpha_{kl} \times x_k) + a_l$$

$$VR^0_l(x_k) = \sum(\beta_{kl} \times x_k) + b_l$$

where :

VR : volatilization rate of $NH_3$, VR = ($V_{NH3}$-$V^0$)/ $N_{rate}$, %;

$\Delta$VR : the change in VR per unit of incremental $N_{rate}$, %×(kgN×ha$^{-1}$)$^{-1}$;

$VR^0$ : initial value of VR without the impact of fertilization, %;

$V^0$ : background $NH_3$ emission when $N_{rate}$=0, kgN×ha$^{-1}$;

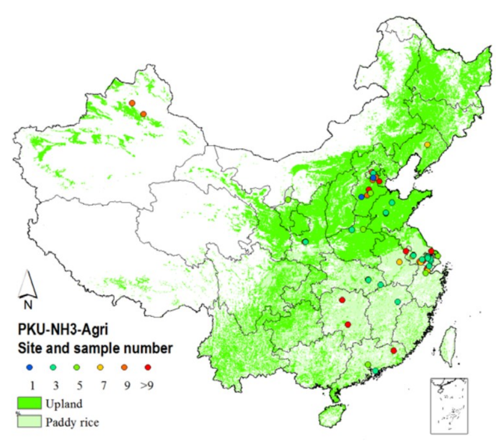
$N_{rate}$ : nitrogen application rate, kgN×ha$^{-1}$;

$l$ : the index of piecewise functions;

$\alpha_{kl}$, $\beta_{kl}$, $a_l$, and $b_l$ : model coefficients for DVR and $VR^0$;

$x_k$ : the environmental factors;

### 2) Observation dataset




The dataset after such data screening comprised 495 site-years, 209 for upland soils (grain crops such as wheat, maize, soybean but excluding rice) and 286 for paddy rice, across 78 sites covering the period from 1990 to 2012.

**Fig. 1** Location and record number of study sites (n = 79) .

## RESULTS: Calibration and validation

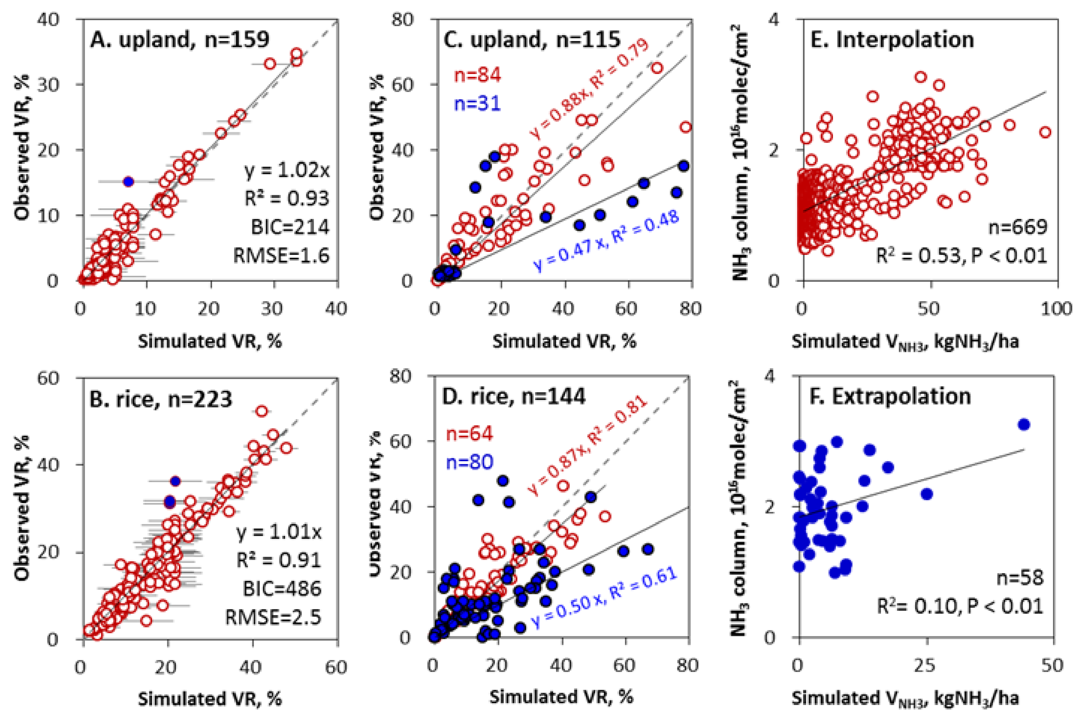



**Fig. 2** Calibration and validation of VR and $V_{NH3}$. A or B: calibration of ΔVRs inside China; C or D: validation of ΔVRs outside China; E or F: validation of $V_{NH3}$ from the annual average total columns of $NH_3$ in 2008 retrieved from IASI satellite observations. Red open circles: The full dataset ; Blue solid circles: significant underestimations and sites or pixels subject to extrapolation.

## RESULTS: Spatial patterns of VRs and $V_{NH3}$

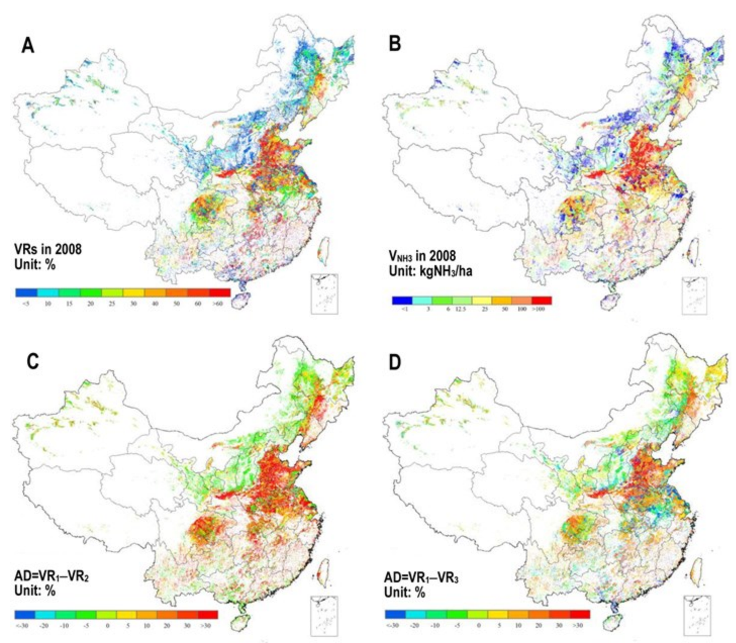


**Fig. 3** 1-km spatial patterns of VRs and $V_{NH3}$, differences with other VR models. Panel A: VRs in 2008, panel B: $V_{NH3}$ in 2008, panel C: difference between PKU-$NH_3$ model and M2 (VRs are modeled as VR = ΔVR·Nrate+$VR^0$ based our data set of NH3 observations ), panel D: difference between PKU-$NH_3$ model and M3(VRs are modeled as VR = ΔVR($x_k$) ·Nrate + $VR^0$ ($x_k$) ).

## RESULTS: Determinants and their effects on VRs

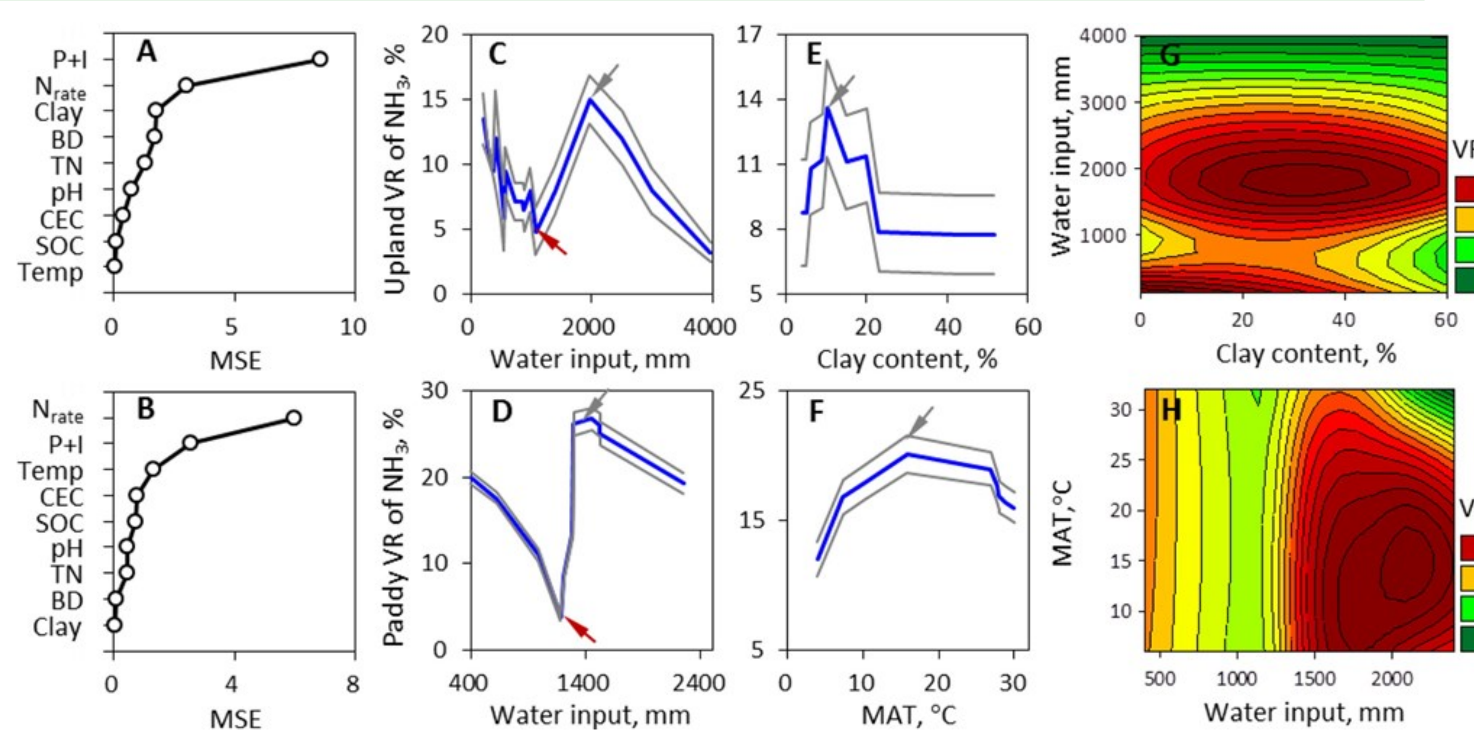



**Fig. 4** Functional dependence of VR upon main environmental determinants. Rank of factors contributing to VR of upland soils (A) and paddy soils (B). VR is calculated for the same reference Nrate of 212 (kg N·ha−1 ), the mean value of the observations used for model calibration. Gray arrows: maximum thresholds; Red arrows: minimum; Gray lines: ±SEM.

## CONCLUSION & REMARKS

- PKU-NH3 is reliable in capturing nonlinear response of VR and VNH3.
- Water input can explain 78% of the spatial variation of VR for upland soils, while Nrate 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.


## REFERENCES

Zhou F, Ciais P, Hayashi K, Galloway JN, Kim DG, Yang C, Li S, Liu B, Shang Z, Gao S (2016). Re-estimating NH3 emissions from Chinese cropland by a new nonlinear model. Environmental science & technology 50 (2):564-572.