Quantifying nitrogen leaching response to fertilizer additions in China's cropland[☆]

Shuoshuo Gao^{a,1}, Peng Xu^{b,1}, Feng Zhou^{a,*}, Hui Yang^a, Chunmiao Zheng^c, Wei Cao^d, Shu Tao^a, Shilong Piao^a, Yue Zhao^e, Xiaoyan Ji^f, Ziyin Shang^a, Minpeng Chen^{g,h,**}

^a Institute of Integrated Watershed Management, Sino-France Institute of Earth Systems Science, Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing, 100871, PR China

^b School of Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen, 518055, PR China

^c School of Environmental Science and Engineering, South University of Science and Technology of China, Shenzhen, 518055, PR China

^d Laboratory of Land Surface Pattern and Simulation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing, 100101, PR China

^e Department of Water Environmental Planning, Chinese Academy for Environmental Planning, Beijing, 100012, PR China

^f State Environmental Protection Key Laboratory of Quality Control in Environmental Monitoring, China National Environmental Monitoring Center, Beijing, 100012, PR China

^g Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences, Beijing, 100081, PR China

^h International Institute for Applied System Analysis, Laxenburg, A-2361, Austria

ARTICLE INFO

Article history:

Received 13 August 2015

Received in revised form

25 December 2015

Accepted 5 January 2016

Available online 14 January 2016

Keywords:

Nitrogen leaching

Nonlinearity

Variability

Spatial pattern

Bayesian inference

ABSTRACT

Agricultural soils account for more than 50% of nitrogen leaching (L_N) to groundwater in China. When excess levels of nitrogen accumulate in groundwater, it poses a risk of adverse health effects. Despite this recognition, estimation of L_N from cropland soils in a broad spatial scale is still quite uncertain in China. The uncertainty of L_N primarily stems from the shape of nitrogen leaching response to fertilizer additions (N_{rate}) and the role of environmental conditions. On the basis of 453 site-years at 51 sites across China, we explored the nonlinearity and variability of the response of L_N to N_{rate} and developed an empirical statistical model to determine how environmental factors regulate the rate of N leaching (LR). The result shows that L_N – N_{rate} relationship is convex for most crop types, and varies by local hydro-climates and soil organic carbon. Variability of air temperature explains a half (~52%) of the spatial variation of LR. The results of model calibration and validation indicate that incorporating this empirical knowledge into a predictive model could accurately capture the variation in leaching and produce a reasonable upscaling from site to country. The fertilizer-induced L_N in 2008 for China's cropland were 0.88 ± 0.23 TgN (1σ), significantly lower than the linear or uniform model, as assumed by Food and Agriculture Organization and MITERRA-EUROPE models. These results also imply that future policy to reduce N leaching from cropland needs to consider environmental variability rather than solely attempt to reduce N_{rate} .

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

As a soluble and mobile contaminant, fertilizer nitrogen not

used by crops is prone to leaching through the root zone into groundwater (Kramer et al., 2006; Wick et al., 2012). When excess levels of nitrate (NO_3^-) accumulate in groundwater, it poses a risk of methaemoglobinemia in infants and risks of gastric and oesophageal cancers (Fewtrell, 2004; Nolan and Hitt, 2006; WHO, 2011). Nitrate in groundwater aquifers has represented a major environmental problem worldwide, particularly in Europe, USA, and South and East Asia (Nolan and Hitt, 2006; Wick et al., 2012; Gu et al., 2013; Rodríguez-Lado et al., 2013). In China, where groundwater provides 20% of the total water supply (Qiu, 2011; Zheng and Liu, 2013), the nitrate levels in more than 25% of samples taken in croplands during 2000–2009 exceeded the World Health

[☆] This paper has been recommended for acceptance by Charles Wong.

* Corresponding author. College of Urban and Environmental Sciences, Peking University, Room 3355, 2nd Yifu Bld, Beijing, 100871, PR China. Tel.: +86 1062758845.

** Corresponding author. Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences, Beijing, 100081, PR China.

E-mail addresses: zhouf@pku.edu.cn (F. Zhou), chenminpeng@caas.cn (M. Chen).

¹ S.S.G and P.X. contributed equally to this work.

Abbreviation

N_{rate}	Nitrogen (N) fertilizer application rate per unit sowing area
L_N	Amount of N leaching
LR	N leaching rate
ΔLR	Change in LR per unit of N_{rate}
L_0	Base N leaching
LR^0	Initial value of LR without the impact of fertilization
f_k	Environmental factors (soil attribute, hydro-climates, sampling Factors)
α_k	Coefficient for f_k in LR term
b	Intercept in LR term
β_k	Coefficient for f_k in LR^0 term
c	Intercept in LR^0 term
Temp	Average air temperature during the observation period
$P+I$	Sum of precipitation and irrigation during the observation period
SOC	Soil organic carbon
pH	Soil pH value
BD	Soil bulk density
Clay	Soil clay content
TN	Soil total nitrogen
Depth	Sampling depth
NPCP	National pollution census program

Organization (WHO) recommended maximum limit of 10 mg/L ($\text{NO}_3\text{-N}$; Gu et al., 2013). Such conditions indicate the likelihood of adverse health effects in nearby rural residents, particularly in north and northwest China (Liu et al., 2006). While fertilizer use accounts for more than 50% of the nitrogen leaching into groundwater in China (Gu et al., 2013), nitrogen loss from cropland is poorly understood (Zheng and Liu, 2013).

Nitrogen leaching depends on the flow rate of infiltrating water and the concentration of nitrogen in the root zone (Riley et al., 2001; Zheng and Bennett, 2002; Li et al., 2006). In the root zone, nitrogen concentrations are controlled by nitrogen additions minus nitrogen losses via ammonia (NH_3) volatilization, denitrification and crop uptake (Van Dreht et al., 2003; Keuskamp et al., 2012; Bouwman et al., 2013). Therefore, the suggested linear relationship between nitrogen application rate (N_{rate} , $\text{kgN}\cdot\text{ha}^{-1}$) and fertilizer-induced nitrogen leaching (L_N , $\text{kgN}\cdot\text{ha}^{-1}$) is inconsistent with the denitrification process within the root zone (IPCC, 2006; Amon-Armah et al., 2015), which in fact varies significantly with nitrogen input (Jahangir et al., 2012; Bouwman et al., 2013; Zhou et al., 2014).

According to a growing number of field observations at specific sites, LR (the rate of N leaching) also varies with environmental conditions (f_k), focusing on hydroclimatic factors or soil properties (Van Dreht et al., 2003; Velthof et al., 2009; Nolan and Hitt, 2006; Chen et al., 2014). First, the sensitivity of leaching rate (LR, %) to N_{rate} (defined as ΔLR , the first-order derivative of LR to N_{rate}) may be controlled by f_k . For example, Wick et al. (2012) observed that ΔLR values were systematically larger after previous cropping or when the amount of precipitation was greater than $281 \text{ mm}\cdot\text{yr}^{-1}$. Second, LR under a given N_{rate} may be regulated by levels of f_k that determine denitrification rates and the residence time of nitrate in the root zone (Van Dreht et al., 2003; Velthof et al., 2009). However, those results only reflect the effects of f_k under a limited range of the environmental factors. When upscaling to national or larger

scale predictions of N leaching rate, unreasonable fluxes may occur widely for environments that are not captured by the small group of field experiments.

To test if it is the similar case in China, the synthesized N leaching measurements were used in this study to investigate the nonlinearity and variability of the response of L_N to N_{rate} for cropland across diverse environmental conditions. A new empirical model (PKU-NLEACH) calibrated by the Bayesian Recursive Regression Tree algorithm (BRRT v2) was also proposed to determine the shape of LR related to controlling factors. The results were then compared with the models without the considerations of nonlinearity and variability, including those used in MITERRA-EUROPE model (Velthof et al., 2009) and FAO Assessment model for soil nutrient balance (de Willigen, 2000; Roy et al., 2003; Liu et al., 2010). In the end, this study assessed how f_k modulates the spatial variability of LR and discussed about the implications on regional budgets.

2. Data and methods

2.1. Field observations in China

Field observations of L_N , N_{rate} , and f_k were collected from sites of both upland and paddy soils from 50 peer-reviewed publications of field trials (80% for upland crops and 20% for paddy rice). Lysimeters were used to quantify the water flow and N movement through agricultural soils. Installation details were as described in Huang et al. (2011). Retained flux measurements had to have at least two levels of N_{rate} , in addition to a zero-N control experiment. Three types of samples were excluded from the analysis: (i) measurements that included the use of such chemicals as nitrification inhibitors that are not widely applied in China, (ii) measurements with the duration not covering all split-applied fertilizations for a crop growing season, and (iii) measurements without zero-N controls. This reduced dataset was comprised of 453 site-years (397 for upland crops and 56 for paddy rice) at 51 sites observed from 1992 to 2013 (Fig. 1 and Data S1), which could produce 338 pairs of LR. However, only 388 site-years at 37 sites with at least three N-input levels could produce 96 pairs of ΔLR .

To interpret the nonlinearity of nitrogen leaching to N_{rate} , we analyzed the f_k (Table 1) known to affect the soil N cycling and transport in the root zone when available in field experiments. However, fertilization methods (e.g., broadcast, incorporation, injection, and deep placement) and tillage practices were not considered due to lack of information about in the surveyed literature. All site-years in the original studies were used and were averaged by replicates if necessary. Few of the missing climate and soil properties within observation periods were supplemented by the 1-km Harmonized World Soil Database (HWSD) v1.2 (<http://www.iiasa.ac.at>) and by the 0.1-degree China Meteorological Forcing Dataset (CMFD; Chen et al., 2011).

2.2. Statistical analysis

The L_N model assumed a quadratic form of nitrogen leaching change along a gradient of N_{rate} : $L_N = [\Delta LR \cdot N_{rate} + LR^0] \cdot N_{rate} + L_0$, because most of control experiments were determined to be well expressed ($R^2 > 0.9$ and $P < 0.01$ for 89% field experiment; Fig. S2). Before investigating the nonlinearity and variability of the response of L_N to N_{rate} , LR was calculated for each non-zero N_{rate} as a difference between nitrogen leaching (L) at N_{rate} and the corresponding control (L^0) divided by N_{rate} (unit: %), and ΔLR is calculated as the change in LR per unit of incremental N_{rate} (unit: $\%\cdot\text{kgN}^{-1}\cdot\text{ha}$). Their meanings were also graphically described in Fig. 2a and b. A Shapiro–Wilk test was then performed to check whether their

Fig. 1. Location and record number of study sites. Upland crops and paddy rice are illustrated as dark and light green, respectively. 37 sites having at least three N-input levels are illustrated as black solid circle, whereas 14 sites having less than three levels are indicated as open circle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

List of environmental factors for the dataset collected from field experiments.

Type	Name of variable	Variable type	Unit
Fertilizer	N application rate (N_{rate}) ^a	Continuous	Kg N ha ⁻¹
Crop	Crop type (Veg) ^b	Discrete	—
Hydroclimatic paramters ^c	Mean air temperature (Temp)	Continuous	°C
	Water input (P+I) ^d	Continuous	mm
Soil ^e	Soil organic carbon content (SOC)	Continuous	%
	Soil nitrogen content (TN)	Continuous	g kg ⁻¹
	Soil pH	Continuous	—
	Bulk density (BD)	Continuous	g cm ⁻³
	Soil clay content (Clay)	Continuous	%
Experiment	Sampling depth (Depth)	Continuous	cm

^a N_{rate} is defined as the sum of split applications within experiment duration.

^b Includes paddy rice, upland crops including wheat, maize, and the others.

^c Cumulative water input and mean air temperature for each observation are calculated as the total amount and mean value during the experiment period, respectively.

^d Water input defined as the sum of precipitation and irrigation rate.

^e Values for topsoil.

distributions were normal. If not, bootstrap resampling was used for analysis of means and confidence intervals (CIs) for all ΔLR and LR. The 96 ΔLR and 338 LR were divided into at least two subgroups or levels based on f_k , where splitting values were identified by a decision tree CART (Fig. 2; Breiman et al., 1984). Levene's test was used to test the homogeneity of variance before comparison of means ΔLR and LR for subgroups on the basis of t-tests. When Levene's test showed no significance ($P > 0.05$), parametric tests were chosen and vice versa (Nolan and Hitt, 2006). If the mean ΔLR was significantly different from zero, L_N to N_{rate} was nonlinear. If mean ΔLR or LR was significantly different between any two sub-

groups, the nonlinear response of nitrogen leaching response to N_{rate} would be varying rather than uniform. All statistical analysis was conducted using RStudio v7.6 (RStudio, Inc) and Matlab R2014 (MathWorks, Inc).

2.3. PKU-NLEACH model

Contrary to previous studies (de Willigen, 2000; Roy et al., 2003; IPCC, 2006; Velthof et al., 2009; Liu et al., 2010), where linear or uniform LR determinations were used, an empirical model (PKU-NLEACH) was applied in this analysis accounting for these

Fig. 2. Effect of N fertilizer rate (N_{rate}) on the N leaching (L_N) and LR_s. (a) Definition of LR; (b) Definition of ΔLR ; (c) Relationship between L_N and N_{rate} based on the field experiments (including 453 site-years at 51 sites) for Chinese cropland, where a part of experiments with at least five N-input levels are indicated as colorful dots and lines; (d) Relationship between LR and N_{rate} , where ΔLR (including 96 pairs) are shown in a boxplot, with statistical information noted beside the bar. Regression between LR and N_{rate} for all field observations has shown in black line.

nonlinear and varying responses of nitrogen leaching to N_{rate} and f_k :

$$LR_j = \Delta LR_j(f_k) \cdot N_{rate} + LR_j^0(f_k), \quad \text{where } f_k \in \Omega_j, \quad \forall j = 1, 2, \dots, J, \quad (1a)$$

and

$$\Delta LR_j(f_k) = \sum (\alpha_{kj} \cdot f_k) + b_j, \quad LR_j^0(f_k) = \sum (\beta_{kj} \cdot f_k) + c_j, \quad (1b)$$

and j and J represent the index and number of piecewise functions, respectively. The BRRT v2 was subsequently used to determine the optimal model structure (i.e., L and $f_k \in \Omega_j = (f_k^{ow}, f_k^p)$) and model coefficients (i.e., $\alpha_{kj}, \beta_{kj}, b_{kj}, c_j$) with a minimum cost function, and to establish the relationships between N leaching rate and N application rate. The cost function in BRRT v2 that was minimized was the Bayesian Information Criterion (BIC). Detailed methodology of the BRRT v2 was described by Zhou et al. (2015). Note that regularized linear regression (Rosset and Zhu, 2007) and condition index were applied for individual bottom nodes within the procedure of BRRT v2, avoiding over-fitting in model calibration and colinearity among different f_k , respectively (Zhou et al., 2015).

PKU-NLEACH model was also used to simulate the spatial patterns of N leaching (under 1-m soil depth) over China's cropland in 2008 at a 1-km scale. The details of model inputs (e.g., N_{rate} , P+I, Temp, SOC, TN, pH, BD, Clay, and crop type) were described in Text

S1 (with Table S1 and Fig. S1). The estimates were then validated by independent observations of groundwater nitrogen concentration at 31 cropland sites collected by Gu et al. (2013) and Wen et al. (2012). To validate the simulated L_N directly, the observed nitrogen concentrations were simply transferred to a 'diagnostic' L_N by multiplying the rate of infiltrating water (= precipitation – evapotranspiration). Precipitation and evapotranspiration, according to site coordinates, were taken from CMFD and Zeng et al. (2014), respectively. Note that inter-site differences of delay and denitrification loss during groundwater transport were ignored (Zheng and Bennett, 2002; Van Dreht et al., 2003).

To evaluate the advantages of incorporating the nonlinearity into PKU-NLEACH model, we designed four types of sensitivity tests. Test M1 ignored the nonlinear term (i.e. $\Delta LR = 0$) and sets LR as an uniform function (i.e., $LR = \sum (\alpha_k \cdot f_k) + b$). Test M2 also ignored the nonlinear term but set LR as a piecewise function (i.e., $LR_j = \sum (\alpha_{kj} \cdot f_k) + b_j$). Test M3 kept a nonlinear model structure but set both ΔLR and LR^0 as constants (i.e., $LR = \Delta LR \cdot N_{rate} + LR^0$). Test M4 maintained the nonlinear term and set both ΔLR and LR^0 as variables (i.e., $LR_j = \Delta LR_j(f_k) \cdot N_{rate} + LR_j^0(f_k)$, see Equation (1)). We also assessed the differences between the PKU-NLEACH model and the linear models recommended by FAO methodology (M5; de Willigen, 2000; Roy et al., 2003; Liu et al., 2010) and MITERRA-EUROPE (M6; Velthof et al., 2009). In test M5 ($LR = a + b \cdot P / (C \cdot D)$, where P, C, and D represent the precipitation, clay content

and sampling depth, respectively), parameters (i.e., a and b) were re-calculated based on China's dataset; Test M6, $LR = LR_{\max} \cdot f_{lu} \cdot \min(f_{p, f_{SOC}}, f_{D, f_T})$, was applied, where $LR_{\max}$ stands for maximum LRs under different soil types, and f_{lu} , f_p , f_{SOC} , f_D , and f_T stand for reduction factors for land use, SOC, precipitation minus evapotranspiration, air temperature and root depth, respectively (Velthof et al., 2009). The R^2 , RMSE, and BIC were applied to assess their predictive accuracy performance.

We finally applied a relative importance analysis (Zhou et al., 2015) to understand the extent to which factors control the difference in $LR-N_{rate}$ relationships and the spatial variation of LR. The relative importance was defined as the magnitude of the increase in the mean squared errors (MSEs) of PKU-NLEACH model when one of the selected f_k is randomly permuted (Zhou et al., 2015).

3. Results

3.1. Nonlinearity of leaching response to N_{rate}

Evidence from control experiments with more than three N -input levels indicate that the nitrogen leaching response to N_{rate} was quadratic or exponential (Fig. 2c), rather than linear, which is consistent with previous analysis (Hansen and Djurhuus, 1996; Lord and Mitchell, 1998; Simmelsgaard and Djurhuus, 1998; Fernández-Escobar et al., 2004; Di and Cameron, 2007; Sun et al., 2008; Huang et al., 2011; Chen et al., 2014; Xue et al., 2014; Amon-Armah et al., 2015). Fig. 2d further confirms that LR grew significantly along the gradient of N_{rate} . Approximately 74% of ΔLR s and 94% of LR were positive, and the remainders were zero or negative (Fig. S3). A following bootstrap resampling performed on all ΔLR showed that the mean (0.0127) was positive, with 95% confidence intervals (CIs) ranging from 0.004 to 0.022 (Fig. 2d).

Additionally, the magnitude and statistical significance of ΔLR across diverse environmental conditions are shown in Fig. 3. Upland crops dominated crop types with a mean positive ΔLR (mean = 0.0128, $P = 0.013$; Fig. 3a) that was almost identical to the mean value for all site-years. All crop types, with the exception of wheat and upland rotation, had positive ΔLR s ($P < 0.05$; Fig. 3a). Among available environmental and sampling factors, ΔLR s were significantly positive where water input ($P+I$) was >524 mm ($P < 0.01$), mean air temperature was ≤ 25.3 °C ($P = 0.03$), SOC were $\leq 6.6\%$ ($P < 0.001$), soil total nitrogen (TN) was $>0.3\%$ ($P = 0.02$), soil pH was ≤ 6.2 ($P < 0.001$), bulk density was >1.37 g/cm³ ($P < 0.001$), clay content was $>16.8\%$ ($P = 0.005$), or sampling depth was >95 cm ($P < 0.001$) (Fig. 3a, b, c). Yet the symmetrical conditions had ΔLR s no different than zero (Fig. 3b, c and Tables S2 and S3).

3.2. Variability of leaching response to N_{rate}

According to China's field observations, L_N responses to N_{rate} varied by environmental conditions (Fig. 2c and d). The t-tests of paired differences between any two sub-groups indicate that maize had the highest positive mean ΔLR (0.025, $P = 0.02$, Fig. 3a), followed by rotation (0.015), paddy rice (0.012), wheat (0.007) and vegetables (0.006). However, no significant difference was detected at the $P < 0.05$ level among crop types (Fig. 3a and Supplementary Table S2). Site-years with higher temperature, greater $P+I$ and greater sampling depth had mean ΔLR significantly larger ($P < 0.05$) than those with the opposite conditions (Fig. 3b). Among soil attributes, the t-tests (Supplementary Table S3) indicate that mean ΔLR were significantly distinct between two subgroups for SOC, pH, bulk density and clay content ($P < 0.05$, Fig. 3c). The results suggest that these interaction terms (e.g. $pH \times N_{rate}$) should be included as potential explanatory variables in the regression models. The

significant differences of LR among crop types were the one between upland and paddy rice ($P = 0.015$) and the ones between vegetable and all wheat ($P < 0.001$), maize ($P = 0.09$) and rotation ($P < 0.001$; Fig. 3d). The mean LR for upland crops (8.8%) was higher than that for paddy rice (1.9%). Site-years with $P+I$ amount of >360 mm, Temperature of >7.2 °C, sampling depth of <100 cm, SOC of <3.5 g/kg, soil pH of >7.6 , bulk density of >1.28 g/cm³, or clay content of $<41\%$ exhibited higher LR ($P = <0.001-0.016$) than that for their opposite levels (Fig. 3e and f, Tables S4 and S5).

3.3. Model calibration and validation

PKU-NLEACH model with 10 response functions for LR (Table 2) was evaluated with coefficient of determination (R^2), Bayesian Information Criterion (BIC) and root-mean-squared error (RMSE) being 0.84, -407, and 4.0% (Fig. 4a), respectively, indicating that most of the variance of LRs is explained by the model with very low associated bias (Fig. 4a). Model performances for the derived ΔLR ($R^2 = 0.77$, RMSE = $0.02\% \cdot \text{kgN}^{-1} \cdot \text{ha}$) and LR^0 ($R^2 = 0.68$, RMSE = 7.4%) further indicate that PKU-NLEACH model can reasonably reproduce these nonlinear and varying responses (Fig. 4b and c).

Maps of LR and L_N (Fig. 5) (excluding the amount of L^0) due to N fertilizer applications (i.e., synthetic fertilizers, manure, and crop residues) were produced over China's territory by the calibrated PKU-NLEACH model (M4) with uncertainties as described in Text S2. The estimate of nitrogen leaching by PKU-NLEACH model was 878 ± 226 GgN·yr⁻¹ (1 σ), with 684 ± 165 GgN·yr⁻¹ for upland crops and 194 ± 61 GgN·yr⁻¹ for paddy rice. Fig. 5a shows that the LR from the PKU-NLEACH model varies across China. The average LR over the Southern China and south part of Sichuan Basin were ~10% and ~12%, respectively, which are approximately 2–3 times greater than that over North China. The highest LR values ($>20\%$) are found in Lake Dongtinghu Watersheds and Sichuan Basin where most of the cereals are produced, while the lowest LR values ($\approx 0\%$) locate in Northwest China. The spatial distribution of fertilizer-induced L_N (Fig. 5b) was similar to that of the LRs (Fig. 5a), but hotspots of L_N (>20 kgN ha⁻¹) were amplified in North China Plain and Northeast Plain and became more discrete in spatial distributions in the South China and Sichuan Basin (Fig. 5b). The spatial differences of LR are highly consistent with the results of 1st national pollution census program (hereafter NPCP) in China (MOA, 2007; Wang et al., 2014).

To verify the spatial pattern of our result, we assessed the reliability in upscaling through validation using the 'diagnostic' L_N derived from the observed TN concentrations in groundwater beneath cropland (Gu et al., 2013). Fig. 6a demonstrates that the results simulated by PKU-NLEACH model compare favorably with geographic patterns of the observation-based 'diagnostic' L_N ($R^2 = 0.73$, $P < 0.01$), except for few wells sampled in a year when water input or N_{rate} greatly differed from those in 2008. Although this result cannot confirm the reliability in actual magnitude of L_N , it provides additional validation of the predictive capabilities of our models, suggesting that PKU-NLEACH model could be acceptable in capturing the spatial patterns of nitrogen leaching.

3.4. Identification of controlling factors

The regression tree for PKU-NLEACH model shown in Fig. 7 further illustrates that the difference of response functions is primarily regulated by hydroclimatic factors and SOC. For example, the variations in LRs were dominated by N_{rate} at low temperatures and low water input (e.g., 1st terminal node in Fig. 7). Conversely, they were controlled by environmental conditions at high temperature and great water input (e.g., 8th – 10th terminal nodes in Fig. 7). The

Fig. 3. Δ LR and LR by crop types (a, d), hydroclimatic and sampling factors (b, e) and soil properties (c, f). Data are shown as mean $\pm$ SEM (standard error of mean), with number of field experiments noted at base of each bar. Asterisks or letters indicate significant differences from 0 (***P < 0.001, **P < 0.01, *P < 0.05) or between mean Δ LRs and LR for subgroups within each category.

grouping of response functions also reflected the difference of Δ LR under diverse environmental conditions (Table 2). For example, Δ LRs were roughly smaller (mean of $0.001\% \cdot \text{kgN}^{-1} \cdot \text{ha}$) compared to those where the air temperature $>16.6^\circ\text{C}$ (mean of $0.04\% \cdot \text{kgN}^{-1} \cdot \text{ha}$). Relative importance analysis of f_k by PKU-NLEACH model also affirms that the variation of LR is primarily affected by hydroclimatic variability. Air temperature was found to be the most important determinant for both crops (Fig. 3b), which alone accounts for 52% of the variance of LR. Water input and clay content are ranked second and third as determinants controlling LR, explaining 18% and 10% of the variance in LR accordingly.

3.5. Performance comparison for modeling LR and L_N

The differences in predictive accuracy between models with and

without the interaction term $\Delta\text{LR} \cdot N_{\text{rate}}$ or varying coefficients (see Methods) were further analyzed. Performance statistics illustrated that the results from PKU-NLEACH model considering nonlinear and varying responses are superior to the other models over the full modeling domain (Table 3 and Fig. S4). The linear and uniform response model (M1), where R^2 , RMSE, and BIC were 0.19, 9.3 and -17.6 , respectively, was unable to capture the variation in LR (Table 3). When only the varying responses were considered, M2 showed significantly improved performance with a higher R^2 (0.58) and lower RMSE (6.7) and BIC (-131) compared to those of M1. However, this model also had low predictive accuracy ($R^2 = 0.23$ and 0.48) for the observations where N_{rate} was lower than the 10% percentile or greater than the 90% percentile (Fig. S5), which was primarily because the effects of interaction terms were neglected. Similarly, when the varying responses were not incorporated into

Table 2Response functions of PKU-NLEACH Model. Model coefficients are shown as mean $\pm$ STD (standard deviation), with applying domain (Ω_j) of f_k noted for each response function.

No. Response function	Applying domain (Ω_j) ^a
1 LR = $-(0.04 \pm 0.01) \cdot [P+I] + (0.88 \pm 0.07) \cdot pH + (0.01 \pm 0.00) \cdot Temp \cdot N_{rate} + (0.04 \pm 0.01) \cdot BD \cdot N_{rate}$	$f_1 \in [0, 131.7] \cap f_2 \in [0, 16.6] \cap f_6 = \text{Non-Vegetable}$
2 LR = $(0.06 \pm 0.01) \cdot [P+I] + (32.73 \pm 4.89)$	$f_1 \in [131.7, +\infty] \cap f_2 \in [0, 16.6] \cap f_3 \in [0, 0.46] \cap f_6 = \text{Non-Vegetable}$
3 LR = $(0.03 \pm 0.01) \cdot [P+I] + (4.43 \pm 0.47) \cdot TN - (1.53 \pm 0.2) \cdot Clay + (9.41E-04 \pm 0.00) \cdot Temp \cdot N_{rate} + (35.79 \pm 5.36)$	$f_1 \in [131.7, +\infty] \cap f_2 \in [0, 16.6] \cap f_3 \in [0.46, +\infty] \cap f_6 = \text{Vegetable}$
4 LR = $(-1.74 \pm 0.35) \cdot TN + (-1.78 \pm 0.4) \cdot pH + (4.19E-03 \pm 0.00) \cdot BD \cdot N_{rate} + (16.13 \pm 3.14)$	$f_1 \in [131.7, +\infty] \cap f_2 \in [0, 16.6] \cap f_3 \in [0.46, +\infty] \cap f_6 = \text{Non-Vegetable}$
5 LR = $(3.4 \pm 0.81) \cdot pH + (0.05 \pm 0.01) \cdot BD \cdot N_{rate} + (8.02 \pm 3.79)$	$f_2 \in [16.6, +\infty] \cap f_4 \in [0, 3.5] \cap f_6 = \text{Non-Vegetable}$
6 LR = $(0.02 \pm 0.00) \cdot [P+I] + (10.39 \pm 1.69) \cdot pH + (7.68E-04 \pm 0.00) \cdot Temp \cdot N_{rate} + (85.22 \pm 15.51)$	$f_2 \in [16.6, +\infty] \cap f_4 \in [3.5, 6.8] \cap f_6 = \text{Non-Vegetable}$
7 LR = $(-6.98E-05 \pm 0.00) \cdot [P+I] \cdot N + (0.02 \pm 0.01) \cdot BD \cdot N_{rate} + (2.33 \pm 1.07)$	$f_1 \in [0, 250] \cap f_2 \in [16.59, +\infty] \cap f_4 \in [3.5, 6.8] \cap f_6 = \text{Non-Vegetable}$
8 LR = $(0.02 \pm 0.00) \cdot [P+I] + (22.5 \pm 1.75)$	$f_1 \in [250, +\infty] \cap f_2 \in [16.6, 25.3] \cap f_4 \in [6.8, +\infty] \cap f_5 \in [0, 6.5] \cap f_6 = \text{Non-Vegetable}$
9 LR = $(0.02 \pm 0.01) \cdot [P+I] - (1.15 \pm 0.30) \cdot Clay + (0.02 \pm 0.00) \cdot SOC \cdot N_{rate} + (66.6 \pm 14.34)$	$f_1 \in [250, +\infty] \cap f_2 \in [25.3, +\infty] \cap f_4 \in [6.8, +\infty] \cap f_5 \in [0, 6.5] \cap f_6 = \text{Non-Vegetable}$
10 LR = $(0.18 \pm 0.02) \cdot SOC - (0.10 \pm 0.01) \cdot Clay + (1.09E-04 \pm 0.00) \cdot Depth \cdot N_{rate} + (1.77E-03 \pm 0.00) \cdot pH \cdot N_{rate}$	$f_1 \in [250, +\infty] \cap f_2 \in [16.6, +\infty] \cap f_4 \in [6.8, +\infty] \cap f_5 \in [6.5, +\infty] \cap f_6 = \text{Non-Vegetable}$

^a f_1 : P+I, f_2 : Temp, f_3 : TN, f_4 : SOC, f_5 : pH. **Fig. 4.** Calibration of LR (a), ΔLR (b), and LR^0 (c) for China's cropland. The full dataset is illustrated as red open circles, while the estimates with disagreement in the magnitude of LR, ΔLR , and LR^0 between simulated and observed results are represented as solid and open blue circles, respectively. The slope, R^2 , BIC, and the root-mean-squared error (RMSE) are indicated in the insets at the bottom-right of each panel. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) **Fig. 5.** 1-km spatial patterns of nitrogen leaching in China. (a) LRs, (b) nitrogen leaching (L1), (c) difference between L1 and M2, and (d) difference between L1 and M3.

Fig. 6. Model comparison in capturing the spatial variation of the observation-based 'diagnostic' L_N . (a) PKU-NEACH model with varying ΔLR and LR^0 : $LR_j = \Delta LR_j(x_k) \cdot N_{rate} + LR_j^0(x_k)$, $\forall j$. (b) M2 model without $x_k \cdot N_{rate}$: $LR_j = LR_j^0(x_k)$, $\forall j$. (c) M3 model: $LR = \Delta LR(x_k) \cdot N_{rate} + LR^0(x_k)$, where the $\Delta LR(x_k)$, $LR^0(x_k)$, and j are described in Section Methods.

Fig. 7. Regression tree of LR (a) and relative importance of f_k (b). The numbers below abbreviations indicate their splitting values of the abbreviations. The symbols " $\leq$ " and " $>$ " represent the splitting rules of the abbreviations. The numbers within circles indicate the number of samples in individual terminal nodes. The numbers, in *italic*, indicate the serial number of terminal nodes. MSE is abbreviation for mean squared errors, and the numbers in Panel b indicate the proportion of variation explained by controlling factors. The numbers within panel b indicate the proportion of variance explained by the corresponding f_k .

Table 3

Model performances of the simulation of nitrogen leaching rate for China's cropland. L_N , $\Delta LR(f_k)$, $LR^0(f_k)$, and L^0 are described in Section Methods.

Model		R ²	RMSE	Factor	BIC	L _N –L ⁰ , GgN yr ^{–1}	
						Upland	Paddy
Linear response (n = 338)							
M1	LR = LR ⁰ (f _k)	0.19	9.3%	5	–17.6	2052	397
M2	LR _j = LR ⁰ _j (f _k), ∀j	0.44	10.3%	24	158	870	154
M5	FAO Methodology	0.03	10.2%	3	38.4	1882	466
M6	MITERRA-EUROPE model	0.01	42.9%	5	1014	5382	1386
Nonlinear response (n = 338)							
M3	LR = ΔLR(f _k)•N _{rate} + LR ⁰ (f _k)	0.26	9.0%	7	–33.5	2130	494
M4	LR _j =ΔLR _j (f _k)•N _{rate} + LR ⁰ _j (f _k), ∀j	0.84	4.0%	35	–407	685	194

LR models, the nonlinear but uniform response model (M3 in Table 3) performed slightly better than Model 1 ($R^2 = 0.26$, RMSE = 9.0, BIC = -33.5), yet this model was unable to characterize the local variations in the $LR-N_{rate}$ relationships. To demonstrate the advantage of the model used in this analysis (M4 in Table 3), we also compared its results to the models used in MITERRA-EUROPE (M5; Velthof et al., 2009) and in the FAO Assessment of Soil Nutrient Balance (M6; Roy et al., 2003). Although these models yielded acceptable R^2 (0.67) values in European cropland (de Willigen, 2000), their performance declined greatly in cases where the model coefficients had been re-calibrated based on observations in China, with R^2 being 0.01–0.03 (Table 3). These results imply that these forms of response functions would be inappropriate choices for estimating LRs for China's cropland. Hence, the

superiority of predictive performance indicates that the models utilizing nonlinear and varying responses (e.g. M4) would be better than those utilizing linear or uniform functions in simulation of the LR distribution.

Model comparison was further undertaken in predicting L_N . Compared to our estimate (M4), Model 2 underestimated the nitrogen leaching from paddy rice (154 ± 76 GgN·yr⁻¹; Table 3). More surprisingly, other models severely overestimated the nitrogen leaching from both crop types (1882–5382 [upland] and 397–1386 [rice] GgN·yr⁻¹). However, the models without the interaction terms $\Delta LR \cdot N_{rate}$ or varying coefficients were unable to capture the spatial variations of the observation-based 'diagnostic' LR ($R^2 = 0.26$ and 0.04 for Model 2 and 3, respectively; Fig. 6b and c). The absolute difference (AD) in spatial pattern between our

estimates (L_1) and those of M2 (L_2) and M3 (L_3) were also assessed and defined as $AD = L_1 - L_2$ or 3. They had patterns of nitrogen leaching in China that are spatially very different compared to the map derived from PKU-NLEACH model (Fig. 5c and d). Contrary to M2, our estimates were approximately 10 kgN ha^{-1} lower in most of the Northeast Plain, but approximately 15 kgN ha^{-1} higher in the Sichuan Basin and south China (Fig. 5c). These findings indicate that, without the interaction term $\Delta LR \cdot N_{rate}$, the model could not capture the impact of N_{rate} on nitrogen leaching, particularly for the regions exhibiting lower and upper percentiles of LR. The difference between the estimates used in this analysis and those used in M3 were amplified in most major cropping zones in China. In particular, overestimations were significant in the North China Plain, Guanzhong Plain, Jiangnan Plain and Lake Dongtinghu Basin (Fig. 5d). This uniform model, therefore, enhanced the positive effects of N_{rate} but lowered the negative effects of f_k on LRs. However, nitrogen leaching in the uniform model was relatively closer to the estimates used in this analysis in low-value regions (Fig. 5d), which experienced less application of nitrogen fertilizer than other croplands throughout China.

4. Discussion and conclusions

Positive mean ΔLR s indicate that nitrogen leaching tends to increase in N leaching in response to an increase in N_{rate} at a rate significantly greater than linear. This result is also consistent with those from most field experiments with five or more N-input levels (Amon-Armah et al., 2015; Blicher-Mathiesen et al., 2014), suggesting that the current constant LR recommended by the latest IPCC guidelines, FAO methodology, and MITERRA-EUROPE model is unsuitable for estimating N leaching for low or high N_{rate} .

The variations of LR shed light on how f_k influences nitrogen fate and transport in agricultural soils at the national scale. Transport factors (i.e., P+I, bulk density, clay content and sampling depth) were positively or inversely related to LR (Fig. 3). Generally, greater water input results in higher LR, particularly when soils become over-saturated (Nolan and Hitt, 2006). As the bulk density of any given agricultural soils increases, soil porosity decreases (Zheng and Bennett, 2002). Although L_N is independent of porosity, the velocity of N leaching (V) is inversely related to porosity (n), given the same flow rate of infiltrating water (Q) (i.e., $V = Q/(A \cdot n)$ where A is cross-sectional area; Zheng and Bennett, 2002). This implies that larger bulk density results in higher nitrogen leaching rate. However, the structure of porosity distribution, not just the value of total porosity, also affects the leaching rate. Thus, it is important to characterize both porosity value and porosity distribution in quantifying the nitrogen leaching rates in future. High clay content, however, decreases the potential of nitrogen leaching, mainly because of its restriction of water and nitrogen fluxes leaching into root zone and groundwater and the increase of the conversion of nitrate to N_2 or N_2O (Bouwman et al., 2002; Gu et al., 2013; Perlman et al., 2014).

Reaction factors with positive signs included mean air temperature, soil pH and TN (Fig. 3). Mean air temperature regulates LR probably by enhancing the reaction rate and vertical transport velocity of reactive nitrogen in soil that promote higher LR. Although air temperature enhances denitrification and NH_3 volatilization, it also stimulates the hydrolysis of fertilizers (e.g. urea) and the vertical movement of nitrogen (McInnes et al., 1986; Reynolds and Wolf, 1987). The increase of soil pH decreases denitrification (Perlman et al., 2014), eventually strengthening the potential of nitrogen leaching. On the contrary, SOC declines the sensitivity of LR to N_{rate} , yet these results do not corroborate the results of previous control experiments at specific sites (Van Drecht et al., 2003; Velthof et al., 2009), which show a positive relationship

between SOC and nitrogen leaching. Possible interpretation is that the SOC used in PKU-NLEACH model are the average values within a whole measurement period, whereas those are variant during experiment period and thus have a broader range.

These findings well agree with most previous analysis. MITERRA-EUROPE model indicated that LR tended to increase with precipitation and to decrease with clay content, SOC, mean air temperature and sampling depth (Velthof et al., 2009), which is in line with ours except mean air temperature. Yet it did not reflect the degree of nonlinearity in their model. Our analysis explicitly tests the changes in LR for different crops with multiple N input levels including zero-N control, arriving at the same general conclusion of the a faster than linear L_N increase but with a quantitative and higher confidence outcome. NPCP provided a collection of 25 regionally-averaged LR based on nationwide observations in 96 upland soils before 2007 (MOA, 2007). This dataset reflects the responses of regionally-averaged LR to the diverse environmental conditions (i.e., TN, SOC and clay content). Such responses seem to imply that LR is positively related to soil TN but negatively related to clay content and SOC (MOA, 2007), which are also in good agreement for same ranges of f_k with ours. FAO methodology provided a qualitative response function between LR and f_k (i.e., precipitation, air temperature, clay content and root depth; de Willigen, 2000; Roy et al., 2003; Liu et al., 2010) but with the relationships of LR to f_k coinciding with ours. One possible explanation is that FAO methodology overestimated the LR from croplands compared to observations and our model (de Willigen, 2000).

Our studies also suggest that the model that considers the nonlinearity and variability of leaching response to N_{rate} is more accurate and reliable for estimating large-scale LRs than other LR models. For example, our estimate of fertilizer-induced L_N in 2008 ($878 \pm 226 \text{ GgN} \cdot \text{yr}^{-1}$) is close to the result of mass-balance-based CHANS model (total: $\sim 1800 \text{ GgN} \cdot \text{yr}^{-1}$; Gu et al., 2013) minus base N leaching ($1068 \pm 432 \text{ GgN} \cdot \text{yr}^{-1} [= L^0 \times \text{cropland area}]$, where regionally-averaged L^0 and their uncertainty ranges were taken from NPCP [MOA, 2007]). Second, PKU-NLEACH model in particular conditions can separately function as an updated tool for other countries or regions that are subject to interpolation.

Nonetheless, there is no sufficient evidence in support of using the calibrated PKU-NLEACH model for regions whose f_k are not captured by our dataset. Most field experiments of nitrogen leaching in China are within temperate or sub-tropical zones with moderate SOC levels, which are different in Southeast Asia, Mid-U.S. and East Europe. PKU-NLEACH model, therefore, would need to be re-calibrated using more observations from these countries or regions to avoid potential extrapolation.

Another significant drawback in this model is the lack of environmental conditions reflecting crop type, fertilizer type and method (Zhou et al., 2014; Xue et al., 2014), the pulse effects of flooding irrigation (Wang et al., 2012; Poch-Massegú et al., 2014) or other cultivation practices (e.g., tillage; Yagioka et al., 2015), because most of them were unavailable in field experiments or for national simulation. For example, the cropland in North China Plain has experienced intensive irrigation primarily for growing season, which leads to a significant increase of LR and L in previous process-based simulation (Li et al., 2014) compared to our estimates using annual average irrigation rate for whole observation period. Additionally, with a highly temporal resolution of response curves for nitrogen leaching to water input and fertilization, the shape of the LR determinations would be updated with high confidence for the irrigated cropland. According to model inference, the estimated LRs in this analysis can only reflect nitrogen leaching induced by inputs of new nitrogen, not residual nitrogen in agricultural soils (Novoa and Tejeda, 2006). Therefore, base N leaching due to residual nitrogen need to be rationally estimated in future studies.

Overall, this study is the first time to comprehensively test and quantify the nonlinearity and variability of leaching response to N_{rate} for China's cropland. The dataset used for model calibration is limited, yet the associated empirical model developed for that purpose better captures the observed nonlinearity and variability, compared to other linear or uniform models that overstate the fertilizer-induced nitrogen leaching in China. The spatial variability of LR strongly depends on local air temperature, followed by water input and clay content. Therefore, we strongly suggest that future policies to reduce N leaching from cropland need to consider environmental variability rather than solely attempt to reduce nitrogen fertilizer applications.

Acknowledgments

Funding for this study was provided by the National Natural Science Foundation of China (Grants 41201077, 71103186, 41561134016), the Research Fund for the Doctoral Program of Higher Education of China (Grant 20120001120129), 111 Project (No. B14001). We appreciated HWSD and CMFD teams for providing soil and climate datasets, and authors who measured, analyzed, and published data of nitrogen leaching used here.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.01.010>.

References

- Amon-Armah, F., Yiridoe, E.K., Jamieson, R., Hebb, D., 2015. Comparison of crop yield and pollution production response to nitrogen fertilization models, accounting for crop rotation effect. *Agroecol. Sust. Food* 39, 245–275.
- Blicher-Mathiesen, G., Andersen, H.E., Larsen, S.E., 2014. Reprint of "Nitrogen field balances and suction cup-measured n leaching in Danish catchments". *Agric. Ecosyst. Environ.* 198, 36–43.
- Bouwman, A., Beusen, A., Griffioen, J., Van Groenigen, J., Hefting, M., Oenema, O., Van Puijenbroek, P., Seitzinger, S., Slomp, C., Stehfest, E., 2013. Global trends and uncertainties in terrestrial denitrification and N_2O emissions. *Philos. Trans. R. Soc. B* 368, 20130112.
- Bouwman, A., Boumans, L., Batjes, N., 2002. Modeling global annual N_2O and NO emissions from fertilized fields. *Glob. Biogeochem. Cycles* 16, 281–289.
- Breiman, L., Friedman, J., Stone, C.J., Olshen, R.A., 1984. *Classification and Regression Trees*. CRC Press.
- Chen, X., Cui, Z., Fan, M., Vitousek, P., Zhao, M., Ma, W., Wang, Z., Zhang, W., Yan, X., Yang, J., 2014. Producing more grain with lower environmental costs. *Nature* 514, 486–489.
- Chen, Y.Y., Yang, K., He, J., Qin, J., Shi, J.C., Du, J.Y., He, Q., 2011. Improving land surface temperature modeling for dry land of China. *J. Geophys. Res.* 116 (D20).
- de Willigen, P., 2000. An analysis of the calculation of leaching and denitrification losses as practised in the NUTMON approach. *Rapport Plant Res. Int.* 18, 20.
- Di, H.J., Cameron, K.C., 2007. Nitrate leaching losses and pasture yields as affected by different rates of animal urine nitrogen returns and application of a nitrification inhibitor - a lysimeter study. *Nutr. Cycl. Agroecosys* 79, 281–290.
- Fernandez-Escobar, R., Benlloch, M., Herrera, E., Garcia-Novelo, J.M., 2004. Effect of traditional and slow-release N fertilizers on growth of olive nursery plants and N losses by leaching. *Sci. Hortic. Amst.* 101, 39–49.
- Fewtrell, L., 2004. Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion. *Environ. Health Perspect.* 112, 1371–1374.
- Gu, B., Ge, Y., Chang, S.X., Luo, W., Chang, J., 2013. Nitrate in groundwater of China: sources and driving forces. *Glob. Environ. Change* 23, 1112–1121.
- Hansen, E.M., Djurhuus, J., 1996. Nitrate leaching as affected by long-term N fertilization on a coarse sand. *Soil Use Manag.* 12, 199–204.
- Huang, M.X., Liang, T., Ou-Yang, Z., Wang, L.Q., Zhang, C.S., Zhou, C.H., 2011. Leaching losses of nitrate nitrogen and dissolved organic nitrogen from a yearly two crops system, wheat-maize, under monsoon situations. *Nutr. Cycl. Agroecosys* 91, 77–89.
- Intergovernmental Panel On Climate Change, 2006. *IPCC Guidelines for National Greenhouse Gas Inventories*. Institute for Global Environmental Strategies, Japan.
- Jahangir, M.M.R., Khalil, M.I., Johnston, P., Cardenas, L.M., Hatch, D.J., Butler, M., Barrett, M., O'flaherty, V., Richards, K.G., 2012. Denitrification potential in subsoils: a mechanism to reduce nitrate leaching to groundwater. *Agric. Ecosyst. Environ.* 147, 13–23.
- Keuskamp, J.A., van Drecht, G., Bouwman, A.F., 2012. European-scale modelling of groundwater denitrification and associated N_2O production. *Environ. Pollut.* 165, 67–76.
- Kramer, S.B., Reganold, J.P., Glover, J.D., Bohannan, B.J.M., Mooney, H.A., 2006. Reduced nitrate leaching and enhanced denitrifier activity and efficiency in organically fertilized soils. *Proc. Natl. Acad. Sci.* 103, 4522–4527.
- Li, C., Farahbakhshazad, N., Jaynes, D.B., Dinnes, D.L., Salas, W., McLaughlin, D., 2006. Modeling nitrate leaching with a biogeochemical model modified based on observations in a row-crop field in Iowa. *Ecol. Model.* 196, 116–130.
- Li, H., Wang, L.G., Qiu, J.J., Li, C.S., Gao, M.F., Gao, C.Y., 2014. Calibration of DNDC model for nitrate leaching from an intensively cultivated region of Northern China. *Geoderma* 223, 108–118.
- Liu, C.Q., Li, S.L., Lang, Y.C., Xiao, H.Y., 2006. Using $\delta^{15}N$ - and $\delta^{18}O$ -values to identify nitrate sources in karst ground water, Guiyang, Southwest China. *Environ. Sci. Technol.* 40, 6928–6933.
- Liu, J., You, L., Amini, M., Obersteiner, M., Herrero, M., Zehnder, A.J., Yang, H., 2010. A high-resolution assessment on global nitrogen flows in cropland. *P. Natl. Acad. Sci.* 107, 8035–8040.
- Lord, E.I., Mitchell, R.D.J., 1998. Effect of nitrogen inputs to cereals on nitrate leaching from sandy soils. *Soil Use Manag.* 14, 78–83.
- McInnes, K., Ferguson, R., Kissel, D., Kanemasu, E., 1986. Ammonia loss from applications of urea-ammonium nitrate solution to straw residue. *Soil Sci. Soc. Am. J.* 50, 969–974.
- Ministry of Agriculture, 2007. *Fertilizer Lost Coefficient Manual – the First National Pollution Census Program*. China Agricultural Press, Beijing.
- Nolan, B.T., Hitt, K.J., 2006. Vulnerability of shallow groundwater and drinking-water wells to nitrate in the United States. *Environ. Sci. Technol.* 40, 7834–7840.
- Novoa, R.S., Tejeda, H.R., 2006. Evaluation of the N_2O emissions from N in plant residues as affected by environmental and management factors. *Nutr. Cycl. Agroecosys* 75, 29–46.
- Perlman, J., Hijmans, R.J., Horwath, W.R., 2014. A metamodeling approach to estimate global N_2O emissions from agricultural soils. *Glob. Ecol. Biogeogr.* 23, 912–924.
- Poch-Masagüé, R., Jiménez-Martínez, J., Wallis, K., de Cartagena, F.R., Candela, L., 2014. Irrigation return flow and nitrate leaching under different crops and irrigation methods in Western Mediterranean weather conditions. *Agric. Water Manag.* 134, 1–13.
- Qiu, J., 2011. China to spend billions cleaning up groundwater. *Science* 334, 745–745.
- Reynolds, C., Wolf, D., 1987. Effect of soil moisture and air relative humidity on ammonia volatilization from surface-applied urea. *Soil Sci.* 143, 144–152.
- Riley, W., Ortiz-Monasterio, I., Matson, P., 2001. Nitrogen leaching and soil nitrate, nitrite, and ammonium levels under irrigated wheat in Northern Mexico. *Nutr. Cycl. Agroecosys* 61, 223–236.
- Rodríguez-Lado, L., Sun, G., Berg, M., Zhang, Q., Xue, H., Zheng, Q., Johnson, C.A., 2013. Groundwater arsenic contamination throughout China. *Science* 341, 866–868.
- Rosset, S., Zhu, J., 2007. Piecewise linear regularized solution paths. *Ann. Stat.* 35, 1012–1030.
- Roy, R.N., Misra, R.V., Lesschen, J.P., Smaling, E., 2003. *Assessment of Soil Nutrient Balance: Approaches and Methodologies*. Food and Agricultural Organization of the United Nations, Rome.
- Simmelsgaard, S.E., Djurhuus, J., 1998. An empirical model for estimating nitrate leaching as affected by crop type and the long-term N fertilizer rate. *Soil Use Manag.* 14, 37–43.
- Sun, B., Chen, D.L., Li, Y., Wang, X.X., 2008. Nitrogen leaching in an upland cropping system on an acid soil in subtropical China: lysimeter measurements and simulation. *Nutr. Cycl. Agroecosys* 81, 291–303.
- Van Drecht, G., Bouwman, A., Knoop, J., Beusen, A., Meinardi, C., 2003. Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater, and surface water. *Glob. Biogeochem. Cycles* 17.
- Velthof, G., Oudendag, D., Witzke, H., Asman, W., Klimont, Z., Oenema, O., 2009. Integrated assessment of nitrogen losses from agriculture in EU-27 using MITERRA-EUROPE. *J. Environ. Qual.* 38, 402–417.
- Wang, X.L., Feng, A.P., Wang, Q., Wu, C.Q., Liu, Z., Ma, Z.S., Wei, X.F., 2014. Spatial variability of the nutrient balance and related NPSP risk analysis for agroecosystems in China in 2010. *Agric. Ecosyst. Environ.* 193, 42–52.
- Wang, X., et al., 2012. Effects of irrigation mode and N application rate on cotton field fertilizer N use efficiency and N losses (in Chinese). *J. Appl. Ecol.* 2751–2758.
- Wen, D.G., et al., 2012. Groundwater quality and contamination assessment in the main plains of Eastern China. *J. China Univ. Geosci.* 37, 220–228.
- World Health Organization, 2011. *Guidelines for Drinking-water Quality*. WHO Press, Geneva.
- Wick, K., Heumesser, C., Schmid, E., 2012. Groundwater nitrate contamination: factors and indicators. *J. Environ. Manag.* 111, 178–186.
- Xue, L.H., Yu, Y.L., Yang, L.Z., 2014. Maintaining yields and reducing nitrogen loss in rice-wheat rotation system in Taihu Lake region with proper fertilizer management. *Environ. Res. Lett.* 9, 115010.
- Yagioka, A., Komatsuzaki, M., Kaneko, N., Ueno, H., 2015. Effect of no-tillage with weed cover mulching versus conventional tillage on global warming potential and nitrate leaching. *Agric. Ecosyst. Environ.* 200, 42–53.
- Zeng, Z.Z., Wang, T., Zhou, F., Ciais, P., Mao, J.F., Shi, X.Y., Piao, S.L., 2014. A worldwide analysis of spatiotemporal changes in water balance-based evapotranspiration from 1982 to 2009. *J. Geophys. Res.* 119, 1186–1202.

- Zheng, C., Bennett, G.D., 2002. *Applied Contaminant Transport Modeling*, second ed. John Wiley Sons, New York.
- Zheng, C.M., Liu, J., 2013. China's "Love Canal" moment? *Science* 340, 810.
- Zhou, F., Shang, Z.Y., Zeng, Z.Z., Piao, S.L., Ciais, P., Raymond, P.A., Wang, X.H., Wang, R., Chen, M.P., Yang, C.L., Tao, S., Zhao, Y., Meng, Q., Gao, S.S., Mao, Q., 2015. New model for capturing the variations of fertilizer-induced emission factors of N₂O. *Global Biogeochem. Cycles* 29, 885–897.
- Zhou, M.H., Zhu, B., Bruggemann, N., Bergmann, J., Wang, Y.Q., Butterbach-Bahl, K., 2014. N₂O and CH₄ emissions, and NO₃ leaching on a crop-yield basis from a subtropical rain-fed wheat-maize rotation in response to different types of nitrogen fertilizer. *Ecosystems* 17, 286–301.