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*Supplement of*

## **Effects of fertilization and stand age on N<sub>2</sub>O and NO emissions from tea plantations: a site-scale study in a subtropical region using a modified biogeochemical model**

**Wei Zhang et al.**

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## Supplementary materials

Table S1 Measured soil properties at 0–15 cm depth of tea plantations transplanted from 2008 (T08) and 2012 (T12).

Cropland	pH (H <sub>2</sub> O)	BD (g cm <sup>-3</sup> )	SOC (g kg <sup>-1</sup> )	TN (g kg <sup>-1</sup> )	Clay (< 0.002 mm; %)	Silt (0.002–0.02 mm; %)	Sand (0.02–2 mm; %)
T08	5.0 (0.1)	1.25 (0.03)	13.6 (0.2)	1.51 (0.10)	12.7 (0.1)	39.3 (0.5)	48.0 (0.6)
T12	5.4 (0.1)	1.21 (0.05)	12.9 (0.2)	1.38 (0.12)	12.2 (0.2)	39.6 (0.5)	48.2 (0.5)

Table S2 Details of the field management practices for tea plantation with observations for model validation.

Date (yyyy-mm-dd)	Management practices <sup>a</sup>
2008-03-10	Transplanting of tea for T6
2012-03-10	Transplanting of tea for T2
2012-10-08	Fertilization (band placement, 10 cm depth; urea : 150 kg N ha <sup>-1</sup> for T6-UN; organic fertilizer : 150 kg N ha <sup>-1</sup> for T6-OM)
2013-10-28	Irrigation (30 mm)
2013-02-18	Fertilization (band placement, 10 cm depth; urea : 300 kg N ha <sup>-1</sup> for T6-UN; organic fertilizer : 300 kg N ha <sup>-1</sup> for T6-OM)
2013-02-23	Irrigation (60 mm)
2013-03-09	Irrigation (30 mm)
2013-04-15	Irrigation (30 mm)
2013-10-06	Fertilization (band placement, 10 cm depth; urea : 150 kg N ha <sup>-1</sup> for T6-UN and T2-UN; organic fertilizer : 150 kg N ha <sup>-1</sup> for T6-OM and T2-OM)
2014-03-01	Fertilization (band placement, 10 cm depth; urea : 300 kg N ha <sup>-1</sup> for T6-UN and T2-UN; organic fertilizer : 300 kg N ha <sup>-1</sup> for T6-OM and T2-OM)
2014-03-26	Irrigation (60 mm)
2014-04-09	Irrigation (30 mm)
2014-05-29	Irrigation (15 mm)
2014-06-10	Irrigation (30 mm)

<sup>a</sup> For the codes of treatments, refer to the text in section 2.2. The above detailed managements were referred to Yao et al., (2015, 2018).

## References

- Yao, Z., Wei, Y., Liu, C., Zheng, X., and Xie, B.: Organically fertilized tea plantation stimulates N<sub>2</sub>O emissions and lowers NO fluxes in subtropical China, *Biogeosciences*, 12, 5915–5928, 2015.
- Yao, Z., Zheng, X., Liu, C., Wang, R., and Butterbach-Bahl, K.: Stand age amplifies greenhouse gas and NO releases following conversion of rice paddy to tea plantations in subtropical China, *Agr. Forest. Meteorol.*, 248, 386–396, 2018.

Table S3 The scientific process related to soil pH dynamics in the original CNMM-DNDC.

**Urea hydrolysis**

$$K_w = K_{w0}f_w \quad (1)$$

$$f_w = 0.1945e^{0.0645T} \quad (2)$$

$$[H^+]_{urea} = 10^{-sph} + 0.005Urea \quad (3)$$

$$sph^* = -\lg([H^+]_{urea}) \text{ (for } 3.0 \leq sph^* \leq 11.0) \quad (4)$$

**Soil buffering effect for urea hydrolysis**

$$sph^{**} = sph^* - 0.06(sph^* - sph) \quad (5)$$

**Manure application**

$$\Delta sph1 = 0.5f_{depth}Fert_{manure}/Fert_{total} \quad (6)$$

$$f_{depth} = dpf_k / \sum_{k=1}^L dpf_k \quad (7)$$

$$dpf_k = 1.0 - \frac{Fert_{depth} - \overline{Dep}}{(Fert_{depth} - \overline{Dep}) + e^{(4.25 - 0.1(Fert_{depth} - \overline{Dep}))}} Dep \quad (8)$$

$$\overline{Dep} = 0.5(Depth_{k+1} + Depth_k) \quad (9)$$

$$Dep = Depth_{k+1} - Depth_k \quad (10)$$

$$sph' = sph^{**} + \Delta sph1 \text{ (for } sph^{**} \leq 7.0, \text{ and } sph^{**} \leq sph' \leq 7.0) \quad (11)$$

$$sph' = sph^{**} - \Delta sph1 \text{ (for } sph^{**} > 7.0, \text{ and } 7.0 \leq sph' \leq sph^{**})$$

$K_w$ ,  $K_{w0}$ ,  $f_w$ ,  $T$ ,  $sph$  and  $sph'$  refers to Section 2.2 of the text.  $sph^*$  and  $sph^{**}$  denote the soil pH after the modification by urea hydrolysis and soil buffering effect.  $[H^+]_{urea}$  is the hydrogen ion concentration modified by urea hydrolysis.  $Fert_{manure}$ ,  $Fert_{total}$  and  $Fert_{depth}$  are the amounts of applied manure and total fertilizers, and the depth of fertilization.  $Depth_k$  is the soil depth of the  $k$ th layer.  $L$  is the soil layer number for the depth of fertilization.

Table S4 Equations for the statistical criteria.

$$IA = 1 - \frac{\sum_{k=1}^n (s_k - o_k)^2}{\sum_{k=1}^n (|s_k - \bar{o}| + |o_k - \bar{o}|)^2} \quad (1)$$

$$NSI = 1 - \frac{\sum_{k=1}^n (o_k - s_k)^2}{\sum_{k=1}^n (o_k - \bar{o})^2} \quad (2)$$

$$R^2 = 1 - \frac{\sum_{k=1}^n (o_k - \hat{o}_k)^2}{\sum_{k=1}^n (o_k - \bar{o})^2} \quad (3)$$

$$MRB = \frac{\sum_{k=1}^n s_k / n}{\sum_{k=1}^n o_k / n} - 1 \quad (4)$$

$$AIC = \ln\left(\sum_{k=1}^n (o_k - \hat{o}_k)/n\right) + 2(K+1)/n \quad (5)$$

In Eqs. S1-4,  $k$  and  $n$  ( $k = 1, 2, \dots, n$ ) denote the  $k$ th pair and the total pair number of the values, respectively,  $\bar{o}$  represents the mean of the observations ( $o$ ),  $\hat{o}$  is the predictions using the ZIR, and  $K$  denotes the number of independent variable.

Table S5 The observed (Obs) and simulated nitrous oxide (N<sub>2</sub>O) and nitric oxide (NO) emissions from tea plantations by original (Ori) and modified (Mod) models. The simulated N<sub>2</sub>O and NO emission from nitrification (Mod-Ni) and denitrification (Mod-De) by the modified model.

Treatment	N <sub>2</sub> O					NO				
	Obs <sup>a</sup>	Ori	Mod	Mod-Ni	Mod-De	Obs	Ori	Mod	Mod-Ni	Mod-De
T08-UN(2013)	21.1 (2.5)	22.4	23.5	8.7	14.8	19.4 (0.3)	18.8	19.3	8.0	11.3
T08-UN(2014)	14.4 (2.6)	25.3	18.5	6.7	11.8	18.3 (0.5)	20.1	15.7	6.4	9.3
T12-UN(2014)	15.4 (0.4)	18.2	17.2	6.1	11.1	13.1 (0.7)	12.6	11.9	4.7	7.2
T08-OM(2013)	32.7 (0.7)	29.9	29.2	10.7	18.5	17.0 (0.4)	15.6	15.2	6.2	9.0
T08-OM(2014)	28.1 (1.3)	31.4	27.6	10.0	17.6	12.3 (1.1)	17.2	15.6	6.4	9.2
T12-OM(2014)	20.7 (0.9)	24.9	23.4	8.3	15.1	9.4 (0.5)	10.0	9.5	3.9	5.6
T08-NN(2013)	6.2 (0.3)	4.0	3.0	1.1	1.9	2.8 (0.5)	3.6	2.7	1.1	1.6
T08-NN(2014)	1.8 (0.1)	1.6	1.3	0.4	0.9	0.3 (0.1)	1.6	1.3	0.5	0.8
T12-NN(2014)	4.3 (0.6)	2.5	2.6	0.8	1.8	0.4 (0.1)	2.2	2.2	0.8	1.4

<sup>a</sup>The value in the parentheses indicated the standard error of four spatial replicates in field observation.

Table S6 Observed (Obs) and simulated urea replacement effects by the original (Ori) and modified (Mod) models on the nitrous oxide (N<sub>2</sub>O) and nitric oxide (NO) emissions.

	N <sub>2</sub> O				NO							
	$E_{ur}^a$ (%)			$\varepsilon_{ur}^a$ (%)	MRB  <sup>b</sup>		$E_{ur}^a$ (%)			$\varepsilon_{ur}^a$ (%)	MRB  <sup>b</sup>	
	Obs	Ori	Mod		Ori	Mod	Obs	Ori	Mod		Ori	Mod
T08(2013)	55	33	24	94	39	56	-12	-17	-21	77	38	72
T08(2014)	95	24	49	106	75	48	-33	-14	-1	60	56	98
T12(2014)	35	37	36	92	7	4	-28	-21	-20	83	27	29
average	62	31	36	97	40	36	-25	-17	-14	73	40	66

<sup>a</sup>The calculation of  $E_{ur}$  and  $\varepsilon_{ur}$  are referred to Eqs. 18–19 in the text. <sup>b</sup>MRB is model relative bias and is referred to Table S3.

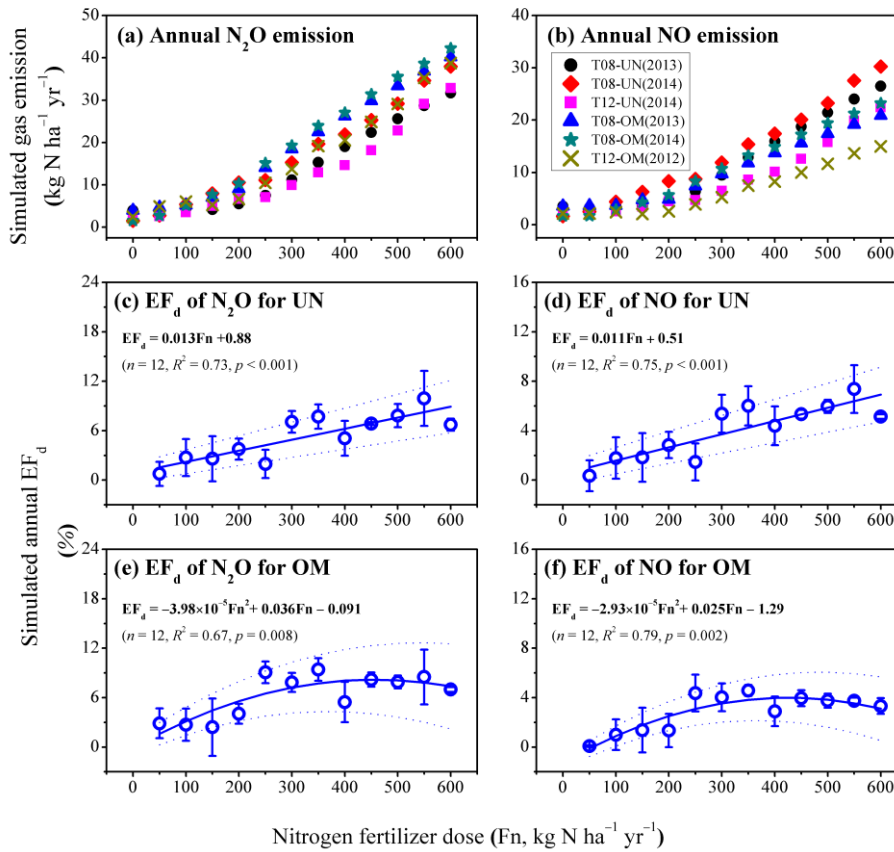
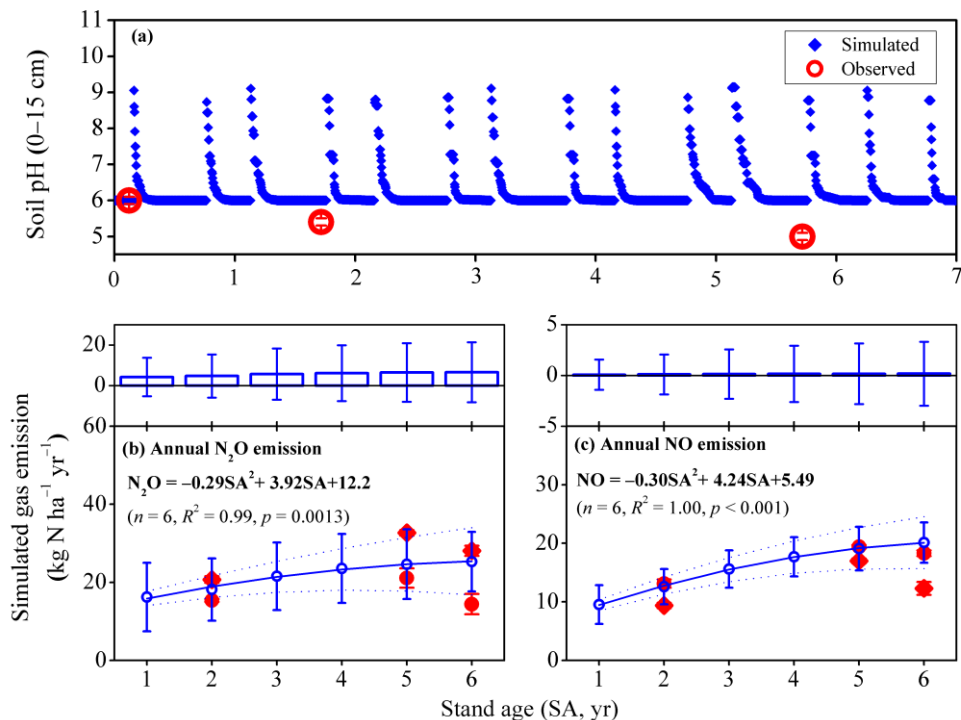


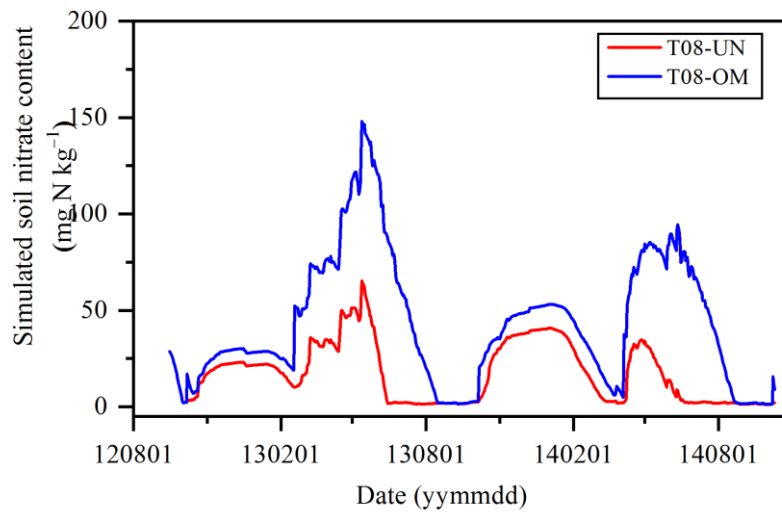
Figure S1: Annual emission and direct emission factor ( $EF_d$ ) of nitrous oxide ( $N_2O$ ) and nitric oxide (NO) from tea plantations with early stand ages against nitrogen fertilizer doses, which were simulated by the original model. The legend in panel b also applies for panel a, wherein T08 and T12 represent the plantations transplanted with seedlings in 2008 and 2012, respectively, UN and OM indicate the fields consecutively applied with urea since tea planting and short-term replacement of urea with oilcake, respectively, and 2013 and 2014 are the years with field observations of gas emissions. Each vertical bar in panel c–f is the standard deviation of the  $EF_d$ s for T08 in 2013 and 2014 and T12 in 2013. Dashed lines are the lower and upper uncertain bounds at the 95% confidence interval for regression curves.



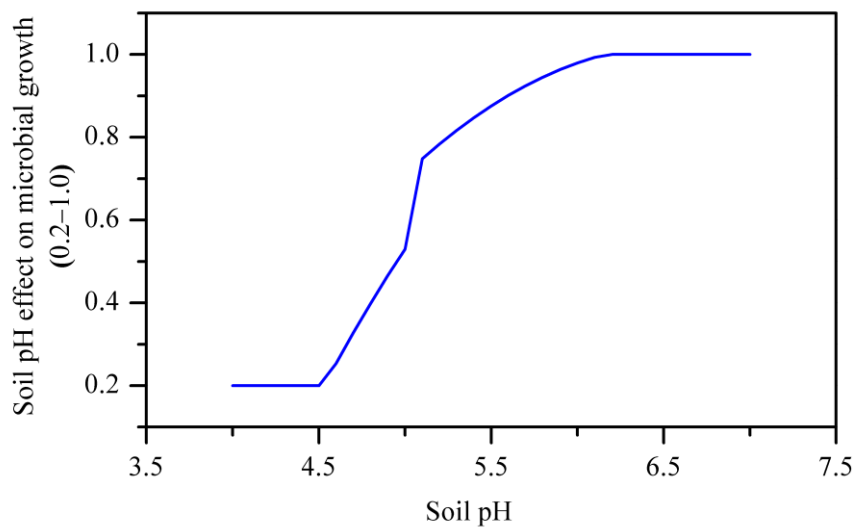


10 **Figure S2: Topsoil (0–15 cm depth) pH and annual emissions of nitrous oxide (N<sub>2</sub>O) and nitric oxide (NO) against early tea stand ages, which were simulated by the original model. The solid lines were the polynomial regression curves. Dashed lines are the lower and upper uncertain bounds at the 95% confidence interval (CI) for regression curves. Each pH datum is given as the daily mean of eight diurnal simulations (3 h for each). The vertical bar crossing each datum point in panel b or c represents the uncertainty (95% CI) induced by those of model inputs. Each box above panels b–c represents total model error that was estimated by referring to mean of model relative errors (MRBs), with vertical bars representing the uncertainties (95% CI) estimated by referring to the double standard deviations of |MRBs|. The red circle and diamond points in panel b or c represent the observed emissions of N<sub>2</sub>O and NO from urea and organic manure treatments.**

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20 **Figure S3: Topsoil (0–10 cm depth) nitrate dynamics of the T08-UN and T08-OM treatments, which were simulated by the modified model.**



**Figure S4: Soil pH (sph) effect factor ( $f_{pH}$ ) (ranging between 0.2–1.0) on microbial growth. For the pH lower than 5.0,  $f_{pH} = -0.1797sph^2 + 2.4158sph - 7.057$ ; otherwise,  $f_{pH} = -0.1225sph^2 + 1.6165sph - 4.3095$ . The parameterization was referred to the program codes of DNDC.**