1	Supplement	of
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2 Insights into Soil NO Emissions and the Contribution to Surface

3 Ozone Formation in China

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- 41 160 μ g/m³)

Temperature dependence factor

$$f(T) = e^{k[^{\circ}C^{-1}]T}$$
 k = 0.103±0.04 Eq. S1

Table S1 Division of regions					
Region	Provinces				
Northeast China	Liaoning, Heilongjiang, Jilin				
North China	Hebei, Inner Mongolia, Tianjin, Beijing, Shanxi				
Central China	Henan, Hubei, Hunan				
East China	Fujian, Jiangsu, Shandong, Zhejiang, Shanghai, Anhui, Jiangxi				
South China	Hainan, Guangdong, Guangxi				
Southwest China	Tibet, Sichuan, Yunnan, Chongqing, Guizhou				
Northwest China	Xinjiang, Qinghai, Gansu, Ningxia and Shaanxi				

Table S2 Statistical index formula

No.	Index	Formula	Note
1	Pearson correlation coefficient (R)	$\frac{\sum [(P_j - \overline{P}) \times (O_j - \overline{O})]}{\sqrt{\sum (P_j - \overline{P})^2 \times \sum (O_j - \overline{O})^2}}$	Unitless, -1≤R≤1
2	mean bias (MB)	$\frac{\sum (P_j - O_j)}{N}$	concentration unit
3	root-mean-square error (RMSE)	$\sqrt{\frac{\sum (P_j - O_j)^2}{N}}$	concentration unit
4	normalized mean bias (NMB)	$\frac{\sum (P_j - O_j)}{\sum O_j} \times 100$	-100%≤NMB≤+∞
5	normalized mean error (NME)	$\frac{\Sigma P_j - O_j }{\Sigma O_j} \times 100$	0%≤NME≤+∞

Region	Annual Soil NO emissions (Gg)	Soil NO emissions during June-August (Ratio of annual totals)	Ratio of soil NO/anthropogenic NOx	Ratio soil NO/anthropogenic NOx (June-August)
Northeast China	94.2	63.7 (67.6%)	12.0%	36.0%
North China	200.5	118.1 (58.9%)	14.9%	36.5%
Central China	281.4	146.7 (52.1%)	35.3%	74.0%
East China	264.3	138.4 (52.4%)	12.8%	26.8%
South China	71.4	20.1 (28.2%)	14.3%	15.8%
Southwest	97 C	24.8 (20.70/)	14 50/	22.00/
China	87.0	34.8 (39.7%)	14.370	23.9%
Northwest	150 /	05 8 (60 59/)	26.89/	67 50/
China	138.4	93.8 (00.5%)	20.8%	07.3%
Total	1157.9	63.7 (53.3%)	12.0%	36.0%

Table 55 Son NO emissions and failo of son NO to antifopogenic NOX by uniferent regions in China for 20	Table S3 Soil NO emissio	ns [*] and ratio of soil NO to anthr	opogenic NOx by differen	nt regions in China for 201
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*Soil NO emissions given in this table are based on the default temperature dependence factor.

Reference	Region	Reference year	Above canopy (Gg N a ⁻¹)	Soil NOx flux (ng N m ⁻² s ⁻¹)	Notes
				generally more than 40 ng N $m^{-2} \ s^{-1}$ (in	
Wang et al. (2005)	China	1999	657	the North China Plain in July) and 20	An empirical modeling approach of Yienger and
				ng N $m^{-2}~s^{-1}$ (in the northeast China in	Levy (YL95)
				July)	

					• • •
Table S4 Com	parison of soil NU	emissions and	flux in China	i reported by	previous studies

					Dynamical and biogenic emissions models, soil
Tie et al. (2006)	China	2004	1375		emissions parameterized with an exponential
					dependence on soil temperature.
					Statistical model based on field measurements
Ver. et al. (2005)	China	100			of NOx fluxes combined with land cover, soil
Yan et al. (2003)	China		480		pH, soil organic carbon, climate, and nitrogen
					fertilizers
II			1226 (ranging		Synthesis of 130 NO emissions sampling points
(2014)	China		from 588.24 to		at 14 locations to estimate soil NO emissions
(2014)			2132.05)		inventory in China.
		2016	1140		
Lu et al. (2010)	China	(Mar-Oct)	1140	PDSNP scheme in GEOS	PDSNP scheme in GEOS Chem
Lu et al. (2019)		2017	1360		BD3NI selelle lii GE63-Chelli
		(Mar-Oct)	1500		
Lu et al. (2021)	China	2017	770 <u>±</u> 40		BDSNP scheme in GEOS-Chem
Wang et al. (2007)	East China	1997-1999	850		Application of YL95 scheme in GEOS-Chem
Lin (2012)	East China	2006	380		Top-down estimates using satellite NO ₂ retrievals
Wang et al. (2022)	The North	2020		10-40 (crop growing season)	Application of MEGAN scheme in WRF-Chem

China plain

Li and Wang	the Pearl River	2005		The average is 47.5 (typical vegetable	NO flux measured by static chamber technique
(2007)	Delta	2003		plot)	in the suburbs of Guangzhou
Li et al. (2007)	South China	2005		The average fluxes of broadleaved forest and pine-leaved forest in the rainy season were 14.9 and 17.1	Sample plots circled in the forest and NO fluxes measured by dynamic flow chamber technique
Liu et al. (2011)	Northern China	2007-2009		Average annual flux of 7.6 (wheat-maize rural)	Experiments NO fluxes were obtained based on automatic measurement systems and intermittent manual measurements
Liu et al. (2017)				The average soil NO flux was 12.9 Vegetable farmland flux is 30.9	Synthesized 520 field observations from 114 publications
			805.2	6.6 (June average, same below)	BDSNP scheme (default fertilizer data)
	China	2018	1157.9 (715.7-1902.6)	9.9	BDSNP scheme (N + compound fertilizer data)
This study			296.1	38.5	BDSNP scheme (default fertilizer data)
-	NCP	2018	455.9 (276.5-762.1)	60.1	BDSNP scheme (N + compound fertilizer data)
				35.4	BDSNP scheme (N + compound fertilizer data and adjusted β value)

	China	NCP	YRD	PRD	Sichuan Basin	Northeast
OBS (µg/m ³)	129.6	172.4	146.5	97.5	108.3	126.1
$MOD~(\mu g/m^3)$	146.7	185.7	171.5	108.4	146.7	128.4
$MB (\mu g/m^3)$	17.1	13.3	25.0	10.9	38.5	2.4
NMB (%)	13.2	7.7	17.1	11.2	35.5	1.9
R	0.89	0.77	0.80	0.58	0.62	0.83

Table S5 Comparison of observed and simulated values in China and five key regions



Figure S1 Anthropogenic NOx emissions and nitrogen fertilizer application during 2010-2017 (Note: anthropogenic NOx emissions are based on MEIC emission inventory; nitrogen fertilizer data from provincial statistical yearbook)



Figure S2 Monthly soil NO emissions (estimated with default temperature dependence factor of 0.103) by region



Figure S3 Soil NO emissions estimated using different fertilizer data (default fertilizer data: International Fertilizer Industry Association from Potter et al. (2010) for year 2010; nitrogen fertilizer and compound fertilizer are from statistical yearbooks at the provincial level for year 2018)



Figure S4 Scatter plot of monthly mean NO_2 concentration (before and after adjusting

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Figure S5 Scatter plot of monthly mean MDA8 ozone concentration (before and after adjusting *k*)



Figure S6 Comparison of OSAT method and Brute force method in China and five key regions



Figure S7 Ozone differences between OSAT method and brute force method under different ozone concentrations in China and five key regions



Figure S8 Spatial distribution of ozone contribution from different source groups based on OSAT results



Figure S9 Relative ozone contribution by emission groups and regions



Figure S10 Area exposed to MDA8 > 160 μ g/m³ under different soil NO emission reduction scenarios (PRD is not shown because MDA8 ozone concentration is less than 160 μ g/m³)



Figure S11 Population exposed to MDA8 > 160 μ g/m³ under different soil NO emission reduction scenarios (PRD is not shown because MDA8 ozone concentration is less than 160 μ g/m³)

Supplementary Information References

- Huang, Y.; Li, D. Soil nitric oxide emissions from terrestrial ecosystems in China: a synthesis of modeling and measurements. Scientific Reports 2014;4:1-8
- Li, D.; Wang, X. Nitric oxide emission from a typical vegetable field in the Pearl River Delta, China. Atmospheric Environment 2007;41:9498-9505
- Li, D.; Wang, X.; Mo, J.; Sheng, G.; Fu, J. Soil nitric oxide emissions from two subtropical humid forests in south China. Journal of Geophysical Research: Atmospheres 2007;112
- Lin, J.-T. Satellite constraint for emissions of nitrogen oxides from anthropogenic, lightning and soil sources over East China on a high-resolution grid. Atmospheric Chemistry and Physics 2012;12:2881-2898
- Liu, C.; Wang, K.; Meng, S.; Zheng, X.; Zhou, Z.; Han, S.; Chen, D.; Yang, Z. Effects of irrigation, fertilization and crop straw management on nitrous oxide and nitric oxide emissions from a wheat-maize rotation field in northern China. Agriculture, Ecosystems & Environment 2011;140:226-233
- Liu, S.; Lin, F.; Wu, S.; Ji, C.; Sun, Y.; Jin, Y.; Li, S.; Li, Z.; Zou, J. A meta-analysis of fertilizerinduced soil NO and combined NO+ N2O emissions. Global Change Biology 2017;23:2520-2532
- Lu, X.; Ye, X.; Zhou, M.; Zhao, Y.; Weng, H.; Kong, H.; Li, K.; Gao, M.; Zheng, B.; Lin, J. The underappreciated role of agricultural soil nitrogen oxide emissions in ozone pollution regulation in North China. Nature communications 2021;12:5021
- Lu, X.; Zhang, L.; Chen, Y.; Zhou, M.; Zheng, B.; Li, K.; Liu, Y.; Lin, J.; Fu, T.-M.; Zhang, Q. Exploring 2016–2017 surface ozone pollution over China: source contributions and meteorological influences. Atmospheric Chemistry and Physics 2019;19:8339-8361
- Potter, P.; Ramankutty, N.; Bennett, E.M.; Donner, S.D. Characterizing the spatial patterns of global fertilizer application and manure production. Earth interactions 2010;14:1-22
- Tie, X.; Li, G.; Ying, Z.; Guenther, A.; Madronich, S. Biogenic emissions of isoprenoids and NO in China and comparison to anthropogenic emissions. Science of the total environment 2006;371:238-251
- Wang, Q.g.; Han, Z.; Higano, Y. An inventory of nitric oxide emissions from soils in China. Environmental pollution 2005;135:83-90
- Wang, R.; Bei, N.; Wu, J.; Li, X.; Liu, S.; Yu, J.; Jiang, Q.; Tie, X.; Li, G. Cropland nitrogen dioxide emissions and effects on the ozone pollution in the North China plain. Environmental Pollution 2022;294:118617
- Wang, Y.; McElroy, M.B.; Martin, R.V.; Streets, D.G.; Zhang, Q.; Fu, T.M. Seasonal variability of NOx emissions over east China constrained by satellite observations: Implications for combustion and microbial sources. Journal of Geophysical Research: Atmospheres 2007;112
- Yan, X.; Ohara, T.; Akimoto, H. Statistical modeling of global soil NOx emissions. Global Biogeochemical Cycles 2005;19