Supplementary Information for

Important contributions of non-fossil fuel nitrogen oxides emissions

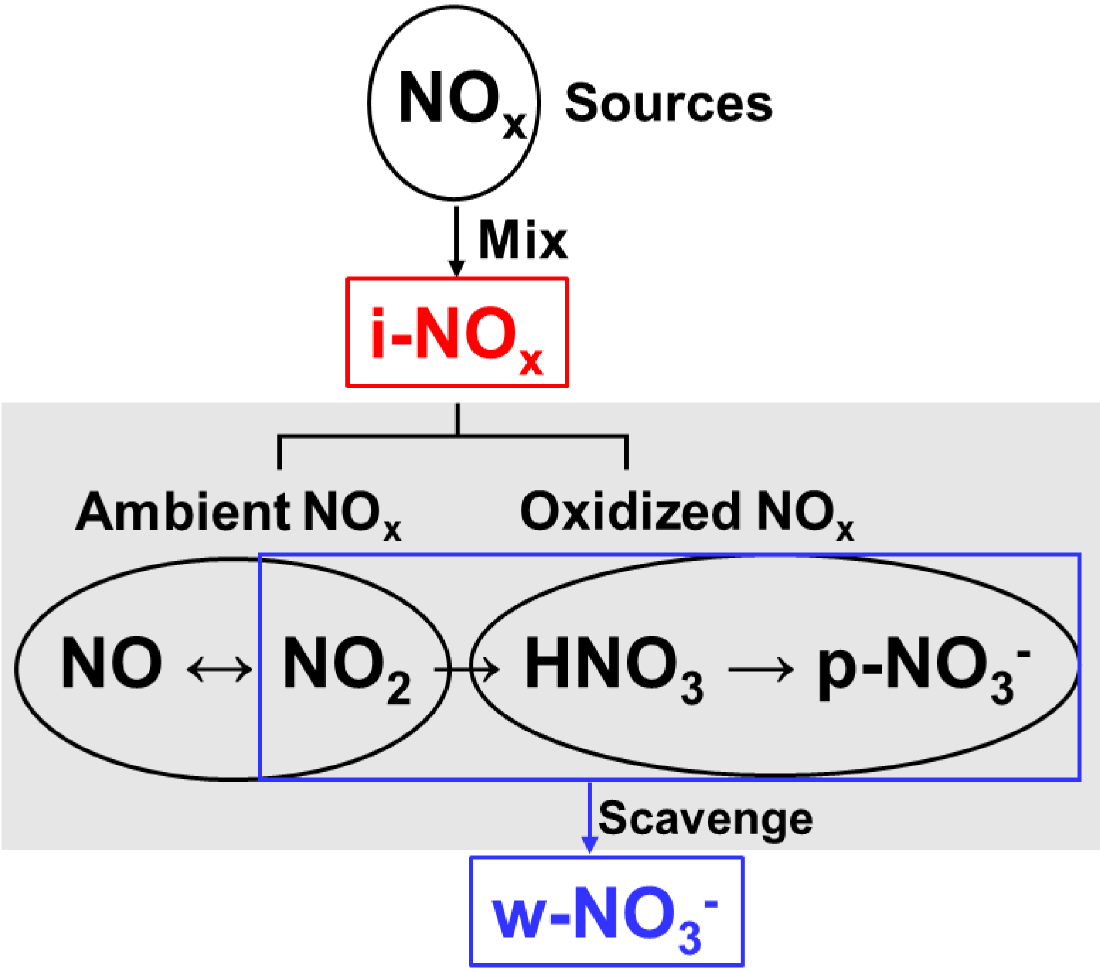
Wei Song[1], Xue-Yan Liu[1], Chao-Chen Hu[1], Guan-Yi Chen[2], Xue-Jun Liu[3], Wendell W. Walters[4], Greg Michalski[5], Cong-Qiang Liu[1]

1. School of Earth System Science, Tianjin University, Tianjin, 300072, China
2. Georgia Tech Shenzhen Institute, Tianjin University, Shenzhen 518071, China
3. College of Resources and Environmental Sciences, China Agricultural University, Beijing, 100193, China
4. Institute at Brown for Environment and Society, Brown University, 85 Waterman St, Providence, RI, 02912, United States
5. Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, 550 Stadium Mall Drive, West Lafayette, IN 47907, United States

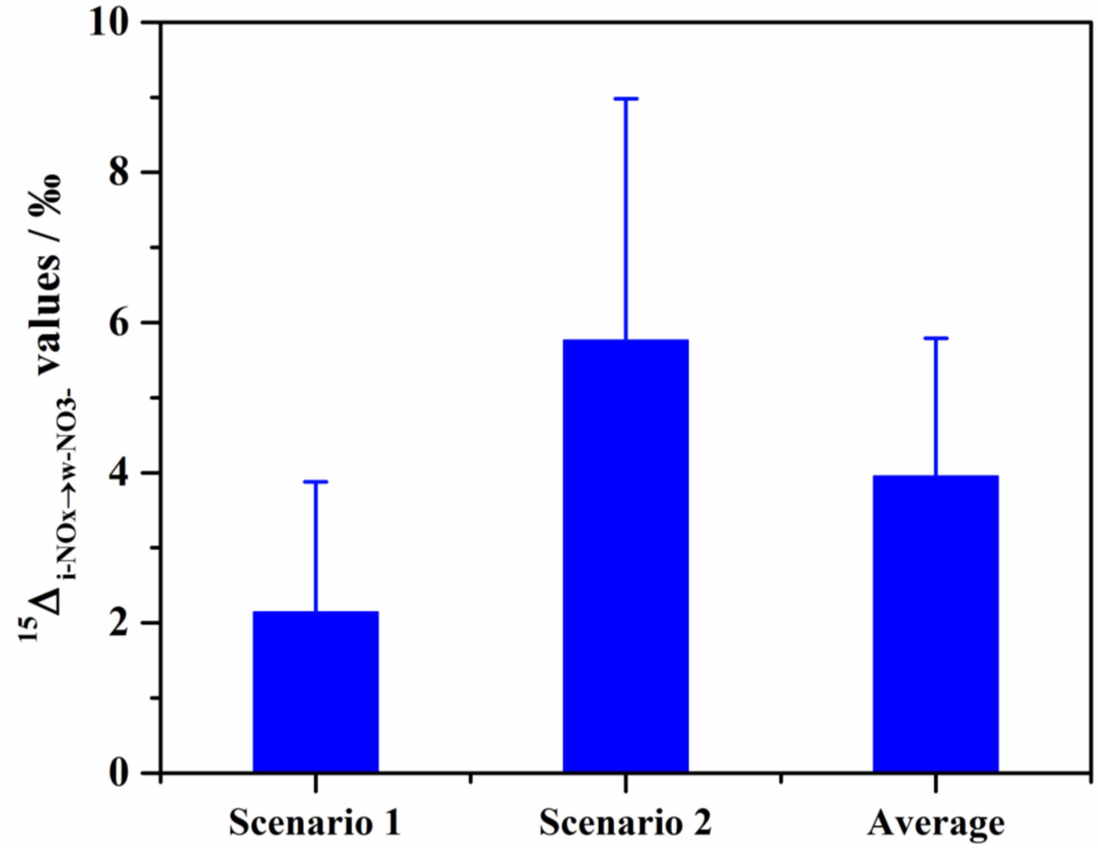
Materials & Correspondence.
Correspondence and requests for materials should be addressed to Xue-Yan Liu (liuxueyan@tju.edu.cn).

This file includes:

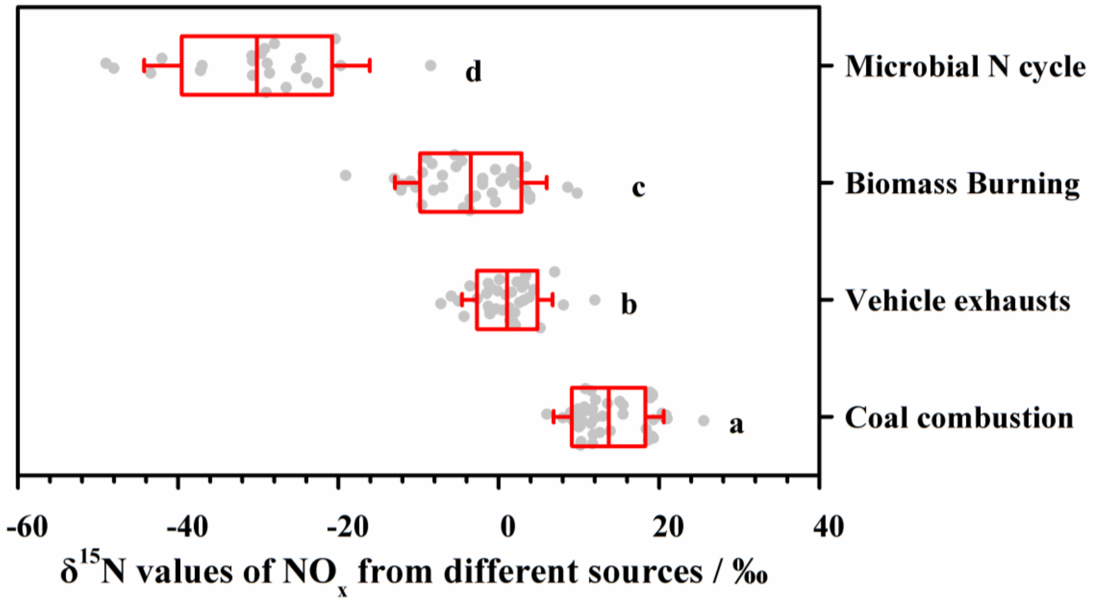
1. **Supplementary Figs. 1–14**
2. **Supplementary Tables. 1–3**
3. **Supplementary Note 1:**
    1) Supplementary references 21−148 in Supplementary Text 1 are publications of $\delta^{15}N_{w\text{-}NO3\text{-}}$ observations.
    2) Supplementary references 149–154 in Supplementary Text 2 are publications of simultaneous observations of HNO_3, p-NO_3^-, and NO_2 concentrations in the atmosphere.
    3) Supplementary references 155−157 in Supplementary Text 3 are data sources of observations of HNO_3, p-NO_3^-, and NO_2 concentrations in the ambient atmosphere.
    4) Supplementary references 158−165 in Supplementary Text 4 are publications of observations of ambient $f_{NO2/NOx}$ values.
    5) Supplementary references 166–169 in Supplementary Text 5 are publications of ambient $\delta^{15}N_{NOx}$ observations.
    6) Supplementary references 170–173 in Supplementary Text 6 are publications of simultaneous $\delta^{15}N$ observations of HNO_3, p-NO_3^-, and w-NO_3^- in the atmosphere.
    7) Supplementary references 174−182 in Supplementary Text 7 are publications of ambient $\delta^{15}N_{HNO3}$ observations.
    8) Supplementary references 183−213 in Supplementary Text 8 are publications of $\delta^{15}N_{p\text{-}NO3\text{-}}$ observations.



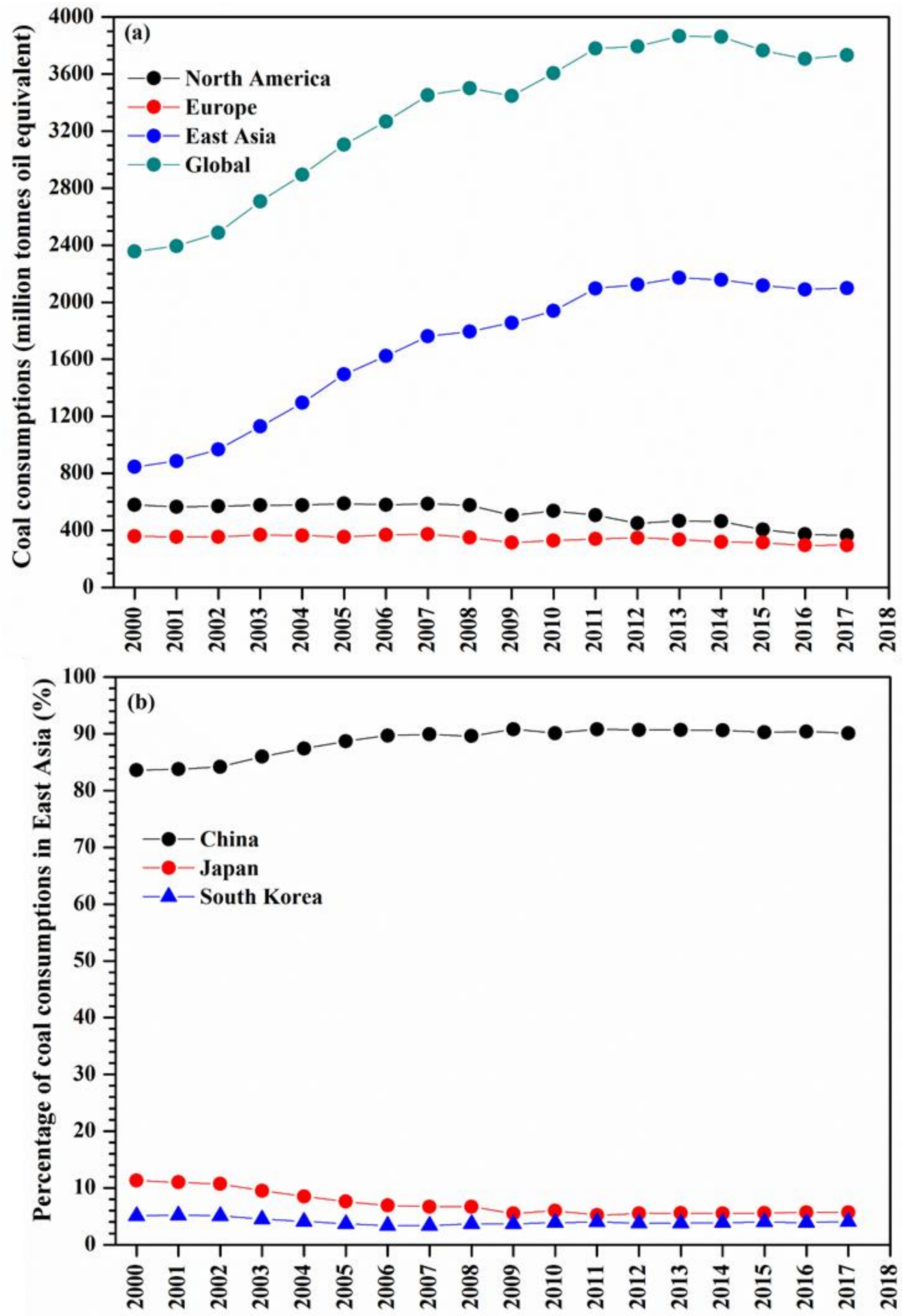
Supplementary Fig. 1 | A schematic map showing relationships between NO_x, HNO_3, p-NO_3^-, and w-NO_3^- in the atmosphere (detailed in Methods)**.**



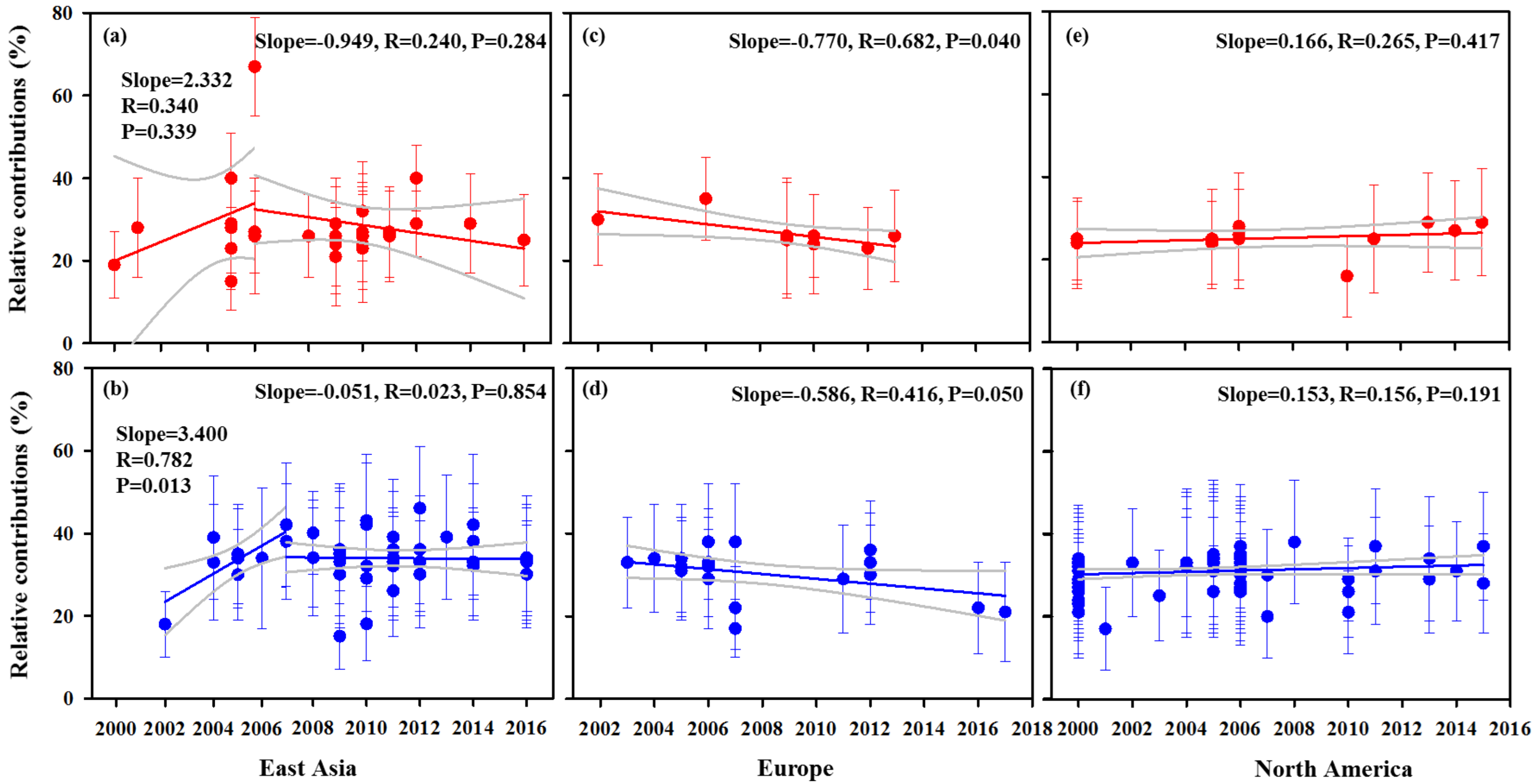
Supplementary Fig. 2 | Differences in $\delta^{15}N$ values between w-NO_3^- and i-NO_x in the atmosphere ($^{15}\Delta_{i\text{-}NOx\rightarrow w\text{-}NO3\text{-}}$ values). Mean ±SD values are shown. Scenarios 1 & 2 show estimations based on simultaneous and non-synchronous observations of atmospheric NO_x, HNO_3, p-NO_3^-, and w-NO_3^- (detailed in Methods). Average: the mean value of mean values of Scenarios 1 & 2.



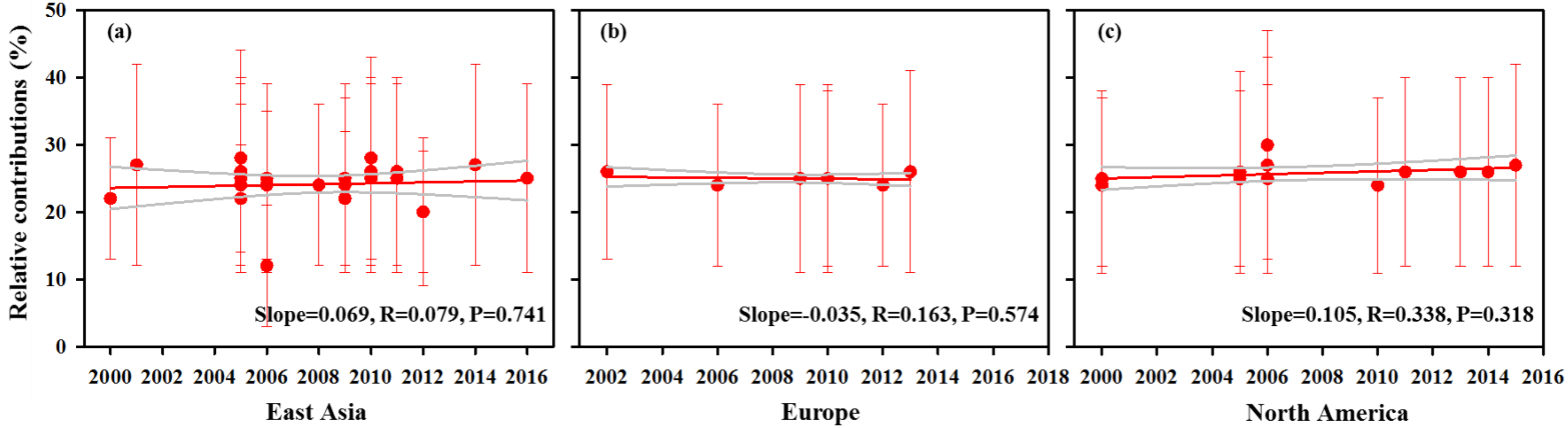
Supplementary Fig. 3 | $\delta^{15}N$ values of NO_x from major sources. Dots around each box show scatter values. The box encompasses the 25^{th}–75^{th} percentiles, whiskers and line in each box are the SD and mean values, respectively. Values with different letters are significantly different at $P<0.05$. Data were cited from refs. 1–9.



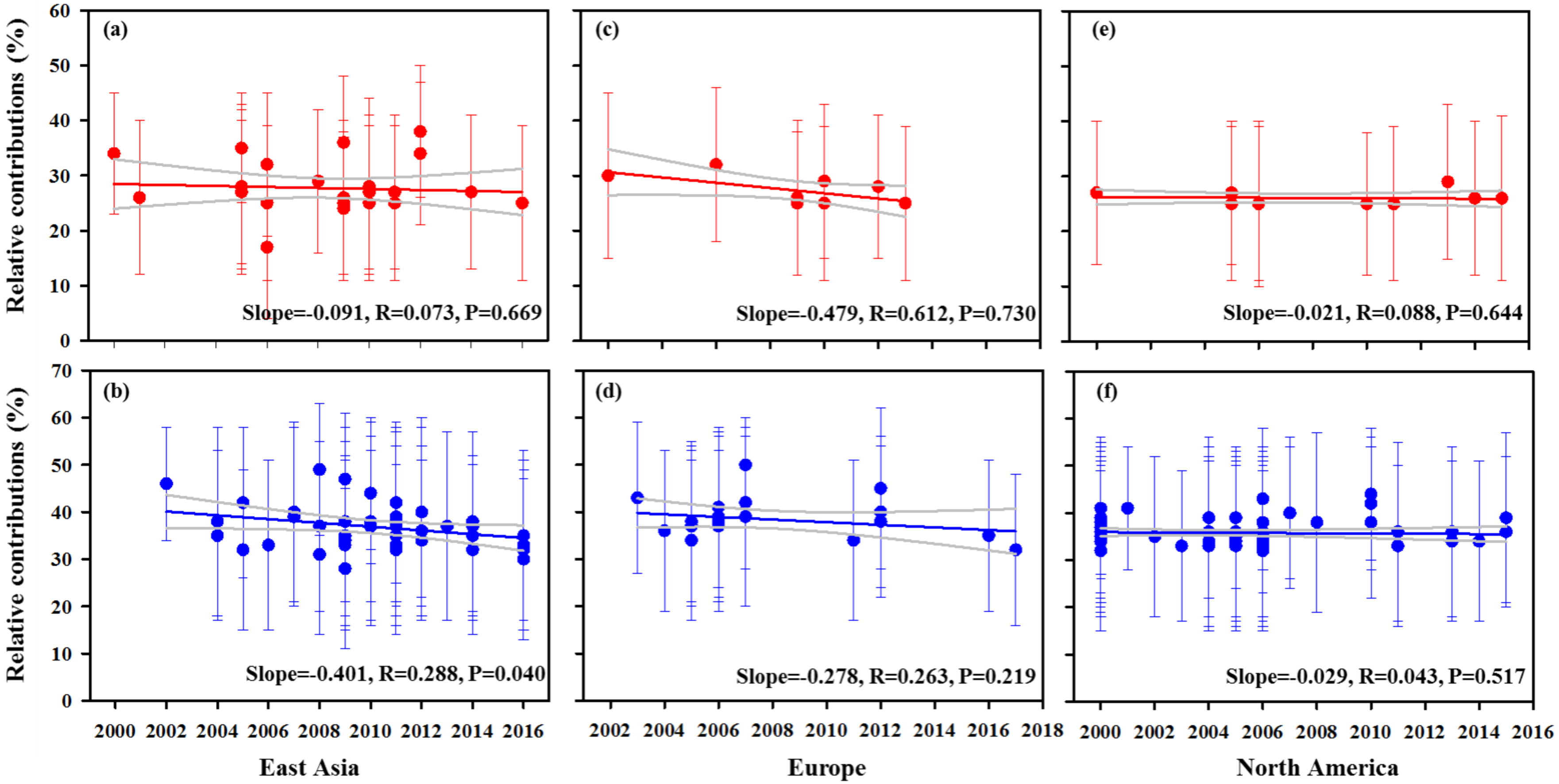
Supplementary Fig. 4 | (a) Coal consumptions in East Asia, Europe, North America, and global between 2000–2017. Data were downloaded from ref. 10. **(b) Percentages of coal consumptions in China, Japan, and South Korea in the total amount of East Asia during 2000–2017.** Data were downloaded from ref. 10.



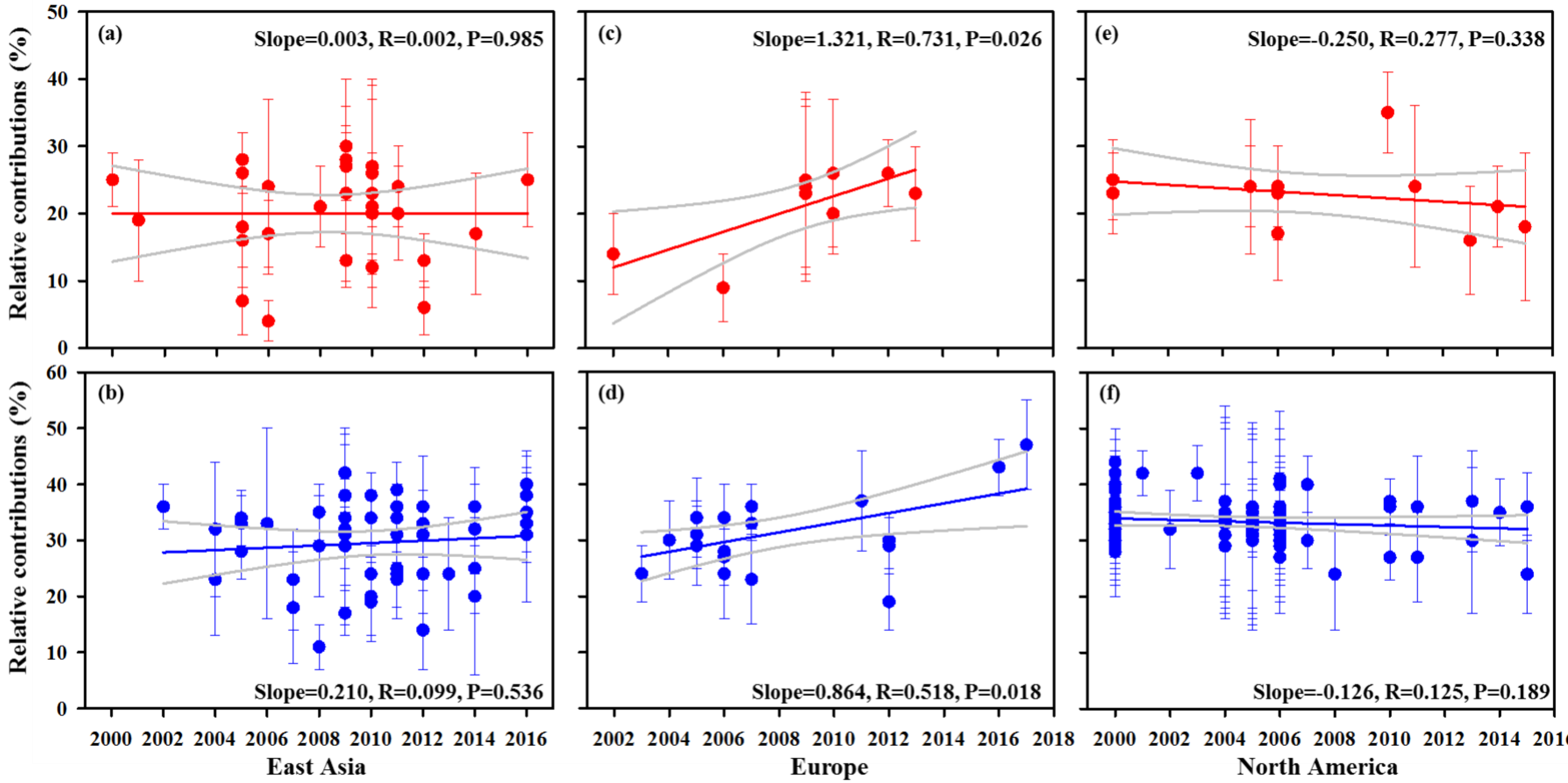
Supplementary Fig. 5 | Variations of relative contributions of NO_x from coal combustion during 2000–2017 at urban (a, c, and e) and non-urban (b, d, and f) sites of East Asia, Europe, and North America, respectively. Mean ± SD values of relative contributions at each site in each year are shown (*n*=28, 9, 13 for panels a, c, e and *n*=47, 21, 88 for panels b, d, f, respectively). Calculations were detailed in Methods. The gray lines were the 95% confidence intervals.



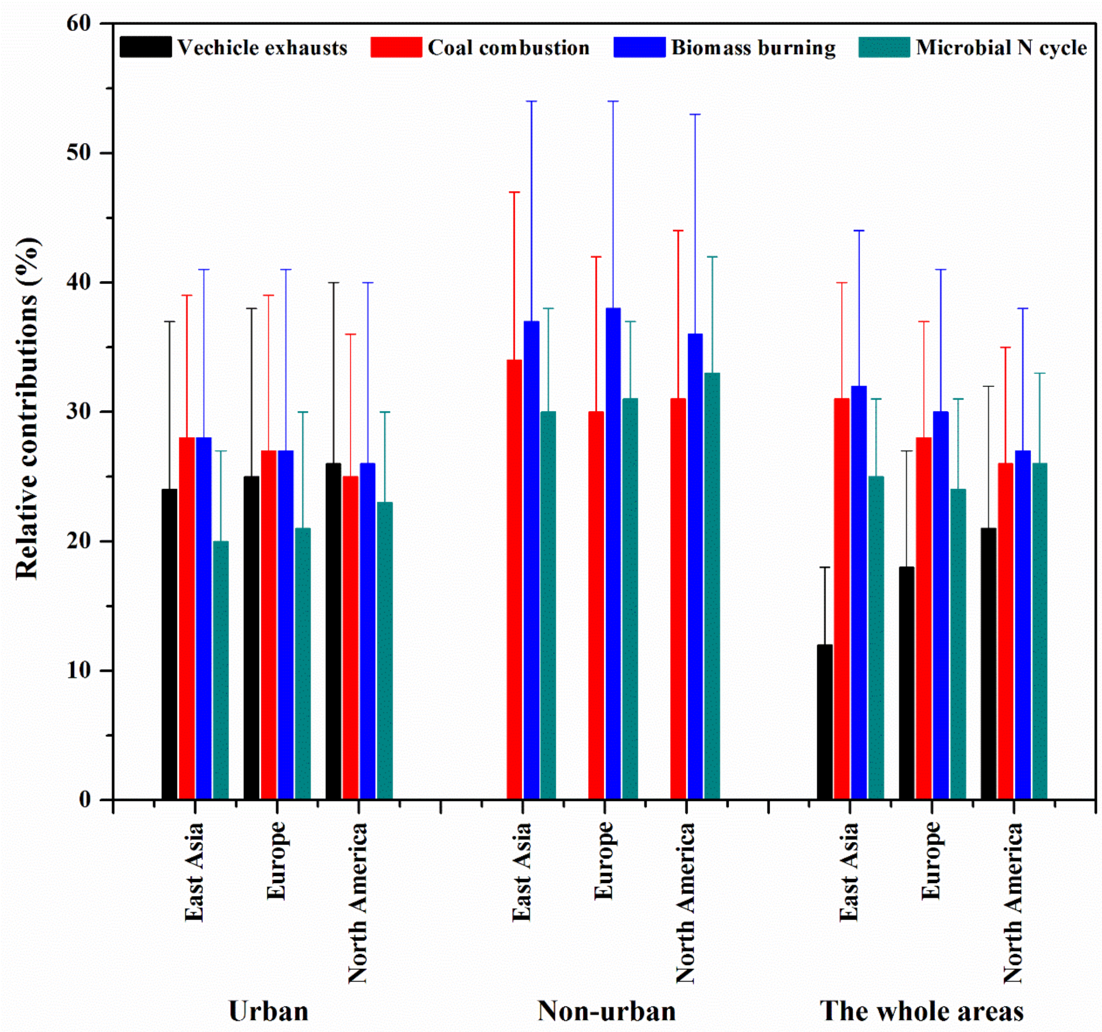
Supplementary Fig. 6 | Variations of relative contributions of NO_x from vehicle exhausts during 2000–2017 at urban (a, b, and c) sites of East Asia, Europe, and North America, respectively. Mean ± SD values of relative contributions at each site in each year are shown (*n*=28, 9, 13 for panels a, b, and c, respectively). Calculations were detailed in Methods. The gray lines were the 95% confidence intervals.



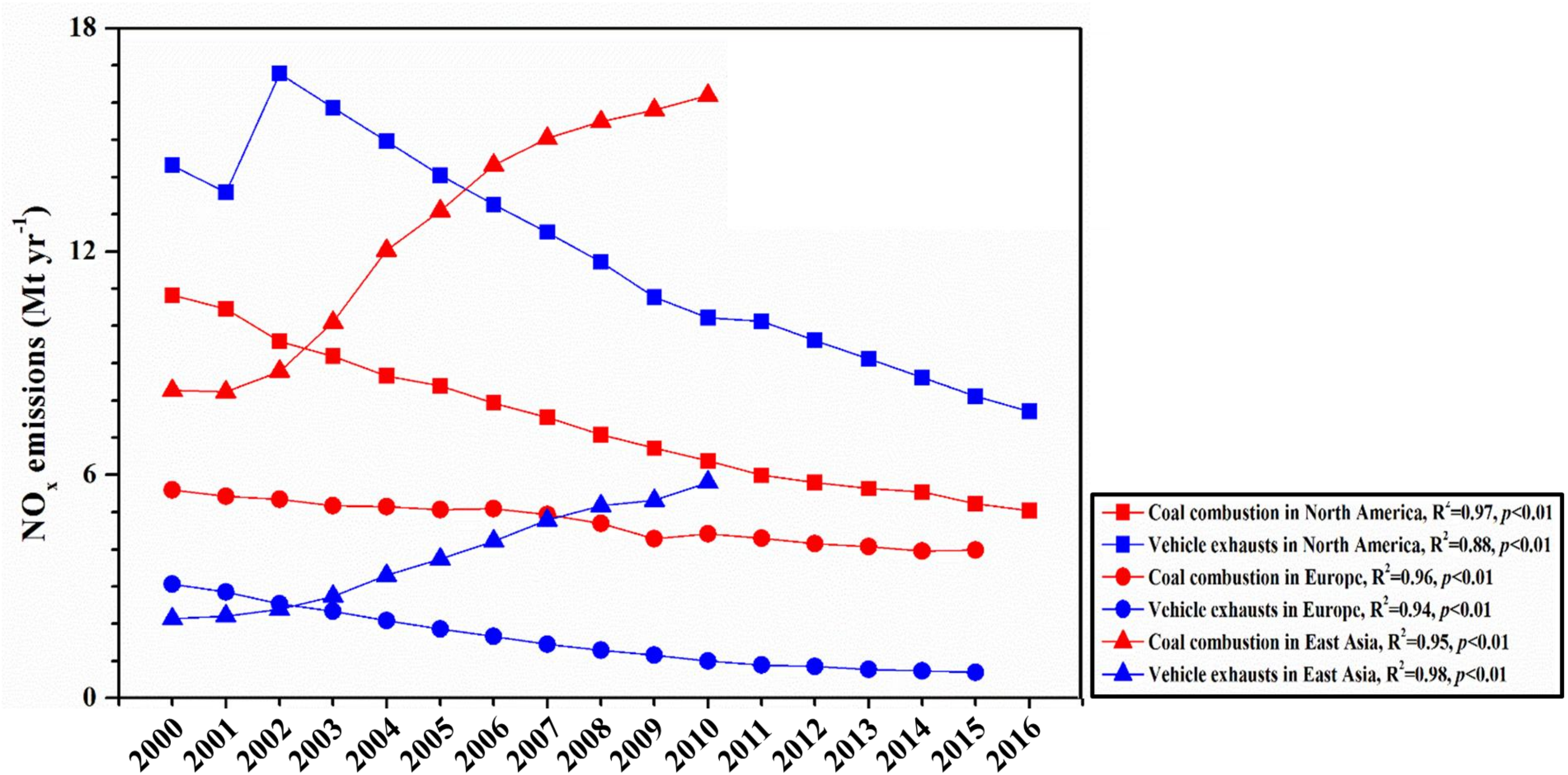
Supplementary Fig. 7 | Variations of relative contributions of NO_x from biomass burning during 2000–2017 at urban (a, c, and e) and non-urban (b, d, and f) sites of East Asia, Europe, and North America, respectively. Mean ± SD values of relative contributions at each site in each year are shown (*n*=28, 9, 13 for panels a, c, e and *n*=47, 21, 88 for panels b, d, f, respectively). Calculations were detailed in Methods. The gray lines were the 95% confidence intervals.



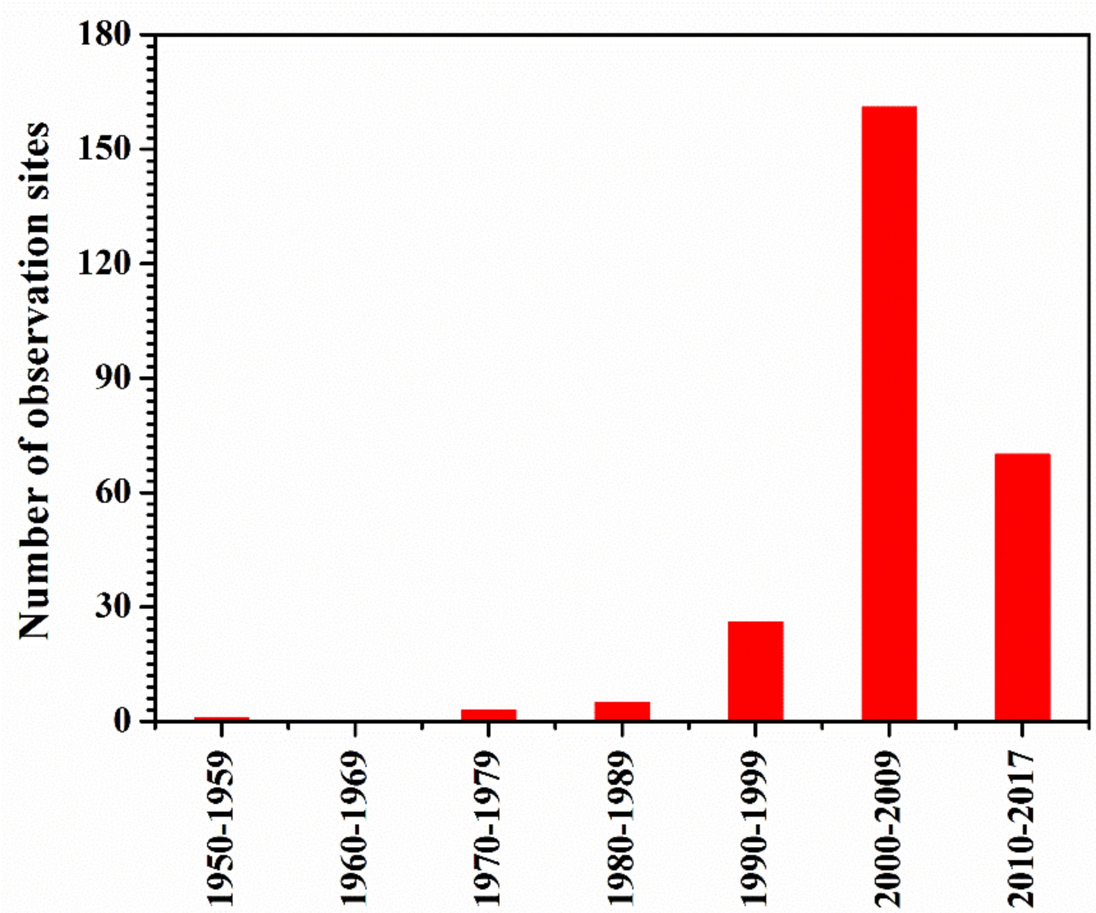
Supplementary Fig. 8 | Variations of relative contributions of NO_x from microbial N cycle during 2000–2017 at urban (a, c, and e) and non-urban (b, d, and f) sites of East Asia, Europe, and North America, respectively. Mean ± SD values of relative contributions at each site in each year are shown (*n*=28, 9, 13 for panels a, c, e and *n*=47, 21, 88 for panels b, d, f, respectively). Calculations were detailed in Methods. The gray lines were the 95% confidence intervals.



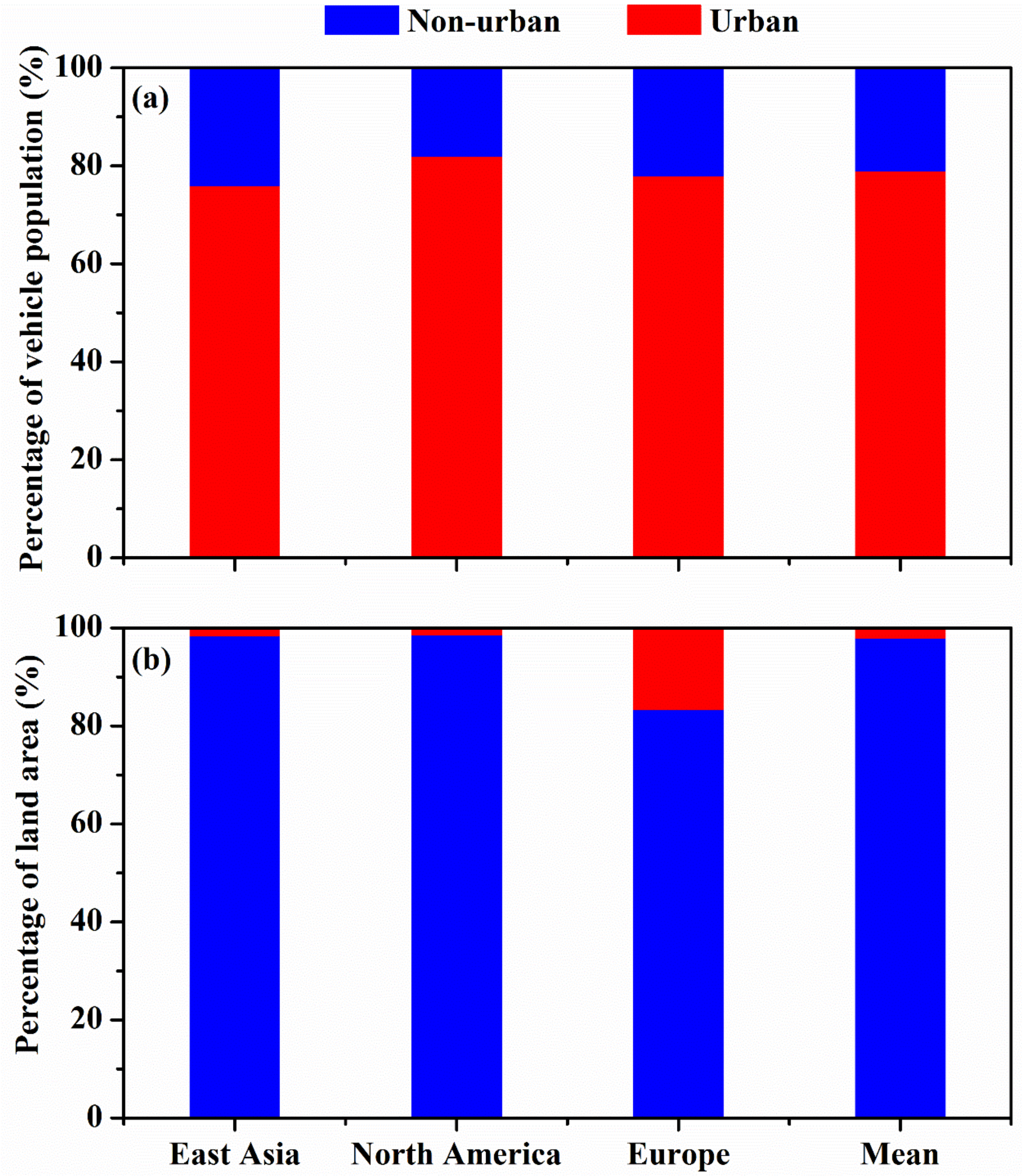
Supplementary Fig. 9 | Annual mean relative contributions of NO_x from vehicle exhausts, coal combustion, biomass burning, and microbial N cycle to precipitation NO_3^- at urban sites, non-urban sites, and the whole areas of East Asia, Europe, and North America, respectively during 2000-2017. Mean ± SD values are shown (replicates are the same as those in Supplementary Figs. 5-8). Calculations were detailed in Methods.



Supplementary Fig. 10 | Annual NO_x emissions from coal combustion and vehicle exhausts during 2000-2010 in East Asia, 2000-2015 in Europe, and 2000-2016 in North America. Data is cited from ref. 11 for East Asia, ref. 12 for Europe and refs. 13 and 14 for North America.



Supplementary Fig. 11 | Temporal distributions of $\delta^{15}N_{w\text{-}NO3\text{-}}$ observations from 1950 to 2017.



Supplementary Fig. 12 | Percentages of vehicle populations of urban and non-urban areas in the total (a), percentages of urban and non-urban areas in the total land areas in different regions (b). Calculating methods and data sources were detailed in Supplementary Tables 2 & 3.

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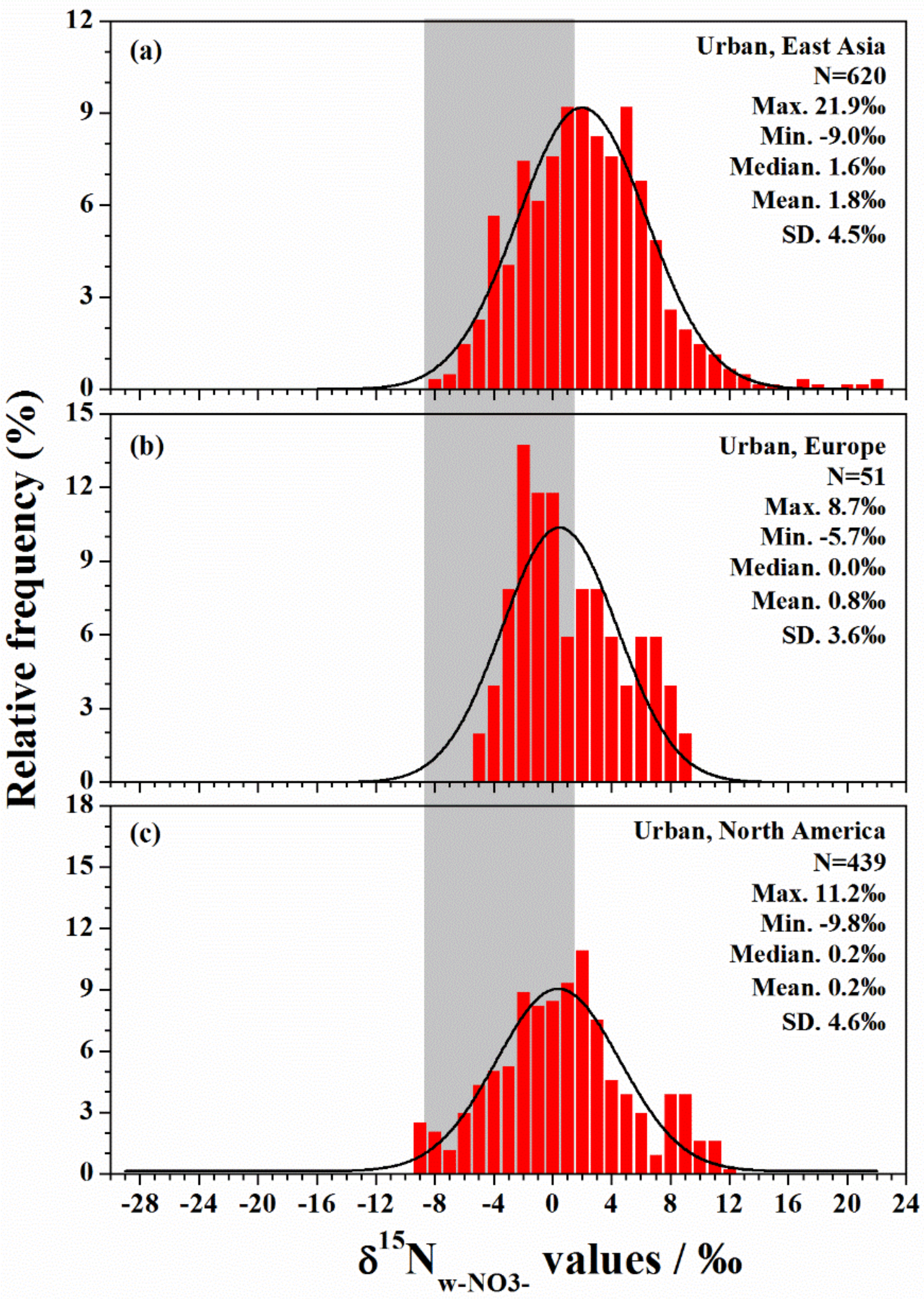
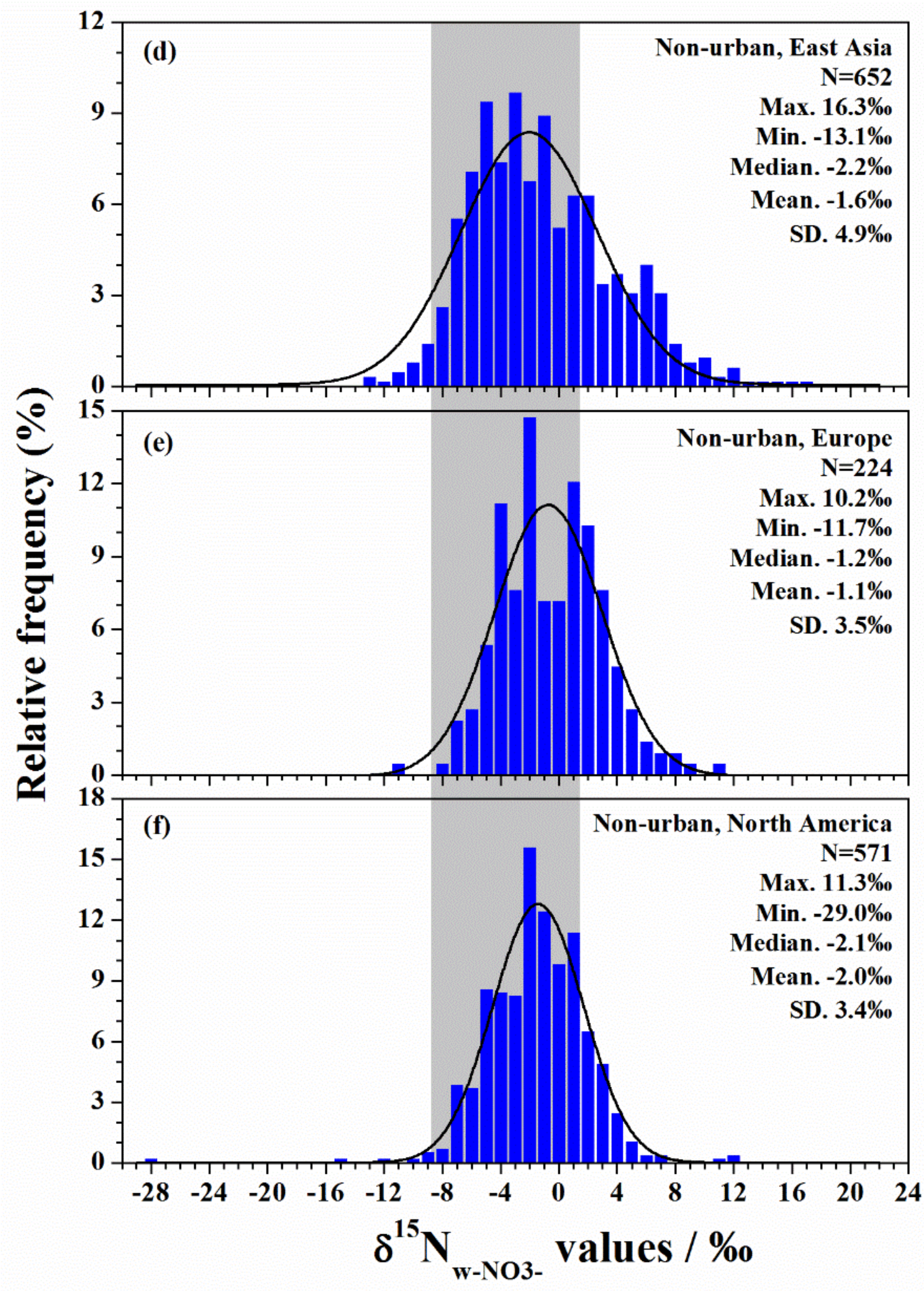
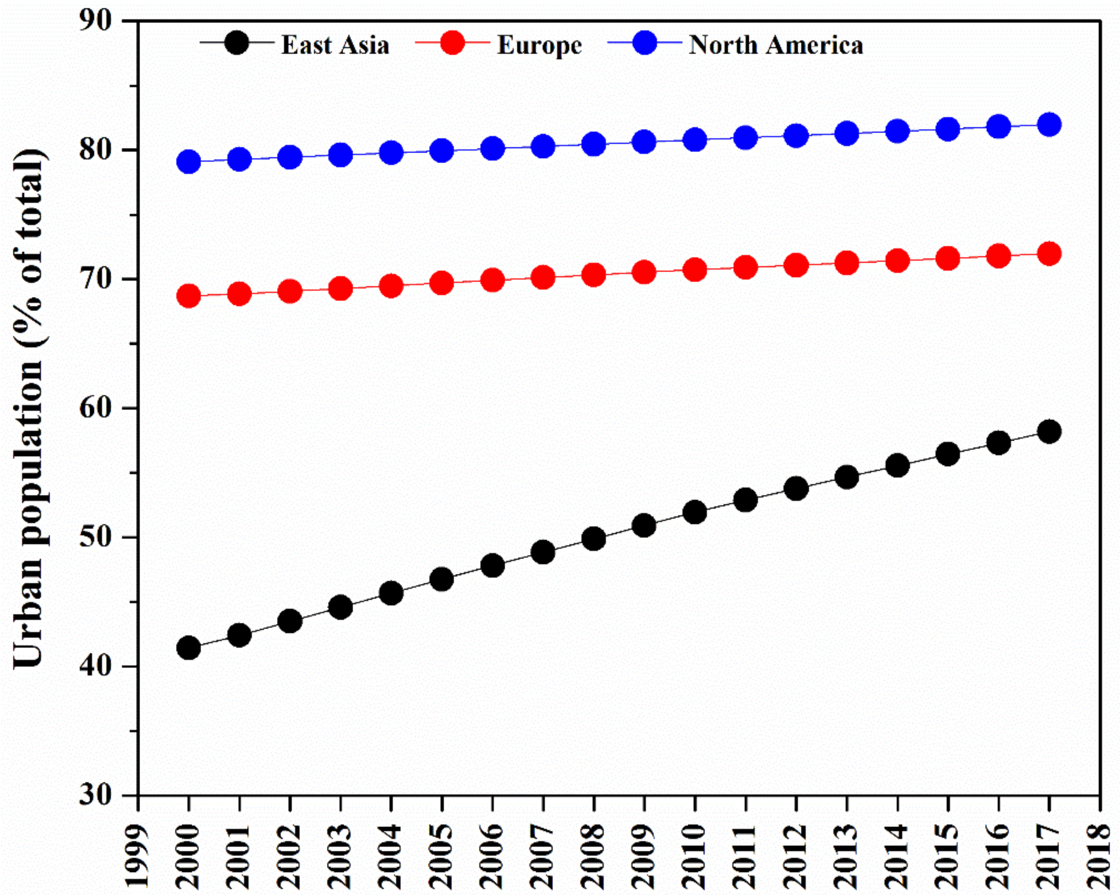


(a)
Urban, East Asia
N=620
Max. 21.9‰
Min. -9.0‰
Median. 1.6‰
Mean. 1.8‰
SD. 4.5‰
(b)
Urban, Europe
N=51
Max. 8.7‰
Min. -5.7‰
Median. 0.0‰
Mean. 0.8‰
SD. 3.6‰
(c)
Urban, North America
N=439
Max. 11.2‰
Min. -9.8‰
Median. 0.2‰
Mean. 0.2‰
SD. 4.6‰
Relative frequency (%)
δ15Nw-NO3- values / ‰



Supplementary Fig. 13 | Relative frequency histograms of $\delta^{15}N_{w\text{-}NO3\text{-}}$ values at urban (a, b, and c) and non-urban (d, e, and d) sites of East Asia, Europe, and North America, respectively. Measurements in independent observation years during 2000–2017 are shown. Trips shaded in the gray show the range of $\delta^{15}N$ of NO_x from vehicle exhausts (detailed in Supplementary Fig. 3).



Supplementary Fig. 14 | Percentages of urban population (expressed as % of total) in East Asia, Europe, and North America between 2000–2017. Data were downloaded from ref. 15.

Supplementary Table 1 | The data sources and values of parameters used for calculating ambient $^{15}\Delta_{i\text{-}NOx\rightarrow w\text{-}NO3\text{-}}$ values. Scenario 1, mean values of regional $\delta^{15}N_{NOx}$ and f_{NO2} values, simultaneously observed values of ambient C_{NO2}, C_{HNO3}, $C_{p\text{-}NO3\text{-}}$, $\delta^{15}N_{HNO3}$, $\delta^{15}N_{p\text{-}NO3\text{-}}$, and $\delta^{15}N_{w\text{-}NO3\text{-}}$ were used. Scenario 2, non-synchronously observed values of ambient f_{NO2}, C_{NO2}, C_{HNO3}, $C_{p\text{-}NO3\text{-}}$, $\delta^{15}N_{NOx}$, $\delta^{15}N_{HNO3}$, $\delta^{15}N_{p\text{-}NO3\text{-}}$, and $\delta^{15}N_{w\text{-}NO3\text{-}}$ were used. (a) data were cited from Supplementary Texts 2 & 3; (b) data were cited from Supplementary Text 4; (c) data were cited from Supplementary Text 5; (d) data were cited from Supplementary Texts 6, 7 & 8; (e) data were cited from Supplementary Text 1.

Observations	Site, Country/Region	NO_2 (μg N m^{-3}) [a]			f_{NO2} (%) [b]			HNO_3 (μg N m^{-3}) [a]			p-NO_3^- (μg N m^{-3}) [a]		
		Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*
Scenario 1	Jülich, Germany	1.0	0.4	19	64.0	10.0	202	0.4	0.1	12	1.2	0.2	12
	Pennsylvania, USA	0.4	0.2	6	64.0	10.0	202	0.2	0.0	11	0.1	0.1	11
	Rishiri, Japan	0.3	0.1	12	64.0	10.0	202	0.1	0.0	12	0.2	0.1	12
	Sapporo, Japan	2.6	0.8	11	64.0	10.0	202	0.1	0.1	12	0.3	0.1	12
	Alberta, Canada	0.9	0.1	7	64.0	10.0	202	0.5	0.2	15	0.3	0.3	15
Scenario 2	East Asia	8.9	1.1	194	64.0	10.0	202	0.2	0.0	532	0.3	0.1	546
	Europe	1.9	0.1	200	64.0	10.0	202	0.2	0.1	200	0.5	0.3	200
	North America	7.3	1.0	162	64.0	10.0	202	0.6	0.1	420	0.2	0.1	421

(continued)

Observations	Site, Country/ Region	$\delta^{15}N_{NOx}$ (‰) [c]			$\delta^{15}N_{HNO3}$ (‰) [d]			$\delta^{15}N_{p\text{-}NO3\text{-}}$ (‰) [d]			$\delta^{15}N_{w\text{-}NO3\text{-}}$ (‰) [e]		
		Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*
Scenario 1	Jülich, Germany	-7.7	2.9	51	-2.5	0.6	12	7.3	2.6	12	-2.4	2.1	12
	Pennsylvania, USA	-7.7	2.9	51	4.3	2.8	11	7.0	3.6	11	0.0	1.7	11
	Rishiri, Japan	-7.7	2.9	51	-0.7	3.3	13	1.8	1.7	12	-3.8	2.7	13
	Sapporo, Japan	-7.7	2.9	51	2.7	1.4	13	6.2	3.1	13	-2.0	1.7	13
	Alberta, Canada	-7.7	2.9	51	-0.9	3.3	5	5.3	2.7	5	-2.1	1.6	5
Scenario 2	East Asia	-7.7	2.9	51	-1.0	4.9	49	2.3	6.4	559	-0.4	4.9	1246
	Europe	-7.7	2.9	51	-2.5	0.9	13	3.9	4.6	248	-1.7	4.1	275
	North America	-7.7	2.9	51	0.4	3.9	287	5.1	5.4	272	-1.1	4.0	994

Supplementary Table 2 | Vehicles per capita, total population, urban and non-urban population (expressed as % in total), urban and non-urban vehicles, % of urban and non-urban vehicles in total, total land area, % of urban land area in total, and urban areas of different countries.

Regions	Countries	Vehicles per capita [a]	Total population ($\times10^8$) [b]	% of urban population [c]	% of non-urban population [d]	Urban vehicles ($\times10^5$)	Non-urban vehicles ($\times10^5$)	% of urban vehicles in total	% of non-urban vehicles in total	Total land areas (10^4 km^2) [e]	% of urban land area in total [f]	Urban land areas (10^4 km^2)
East Asia	China	0.06	13.71	56.0	44.0	460.7	361.9	56.0	44.0	956.3	1.0	9.5
	Japan	0.78	1.27	91.0	9.0	901.5	89.2	91.0	9.0	37.8	14.3	5.4
	Korea	0.55	0.51	82.0	18.0	230.0	50.5	82.0	18.0	10.0	16.6	1.7
North America	USA	0.82	3.21	82.0	18.0	2158.4	473.8	82.0	18.0	983.2	2.6	25.8
	Canada	0.80	0.36	81.0	19.0	231.3	54.3	81.0	19.0	998.5	0.3	2.7
Europe	England	0.71	0.65	83.0	17.0	383.6	78.6	83.0	17.0	24.4	5.9	1.5
	France	0.74	0.66	80.0	20.0	390.7	97.7	80.0	20.0	54.9	12.4	6.8
	Germany	0.77	0.82	77.0	23.0	484.4	144.7	77.0	23.0	35.7	27.5	9.8
	Italy	0.77	0.61	70.0	30.0	327.2	140.2	70.0	30.0	30.1	20.1	6.1

(a) data were cited from ref. 16.
(b-e) data were downloaded from ref. 17.
(f) data were downloaded from refs. 18–20.

**Supplementary Table 3 | ** Urban and non-urban vehicles, % of urban and non-urban vehicles in total, total land areas, urban land areas, and % of urban and non-urban land areas of different three regions.

Regions	Urban vehicles (×10^5)	Non-urban vehicles (×10^5)	% of urban vehicles	% of non-urban vehicles	Total land areas (10^4 km^2)	Urban land areas (10^4 km^2)	% of urban land areas	% of non-urban land areas
East Asia	1592.1	501.6	76.0	24.0	1004.1	16.5	1.7	98.4
North America	2389.7	528.1	82.0	18.0	1981.6	28.5	1.4	98.6
Europe	1585.9	461.2	78.0	22.0	145.1	24.1	16.6	83.4
All three regions	5567.8	1490.8	79.0	21.0	3130.9	69.1	2.2	97.8

Supplementary References:

(1) Felix, J. D., Elliott, E. M. & Shaw, S. L. The isotopic composition of coal-fired power plant NOx: The influence of emission controls and implications for global emission inventories. Environ. Sci. Technol. 46, 3528–3535 (2012).

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(12) National emission ceilings directive emissions data viewer 1990-2017. Data were downloaded from https://www.eea.europa.eu/data-and-maps/dashboards/necd-directive-data-viewer-2.

(13) Air pollutant emissions trends data. Data were downloaded from https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data.

(14) Air pollutants emissions inventory online search. Data were downloaded from https://pollution-waste.canada.ca/air-emission-inventory.

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(19) https://new.qq.com/rain/a/20150724017824.

(20) http://finance.people.com.cn/n1/2017/1228/c1004-29734355.html.

Supplementary Text 1 | Publications of $\delta^{15}N_{w\text{-}NO3\text{-}}$ observations.

(21) Altieri, K. E., Hastings, M. G., Gobel, A. R., Peters, A. J. & Sigman, D. M. Isotopic composition of rainwater nitrate at bermuda: the influence of air mass source and chemistry in the marine boundary layer. J. Geophys. Res. Atmos. **118**, doi:10.1002/jgrd.50829 (2013).

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