Supplement of

Enhanced sulfate formation through SO_2+NO_2 heterogeneous reactions during heavy winter haze in the Yangtze River Delta region, China

Ling Huang et al.

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Table S1. Summary of parameters representing clean, transition, and polluted conditions during Beijing 2015. Temperature (T) and relative humidity (RH) are directly adopted from Table S2 of Wang et al. (2016). NO_2 concentrations are assumed to be 50 % of NOx. Liquid water content (LWC) and aerosol pH are calculated by ISORROPIA assuming a metastable aerosol in CAMx.

Conditions	Temperature [K]	RH [%]	NO_2(g) [ppb]	LWC [$\mu g\ m^{-3}$]	Aerosol pH [-]
Clean	273.4	21	32	1.24	5.5
Transition	274.4	41	58	12.3	4.2
Polluted	273.9	56	45.5	35.8	4.1

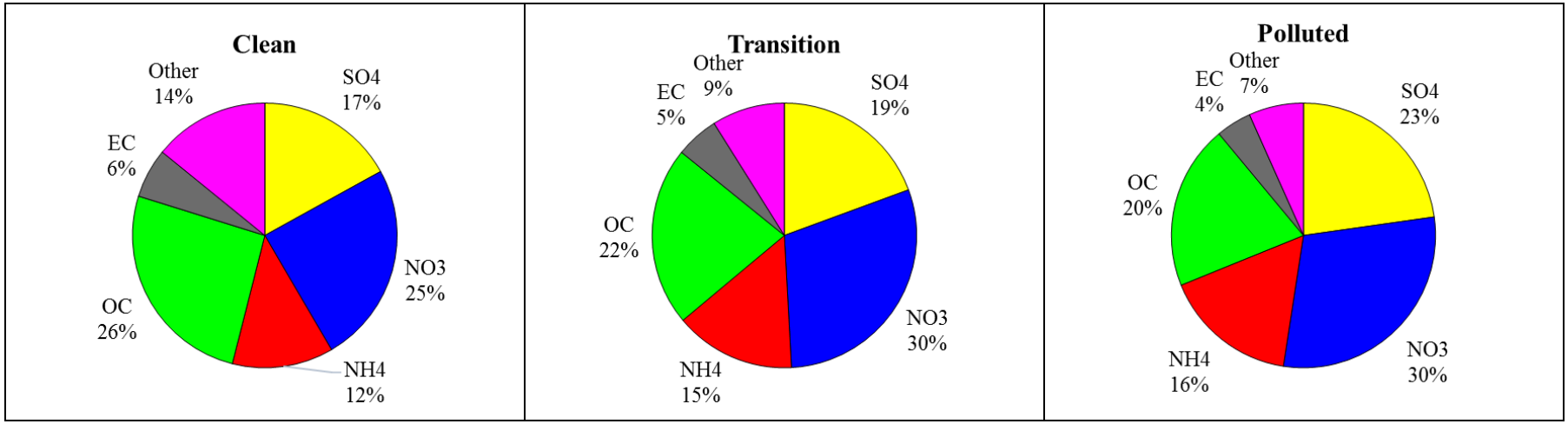


Figure S1. Mass fractions of major PM species for clean, transition, and polluted periods during 1 to 29 December 2013 at SAES site.

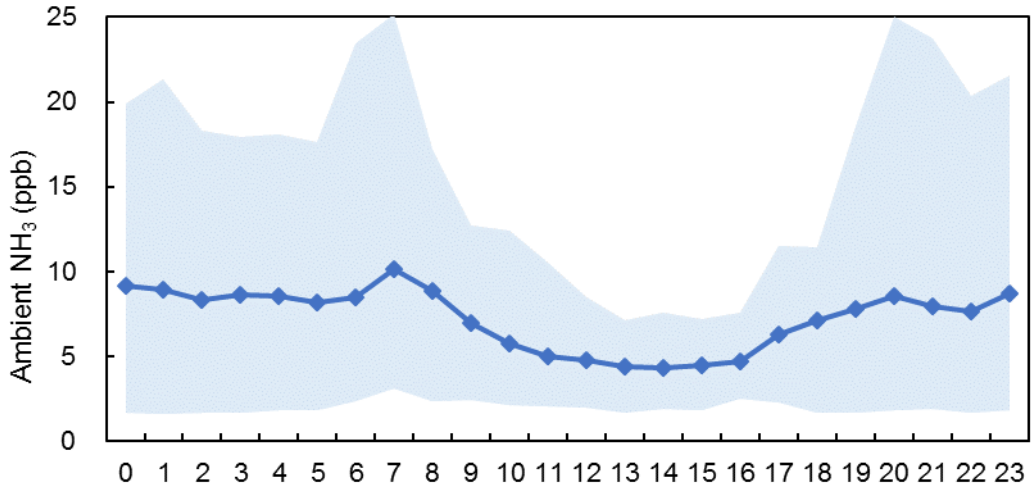


Figure S2. Diurnal profiles of ammonia concentrations (ppb) at FDU site during 1 to 29 December 2013. Shaded areas constrain maximum and minimum concentrations.

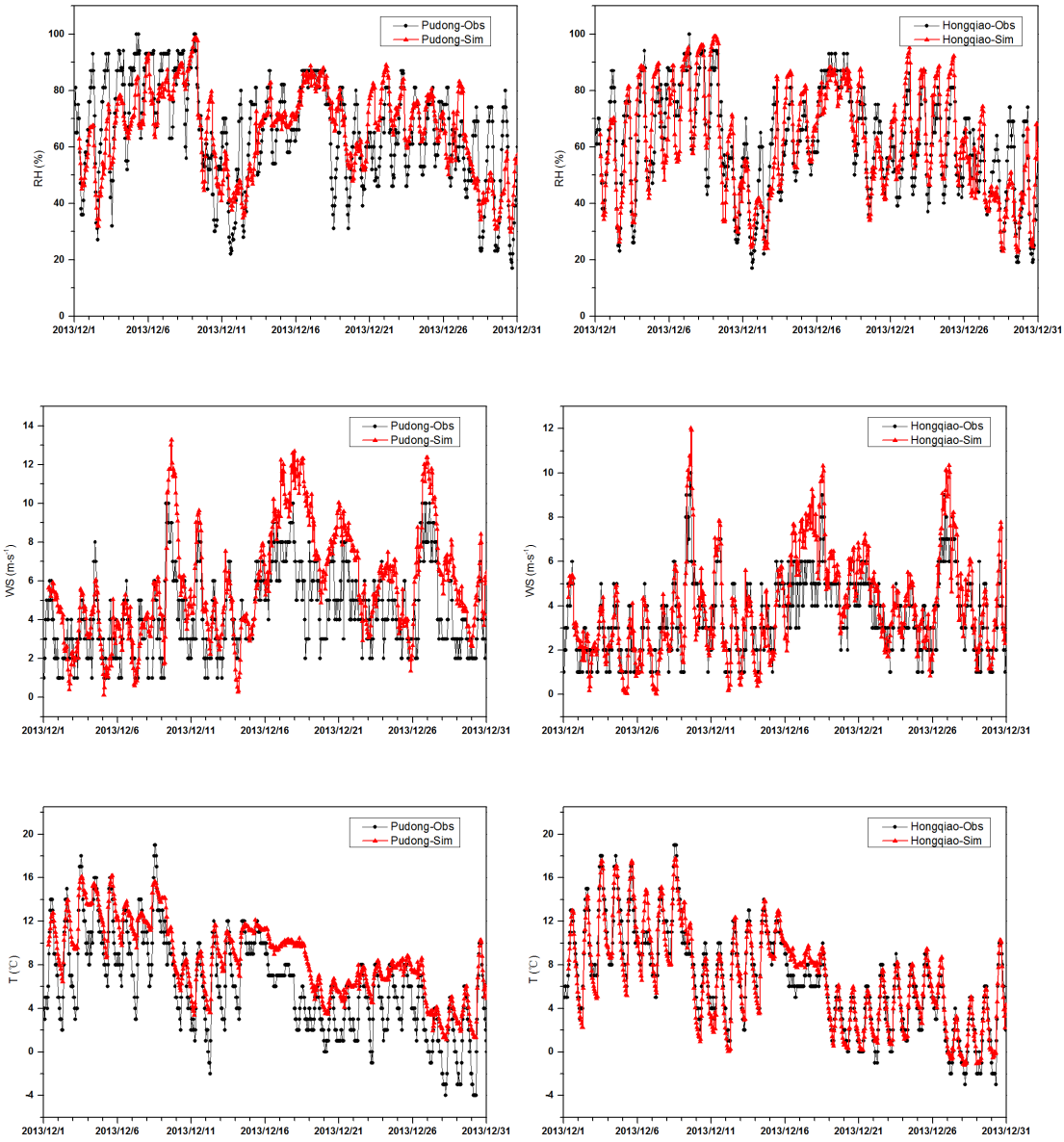


Figure S3. Comparison of observed (black dot-line) and simulated (red dot-line) hourly relative humidity (top row), wind speed (WS, middle row) and temperature (bottom row) at Pudong (left column) and Hongqiao (right column) airport monitoring site.

Table S2. Statistical summary of monthly $PM_{2.5}$ simulated from noHet and Het_2NH_3 scenarios at 23 monitoring sites in Zhejiang, Jiangsu and Anhui province during 1 to 29 December 2013.

No.	Province	City	Latitude	Longitude	Observed mean	noHet				Het_2NH_3			
						Modeled mean	MB	NMB	IOA	Modeled mean	MB	NMB	IOA
1		Hangzhou	29.64	119.03	66.5	60.1	-6.4	-10%	0.74	74.0	7.5	11%	0.75
2		Ningbo	29.85	121.52	153.0	108.9	-44.1	-29%	0.71	122.5	-30.5	-20%	0.78
3		Wenzhou	28.02	120.67	86.6	56.5	-30.1	-35%	0.71	69.3	-17.3	-20%	0.75
4		Jiaxing	30.76	120.76	131.9	102.5	-29.5	-22%	0.73	116.5	-15.4	-12%	0.80
5		Huzhou	30.86	120.09	189.3	119.8	-69.6	-37%	0.67	140.6	-48.7	-26%	0.77
6	Zhejiang	Quzhou	28.94	118.87	71.4	82.8	11.4	16%	0.72	89.8	18.5	26%	0.66
7		Zhoushan	30.02	122.12	99.0	59.5	-39.5	-40%	0.67	72.2	-26.8	-27%	0.75
8		Taizhou	28.65	121.42	106.9	75.3	-31.7	-30%	0.76	88.8	-18.2	-17%	0.82
9		Lishui	28.45	119.91	91.0	61.5	-29.5	-32%	0.62	75.1	-15.9	-17%	0.68
10		Shaoxing	30.01	120.58	198.7	138.8	-60.0	-30%	0.64	166.1	-32.6	-16%	0.72
11		Jinhua	29.11	119.65	164.3	88.2	-76.1	-46%	0.59	105.5	-58.8	-36%	0.68
12		Nanjing	32.01	118.74	170.5	139.4	-31.1	-18%	0.76	152.5	-18.0	-11%	0.80
14		Xuzhou	34.28	117.29	142.0	139.5	-2.4	-2%	0.70	150.0	8.0	6%	0.71
15		Changzhou	31.76	120.00	144.9	127.1	-17.8	-12%	0.83	141.8	-3.1	-2%	0.86
16		Suzhou	31.25	120.56	154.8	119.3	-35.5	-23%	0.74	132.7	-22.1	-14%	0.79
17		Nantong	31.93	120.94	132.1	92.9	-39.2	-30%	0.73	104.3	-27.8	-21%	0.78
18	Jiangsu	Huai'an	33.60	119.04	200.1	109.7	-90.4	-45%	0.55	120.5	-79.6	-40%	0.57
19		Yancheng	33.37	120.13	145.1	130.8	-14.3	-10%	0.75	140.2	-4.9	-3%	0.76
20		Yangzhou	32.38	119.39	144.9	137.6	-7.3	-5%	0.75	149.7	4.8	3%	0.77
21		Zhenjiang	32.21	119.43	143.5	140.7	-2.7	-2%	0.78	154.1	10.7	7%	0.79
22		Taizhou	32.49	119.90	158.0	119.1	-39.0	-25%	0.73	126.9	-31.2	-20%	0.77
23		Suqian	33.95	118.29	139.9	115.9	-24.0	-17%	0.74	126.4	-13.5	-10%	0.74
24	Anhui	Hefei	31.91	117.16	132.2	115.0	-17.1	-13%	0.77	126.8	-5.4	-4%	0.77

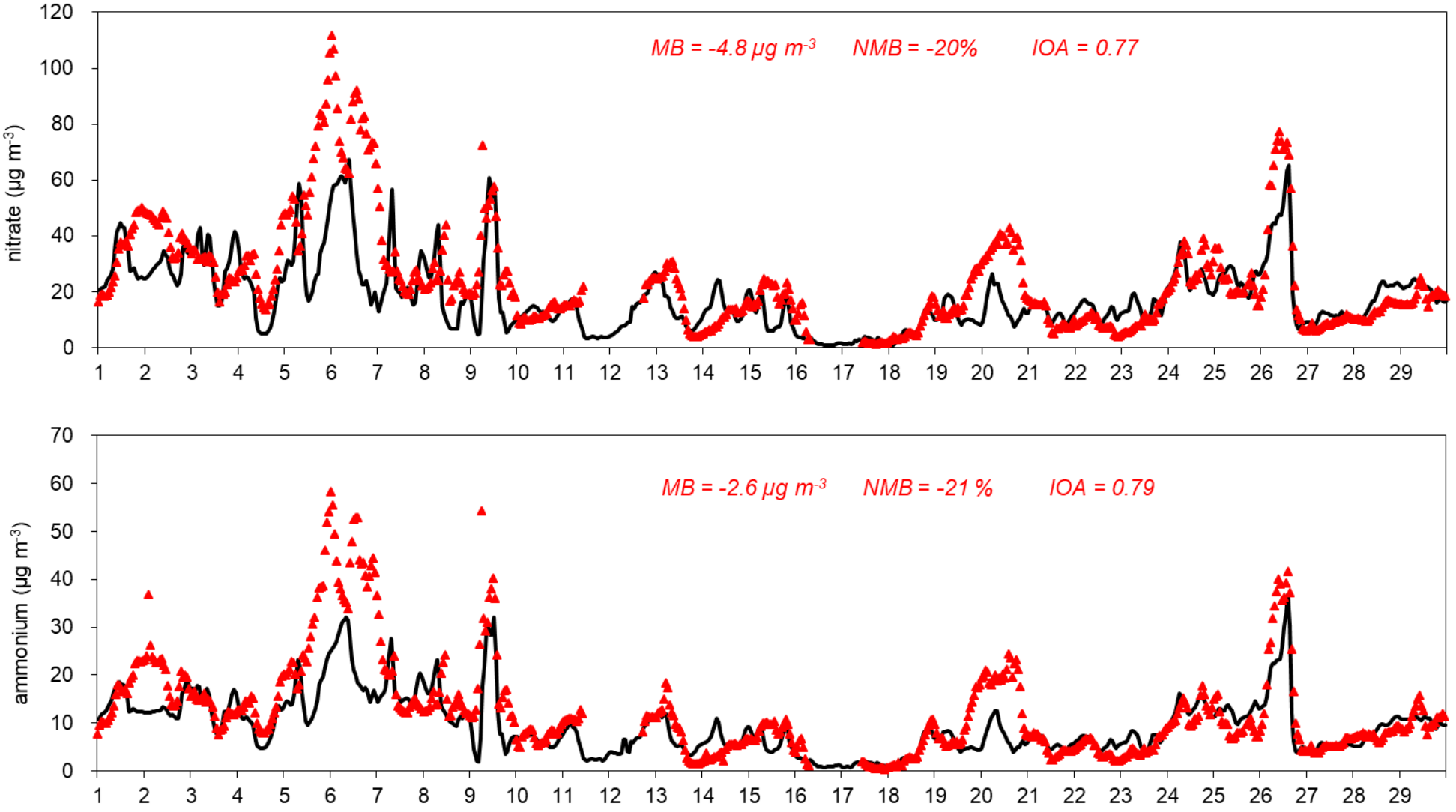
Table S3. Statistic summary of WRF simulated meteorological parameters during December 2013 at Pudong and Hongqiao airport monitoring site.

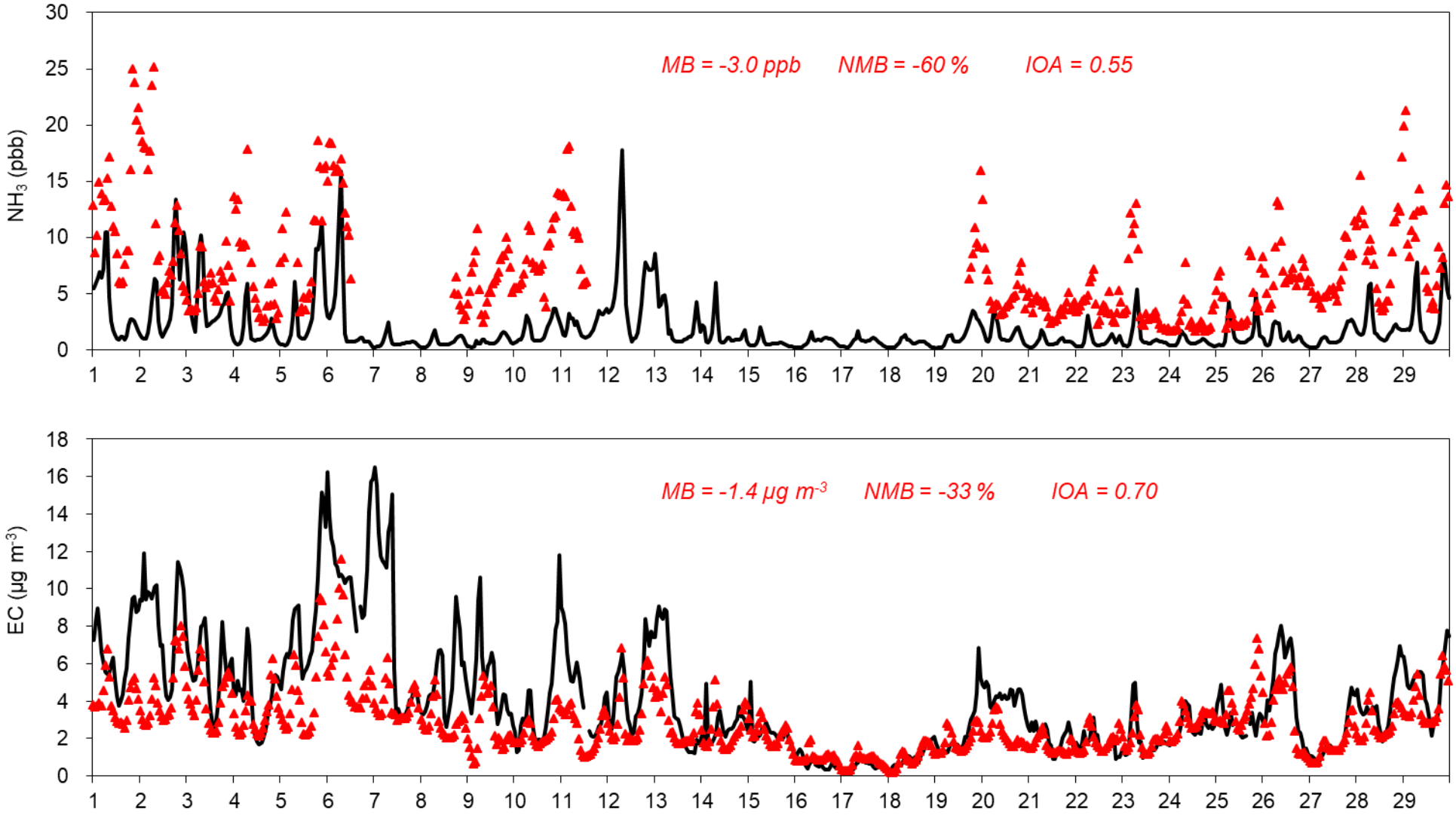
Meteorological parameter	Statistics metric	Pudong	Hongqiao
Temperature [℃]	NMB	0.37	0.01
	NME	0.41	0.16
	IOA	0.86	0.98
Relative humidity [%]	NMB	0.00	0.01
	NME	0.16	0.14
	IOA	0.85	0.92
Wind speed [m s^{-1}]	NMB	0.33	0.14
	NME	0.42	0.29
	IOA	0.79	0.89
Wind direction	Bias	0.13	0.31

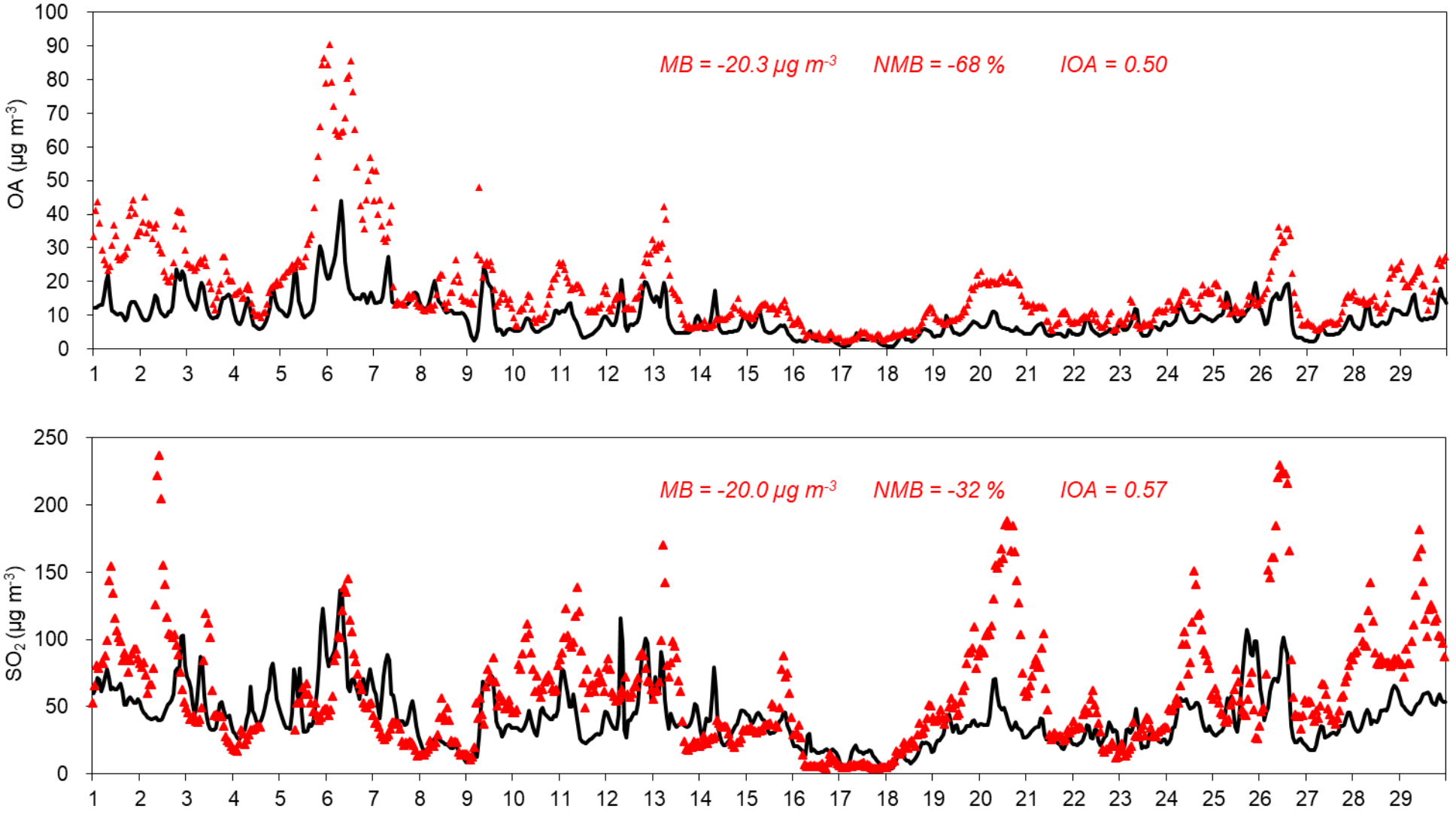
Table S4. Statistical analysis of base case model performance

Species	Observed mean [μg m^{-3}]*	Modeled mean [μg m^{-3}]*	MB	NMB	IOA
O_3	20.1	13.5	-6.6	-33%	0.76
NO_2	71.5	67.7	-3.8	-5%	0.79
SO_2	62.9	42.9	-20.0	-32%	0.57
NH_3	7.4	2.2	-5.2	-72%	0.52
$PM_{2.5}$	118.7	106.7	-12.0	-10%	0.78
sulfate	17.2	14.5	-2.7	-16%	0.80
ammonium	12.7	9.7	-3.0	-21%	0.79
nitrate	24.4	19.6	-4.8	-20%	0.77
EC	4.3	2.9	-1.4	-32%	0.72
OC	18.7	9.6	-9.1	-49%	0.60

*Units for all species except NH_3 are μg m^{-3}; unit for NH_3 is ppb.


MB = -4.8 µg m-3 NMB = -20% IOA = 0.77
nitrate (µg m-3)
0
20
40
60
80
100
120
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29
MB = -2.6 µg m-3 NMB = -21 % IOA = 0.79
ammonium (µg m-3)
0
10
20
30
40
50
60
70
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29


MB = -3.0 ppb
NMB = -60 %
IOA = 0.55
NH3 (ppb)
MB = -1.4 µg m-3
NMB = -33 %
IOA = 0.70
EC (µg m-3)


OA (µg m-3)
MB = -20.3 µg m-3
NMB = -68 %
IOA = 0.50
SO2 (µg m-3)
MB = -20.0 µg m-3
NMB = -32 %
IOA = 0.57

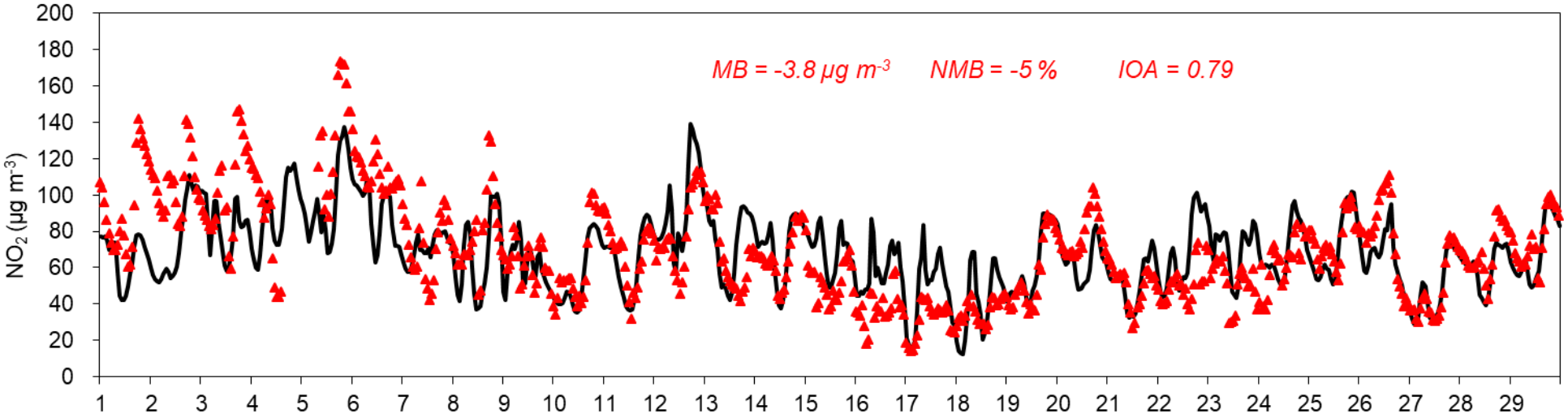


Figure S4. Time series of observed and modeled concentrations for ozone, NH_3, nitrate, ammonium, EC, OA, SO_2 and NO_2 at SAES site during 1 to 29 December 2013

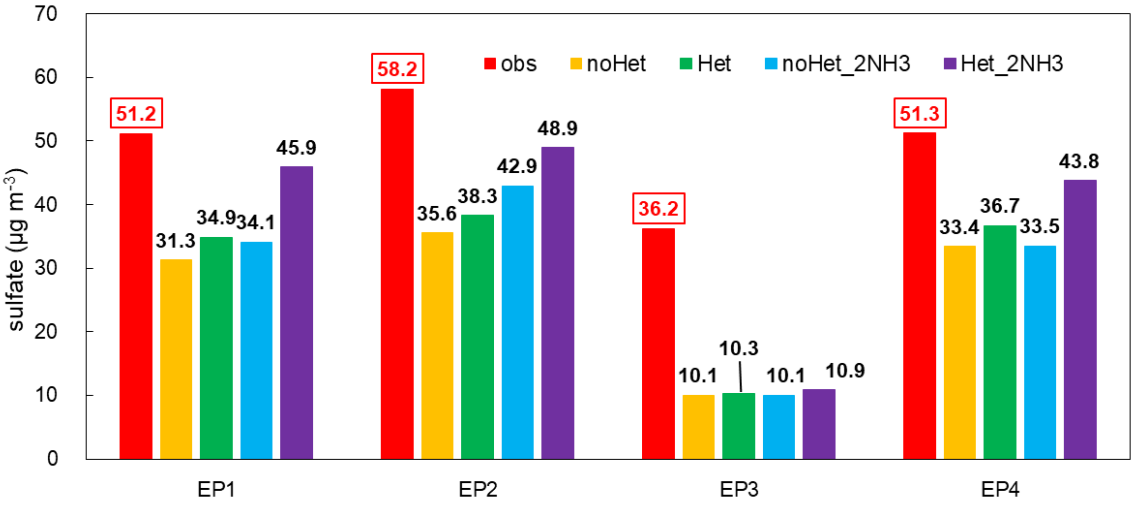


Figure S5. Observed and predicted average sulfate concentrations for four selected heavy haze episodes during 1 to 29 December 2013.

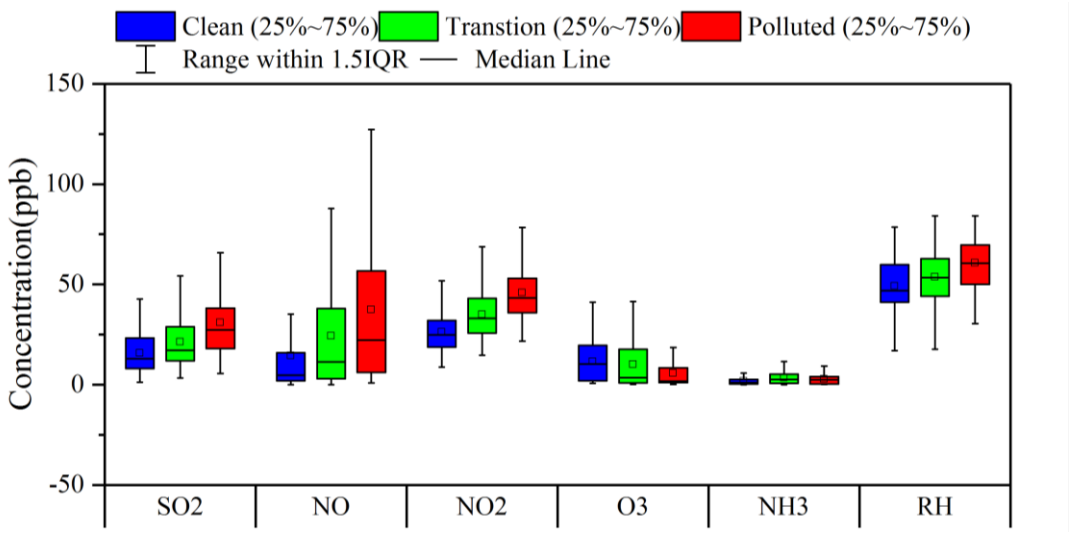


Figure S6. Box and whisker plot of observations by clean, transition and polluted periods during 1 to 29 December 2013 at SAES site.

Table S5. Statistical metrics of sulfate for different scenarios at SAES site during 1 to 29 December 2013

Scenario	Period	Mean observed sulfate [μg m^{-3}]	Mean modeled sulfate [μg m^{-3}]	MB [μg m^{-3}]	NMB [-]	IOA [-]
noHet	all	17.2	14.4	-2.8	-16%	0.80
	clean	6.7	7.8	1.1	16%	0.68
	transition	14.2	14.7	0.5	4%	0.63
	polluted	36.1	23.1	-13.0	-36%	0.59
Het	all	17.2	15.1	-2.1	-12%	0.83
	clean	6.7	8.0	1.2	18%	0.65
	transition	14.2	15.3	1.2	8%	0.62
	polluted	36.1	24.6	-11.5	-32%	0.63
noHet_2NH_3	all	17.2	15.2	-2.1	-12%	0.83
	clean	6.7	8.6	1.9	28%	0.65
	transition	14.2	15.0	0.8	6%	0.63
	polluted	36.1	24.5	-11.6	-32%	0.64
Het_2NH_3	all	17.2	17.0	-0.2	-1%	0.86
	clean	6.7	9.1	2.3	34%	0.59
	transition	14.2	16.3	2.1	15%	0.58
	polluted	36.1	29.1	-6.9	-19%	0.72

Table S6. Statistical metrics of nitrate for different scenarios at SAES site during 1 to 29 December 2013

Scenario	Period	Mean observed nitrate [μg m^{-3}]	Mean modeled nitrate [μg m^{-3}]	MB [μg m^{-3}]	NMB [-]	IOA [-]
noHet	all	24.4	19.6	-4.8	-20%	0.77
	clean	9.6	12.0	2.4	25%	0.74
	transition	22.0	20.8	-1.2	-5%	0.76
	polluted	48.4	28.3	-20.1	-42%	0.62
Het	all	24.4	19.6	-4.8	-20%	0.77
	clean	9.6	12.1	2.5	26%	0.73
	transition	22.0	20.9	-1.1	-5%	0.75
	polluted	48.4	28.1	-20.2	-42%	0.62
noHet_2NH_3	all	24.4	26.8	2.3	10%	0.82
	clean	9.6	15.9	6.3	66%	0.55
	transition	22.0	28.7	6.7	31%	0.56
	polluted	48.4	38.9	-9.5	-20%	0.72
Het_2NH_3	all	24.4	27.4	2.9	12%	0.83
	clean	9.6	16.2	6.6	69%	0.55
	transition	22.0	29.3	7.3	33%	0.57
	polluted	48.4	40.0	-8.4	-17%	0.75

Table S7. Statistical metrics of ammonium for different scenarios at SAES site during 1 to 29 December 2013

Scenario	Period	Mean observed ammonium [μg m^{-3}]	Mean modeled ammonium [μg m^{-3}]	MB [μg m^{-3}]	NMB [-]	IOA [-]
noHet	all	12.7	10.1	-2.6	-21%	0.79
	clean	4.9	5.8	0.9	19%	0.80
	transition	11.0	10.5	-0.4	-4%	0.76
	polluted	26.2	15.4	-10.8	-41%	0.61
Het	all	12.7	10.4	-2.4	-19%	0.80
	clean	4.9	5.9	1.0	20%	0.79
	transition	11.0	10.8	-0.2	-1%	0.77
	polluted	26.2	15.9	-10.3	-39%	0.63
noHet_2NH_3	all	12.7	11.6	-1.2	-9%	0.84
	clean	4.9	6.4	1.6	32%	0.70
	transition	11.0	12.0	1.1	10%	0.66
	polluted	26.2	18.1	-8.1	-31%	0.68
Het_2NH_3	all	12.7	12.4	-0.4	-3%	0.87
	clean	4.9	6.6	1.8	36%	0.70
	transition	11.0	12.6	1.7	15%	0.67
	polluted	26.2	20.0	-6.2	-24%	0.75

Table S8. Statistical metrics of $PM_{2.5}$ for different scenarios at SAES site during 1 to 29 December 2013

Scenario	Period	Mean observed $PM_{2.5}$ [μg m^{-3}]	Mean modeled $PM_{2.5}$ [μg m^{-3}]	MB [μg m^{-3}]	NMB [-]	IOA [-]
noHet	all	118.7	106.7	-12.0	-10%	0.78
	clean	52.8	69.4	16.6	31%	0.73
	transition	103.1	112.9	9.7	9%	0.74
	polluted	232.3	149.2	-83.0	-36%	0.63
Het	all	118.7	107.7	-11.0	-9%	0.79
	clean	52.8	69.8	16.9	32%	0.73
	transition	103.1	113.9	10.8	10%	0.74
	polluted	232.3	151.2	-81.0	-35%	0.64
noHet_2NH_3	all	118.7	116.0	-2.7	-2%	0.80
	clean	52.8	74.8	22.0	42%	0.68
	transition	103.1	122.5	19.3	19%	0.67
	polluted	232.3	163.7	-68.5	-30%	0.66
Het_2NH_3	all	118.7	119.4	0.7	1%	0.82
	clean	52.8	75.7	22.9	43%	0.68
	transition	103.1	125.1	22.0	21%	0.68
	polluted	232.3	171.7	-60.6	-26%	0.71

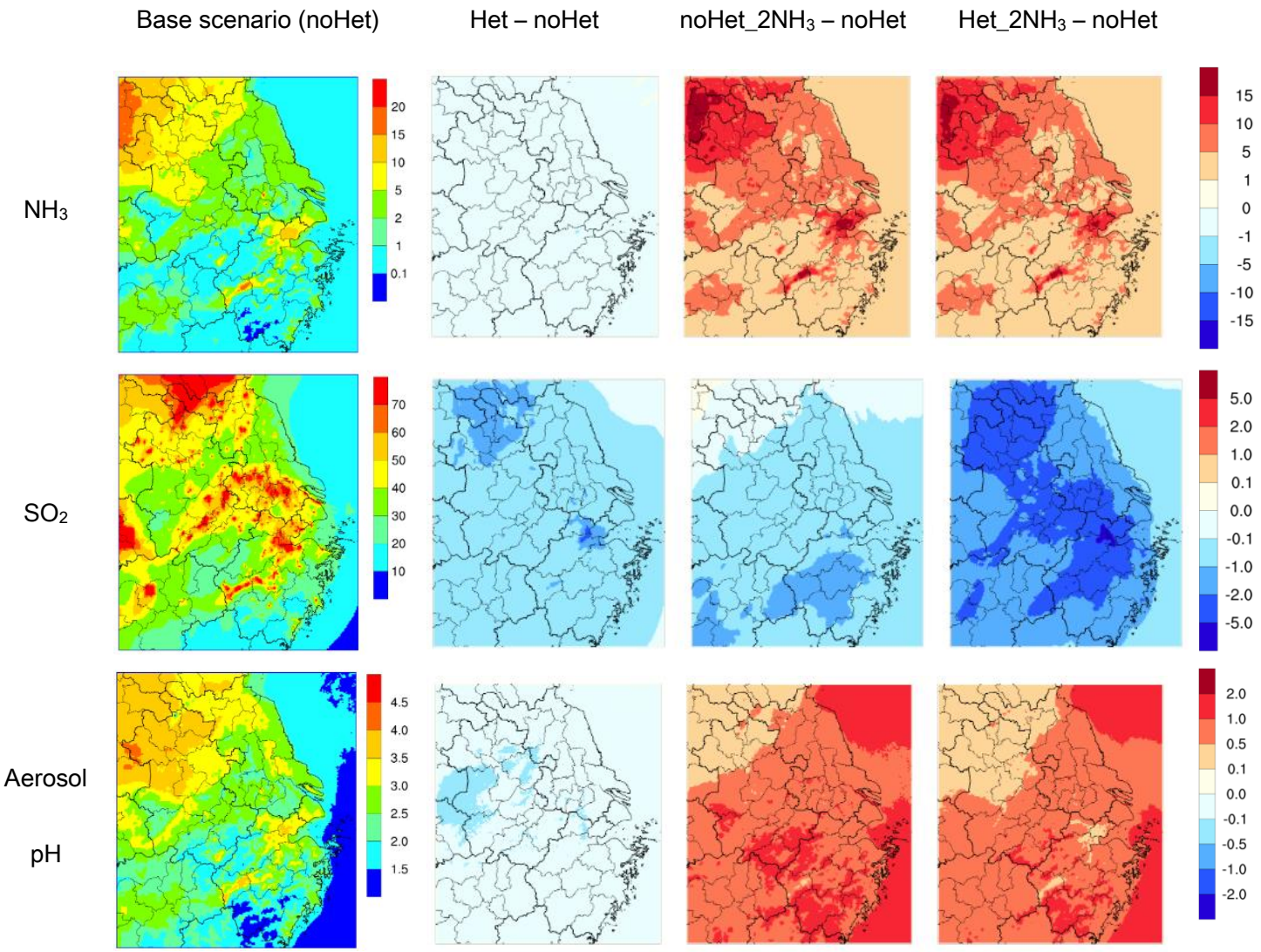


Figure S7: Spatial distribution of simulated monthly average NH_3 (μg m^{-3}, top row), SO_2 (μg m^{-3}, second row), and aerosol pH (bottom row) over the YRD region for the base case scenario (first column) and the changes between the base case and the other three sensitivity runs: Het (second column), noHet_2NH_3 (third column) and Het_2NH_3 (fourth column).

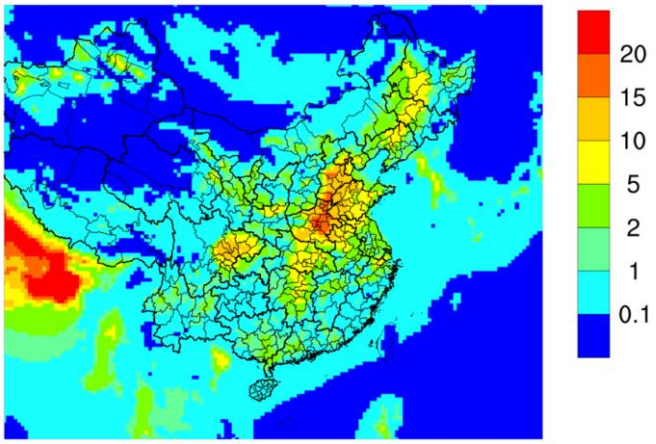


Figure S8: Spatial distribution of base case simulated monthly average NH_3 (μg m^{-3}) concentrations over China.