Assessing the nonlinear response of fine particles to precursor emissions: development and application of an Extended Response Surface Modeling technique (ERSM v1.0)

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1 Evaluation of WRF/CMAQ performance

The meteorological prediction lays the foundation for the air quality simulation. In this study, the meteorological parameters simulated by WRF were compared with the observational data obtained from the National Climatic Data Center (NCDC), where hourly or every third hour observations are available for 57 sites scattering within the innermost domain. Due to the limited observational data available, the statistical evaluation was restricted to the temperature at 2 m, wind speed and wind direction at 10 m, and humidity at 2 m. The statistical indices used include the bias, gross error (GE), the root mean square error (RMSE), and the index of agreement (IOA). A detailed explanation of these indices can be found in Baker (2004).

Table S1 lists the model performance statistics and the benchmarks suggested by Emery et al. (2001). These benchmark values were derived based on performance statistics of the Fifth-Generation NCAR/Penn State Mesoscale Model (MM5) from a number of studies over the U.S. domain (mostly at grid resolution of 12km or 4km), and have been widely accepted in many regional air quality modeling studies. We expect these standards should also be applicable in our simulation domain. For wind speed and humidity, all statistical indices are within the benchmark range. For temperature, the bias for the August simulation slightly exceeds this benchmark (-0.61K vs ±0.5K), but the bias for January, and the values of GE and IOA are all within the benchmarks, indicating an acceptable performance. While the biases for wind direction are below 10 degrees, the GEs are slightly larger than the 30 degrees benchmark value. As indicated in the previous research (Wang et al., 2010; Zhang et al., 2006), the large gross errors may result from a caveat in treating the wind direction vector as a scalar in the evaluation method, where error calculations are performed inconsistently when determining the differences between simulated and observed values. On a wind rose plot, both 0 and 360 degrees represent the direction of north. Therefore, for instance, if the observed wind is in the north direction and the predicted value is 190 degrees, the actual difference can be 190-0=190 degrees or 360-190=170 degrees. If the first value (i.e., 190) is selected in calculating the gross errors, this increases the actual difference in the gross errors by 20 degrees. The observed temperature and humidity are reproduced quite well, with all the statistical indices significantly better than the benchmark values. In summary, these statistics indicate an overall satisfactory performance of meteorological predictions.

Table S 1. Penetrations of major control technologies for industrial process in China.

Item	Wind speed (m/s)				Wind direction (deg)		Temperature (K)				Humidity (g/kg)			
	Bias	GE	RMSE	IOA	Bias	GE	Bias	GE	RMSE	IOA	Bias	GE	RMSE	IOA
Ref.	<±0.5		<2	>0.6	<±10	<30	< ± 0.5	<2		>0.8	<±1	<2		>0.6
Jan	0.41	1.16	1.52	0.81	4.02	33.00	0.46	1.35	1.74	0.93	0.28	0.56	0.76	0.85
Aug	0.40	1.13	1.47	0.78	-1.21	36.80	-0.61	1.58	2.03	0.91	0.73	1.47	1.9	0.73

During the simulation period, the Ministry of Environmental Protection of China (MEP) reported daily primary pollutant and its air pollution index (API) for 12 major cities in the innermost domain on its official website (http://datacenter.mep.gov.cn). Using each city's API

and primary pollutant, it is possible to back-calculate the daily average concentration for the primary pollutant. PM_{10} is the primary air pollutant on most of the days. The simulated and API-derived PM_{10} concentrations are therefore compared, as shown in Fig. S1. The simulated values used in the comparison are the average concentrations of the urban area (see Fig. 2 in the main text). The observation of a specific city was adopted if the API-derived PM_{10} concentrations were available for more than 70% days during the simulation period (62 days in total).

A number of statistical indices including mean observation, mean simulation, normalized mean bias (NMB), normalized mean error (NME), mean fractional bias (MFB), and mean fractional error (MFE), were calculated for the cities to give a quantitative assessment of the model performance, as shown in Table S2. The benchmarks proposed by Boylan (2005) and Morris et al. (2005) are also listed in Table S2. It can be seen that the PM_{10} concentrations are underestimated both months. This underestimation may be mainly attributable to the exclusion of fugitive dust emissions, and the underestimation of secondary organic aerosols (SOA). All the statistical indices meet the criteria, indicating a satisfactory modeling performance.

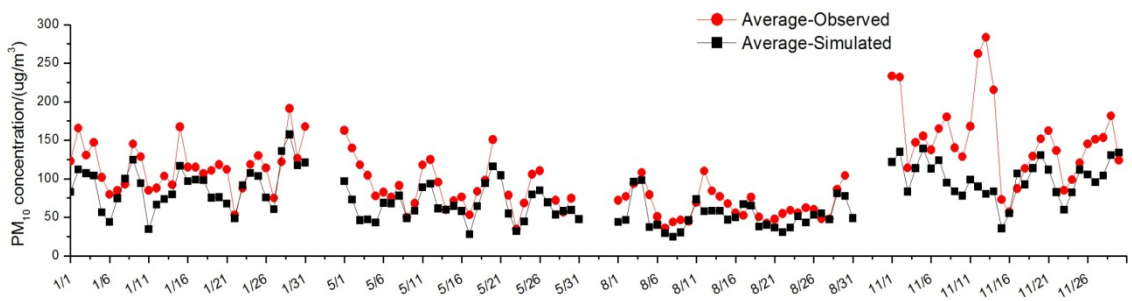

Figure S 1. Comparison of PM_{10} simulation with API-derived observation in 12 major cities

Table S 2. Statistical results for the comparison of simulated PM_{10} concentrations with API-derived observations.

Month	Mean observation (μg/m^3)	Mean simulation (μg/m^3)	Normalized mean bias (NMB)	Normalized mean error (NME)	Mean fractional bias (MFB)	Mean fractional error (MFE)
Benchmark					±50-60%	75%
Jan	116.0	90.3	-22.2%	31.7%	-26.6%	36.9%
Aug	65.3	51.7	-20.8%	36.5%	-26.9%	43.3%

The observational data of fine particles are very sparse and not publicly available during the simulation period (January and August, 2010). In order to evaluate the model performance in simulating fine particle pollution, we conducted extra simulations for two field campaign periods (July 15-30 and December 15-30) in 2011 and compared the simulated $PM_{2.5}$ concentrations with observations (unpublished data of Tsinghua University), as shown in Fig. S2. Note that the observations are not available in January for the Shanghai-Xushui site. The comparison results indicate that the modeling system can capture the temporal variation of $PM_{2.5}$ concentrations fairly well. The simulated average concentrations agree very well with observations for most periods, with NMBs ranging between -15% and +24%. Relatively large underestimation occurs in Shanghai-Pudong site during July (-38%) and relatively large overestimation occurs in Nanjing during December (+58%).

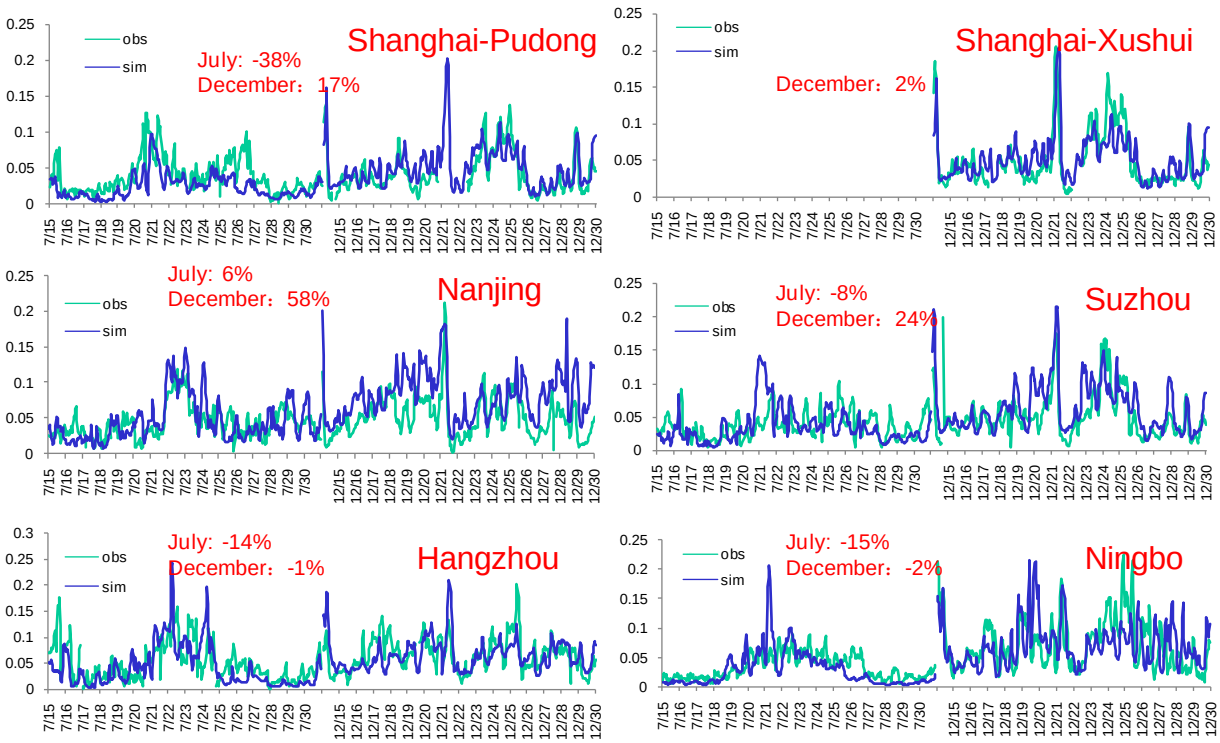

Figure S 2. Comparison of simulated hourly $PM_{2.5}$ concentrations with observations during a field campaign in 2011 (unit: $\mu g/m^3$). The percentage in the figure represents the normalized mean bias (NMB).

The simulated concentrations of inorganic aerosols are compared with the observational data at the Shanghai-Xushui site during December, 2011 (Fig. S3). It can be seen that the modeling system can capture the temporal trends of SO_4^{2-}, NO_3^-, and NH_4^+ fairly well. There is an overestimation for NO_3^- (25%), underestimation for SO_4^{2-} (-37%), and good agreement for NH_4^+ (14%). The overestimation of NO_3^- and underestimation for SO_4^{2-} to a certain extent are consistent with previous studies, probably attributable to the lack of some chemical formation pathways in the modeling system (Wang et al., 2011; Wang et al., 2013).

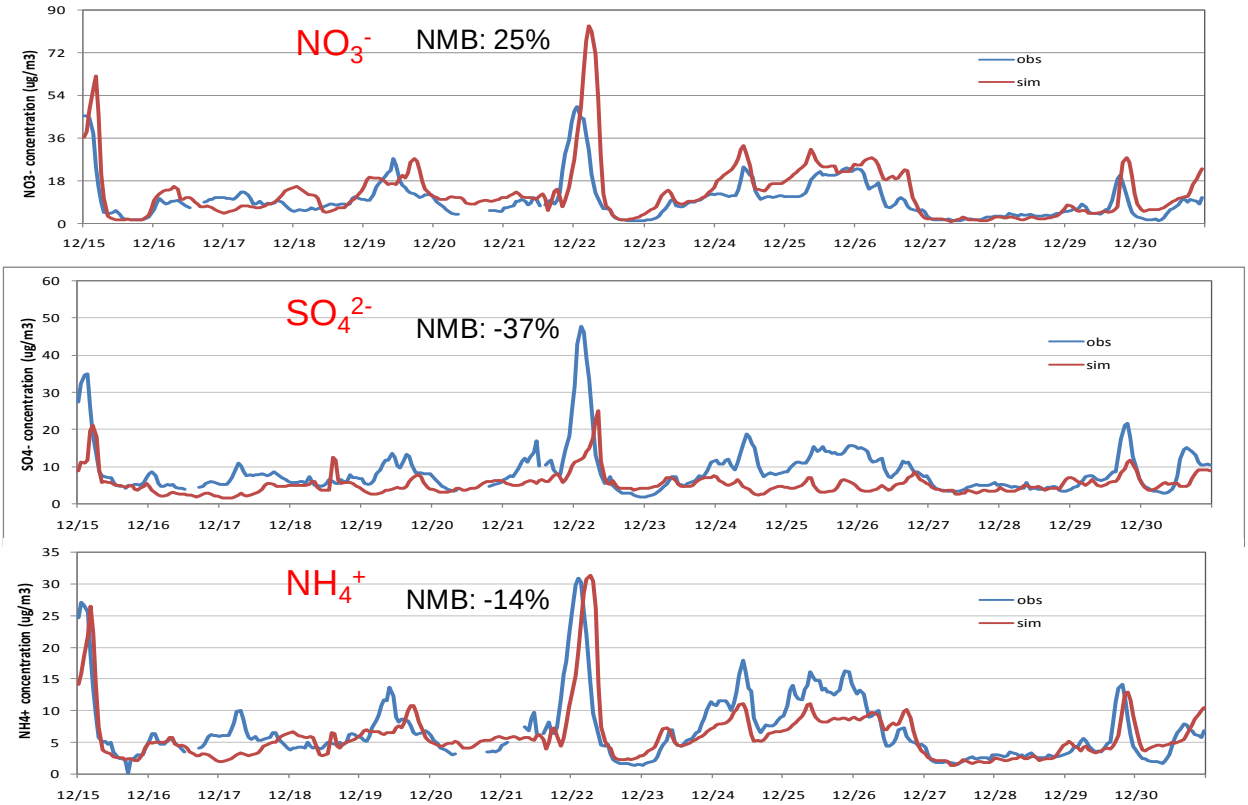

Figure S 3. Comparison of simulated inorganic aerosol concentrations with observations at the Shanghai-Xushui site during a field campaign in 2011.

2 Validation of ERSM performance

Table S 3. Description of out-of-sample scenarios

Case number	Description
1-6	Control variables of gaseous precursors in Shanghai change but the other variables stay

	the same as the base case. For case 1-3, the emission ratios (defined as the ratios of the changed emissions to the emissions in the base case) of all control variables of gaseous precursors in Shanghai are set to 0.1, 0.5, and 1.45, respectively. Case 4-6 are generated randomly by applying LHS method for the control variables of gaseous precursors in Shanghai.
7-12	The same as case 1-6 but for Jiangsu.
13-18	The same as case 1-6 but for Zhejiang.
19-24	The same as case 1-6 but for Others.
25-32	Control variables of gaseous precursors change but those of primary $PM_{2.5}$ stay the same as the base case. For case 25-27, the emission ratios of all control variables of gaseous precursors are set to 0.1, 0.5, and 1.45, respectively. Case 28-32 are generated randomly by applying LHS method for the control variables of gaseous precursors.
33-36	Control variables of primary $PM_{2.5}$ change randomly (with LHS method applied) but those of gaseous precursors stay the same as the base case.
37-40	Case 37-40 are generated randomly by applying LHS method for all control variables.

Table S 4. Comparison of $PM_{2.5}$ concentrations predicted by the ERSM technique with out-of-sample CMAQ simulations in January.

Case	ERSM prediction			CMAQ simulation			Normalized Error (NE)		
number	Shanghai	Jiangsu	Zhejiang	Shanghai	Jiangsu	Zhejiang	Shanghai	Jiangsu	Zhejiang
1	59.3	80.9	70.7	61.7	80.8	70.8	3.9%	0.1%	0.2%
2	62.9	80.6	71.1	64.3	81.0	71.2	2.2%	0.5%	0.1%
3	67.2	81.0	71.2	65.7	80.8	71.1	2.3%	0.2%	0.1%
4	63.8	80.8	71.1	63.8	80.8	71.1	0.0%	0.0%	0.0%
5	63.3	80.1	71.1	65.0	80.9	71.1	2.6%	1.0%	0.1%
6	65.0	81.2	71.4	66.2	81.2	71.4	1.9%	0.1%	0.1%
7	63.5	73.9	69.0	63.9	75.2	69.3	0.6%	1.8%	0.4%
8	64.7	78.6	70.4	64.8	80.2	70.6	0.3%	2.0%	0.3%
9	65.6	82.8	71.6	65.4	81.1	71.4	0.4%	2.0%	0.3%
10	64.5	79.1	70.4	64.6	79.2	70.6	0.1%	0.1%	0.2%
11	64.8	78.9	70.9	65.0	80.7	71.1	0.4%	2.2%	0.3%
12	65.7	81.5	71.2	65.8	82.4	71.3	0.1%	1.2%	0.1%
13	63.9	78.2	60.4	64.0	78.3	63.2	0.2%	0.2%	4.3%
14	64.8	80.0	68.0	64.9	80.1	69.0	0.1%	0.2%	1.5%
15	65.4	81.2	73.3	65.3	81.0	72.5	0.2%	0.2%	1.1%
16	64.8	80.1	68.0	64.8	80.2	68.2	0.1%	0.1%	0.3%
17	65.1	80.7	68.9	65.2	80.8	70.5	0.1%	0.2%	2.3%
18	65.2	80.6	71.5	65.2	80.6	72.0	0.0%	0.1%	0.7%
19	64.2	79.3	69.5	64.3	79.4	69.5	0.2%	0.1%	0.1%
20	64.7	80.2	70.4	64.8	80.2	70.4	0.1%	0.1%	0.1%
21	65.6	81.5	71.8	65.5	81.4	71.7	0.2%	0.1%	0.1%
22	64.8	80.4	70.6	64.9	80.5	70.6	0.1%	0.0%	0.0%
23	65.1	80.8	71.0	65.2	80.8	71.1	0.1%	0.1%	0.1%
24	65.1	80.6	70.8	65.1	80.6	70.9	0.0%	0.0%	0.0%

25	52.4	65.9	52.4	53.9	66.6	55.3	2.8%	1.1%	5.2%
26	61.2	76.5	66.2	62.7	78.0	66.7	2.5%	2.0%	0.9%
27	67.9	83.7	74.7	66.2	81.5	73.0	2.7%	2.7%	2.4%
28	63.6	77.4	67.8	64.5	79.7	68.0	1.3%	3.0%	0.4%
29	64.4	80.3	69.1	65.1	80.5	70.5	1.2%	0.3%	2.0%
30	62.5	77.6	59.4	63.6	77.7	58.6	1.7%	0.1%	1.4%
31	63.5	81.1	73.2	63.0	80.7	72.3	0.9%	0.4%	1.2%
32	64.6	78.5	70.4	65.4	81.0	71.8	1.2%	3.0%	2.0%
33	59.8	69.3	78.9	59.8	69.3	78.9	0.0%	0.0%	0.0%
34	53.9	78.0	62.8	53.9	78.0	62.8	0.1%	0.1%	0.1%
35	66.4	73.7	66.1	66.4	73.7	66.1	0.0%	0.0%	0.0%
36	58.0	82.3	72.2	58.1	82.3	72.2	0.0%	0.0%	0.0%
37	44.2	66.6	50.6	45.1	68.3	52.4	2.1%	2.4%	3.4%
38	45.6	74.3	65.4	47.7	75.2	66.1	4.5%	1.2%	1.1%
39	66.7	65.6	71.6	66.4	65.6	73.7	0.4%	0.1%	2.8%
40	61.3	83.6	67.7	61.9	82.9	67.5	1.0%	0.8%	0.3%

Table S 5. Comparison of $PM_{2.5}$ concentrations predicted by the ERSM technique with out-of-sample CMAQ simulations in August.

Case	ERSM prediction			CMAQ simulation			Normalized Error (NE)		
number	Shanghai	Jiangsu	Zhejiang	Shanghai	Jiangsu	Zhejiang	Shanghai	Jiangsu	Zhejiang
1	32.0	54.5	38.7	32.1	54.5	39.5	0.1%	0.1%	2.0%
2	36.2	55.0	39.0	36.1	55.0	39.7	0.3%	0.0%	1.7%
3	40.3	55.6	39.1	40.2	55.5	40.0	0.2%	0.1%	2.1%
4	36.2	55.1	39.2	36.0	55.1	39.7	0.4%	0.0%	1.5%
5	37.5	55.2	39.1	38.0	55.2	39.7	1.3%	0.0%	1.6%
6	38.7	55.3	39.2	38.5	55.3	39.8	0.7%	0.0%	1.4%
7	36.7	41.2	38.1	36.7	41.4	38.7	0.1%	0.5%	1.6%
8	37.8	49.0	38.6	37.8	49.0	39.3	0.0%	0.1%	1.8%
9	39.4	59.9	39.5	39.3	59.8	40.2	0.2%	0.2%	1.9%
10	38.1	50.2	38.8	38.1	50.1	39.5	0.1%	0.3%	1.9%
11	38.3	52.7	38.9	38.3	52.3	39.6	0.0%	0.8%	1.8%
12	38.2	54.3	38.9	38.2	54.4	39.5	0.0%	0.3%	1.3%
13	31.7	49.1	27.3	31.7	49.2	28.2	0.1%	0.3%	3.0%
14	34.8	52.3	33.9	34.8	52.2	33.8	0.0%	0.3%	0.3%
15	41.8	57.9	43.9	41.8	57.7	44.4	0.0%	0.4%	1.0%
16	36.6	53.6	35.7	36.6	53.6	35.6	0.2%	0.1%	0.5%
17	38.2	54.6	37.2	38.2	54.6	37.5	0.0%	0.1%	0.8%
18	34.8	52.6	37.0	34.8	52.5	36.4	0.1%	0.0%	1.5%
19	36.5	53.1	37.1	36.5	53.0	37.7	0.0%	0.2%	1.6%
20	37.5	54.2	37.9	37.5	54.1	38.7	0.0%	0.1%	1.9%
21	39.8	56.5	40.2	39.8	56.5	40.9	0.0%	0.0%	1.8%
22	38.1	54.7	38.5	38.1	54.7	39.3	0.1%	0.0%	1.9%
23	38.7	55.0	39.0	38.7	55.0	39.6	0.0%	0.0%	1.6%

24	37.7	54.6	38.1	37.6	54.6	38.7	0.0%	0.1%	1.6%
25	21.1	31.5	23.2	23.4	34.1	25.7	10.2%	7.7%	9.6%
26	30.9	44.9	31.7	30.6	44.2	32.0	1.1%	1.5%	0.8%
27	45.8	64.1	45.5	44.8	63.1	45.9	2.1%	1.6%	0.9%
28	35.4	50.4	35.6	35.3	50.4	36.4	0.4%	0.2%	2.2%
29	36.3	49.4	38.9	36.1	49.7	38.4	0.7%	0.6%	1.4%
30	33.3	48.5	28.3	32.8	48.5	28.7	1.6%	0.1%	1.2%
31	34.9	54.1	38.4	34.7	54.1	40.1	0.8%	0.0%	4.1%
32	38.7	51.9	38.2	37.9	52.0	39.0	2.0%	0.2%	2.2%
33	36.3	47.5	46.1	36.3	47.5	46.0	0.0%	0.1%	0.2%
34	31.2	53.3	33.8	31.3	53.4	33.9	0.1%	0.1%	0.2%
35	38.9	49.7	36.2	38.9	49.8	36.2	0.0%	0.0%	0.0%
36	34.4	56.4	40.5	34.4	56.4	40.4	0.0%	0.1%	0.1%
37	19.5	38.4	21.2	20.0	38.2	21.6	2.7%	0.5%	1.8%
38	24.2	41.9	32.6	23.2	42.0	32.9	4.2%	0.2%	0.9%
39	37.6	39.1	40.3	36.5	38.2	39.9	2.9%	2.5%	1.0%
40	32.0	52.9	34.1	32.0	52.8	34.7	0.0%	0.1%	1.8%

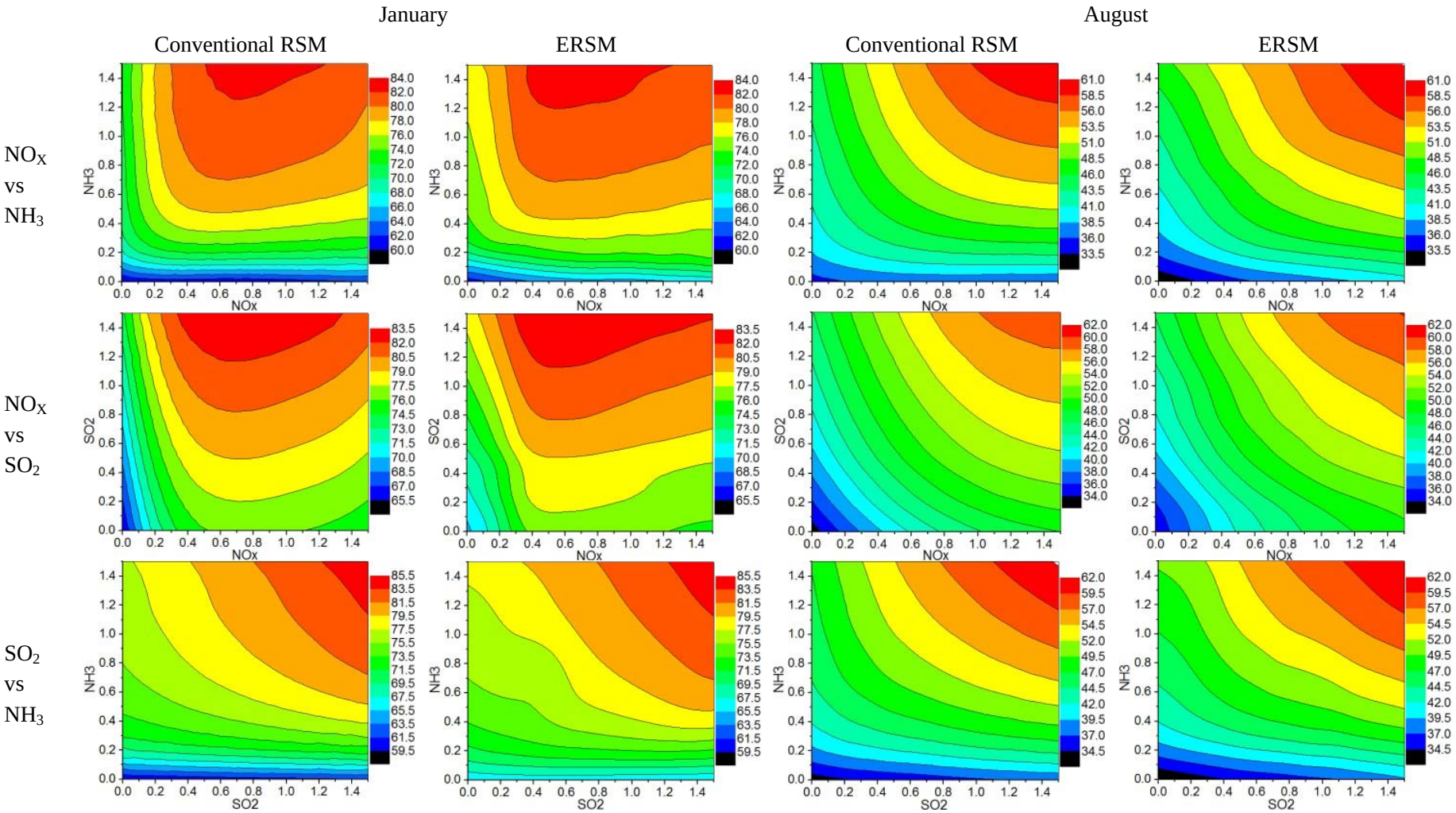

Figure S 4. The same as Fig. 4 but for the region of Jiangsu.

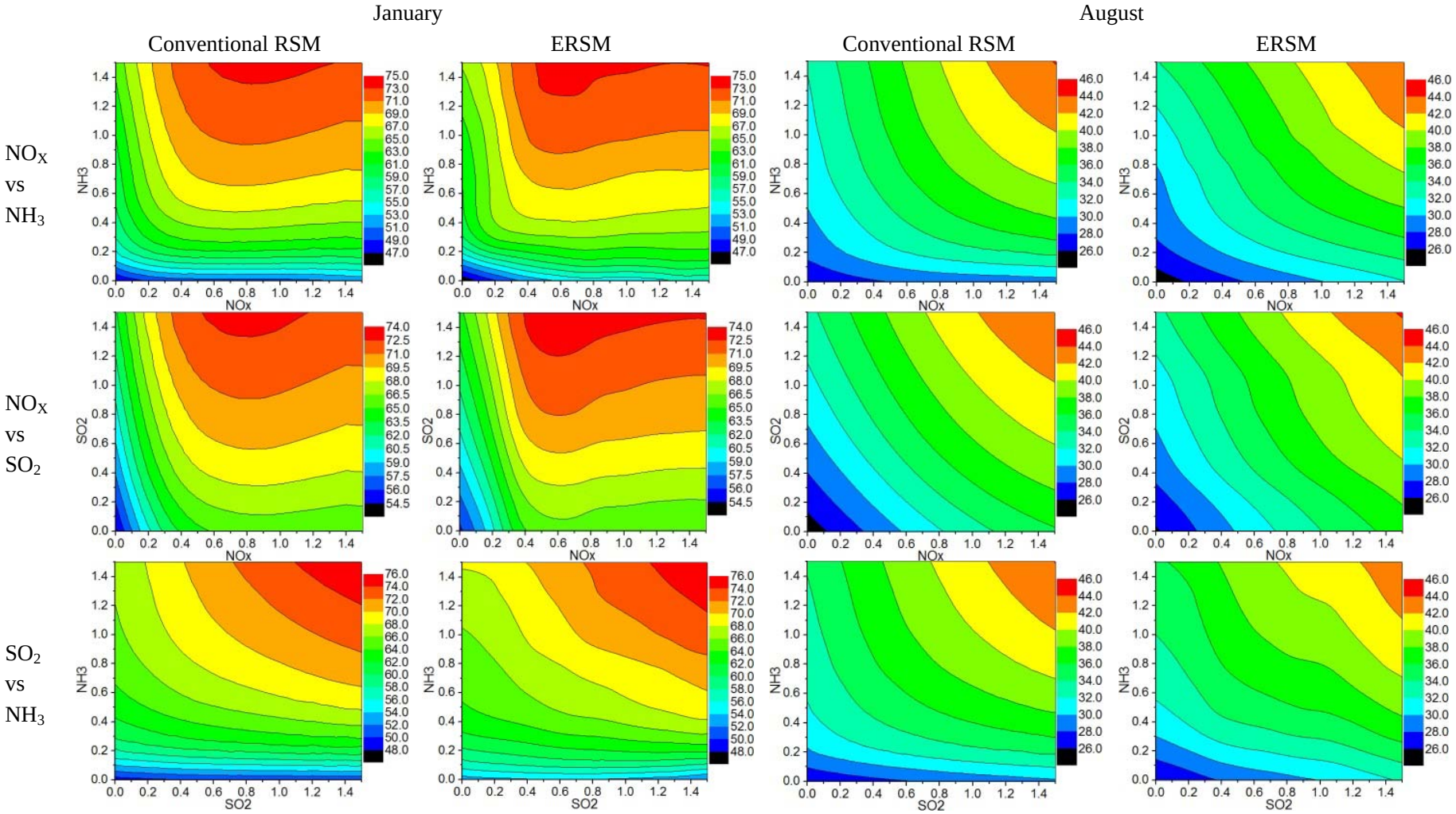

Figure S 5. The same as Fig. 4 but for the region of Zhejiang.

3 Response of $PM_{2.5}$, SO_4^{2-} and NO_3^- to precursor emissions.

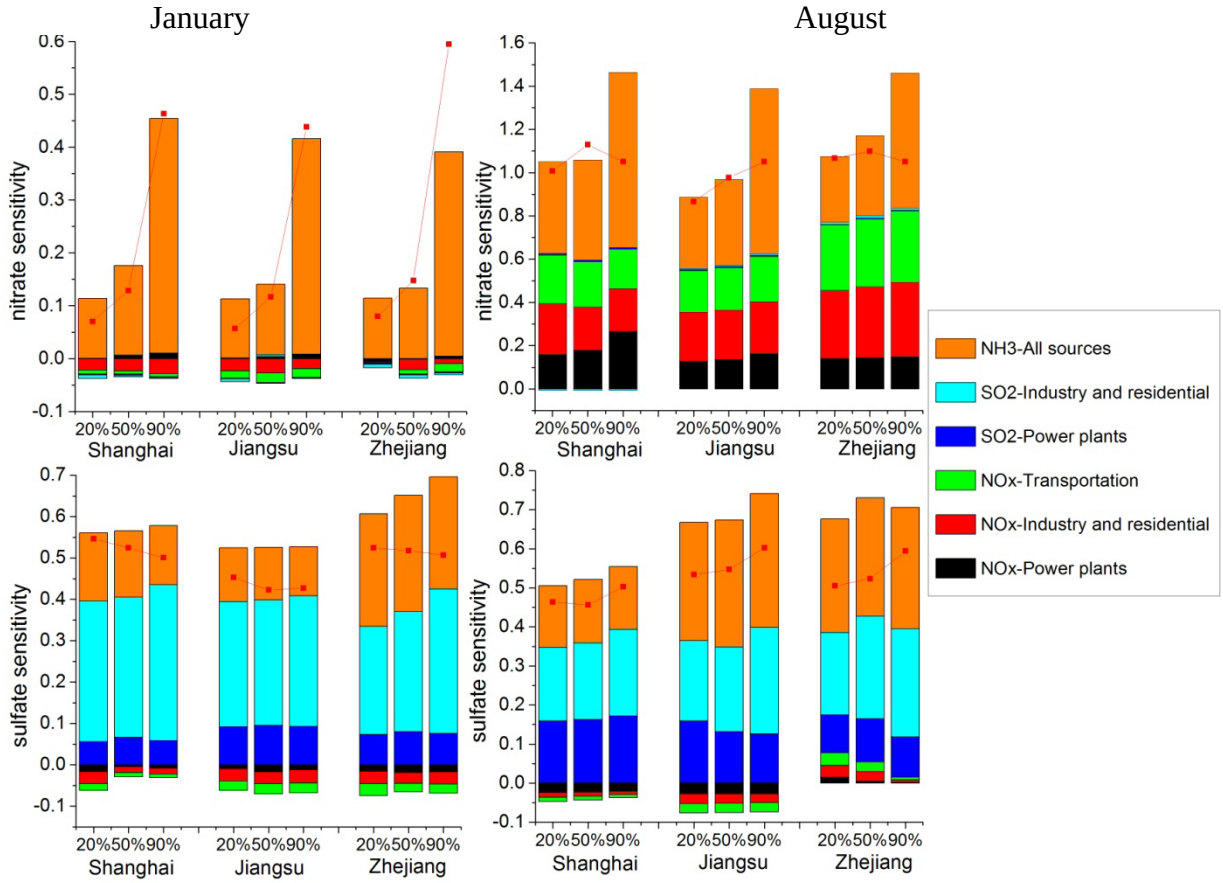

Figure S 6. Sensitivity of NO_3^- and SO_4^{2-} concentrations to the stepped control of individual air pollutants from individual sectors. The X-axis shows the reduction ratio (= 1 – emission ratio). The Y-axis shows NO_3^-/SO_4^{2-} sensitivity, which is defined as the change ratio of NO_3^-/SO_4^{2-} concentration divided by the reduction ratio of emissions. The colored bars denote the NO_3^-/SO_4^{2-} sensitivities when a particular emission source is controlled while the others stay the same as the base case; the red dotted line denotes the NO_3^-/SO_4^{2-} sensitivity when all emission sources are controlled simultaneously.

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