Supplement of

Enhanced sulfate formation through \( \text{SO}_2 + \text{NO}_2 \) 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). NO₂ 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 [%] | NO₂(g) [ppb] | LWC [μg 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 | Modeled mean | MB      | NMB     | IOA     | Modeled mean | MB      | NMB     | IOA     |
|-----|----------|--------|----------|-----------|---------------|--------------|---------|---------|---------|--------------|---------|---------|---------|
| 1   | Zhejiang | 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  | Jiangsu  | Nanjing | 32.01    | 118.74    | 170.5         | 139.4        | -31.1   | -18%    | 0.76    | 152.5        | -18.0   | -11%    | 0.80    |
| 13  |          | Xuzhou  | 34.28    | 117.29    | 142.0         | 139.5        | -2.4    | -2%     | 0.70    | 150.0        | 8.0     | 6%      | 0.71    |
| 14  |          | Changzhou| 31.76   | 120.00    | 144.9         | 127.1        | -17.8   | -12%    | 0.83    | 141.8        | -3.1    | -2%     | 0.86    |
| 15  |          | Suzhou  | 31.25    | 120.56    | 154.8         | 119.3        | -35.5   | -23%    | 0.74    | 132.7        | -22.1   | -14%    | 0.79    |
| 16  |          | Nantong | 31.93    | 120.94    | 132.1         | 92.9         | -39.2   | -30%    | 0.73    | 104.3        | -27.8   | -21%    | 0.78    |
| 17  |          | Hua’ian | 33.60    | 119.04    | 200.1         | 109.7        | -90.4   | -45%    | 0.55    | 120.5        | -79.6   | -40%    | 0.57    |
| 18  |          | Yancheng| 33.37    | 120.13    | 145.1         | 130.8        | -14.3   | -10%    | 0.75    | 140.2        | -4.9    | -3%     | 0.76    |
| 19  |          | Yangzhou| 32.38    | 119.39    | 144.9         | 137.6        | -7.3    | -5%     | 0.75    | 149.7        | 4.8     | 3%      | 0.77    |
| 20  |          | Zhenjiang| 32.21  | 119.43    | 143.5         | 140.7        | -2.7    | -2%     | 0.78    | 154.1        | 10.7    | 7%      | 0.79    |
| 21  |          | Taizhou | 32.49    | 119.90    | 158.0         | 119.1        | -39.0   | -25%    | 0.73    | 126.9        | -31.2   | -20%    | 0.77    |
| 22  |          | Suqian  | 33.95    | 118.29    | 139.9         | 115.9        | -24.0   | -17%    | 0.74    | 126.4        | -13.5   | -10%    | 0.74    |
| 23  | 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 [°C]         | 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  |
|---------|---------------------------|--------------------------|--------|---------|------|
| O₃      | 20.1                      | 13.5                     | -6.6   | -33%    | 0.76 |
| NO₂     | 71.5                      | 67.7                     | -3.8   | -5%     | 0.79 |
| SO₂     | 62.9                      | 42.9                     | -20.0  | -32%    | 0.57 |
| NH₃     | 7.4                       | 2.2                      | -5.2   | -72%    | 0.52 |
| PM₂.₅   | 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 NH₃ are µg m⁻³; unit for NH₃ is ppb.
MB = -4.8 μg m⁻³  NMB = -20%  IOA = 0.77

MB = -2.6 μg m⁻³  NMB = -21%  IOA = 0.79
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     | 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_2NH₃ | 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_2NH₃  | 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 | 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 |
| Scenario  | Period | Mean observed ammonium [µg m⁻³] | Mean modeled ammonium [µg m⁻³] | MB   | 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_2NH₃| 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_2NH₃ | 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 |
| Scenario      | Period   | Mean observed PM$_{2.5}$ [µg m$^{-3}$] | Mean modeled PM$_{2.5}$ [µg m$^{-3}$] | MB  | NMB  | IOA |
|---------------|----------|---------------------------------------|---------------------------------------|-----|------|-----|
| noHet         | all      | 118.7                                 | 106.7                                 | -12 | -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.