Supplement of "Organosulfates in atmospheric aerosols in Shanghai, China: seasonal and interannual variability, origin, and formation mechanisms"

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Table S1. Summary of average (standard deviation) values of meteorological parameters, trace gases, aerosol liquid water content (ALWC), aerosol [$H^+$], PM$_{2.5}$ and components of PM$_{2.5}$ in four seasons and throughout the year in 2015/2016 and 2018/2019.

|                  | Spring          | Summer          | Autumn          | Winter          | Annual          |
|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                  | 2015            | 2019            | 2015            | 2019           | 2015-2016       | 2018-2019       |
| $T$ (°C)         | 16.6 (3.8)      | 17.2 (2.3)      | 30.2 (2.3)      | 30.5 (3.1)     | 16.4 (1.1)      | 17.9 (1.9)      | 7.2 (0.8)  | 6.2 (0.7)  | 18.2 (1.7) | 18.4 (9.3) |
| RH               | 0.6 (0.1)       | 0.7 (0.1)       | 0.7 (0.1)       | 0.7 (0.1)      | 0.8 (0.1)       | 0.7 (0.1)       | 0.7 (0.1) | 0.7 (0.1) | 0.7 (0.1) | 0.7 (0.1) |
| wind speed (m s$^{-1}$) | 3.8 (1.5)    | 4.0 (1.2)       | 4.4 (1.3)       | 4.4 (1.2)      | 3.6 (1.0)       | 4.3 (1.0)       | 3.3 (1.0) | 3.4 (1.0) | 3.8 (1.0) | 3.8 (1.0) |
| NO$_2$ (ppb)     | 30.4 (11.5)     | 22.4 (6.1)      | 14.9 (5.2)      | 11.7 (4.0)     | 28.5 (7.4)      | 20.1 (7.1)      | 21.1 (9.4) | 14.1 (6.8) | 32.6 (14.9)| 27.0 (13.0)| 21.3 |
| O$_3$ (ppb)      | 35.9 (8.9)      | 41.2 (11.0)     | 38.5 (18.9)     | 30.7 (13.8)    | 19.2 (8.8)      | 31.7 (7.8)      | 21.1 (9.5) | 14.9 (6.7) | 29.8 (15.2)| 29.6 (13.9)|
| SO$_2$ (ppb)     | 6.3 (2.4)       | 2.2 (0.6)       | 3.5 (2.1)       | 1.5 (0.3)      | 4.8 (1.8)       | 3.5 (1.3)       | 8.4 (3.5)  | 2.8 (1.1)  | 5.7 (1.1)  | 2.5 (1.1)  |
| ALWC (μg m$^{-3}$) | 14.0 (15.4)    | 12.0 (8.5)      | 9.6 (4.5)       | 5.0 (3.3)      | 52.7 (43.7)     | 14.6 (32.4)     | 25.7 (16.8)| 29.2 (19.8)| 24.4 (16.8)| 27.0 (13.0)| 14.8 |
| [$H^+$]          | 2.4E-4 (3.5E-4) | 7.0E-5 (7.5E-5)| 7.3E-3 (6.7E-3)| 2.0E-3 (2.4E-3)| 1.9E-4 (1.2E-4)| 9.7E-5 (9.7E-5)| 6.1E-5 (7.2E-5)| 3.0E-3 (1.1E-2)| 2.3E-3 (4.8E-3)| 1.4E-3 (5.7E-3)|
| OM (μm)          | 15.9 (7.4)      | 10.6 (5.2)      | 7.4 (5.5)       | 6.2 (4.5)      | 11.5 (6.3)      | 8.3 (5.4)       | 8.3 (8.9)  | 2.2 (6.0)  | 11.1 (3.4) | 12.7 (5.5) |
| EC (μm)          | 3.9 (1.7)       | 3.4 (1.2)       | 2.5 (1.1)       | 1.5 (0.8)      | 3.2 (1.2)       | 1.8 (0.8)       | 4.0 (1.8)  | 2.2 (1.0)  | 4.0 (1.6)  | 2.2 (1.2)  |
| CF (μm)          | 0.5 (0.7)       | 0.4 (0.2)       | 0.1 (0.2)       | 0.3 (0.2)      | 1.1 (0.8)       | 0.3 (0.8)       | 1.5 (1.0)  | 1.0 (0.6)  | 1.5 (0.9)  | 0.7 (0.4)  |
| NO$_2^+$ (ppb)   | 9.4 (5.7)       | 9.9 (6.3)       | 1.0 (1.1)       | 3.4 (3.2)      | 9.6 (8.2)       | 6.7 (6.5)       | 16.6 (10.0)| 14.1 (10.0)| 16.6 (10.0)| 8.4 (7.8)  |
| SO$_2^+$ (ppb)   | 8.9 (5.2)       | 5.3 (3.1)       | 7.4 (2.0)       | 4.2 (2.0)      | 9.4 (5.7)       | 4.0 (1.9)       | 11.1 (5.1) | 9.2 (5.3)  | 9.1 (4.6)  | 5.7 (3.8)  |
| NH$_4^+$ (ppb)   | 5.9 (3.1)       | 4.6 (2.6)       | 2.7 (1.7)       | 1.4 (1.1)      | 7.0 (4.8)       | 3.1 (2.6)       | 10.2 (5.1) | 6.2 (4.1)  | 6.2 (4.6)  | 3.8 (3.3)  |
| PM$_{2.5}$ (μg m$^{-3}$) | 59.1 (21.4)    | 44.6 (20)       | 30.8 (13.5)     | 22 (11.1)      | 59.7 (35.0)     | 34.2 (17.7)     | 47.5 (29.9)| 55.9 (29.9)| 59.0 (37.9)| 38.6 (24.0)|

Units: $T$ (°C), wind speed (m s$^{-1}$), NO$_2$ (ppb), O$_3$ (ppb), SO$_2$ (ppb), ALWC (μg m$^{-3}$), aerosol [$H^+$] (mol L$^{-1}$), and major aerosol components (μg m$^{-3}$).
Table S2. Recoveries of OS standards spiked in the blank filter.

| OS standard                  | Spike concentration (ppm) | Recovery  |
|------------------------------|---------------------------|-----------|
| Limonaketone sulfate         | 2.50                      | 88.5%     |
| α-Pinene sulfate             | 2.86                      | 88.7%     |
| Δ-Carene sulfate             | 3.26                      | 66.4%     |
| β-Caryophyllene sulfate      | 1.82                      | 84.2%     |
| Octyl sulfate                | 1.94                      | 82.6%     |
| Methyl sulfate               | 1.92                      | 88.0%     |
| Phenyl sulfate               | 1.57                      | 87.7%     |
| Camphorsulfonate             | 2.27                      | 94.3%     |
| Lactic acid sulfate          | 5.05                      | 72.5%     |
| Glycolic acid sulfate        | 4.82                      | 77.8%     |

Table S3. Dates and concentrations of major components of aerosol samples used for matrix effect evaluation, as well as the ratios of the signal response of OS standards in different sample extracts to that in pure solvent.

| Exp. 1                  | Exp. 2                  | Exp. 3                  | Exp. 4                  |
|-------------------------|-------------------------|-------------------------|-------------------------|
| Date of sample          | 19/01/2019              | 19/01/2019              | 31/07/2019              | 01/08/2019              |
| OM                      | 22                      | 22                      | 4                       | 4                       |
| NO$_3^-$                 | 34                      | 34                      | 0.4                     | 0.7                     |
| SO$_4^{2-}$              | 15                      | 15                      | 2                       | 2                       |

| OS standard              | Exp. 1                  | Exp. 2                  | Exp. 3                  | Exp. 4                  |
|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Limonaketone sulfate    | 0.93 (1.3)              | 0.93 (7.8)              | 1.09                    | 1.15                    |
| α-Pinene sulfate        | 0.90 (1.4)              | 0.98 (9.0)              | 1.02                    | 1.06                    |
| Δ-Carene sulfate        | 0.81 (1.6)              | 0.91 (10.2)             | 1.02                    | 1.08                    |
| β-Caryophyllene sulfate | 0.96 (0.9)              | 1.08 (5.7)              | 1.07                    | 1.10                    |
| Octyl sulfate           | 0.87 (1.0)              | 1.00 (6.1)              | 1.10                    | 1.14                    |
| Methyl sulfate          | 0.20 (1.0)              | 0.16 (6.0)              | 0.51                    | 0.55                    |
| Phenyl sulfate          | 1.01 (0.8)              | 0.96 (4.9)              | 1.06                    | 1.12                    |
| Camphorsulfonate        | 0.89 (1.1)              | 1.07 (7.1)              | 1.06                    | 1.11                    |
| Lactic acid sulfate     | 0.93 (1.0)              | 0.86 (6.3)              | 1.35                    | 1.38                    |
| Glycolic acid sulfate   | 0.17 (1.0)              | 0.31 (6.0)              | 0.45                    | 0.53                    |

Units: OM, NO$_3^-$ and SO$_4^{2-}$ (μg m$^{-3}$). The values in parentheses are the concentrations (ppm) of the OS standards added to the aerosol sample extracts. The OS standard concentrations in experiments 2-4 are the same.
Table S4. Molecular formulas of high-molecular-weight CHOS species observed during the pollution periods of winter and summer in 2019.

| Formula          | m/z      | Formula          | m/z      |
|------------------|----------|------------------|----------|
| C_{19}H_{33}O_{8}S | 409.1896 | *C_{19}H_{33}O_{8}S_{2} | 421.0052 |
| C_{20}H_{37}O_{8}S | 421.226  | C_{22}H_{43}O_{8}S | 429.1008 |
| C_{19}H_{37}O_{8}S | 425.2209 | C_{18}H_{33}O_{14}S | 437.0026 |
| C_{22}H_{43}O_{8}S | 435.278  | C_{18}H_{33}O_{14}S | 451.0183 |
| *C_{10}H_{20}O_{10}S_{2} | 439.0733 | C_{18}H_{33}O_{14}S | 453.0339 |
| C_{18}H_{33}O_{10}S | 439.1638 | *C_{12}H_{33}O_{12}S_{2} | 455.0318 |
| C_{22}H_{43}O_{8}S | 485.2209 | C_{12}H_{33}O_{12}S | 467.0132 |
| C_{30}H_{57}O_{14}S | 611.1223 | C_{24}H_{57}O_{14}S | 485.2209 |
| C_{31}H_{57}O_{14}S | 637.3199 | C_{30}H_{57}O_{14}S | 569.3301 |
| C_{31}H_{57}O_{14}S | 685.3469 | C_{30}H_{57}O_{14}S | 601.3563 |
|                 |          | C_{30}H_{57}O_{14}S | 607.3093 |
|                 |          | C_{30}H_{57}O_{14}S | 637.3199 |
|                 |          | C_{30}H_{57}O_{14}S | 647.3981 |
|                 |          | C_{30}H_{57}O_{14}S | 691.4396 |

*The high-molecular-weight CHOS species with two sulfur atoms may be accretion products of smaller CHOS species.
### Table S5. Summary of individual organosulfate concentration (in ng m\(^{-3}\)) in four seasons in 2015/2016 and 2018/2019.

| Category | Formula | [M-H]⁻ | Spring | Summer | Autumn | Winter |
|----------|---------|---------|--------|--------|--------|--------|
|          |         | 2015    | 2019   | 2015   | 2019   | 2015   | 2018   | 2016   | 2019   |
| C₂/C₃ OS | C₃H₅O₄S⁻ | 0.53    | 0.35   | 0.67   | 0.82   | 0.59   | 0.28   | 0.67   | 0.48   |
|          | C₃H₅O₅S⁻ | 1.29    | 1.15   | 4.56   | 3.77   | 1.50   | 0.92   | 1.35   | 0.93   |
|          | C₂H₂O₄S⁻ | 2.58    | 2.55   | 3.79   | 3.19   | 2.43   | 1.80   | 2.58   | 1.33   |
|          | C₃H₆O₅S⁻ | 0.75    | 0.53   | 0.63   | 1.24   | 2.59   | 0.33   | 1.27   | 0.63   |
|          | C₃H₆O₆S⁻ | 2.25    | 2.32   | 2.06   | 1.97   | 2.15   | 1.74   | 2.49   | 1.72   |
|          | C₄H₇O₄S⁻ | 2.29    | 2.18   | 2.31   | 1.30   | 1.75   | 1.23   | 1.77   | 2.33   |
|          | C₅H₇O₆S⁻ | 0.85    | 0.63   | 0.79   | 1.14   | 0.69   | 0.48   | 0.95   | 0.69   |
|          | C₆H₉O₆S⁻ | 0.94    | 0.54   | 0.37   | 0.34   | 0.99   | 0.54   | 1.86   | 1.95   |
|          | C₆H₆O₅S⁻ | 0.35    | 0.08   | 0.37   | --     | 0.41   | 0.13   | 0.34   | 0.12   |
|          | C₇H₈O₅S⁻ | 0.33    | 0.11   | 0.32   | 0.28   | 0.43   | 0.11   | 0.33   | 0.16   |
|          | C₅H₈O₄S⁻ | 1.06    | 0.56   | 1.09   | 0.47   | 1.13   | 0.80   | 1.49   | 1.28   |
|          | C₆H₇O₆S⁻ | 1.40    | 1.06   | 3.34   | 2.98   | 0.90   | 1.04   | 0.70   | 0.68   |
|          | C₆H₆O₉S⁻ | 1.05    | 1.41   | 1.02   | 1.91   | 1.09   | 0.97   | 1.35   | 1.50   |
|          | C₇H₇O₆S⁻ | 1.51    | 1.96   | 6.35   | 4.19   | 1.68   | 1.14   | 1.41   | 1.06   |
|          | C₇H₈O₆S⁻ | 1.33    | 2.34   | 2.87   | 1.69   | 1.61   | 1.49   | 1.69   | 1.35   |
|          | C₈H₉O₆S⁻ | 1.62    | 2.16   | 4.57   | 4.49   | 1.03   | 1.84   | 1.26   | 1.16   |
|          | C₉H₁₀O₆S⁻ | 0.53    | 0.64   | 0.74   | 1.21   | 0.54   | 0.42   | 0.52   | 0.40   |
|          | C₈H₇O₇S⁻ | 2.89    | 3.96   | 13.14  | 8.85   | 2.67   | 2.55   | 3.81   | 3.06   |
|          | C₉H₈O₇S⁻ | 1.57    | 2.56   | 9.66   | 9.74   | 1.19   | 1.40   | 1.33   | 1.06   |
|          | C₁₀H₁₇O₅S⁻ | 1.26    | 1.23   | 35.80  | 30.52  | 0.52   | 0.57   | 0.48   | 0.37   |
|          | C₁₀H₁₅O₆S⁻ | 0.48    | 0.50   | 0.96   | 0.87   | 0.45   | 0.36   | 0.45   | 0.33   |
|          | C₁₀H₉O₈S⁻ | 0.82    | 0.60   | 2.64   | 6.82   | --     | 0.40   | 0.20   | 0.24   |
|          | C₁₀H₁₆NO₇S⁻ | 0.57    | 0.59   | 2.14   | 7.39   | --     | 0.26   | --     | --     |
|          | C₁₀H₁₇NO₇S⁻ | 1.06    | 1.01   | 2.64   | 2.90   | 0.81   | 0.72   | 0.86   | 0.49   |
|          | C₁₀H₁₈NO₇S⁻ | 1.58    | 2.05   | 3.35   | 4.17   | 1.28   | 0.95   | 1.31   | 0.56   |
|          | C₁₀H₁₉O₇S⁻ | 0.32    | 0.04   | 0.29   | 0.14   | 0.31   | 0.10   | 0.37   | 0.27   |
|          | C₁₀H₂₀O₇S⁻ | 1.56    | 1.10   | 1.47   | 0.91   | 0.95   | 1.06   | 1.20   | 0.99   |
|          | C₁₀H₂₁O₇S⁻ | 1.11    | 2.24   | 2.20   | 3.90   | 1.01   | 1.10   | 1.07   | 0.61   |
|          | C₁₀H₂₂O₇S⁻ | 2.79    | 4.37   | 3.35   | 6.45   | 1.77   | 3.12   | 3.72   | 3.57   |
|          | C₁₀H₂₃O₇S⁻ | 0.31    | 0.22   | 0.45   | 0.20   | 0.31   | 0.20   | 0.29   | --     |
|          | C₁₀H₂₄NO₉S⁻ | 11.20   | 6.57   | 6.50   | 4.92   | 3.00   | 5.52   | 3.04   | 5.39   |
|          | C₁₀H₂₅NO₉S⁻ | 2.28    | 3.00   | 1.21   | 1.22   | 1.36   | 3.65   | 1.57   | 1.53   |
|          | C₁₀H₂₆NO₉S⁻ | 1.70    | 2.06   | 1.24   | 1.60   | 1.13   | 1.59   | 1.11   | 1.11   |

**SUM** 51.04 51.53 114.13 102.09 38.15 37.98 44.48 35.99
Figure S1. MS² spectra of quantified OS species with S-containing fragments being labeled. The collision energy was 6-10 eV for C₅H₈NO₈S⁻, 12-25 eV for C₃H₅O₄S⁻, C₂H₃O₅S⁻, C₄H₅O₅S⁻, and C₁₀H₁₆NO₁₀S⁻, 20-50 eV for C₆H₅O₄S⁻, and 10-35 eV for the rest.