



Supplement of

Enhancement of secondary organic aerosol formation and its oxidation state by SO₂ during photooxidation of 2-methoxyphenol

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1 1 Chemicals

Guaiacol (Sigma-Aldrich, > 99%), sodium chloride (Sinopharm Chemical Reagent Co.,
Ltd., > 99.8%), and ammonium sulfate (Sinopharm Chemical Reagent Co., Ltd., > 99%)
were used in the experiments as received. NO (963 ppm) and SO₂ (3000 ppm) were
purchased from Beijing Huayuan Gas Chemical Industry Co., Ltd.

6 2 Positive matrix factorization (PMF) analysis

7 Positive Matrix Factorization (PMF) is a receptor model and a multivariate factor 8 analysis tool, which could decompose a matrix of speciated sample data into two 9 matrices, namely factor contributions and factor profiles (Paatero, 1997). In recent years, 10 the PMF model was widely used for the analysis of high resolution (HR) mass spectra 11 data, which could provide better separation of different organic components (DeCarlo 12 et al., 2010; Docherty et al., 2008). This model is expressed as a bilinear factor model, namely, $x_{ij} = \sum_{p} g_{ip} f_{pj} + e_{ij}$, where i and j refer to values of j species in i samples, 13 14 respectively, p is the number of factors in the solution and is used a least-squares fitting 15 process to minimize the quality of fit parameter. In this work, the HR mass spectra (m/z 16 12–115) was analyzed by the PMF software coupled with a modified version of the CU 17 AMS PMF Execute Calcs Tool version 2.06 developed by Ulbrich et al. (2009). The 18 concentration and uncertainty matrices input into the PMF analysis were generated 19 from the PIKA version 1.15D. Ions were classified and down-weighted according to 20 the signal to noise ratios (SNR). 0.2 < SNR < 2 was classified as the weak ions and 21 down-weighted by a factor of 2, SNR < 0.2 was bad ions and removed from the analysis,

and the uncertainty values of CO₂⁺-related peaks at m/z 16 (O), 17 (HO), 18 (H₂O), 28
(CO), and 44 (CO₂) were down-weighted.

24 **3** Timescale calculation

The average gas-particle partitioning timescale $(\bar{\tau}_{g-p})$ over the course of experiment could be expressed as Eq. (S1) (Zhang et al., 2014; Seinfeld and Pandis, 2006), and the vapor wall deposition timescale (τ_{g-w}) is calculated using Eq. (S2) (Zhang et al., 2015).

28
$$\overline{\tau}_{g-p} = \frac{1}{2\pi \overline{N}_p \overline{D}_p D_{gas} F_{FS}}$$
(S1)

$$\tau_{g-w} = \frac{1}{k_w}$$
(S2)

30
$$k_{\rm w} = \left(\frac{A}{V}\right) \left(\frac{\alpha_{\rm w}\overline{c}/4}{\pi\alpha_{\rm w}\overline{c}/8\left(D_{\rm gas}k_{\rm e}\right)^{0.5}+1}\right)$$
(S3)

where \bar{N}_{p} is the average particle number concentration for the whole experimental 31 process since UV lamps were turned on, \bar{D}_{p} is the number mean diameter, D_{gas} is the 32 gas-phase diffusivity, $F_{\rm FS}$ is the Fuchs-Sutugin correction to the mass transfer flux due 33 34 to noncontinuum effects and imperfect accommodation (Seinfeld and Pandis, 2006), $k_{\rm w}$ is the overall wall loss rate of organic vapors (Eq. (S3)), A/V is the surface to volume 35 36 ratio of the chamber, $\alpha_{\rm w}$ is the mass accommodation coefficient of vapors deposition to the wall (~10⁻⁵) (Zhang et al., 2014; Matsunaga and Ziemann, 2010), \overline{c} is the mean 37 thermal speed of the molecules, and k_e is the coefficient of eddy diffusion (0.015 s⁻¹) 38 39 (Zhang et al., 2014). Considering that the chamber volume in this work (30 m³) is very close to that (28 m³) used by Zhang et al. (2014), thus the values of $k_{\rm e}$ and $\alpha_{\rm w}$ 40 reported by them were applied to calculate $k_{\rm w}$. In addition, we considered that the 41

42 equilibrium was established for vapor wall losses after 4 hours photooxidation, because 43 Matsunaga and Ziemann (2010) and Yeh and Ziemann (2014) reported the rapid equilibrium established within less than an hour for vapor wall losses in Teflon 44 45 chambers. Meanwhile, it was assumed that the chamber wall was essential an absorbing medium of infinite extent. In this case, k_w could be calculated using Eq. (S3) (Zhang 46 et al., 2015). Since this method could not separate the evaporation of adsorbed organic 47 48 materials from the wall, the effect of vapor wall loss in this calculation might be 49 overestimated. It is assumed that D_{gas} of organic vapor changes with the molecular weight (MW) 50 and is equal to D_{CO_2} (MW_{CO2}/MW). The value of D_{CO_2} is 1.38 × 10⁻⁵ m² s⁻¹ (Zhang et 51 al., 2014). Conventionally, MW of 98 g mol⁻¹ (H₂SO₄) is widely used for the Fuchs-52 53 Sutugin correction, but a number more like 300 g mol⁻¹ might be more representative of the condensable organic vapors. Thus, MW of 300 g mol⁻¹ was selected in this work. 54

55 The Fuchs-Sutugin correction is expressed as the following equation:

56
$$F_{\rm FS} = \frac{0.75\alpha(1+Kn)}{Kn^2 + Kn + 0.283Kn\alpha + 0.75\alpha}$$
(S4)

57 where α is the mass accommodation coefficient onto particles (~0.002) (Zhang et al., 58 2014) and *Kn* is the Knudsen number, expressed as follows:

59 $Kn = \frac{\lambda}{R_{\rm p}}$ (S5)

60 $R_{\rm p}$ is the particle radius and λ is the gas mean free path, which is calculated using Eq. 61 (S6):

$$\lambda = \frac{3D_{\text{gas}}}{\overline{c}} \tag{S6}$$

63
$$\overline{c} = \sqrt{\frac{8N_A kT}{\pi MW}}$$
(S7)

64 where N_A , k, and T are Avogadro's number, Boltzmann constant, and temperature, 65 respectively.

66 4 Organosulfate concentration calculation

67 Considering that methyl sulfate is the simplest organosulfate, the fraction of $C_xH_yO_zS$ 68 is more likely to be lower than that of methyl sulfate (Huang et al., 2015). In addition, 69 more information about the varieties of organosulfates could not be obtained in this 70 work. Therefore, a conservative low-bound of organosulfate concentration has been 71 estimated according to the method described by Huang et al. (2015), as shown in Eq. 72 (S8).

73
$$C_{\rm OS_{min}} = f_{\rm OS} \times (C_{\rm org} + C_{\rm SO_4})$$
(S8)

74
$$f_{\rm OS} = \frac{\frac{\sum_{h} I_{\rm OS,h}}{\rm RIE_{\rm OS}}}{\frac{\sum_{n} I_{\rm org,n}}{\rm RIE_{\rm org}} + \frac{\sum_{t} I_{\rm SO_{4},t}}{\rm RIE_{\rm SO_{4}}}}$$
(S9)

where $C_{\text{OS}_{\min}}$ is the minimum concentration of organosulfates; f_{OS} is the factor that represents for the fractional contribution of organosulfates to the lumped species of organics and sulfate in W-mode data; C_{org} and C_{SO_4} are the concentrations of organics and sulfate calculated from V-mode data, respectively; h, n, and t indicate the fragments of organosulfates, organics, and sulfate, respectively; $\sum_{h} I_{\text{OS},h}$, $\sum_{n} I_{\text{org},n}$, and $\sum_{l} I_{\text{SO}_4, l}$ are the total signal intensities of organosulfates, organics, and sulfate,

- 81 respectively, obtained from W-mode data; RIE_{os} is the relative ionization efficiency
- for organosulfates, which is estimated as the average of $RIE_{org} = 1.4$ and $RIE_{SO_{c}} = 1.2$

83 (Barnes et al., 2006).

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Figure S1. Schematic of the RCEES-CAS smog chamber facility.



131 Figure S2. SOA mass concentration (M_o) vs. the consumed guaiacol concentration





133

Figure S3. Formation of SOA, sulfate, and nitrate as a function of SO₂ concentration for guaiacol photooxidation. The k values are the slopes of the fitted lines for each species.



138 Figure S4. Variations in the concentrations of sulfate and nitrate at different SO₂





Figure S5. Decays of guaiacol as a function of irradiation time at different conditions

142 (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$)).



Figure S6. Decays of NO_x as a function of irradiation time at different conditions (a:

145 no seed, b: NaCl, c: (NH₄)₂SO₄)).



Figure S7. Decays of SO₂ as a function of irradiation time with different seed particles.



Figure S8. Variations in the concentrations of ammonium salt as function of irradiation

150 time at different SO₂ concentrations (without seed particles).



152 Figure S9. Variations in the mass concentrations of NO^+ and NO_2^+ , as well as

153 NO^+/NO_2^+ ratio as a function of irradiation time at different SO₂ concentrations

154 (without seed particles).



Figure S10. Variations in H/C, O/C, and N/C ratios at different SO₂ concentrations as

157 a function of irradiation time (without seed particles).



Figure S11. Time-dependent curves of Factor 1 (a) and Factor 2 (b) at three different

160 SO₂ concentrations (without seed particles).



Figure S12. Variations in the fraction of organic ion groups as a function of irradiation



164 NaCl, c: (NH₄)₂SO₄).



Figure S13. Differences among the normalized mass spectra of SOA formed at different
SO₂ concentrations without seed particles (a: 33 ppbv SO₂ – no SO₂; b: 56 ppbv SO₂ –
33 ppbv SO₂).



170 Figure S14. Fitted peaks of average W-mode mass spectrum of methyl sulfate obtained





Figure S15. Variations in the gas-phase concentrations of acetic acid as function of
irradiation time in the presence of different seed particles and SO₂ concentrations (a: no

175 seed, b: NaCl, c: (NH₄)₂SO₄).



Figure S16. Variations in H/C, O/C, and N/C ratios at different SO₂ concentrations as

178 a function of irradiation time with NaCl seed particles.



180 Figure S17. Variations in H/C, O/C, and N/C ratios at different SO₂ concentrations as

181 a function of irradiation time with (NH₄)₂SO₄ seed particles.



182

183 Figure S18. Difference between the normalized mass spectra of SOA formed with

184 different seed particles (NaCl seeded SOA – (NH₄)₂SO₄ seeded SOA).



Figure S19. Variations in the concentrations of sulfate as function of irradiation time in
the presence of different seed particles and SO₂ concentrations (a: no seed, b: NaCl, c:
(NH₄)₂SO₄). The sulfate concentrations shown in Figure S19c are the net concentrations
formed via SO₂ oxidation, i.e., do not include the (NH₄)₂SO₄ concentration added in the
smog chamber.



191

192 Figure S20. Mass spectra of SOA with NaCl (a) and (NH₄)₂SO₄ (b) as seed particles

193 obtained by HR-ToF-AMS at different SO₂ concentration (red bars: without SO₂; olive

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194 markers: 30 ppbv SO<sub>2</sub> for a and 33 ppbv SO<sub>2</sub> for b; blue markers: 54 ppbv SO<sub>2</sub>).
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Figure S21. Differences among the normalized mass spectra of SOA formed at different

 SO_2 concentrations with (NH₄)₂SO₄ seed particles (a: 33 ppbv SO₂ – no SO₂; b: 54 ppbv

¹⁹⁸ SO₂ – 33 ppbv SO₂).



Figure S22. Differences among the normalized mass spectra of SOA formed at different
SO₂ concentrations with NaCl seed particles (a: 30 ppbv SO₂ – no SO₂; b: 54 ppbv SO₂
- 30 ppbv SO₂).