SUPPLEMENTARY INFORMATION

for

Unraveling the role of silicon in atmospheric aerosol secondary formation: A new conservative tracer for aerosol chemistry

Dawei Lu[1], Jihua Tan[2], Xuezhi Yang[1,2], Xu Sun[1], Qian Liu[1,2,3], Guibin Jiang[1,2]

[1]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[2]College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 100049, China

[3]Institute of Environment and Health, Jianghan University, Wuhan 430056, China

Email: qianliu@rcees.ac.cn

Content

1. Supplementary experimental details

1.1 Sampling of primary source samples of $PM_{2.5}$

For the primary sources of $PM_{2.5}$, seven major sources were collected as literature reported (Ge et al., 2004; Li et al., 2011; Das et al., 2010; Zhao et al., 2006; Chow et al., 2003; Fraser et al., 1998; Hu et al., 2013; Huang et al., 2014; Zhang et al., 2013; Reff et al., 2009; Song et al., 2007; He et al., 2001), including soil dust, industrial emission, coal combustion, vehicle exhaust, biomass burning, urban fugitive dust, and construction dust. The soil dusts were collected at different directions and different depths around Beijing. The industrial emission samples were collected by air sleeves or electrostatic filters installed in the chimneys in steel and power plants in Tangshan, Hebei, which is adjacent to Beijing. The coal combustion samples were fly ashes from burning of honeycomb briquette and lump coals. The fly ashes were drawn through a dilution system (Ge et al., 2004) and then collected onto polypropylene membrane filters by an impactor at a flow rate of 36 L/min. The vehicle exhaust samples were collected following a previously reported method (Fraser et al., 1998) in the middle section of a highway tunnel (Tanyugou Tunnel, Changping, Beijing; 3455 m length) by a high-volume air sampler (Echo Hi-Vol, Milan, Italy) onto Whatman Teflon membrane filters. This tunnel is only open to motor vehicles (mainly diesel- and gasoline-powered vehicles) and the $PM_{2.5}$ concentration outside the tunnel was low ($< 15\ \mu g/m^3$), so the collected samples could represent the vehicle emission. The biomass burning samples were collected from burnt straws from Daxing and Tongzhou Districts, Beijing. The urban fugitive dusts were collected in the city of Beijing at an altitude of 20 m by an SYC-3 auto-sampler (Laoshan Instruments, Qingdao, China). The construction dusts were obtained from several construction sites in Beijing and mainly consisted of fine sands, cement dusts and brick dusts.

1.2 Measurement of Si isotopic composition

The Si isotopic composition was measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) on a Nu Plasma II MC-ICP-MS (Wrexham, UK) working in medium-resolution mode coupled to a DSN-100 DeSolvation Nebulizer System. The samples were diluted with HCl solution to obtain a Si concentration of ~300 ng/mL, at which the intensities of ^{28}Si, ^{29}Si and ^{30}Si were about 2, 0.11, and 0.08 V. A PFA nebulizer was used for sample injection at 70 μL/min in dry mode. The optimized instrumental parameters and the Faraday cup configuration are the same as in our previous study (Lu et al., 2018). The procedure blank of the Faraday detector noise was subtracted in the electrostatic analyzer for 30 s prior to each measurement. After each measurement, the system was rinsed with HCl solution (pH 2) for 120 s to reduce the background intensity to < 0.03 V. Three parallel measurements were performed for all experiments ($n = 3$). The Si isotopic composition was expressed as a δ value (δ^{30}Si and δ^{29}Si) relative to a standard material (NIST SRM-8546) as follows:

$$\delta^{29}\mathrm{Si} = \left(\frac{\left(^{29}\mathrm{Si}/^{28}\mathrm{Si}\right)_{\mathrm{sample}}}{\left(^{29}\mathrm{Si}/^{28}\mathrm{Si}\right)_{\mathrm{standard}}} - 1\right) \times 1000 \qquad \text{(S1)}$$

$$\delta^{30}\mathrm{Si} = \left(\frac{\left(^{30}\mathrm{Si}/^{28}\mathrm{Si}\right)_{\mathrm{sample}}}{\left(^{30}\mathrm{Si}/^{28}\mathrm{Si}\right)_{\mathrm{standard}}} - 1\right) \times 1000 \qquad \text{(S2)}$$

The mass bias of a sample was corrected by using a standard-sample-standard bracketing method based on the mean values of the isotope ratios from two adjacent standard measurements (Lu et al., 2016). Two standard reference materials (NIST SRM-8546 and IRMM-017) were used to validate the method. The δ^{30}Si value of NIST SRM-8546 solution with a Si concentration of 300 ng/mL was measured to be -0.08 ± 0.11‰ (mean ± 2SD, n = 40), and the δ^{30}Si value of IRMM-017 was measured to be -1.38 ± 0.18‰ (mean ± 2SD, n = 36). The δ^{30}Si value of IRMM-017 was highly consistent with the literature reported value (Zambardi and Poitrasson, 2011), confirming the high accuracy and precision of the method.

1.3 Measurement of OC and EC in $PM_{2.5}$

OC and EC were measured by using a DRI Thermal/Optical Carbon Analyzer. The temperature program of the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evolution protocol was adopted. A punch aliquot of a sample quartz filter was heated stepwise at temperatures of 120 °C (OC1), 250 °C (OC2), 450 °C (OC3), and 550 °C (OC4) in a non-oxidizing He atmosphere, and 550 °C (EC1) and 700 °C (EC2) in an oxidizing atmosphere of 2% oxygen in a balance of He. The carbon that evolved at each temperature is oxidized to CO_2 and then reduced to methane (CH_4) for quantification with a flame ionization detector. The analyzer was calibrated daily with CH_4. Quartz filter blanks were processed concurrently with field blank samples and used to obtain detection limits (LODs). The blank based LODs, calculated as three times the average field blanks, were < 1.0 $\mu g/m^3$ for both OC and EC. Replicate analyses were performed at the rate of one per group of 10 samples. The RSDs were less than 5% (Cao et al., 2003).

1.4 Estimation of SOC in $PM_{2.5}$

It has been reported that the minimum value of OC/EC occurred simultaneously in urban and rural areas both in winter and summer (Castro et al., 1999), and particles with the minimum OC/EC ratios were regarded as being dominated by primary aerosols. Thus, the minimum value of OC/EC ratio can be used to estimate the amount of SOC in aerosols and the concentration of SOC can be calculated by the following equation:

$$\mathrm{SOC} = \mathrm{OC}_{\mathrm{total}} - (\mathrm{OC/EC})_{\min} \times \mathrm{EC} \qquad \text{(S9)}$$

where $\mathrm{OC}_{\mathrm{total}}$ is the total OC, and $(\mathrm{OC/EC})_{\min}$ is the estimated minimum OC/EC ratio (Turpin and Huntzicker, 1995).

1.5 Measurement of water soluble inorganic ions in $PM_{2.5}$

The water-soluble inorganic ions were analyzed according to previously reported methods (Tan et al., 2009a; Tan et al., 2009b). The $PM_{2.5}$ filter samples were extracted by an ultrasonication method, and normally > 98% of sulfate, nitrate, and ammonium could be extracted. The filter was submerged in a vial with 10 mL of water, sealed and subjected to ultrasonication for 20 min. The extraction was repeated twice. The extracts were filtered through a 0.45 μm Teflon filter and then analyzed by ion chromatography (Dionex ICS 600 and 2100) to determine the concentrations of water soluble inorganic ions. The recoveries of ions (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) were in the range of 90-110%. The RSDs of the results were < 5%.

1.6 Estimation of secondary aerosols by using the traditional method

Following the traditional method, the secondary aerosol (SA) contribution was estimated by the combination of SIA and SOA. The SIA was the sum of secondary ions (NH_4^+, NO_3^-, and SO_4^{2-}), and the SOA was obtained by multiplying SOC by an OM/OC ratio of 1.6 (Xing et al., 2013).

1.7 Analysis of atmospheric concentration of SO_2 and NO_x and relative humidity

The atmospheric concentrations of SO_2 and NO_x were monitored by a Thermo Scientific Model 43i Sulfur Dioxide Analyzer and a Thermo Scientific Model 42i NO-NO_2-NO_x Analyzer, respectively. The relative humidity (RH) was measured by a Vaisala HUMICAP Humidity and Temperature Probe HMP155 (Helsinki, Finland).

2. Supporting figures

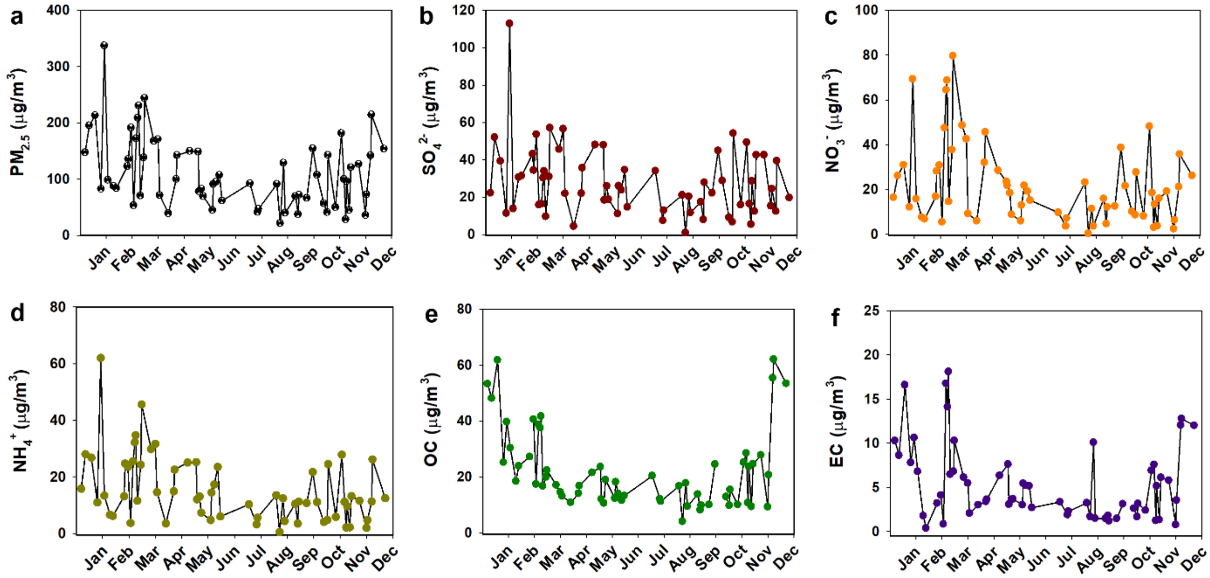

Figure S1. Daily concentration profile of $PM_{2.5}$ (**a**) and secondary species in $PM_{2.5}$ (SO_4^{2-} (**b**), NO_3^- (**c**), NH_4^+ (**d**), OC (**e**), and EC (**f**)) on haze days in 2013. The $PM_{2.5}$ samples were collected around Beijing on random haze days in 2013 (Lu et al., 2018). From (**a**), the $PM_{2.5}$ concentration showed large variations among different days ranging from 28.4 to 337.1 μg/m^3 with an annual mean value of 112.4 μg/m^3. The pollution level in spring and winter was higher than that in summer and autumn probably due to the larger emission of coal combustion in spring and winter in this region (Lu et al., 2018; Liu et al., 2016). From (**b**)-(**f**), all secondary species in $PM_{2.5}$ showed a similar seasonal trend with the $PM_{2.5}$ (i.e., higher in spring/winter than in summer/autumn), because secondary aerosols are a major component of $PM_{2.5}$ in Beijing (Huang et al., 2014). While for individual days, the concentrations of different secondary species showed large differences, suggesting different sources and secondary particle contribution to $PM_{2.5}$ on different haze days.

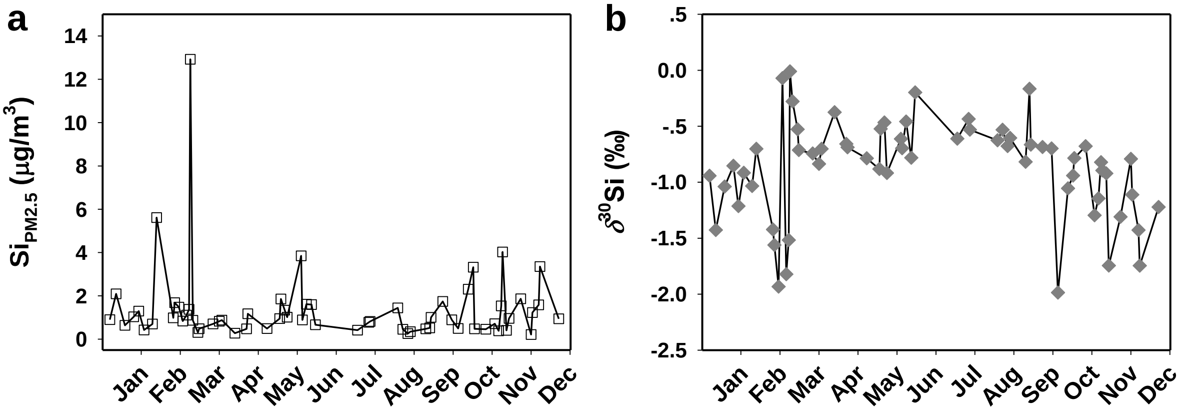

Figure S2. The daily mean Si$_{PM2.5}$ (**a**) and Si isotopic composition (δ^{30}Si) of PM$_{2.5}$ (**b**) on different haze days in 2013. The sample information was the same as in Fig. S1. From (**a**), the Si$_{PM2.5}$ did not show any seasonal trend, which was totally different from the concentration profiles of PM$_{2.5}$ and secondary species in PM$_{2.5}$ (as shown in Fig. S1). However, for δ^{30}Si of PM$_{2.5}$ (**b**), a clear seasonal trend that more negative in spring/winter than in summer/autumn was observed. It should be noted that the Si isotopic signature could indicate the primary sources of PM$_{2.5}$ (Lu et al., 2018). Thus, the results in (**b**) suggested that ^{30}Si-depleted sources (e.g., coal combustion and industrial emission (Lu et al., 2018)) contributed more to aerosols in spring/winter than in summer/autumn. The discussion above evidenced that the airborne Si in PM$_{2.5}$ was only related with the primary source emission but did not depend on the aerosol formation.

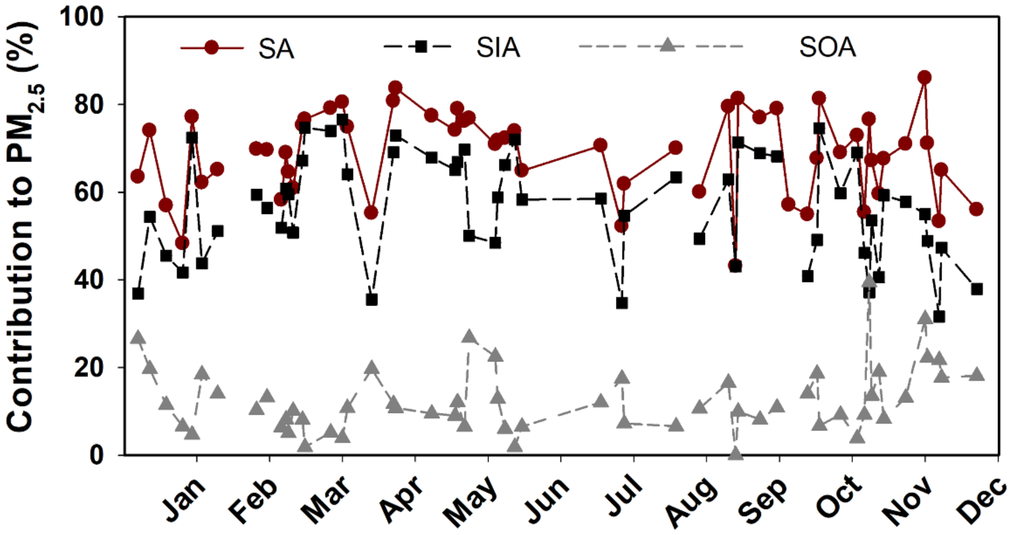

Figure S3. Contribution of secondary aerosol (SA), secondary inorganic aerosol (SIA), and secondary organic aerosol (SOA) to PM$_{2.5}$ estimated by using the traditional method. The contributions were estimated based on the chemical compositions of PM$_{2.5}$ (e.g., SO_4^{2-}, NO_3^-, NH_4^+, OC, and EC). It can be seen that the SA contribution was quite high all through the year, and the contribution of SIA was much higher than that of SOA.

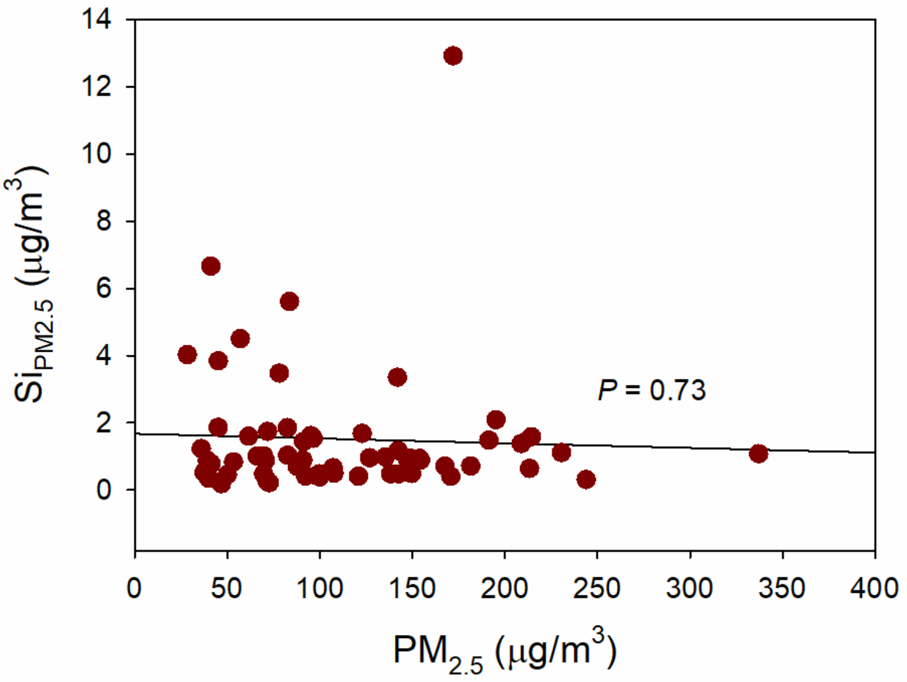

Figure S4. Correlation analysis of total Si in $PM_{2.5}$ ($Si_{PM2.5}$) with $PM_{2.5}$ concentration on haze days. The Si in $PM_{2.5}$ did not show any correlation with the $PM_{2.5}$ concentration (P = 0.73). With the increase of $PM_{2.5}$ concentration, the $Si_{PM2.5}$ was unaffected and kept a steady trend. Considering the high secondary aerosol contribution to $PM_{2.5}$ in the studied region, this results also suggested that the airborne Si might not be involved in the secondary aerosol formation.

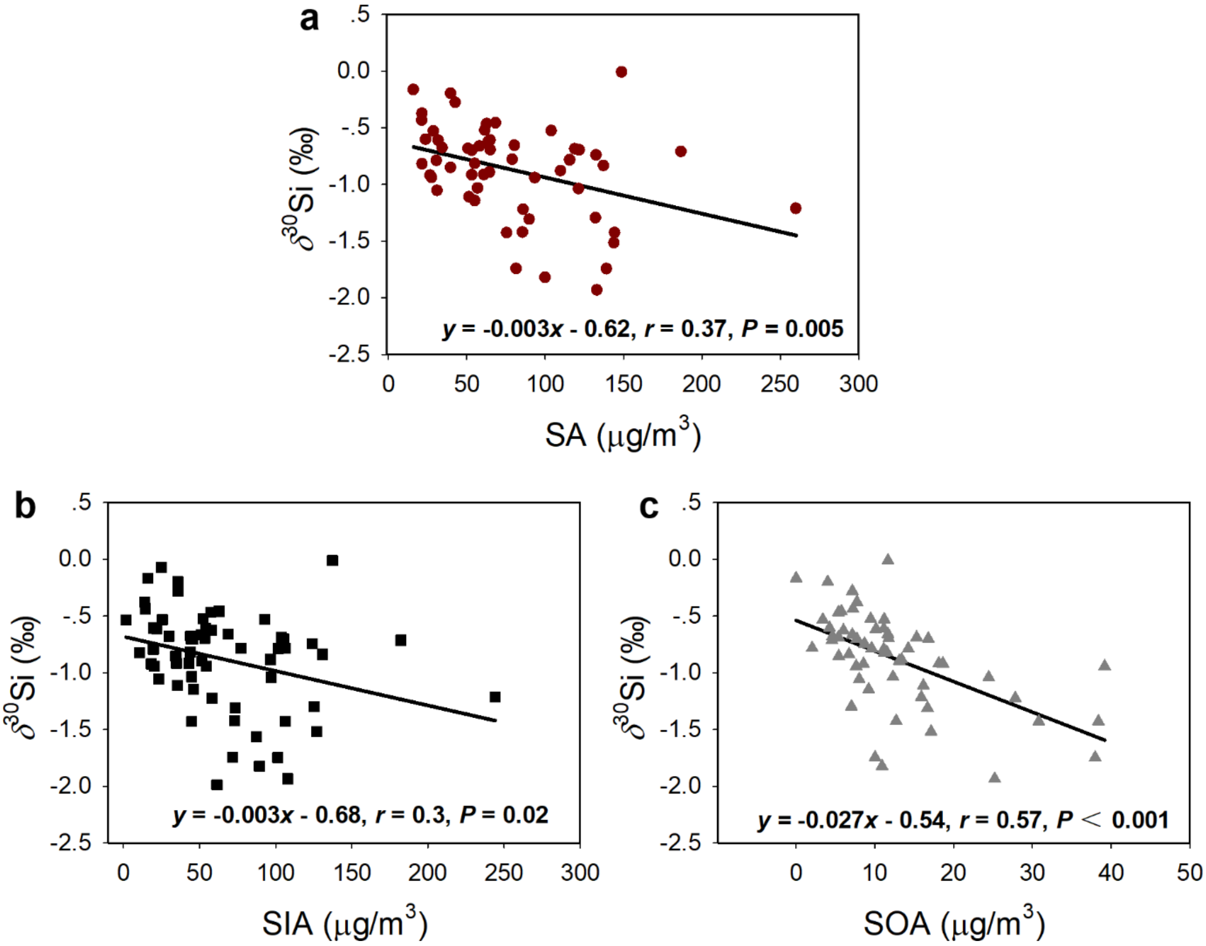

Figure S5. Correlation analysis of Si isotopic composition (δ^{30}Si) of $PM_{2.5}$ with the secondary aerosols (SA (**a**), SIA (**b**), and SOA (**c**)).

3. Supporting tables

Table S1. Concentrations of chemical components indicative of secondary aerosols (NH_4^+, NO_3^-, SO_4^{2-}, OC, and EC) in $PM_{2.5}$ samples in 2013.

Date	SO_4^{2-} (μg/m^3)	NO_3^- (μg/m^3)	NH_4^+ (μg/m^3)	OC (μg/m^3)	EC (μg/m^3)
6/1/2013	22.20	16.41	15.80	53.32	10.29
11/1/2013	52.01	26.14	27.96	48.17	8.63
18/1/2013	39.27	31.00	26.74	61.79	16.61
25/1/2013	11.34	12.15	10.94	25.24	7.80
29/1/2013	112.87	69.30	62.00	39.70	10.63
2/2/2013	13.81	15.80	13.37	30.39	6.81
8/2/2013	30.69	7.56	6.58	18.49	1.80
11/2/2013	31.45	6.78	6.21	23.94	0.39
23/2/2013	43.09	16.82	13.11	27.23	3.21
24/2/2013	34.33	28.19	24.68	-	-
27/2/2013	53.59	30.75	23.56	40.57	4.13
2/3/2013	15.88	5.45	3.693	17.43	0.84
5/3/2013	16.28	47.41	25.53	38.70	16.77
6/3/2013	30.27	64.43	32.21	37.54	14.12
7/3/2013	33.92	68.69	34.65	41.69	18.10
10/3/2013	9.62	14.58	11.55	16.77	6.47
14/3/2013	30.91	37.69	24.31	19.93	6.81
15/3/2013	57.06	79.63	45.59	22.42	10.29
26/3/2013	45.55	48.632	29.78	17.11	6.14
31/3/2013	56.52	42.553	31.61	14.61	5.48
2/4/2013	21.91	9.255	14.57	13.13	2.07
12/4/2013	4.38	6.024	3.52	10.89	3.03
21/4/2013	22.03	32.014	14.88	14.11	3.40
22/4/2013	35.62	45.611	22.54	16.85	3.64
6/5/2013	48.02	28.485	25.04	21.59	6.34
7/5/2013	47.84	23.580	25.21	23.62	7.62
17/5/2013	18.41	21.773	12.04	12.07	3.07
18/5/2013	25.90	18.503	13.08	10.65	3.64
21/5/2013	18.76	8.778	7.31	19.03	3.69

23/5/2013	11.10	6.024	4.73	12.40	3.03
3/6/2013	25.99	12.995	14.45	18.22	5.44
4/6/2013	23.83	21.773	17.29	14.01	5.20
7/6/2013	34.51	19.191	23.49	11.60	5.16
11/6/2013	14.68	15.18	5.98	13.32	2.70
14/6/2013	34.01	9.72	10.29	20.41	3.36
17/7/2013	7.49	3.60	3.24	12.17	1.91
26/7/2013	12.86	7.14	5.56	11.29	2.29
27/7/2013	21.09	23.23	13.51	16.77	3.25
18/8/2013	0.88	0.36	0.53	4.10	1.70
22/8/2013	20.34	11.43	12.39	17.80	10.10
26/8/2013	11.72	3.61	4.40	9.51	1.52
28/8/2013	17.46	15.92	10.44	13.85	1.47
1/9/2013	7.96	4.71	3.47	8.20	1.82
9/9/2013	27.84	12.15	11.20	9.87	1.20
13/9/2013	22.21	12.59	10.76	10.07	1.48
29/9/2013	44.85	38.64	21.69	24.57	3.13
4/10/2013	28.76	21.57	11.08	-	-
12/10/2013	9.04	10.17	4.07	12.93	2.63
16/10/2013	6.72	8.66	4.76	9.81	1.68
17/10/2013	54.13	27.74	24.45	15.47	3.15
26/10/2013	15.86	8.17	5.85	10.12	2.41
2/11/2013	49.28	48.17	27.82	25.18	6.92
5/11/2013	16.40	18.51	11.19	28.52	7.58
7/11/2013	5.39	3.03	2.13	10.76	1.25
8/11/2013	28.60	13.40	9.62	23.68	5.16
11/11/2013	12.42	3.70	2.18	9.416	1.35
13/11/2013	42.57	15.95	13.16	24.65	6.12
22/11/2013	42.58	19.20	11.56	27.82	5.79
30/11/2013	15.29	2.44	1.98	9.30	0.78
1/12/2013	24.42	6.41	4.69	20.73	3.54
6/12/2013	12.41	21.17	11.29	55.41	12.05
7/12/2013	39.42	35.77	26.13	62.06	12.78
22/12/2013	19.66	26.21	12.43	53.43	12.01

4. References for SI

Cao, J. J., Lee, S. C., Ho, K. F., Zhang, X. Y., Zou, S. C., Fung, K., Chow, J. C., and Watson, J. G.: Characteristics of carbonaceous aerosol in Pearl River Delta Region, China during 2001 winter period, Atmos. Environ., 37, 1451-1460, 10.1016/S1352-2310(02)01002-6, 2003.

Castro, L. M., Pio, C. A., Harrison, R. M., and Smith, D. J. T.: Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations, Atmos. Environ., 33, 2771-2781, Doi 10.1016/S1352-2310(98)00331-8, 1999.

Chow, J. C., Watson, J. G., Ashbaugh, L. L., and Magliano, K. L.: Similarities and differences in PM_{10} chemical source profiles for geological dust from the San Joaquin Valley, California, Atmos. Environ., 37, 1317-1340, 2003.

Das, O., Wang, Y., and Hsieh, Y.-P.: Chemical and carbon isotopic characteristics of ash and smoke derived from burning of C_3 and C_4 grasses, Org. Chem., 41, 263-269, 2010.

Fraser, M. P., Cass, G. R., and Simoneit, B. R.: Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel, Environ. Sci. Technol., 32, 2051-2060, 1998.

Ge, S., Xu, X., Chow, J. C., Watson, J., Sheng, Q., Liu, W., Bai, Z., Zhu, T., and Zhang, J.: Emissions of air pollutants from household stoves: honeycomb coal versus coal cake, Environ. Sci. Technol., 38, 4612-4618, 2004.

He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C. K., Cadle, S., Chan, T., and Mulawa, P.: The characteristics of $PM_{2.5}$ in Beijing, China, Atmos. Environ., 35, 4959-4970, 2001.

Hu, J., Zheng, M., Liu, W., Li, C., Nie, Z., Liu, G., Xiao, K., and Dong, S.: Occupational exposure to polychlorinated dibenzo-*p*-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls, and polychlorinated naphthalenes in workplaces of secondary nonferrous metallurgical facilities in China, Environ. Sci. Technol., 47, 7773-7779, 10.1021/es4016475, 2013.

Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218-222, 10.1038/nature13774, 2014.

Li, H., Zhang, J., Zhao, Y., Wu, C.-Y., and Zheng, C.: Wettability of fly ashes from four coal-fired power plants in China, Indus. Eng. Chem. Res., 50, 7763-7771, 10.1021/ie2001378, 2011.

Liu, J., Mauzerall, D. L., Chen, Q., Zhang, Q., Song, Y., Peng, W., Klimont, Z., Qiu, X., Zhang, S., Hu, M., Lin, W., Smith, K. R., and Zhu, T.: Air pollutant emissions from Chinese households: A major and underappreciated ambient pollution source, Proc. Natl. Acad. Sci. U. S. A., 113, 7756-7761, 10.1073/pnas.1604537113, 2016.

Lu, D., Liu, Q., Zhang, T., Cai, Y., Yin, Y., and Jiang, G.: Stable silver isotope fractionation in the natural transformation process of silver nanoparticles, Nat. Nanotechnol., 11, 682-686, 2016.

Lu, D., Liu, Q., Yu, M., Yang, X., Fu, Q., Zhang, X., Mu, Y., and Jiang, G.: Natural Silicon Isotopic Signatures Reveal the Sources of Airborne Fine Particulate Matter, Environ. Sci. Technol., 52, 1088-1095, 2018.

Reff, A., Bhave, P. V., Simon, H., Pace, T. G., Pouliot, G. A., Mobley, J. D., and Houyoux, M.: Emissions inventory of $PM_{2.5}$ trace elements across the United States, Environ. Sci. Technol., 43, 5790-5796, 10.1021/es802930x, 2009.

Song, Y., Tang, X., Xie, S., Zhang, Y., Wei, Y., Zhang, M., Zeng, L., and Lu, S.: Source apportionment of $PM_{2.5}$ in Beijing in 2004, J. Hazard. Mater., 146, 124-130, 2007.

Tan, J. H., Duan, J. C., Chen, D. H., Wang, X. H., Guo, S. J., Bi, X. H., Sheng, G. Y., He, K. B., and Fu, J. M.: Chemical characteristics of haze during summer and winter in Guangzhou, Atmos. Res., 94, 238-245, 10.1016/j.atmosres.2009.05.016, 2009a.

Tan, J. H., Duan, J. C., He, K. B., Ma, Y. L., Duan, F. K., Chen, Y., and Fu, J. M.: Chemical characteristics of PM2.5 during a typical haze episode in Guangzhou, J. Environ. Sci., 21, 774-781, 10.1016/S1001-0742(08)62340-2, 2009b.

Turpin, B. J., and Huntzicker, J. J.: Identification of Secondary Organic Aerosol Episodes and Quantitation of Primary and Secondary Organic Aerosol Concentrations during Scaqs, Atmos. Environ., 29, 3527-3544, Doi 10.1016/1352-2310(94)00276-Q, 1995.

Xing, L., Fu, T. M., Cao, J. J., Lee, S. C., Wang, G. H., Ho, K. F., Cheng, M. C., You, C. F., and Wang, T. J.: Seasonal and spatial variability of the OM/OC mass ratios and high regional correlation between oxalic acid and zinc in Chinese urban organic aerosols, Atmos. Chem. Phys., 13, 4307-4318, 10.5194/acp-13-4307-2013, 2013.

Zambardi, T., and Poitrasson, F.: Precise determination of silicon isotopes in silicate rock reference materials by MC-ICP-MS, Geostand. Geoanal. Res., 35, 89-99, 10.1111/j.1751-908X.2010.00067.x, 2011.

Zhang, R., Jing, J., Tao, J., Hsu, S.-C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., and Zhao, Y.: Chemical characterization and source apportionment of $PM_{2.5}$ in Beijing: seasonal perspective, Atmos. Chem. Phys., 13, 7053-7074, 2013.

Zhao, P., Feng, Y., Zhu, T., and Wu, J.: Characterizations of resuspended dust in six cities of North

China, Atmos. Environ., 40, 5807-5814, 2006.