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1 **PM_{2.5}-bound silicon-containing secondary organic aerosols (Si-SOA)**
2 **in Beijing ambient air**

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16

17 **Abstract**

18 Volatile methyl siloxanes (VMS) have been widely used in personal care products and
19 industrial applications, and are an important component of VOCs (volatile organic
20 compounds) indoors. They have sufficiently long lifetimes to undergo long-range
21 transport and to form secondary aerosols through atmospheric oxidation. To investigate
22 these silicon-containing secondary organic aerosols (Si-SOA), we collected PM_{2.5}

23 samples during 8th-21st August 2018 (summer) and 3rd-23rd January 2019 (winter) at an
24 urban site of Beijing. As the oxidation of VMS mainly results in hydrophilic polar semi-
25 volatile and non-volatile oxidation products, the differences between total water-
26 soluble Si and total water-soluble inorganic Si were used to estimate water-soluble
27 organic Si, considered to be secondary organic Si (SO-Si). The average concentrations
28 of SO-Si during the summer and winter campaigns were 4.6 ± 3.7 and 13.2 ± 8.6 ng m⁻³,
29 accounting for approximately 80.1 ± 10.1 % and 80.2 ± 8.7 % of the total water-soluble
30 Si, and 1.2 ± 1.2 % and 5.0 ± 6.9 % of total Si in PM_{2.5}, respectively. The estimated Si-
31 SOA concentrations were 12.7 ± 10.2 ng m⁻³ and 36.6 ± 23.9 ng m⁻³ on average in summer
32 and winter, which accounted for 0.06 ± 0.07 % and 0.16 ± 0.22 % of PM_{2.5} mass, but
33 increased to 0.26% and 0.92% on certain days. We found that net solar radiation is
34 positively correlated with SO-Si levels in the summer but not in winter, suggesting
35 seasonally different formation mechanisms.

36 **Keywords:** PM_{2.5}, silicon, secondary organic aerosol, volatile methylsiloxanes

37

38 **1. Introduction**

39 Silicon (Si)-containing compounds such as siloxane and polysiloxane (silicone) are
40 widely used in personal care products and industrial applications. They have a high
41 potential to form secondary organic aerosols (SOA). Recent studies of Si-containing
42 SOA (Si-SOA) from oxidation of siloxanes include: physical properties
43 characterization of Si-SOA produced from an oxidation flow reactor (OFR) (Janecek
44 et al., 2019), molecular characterization of Si-SOA with high-performance mass
45 spectrometry (Wu and Johnston, 2016, 2017), experimental and theoretical
46 investigation of the kinetics and mechanism of volatile methylsiloxanes (VMS)
47 oxidation by hydroxyl radical (Xiao et al., 2015), modelling for the estimation of the
48 production rates of dimethylsilanediol (DMSD) from VMS (Muirhead et al., 2018),
49 modelling for quantification of three VMS and their oxidation products (Janecek et al.,
50 2017), and assessment of health impacts of Si-SOA on human lung cells (King et al.,
51 2020). Due to the complex oxidation processes of siloxanes to form various types of
52 Si-SOA (Xiao et al., 2015), the total concentration of Si-SOA has never been reported.

53 The main sources of silicon in the troposphere include resuspended silicon containing
54 dust from natural or anthropogenic sources and emissions of silicon-containing
55 compounds, such as from industry and fuel consumption (Wang et al., 2001).
56 Organosilicon compounds have not been identified in natural sources (Muirhead et al.,
57 2018), and therefore, organosilicon compounds are assumed to arise mainly from
58 human activities. It was reported that siloxanes were the most abundant volatile organic
59 compounds (VOCs) emitted from a university classroom (Tang et al., 2015).

60 All siloxanes with the number of silicon atoms > 1 are considered to be oligomers or
61 polymers. The global production of polysiloxane is enormous. China was the largest
62 manufacturer and consumer of polysiloxane in the world in 2009, with the output and
63 consumption of 270 000 and 430 000 tons in 2009, respectively (CRCSI, 2010). In
64 2018, the output and consumption of polysiloxane in China has reached 1.04 and 1.13
65 million tons, respectively (CBIRI, 2019). Organosilicon compounds like methyl
66 siloxanes are widely applied in industrial applications and consumer products due to
67 their high thermal stability, water repellence, smooth texture and low surface tension
68 (Xu et al., 2015). VMS, polydimethylsiloxane and polyethermethylsiloxane are three
69 organosilicon classes, which have noteworthy environmental loadings (Wang et al.,
70 2013). The hydrolysis or thermal decomposition of polydimethylsiloxane and
71 polyethermethylsiloxane can also generate highly volatile cyclic dimethylsiloxanes or
72 volatile linear siloxane diols such as dimethylsilanediol (Tuazon et al., 2000; Wang et
73 al., 2001).

74 VMS can be classified as volatile linear or cyclic methylsiloxanes. Consisting of –
75 $(\text{CH}_3)_2\text{SiO}$ – structural units, linear- (lVMS) and cyclic- volatile methylsiloxanes
76 (cVMS) are widely used in cleaning agents, lubricants, and personal care products, such
77 as cosmetics, antiperspirants, and skin and hair care products (Horii and Kannan, 2008;
78 Wang et al., 2009a; Xiao et al., 2015). Worldwide production of cVMS is huge, with
79 cVMS production in the European Union and North America nearly 100 million kg per
80 year (Xiao et al., 2015), and more than 90% of the environmental loading of cVMS in
81 the United States in 1993 was released to the atmosphere, with the remaining cVMS

82 discharged to wastewater (Genualdi et al., 2011). China is leading the world in the
83 production capacity of cyclic siloxanes, with its production reaching about 800 million
84 kg in 2008 (Xu et al., 2013). cVMS can easily partition into the atmosphere as vapour
85 due to their low water solubilities, high Henry's Law constants and high vapor pressures
86 (Wang et al., 2013). The environmental properties and consequent concerns over cVMS,
87 such as bioaccumulation, toxicity, and degradation, were addressed in a review paper
88 on organosiloxanes (Rücker and Kümmerer, 2015). A number of cVMS including
89 octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and
90 dodecamethylcyclohexasiloxane (D6) have been prioritized in several regulatory
91 jurisdictions due to their persistence and bioaccumulation potential and environmental
92 toxicity (Kierkegaard and McLachlan, 2013; Wang et al., 2013). In indoor air samples
93 collected from the UK and Italy, the average concentration of IVMS (L2~L5) and
94 cVMS (D3~D6) together could reach 240 $\mu\text{g m}^{-3}$ in Italy and 350 $\mu\text{g m}^{-3}$ in the UK
95 (Pieri et al., 2013). The half-lives of L3 and L4 are reported as 8.77 and 6.03 days,
96 respectively (Whelan et al., 2004), while for D3, D4 and D5, they can extend to around
97 10-30 days (Xiao et al., 2015), which indicates that they can exist in the atmosphere
98 sufficiently long to undergo oxidation to generate secondary products and undergo
99 long-range transport to affect the air quality regionally. The atmospheric half-lives and
100 concentrations of some major IVMS and cVMS in the outdoor environment are
101 summarized in Table 1.

102 Table 1 Atmospheric outdoor concentrations of major IVMS and cVMS compounds (ng m^{-3})

| | | L3 | L4 | L5 | L6 | D3 | D4 | D5 | D6 | References |
|-----------------|-------|-----------|-----------|-----------|----|-----------|---------|---------|-----------|-----------------------|
| Toronto, Canada | 2010- | 1.3 ± 1.0 | 2.1 ± 1.3 | 1.9 ± 1.0 | | 1.6 ± 1.1 | 16 ± 12 | 91 ± 54 | 7.3 ± 4.2 | (Ahrens et al., 2014) |

| | | | | | | | | | | |
|---|------|-------|-------|-------|-------|------|--------|----------|------|-----------------------------------|
| (Semiurban) | 2011 | | | | | | | | | |
| Guangzhou, China (Urban) | 1996 | | | | 2900 | 900 | | | | (Wang et al., 2001) |
| Paris, France (Urban) | 2009 | 0.029 | 0.057 | 0.12 | 30 | 50 | 280 | 53 | | |
| Downsview, ON, Canada (Urban) | 2009 | 0.12 | 0.66 | 0.45 | 18 | 11 | 55 | 6.2 | | (Genualdi et al., 2011) |
| Sydney, FL, USA (Urban) | 2009 | | 0.16 | 0.081 | 0.65 | 5.4 | 82 | 4.0 | | |
| Chicago, USA (Urban) | | | | | | | 18-190 | 100-1100 | 0-50 | (Yucuis et al., 2013) |
| Tystberga, Sweden (regional background) | 2011 | 0.2 | 0.025 | 0.013 | 0.022 | 0.94 | 3.5 | 13 | 1.0 | (Kierkegaard and McLachlan, 2013) |

103 *Note: L3: Octamethyltrisiloxane; L4: Decamethyltetrasiloxane; L5: Dodecamethylpentasiloxane; L6:*
104 *Tetradecamethylhexasiloxane; D3: Hexamethylcyclotrisiloxane; D4: Octamethylcyclotetrasiloxane; D5:*
105 *Decamethylcyclopentasiloxane; D6: Dodecamethylcyclohexasiloxane;*

106

107 Because of the increasing production and consumption of VMS, many studies have
108 been conducted to investigate their physical/ chemical properties (Xu and Wania, 2013;
109 Xu et al., 2014), develop analytical methods (Badjagbo et al., 2009; Kierkegaard et al.,
110 2010), and to determine their atmospheric concentrations (Genualdi et al., 2011;
111 Kierkegaard and McLachlan, 2013; Lu et al., 2010; Krogseth et al., 2013; Buser et al.,
112 2013) as well as their bioaccumulation effects (Kierkegaard et al., 2011; Kierkegaard
113 et al., 2013). Si has been frequently detected in atmospheric nanoparticles, which
114 occurred in up to 50% of atmospheric nanoparticles with a mole fraction >0.01 in
115 Pasadena, suggesting the possible contribution from Si-containing VOCs to
116 nanoparticulate Si formation through photochemical reactions (Bzdek et al., 2014).

117 VMS compounds may undergo oxidation with atmospheric oxidants to form new
118 particles or partition onto existing particles. VMS were reported not to be reactive
119 toward ozone and NO₃ radicals (Kim and Xu, 2017). The predominant degradation
120 pathways of atmospheric VMS is through oxidation of vapour by hydroxyl radical,

121 which can produce compounds including silanols, silanediols and silanetriols (Wu and
122 Johnston, 2017; Xiao et al., 2015). A previous study showed that the reaction with
123 hydroxyl radical in the first oxidation step is a major VMS degradation pathway (Kim
124 and Xu, 2017). The hydroxyl radical is reported to be abundant (Slater et al., 2020) and
125 to play an important role in the atmospheric chemistry of Beijing (Whalley et al., 2021).
126 It is reported that the silanols can quickly partition into the particle phase in the
127 atmosphere (Chandramouli and Kamens, 2001). Chamber studies have shown that the
128 nonvolatile and semi-volatile oxidation products of VMS by OH radical can form
129 secondary aerosols (Chandramouli and Kamens, 2001; Wu and Johnston, 2016, 2017).
130 Wu and Johnson (2016) investigated the chemical composition of secondary aerosol
131 formed from D4 and D5 oxidation by OH radical, which showed that the oxidation led
132 predominantly to the substitution of one or more CH₃ groups by OH, CH₂OH or
133 CH₂OOH groups. Due to the various pathways of the VMS oxidation process and
134 numerous oxidation products (Lamaa et al., 2014; Wu and Johnston, 2017; Xiao et al.,
135 2015), it is difficult to identify all oxidation products, and unlikely to be able to quantify
136 all of them in ambient aerosol samples. In the work of Janecek et al. (2017), they only
137 calculated the concentrations of the oxidation products of D5 (namely o-D5) applying
138 a Community Multiscale Air Quality (CMAQ) model with the experimentally
139 determined D5 as input. Si-SOA tracers in fine particles are also starting to be
140 determined through laboratory analysis, but total Si-SOA remained unquantified
141 (Milani et al., 2021).

142 In this work, we propose a conservative estimation of SO-Si and Si-SOA, which does

143 not require information on the precursor concentrations to estimate the SO-Si and Si-
144 SOA concentrations in ambient fine particles for the first time.

145

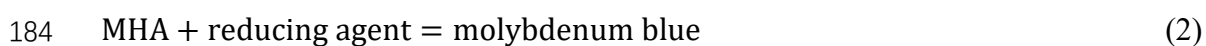
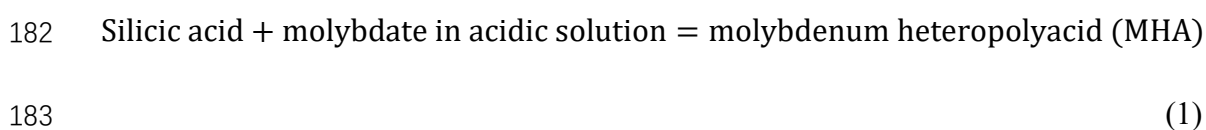
146 **2. Experimental**

147 2.1 Method introduction

148 The introduction of hydroxyl groups into IVMS and cVMS molecules improves their
149 attractive interactions with water molecules, which leads to an increase of the water
150 solubility the VMS oxidation products (Wang et al., 2013; Atkinson, 1991; R cker and
151 K mmerer, 2015). Compounds like dimethylsilanediol (DMSD) and methylsilanetriol
152 (MST) are extremely water soluble (Muirhead et al., 2018; R cker and K mmerer,
153 2015). The water solubility of $(\text{CH}_3)_3\text{SiOH}$ is 7.2 g/100 g H_2O and 1,2-
154 dihydroxytetramethyldisilane is 12.4 g/100 g H_2O (R cker and K mmerer, 2015).
155 Because the absolute mass of $\text{PM}_{2.5}$ on the filters for extraction are usually very low (<
156 4mg per 10 mL water in this study) and the absolute mass of Si-SOA are even lower,
157 all Si-SOA should be solubilized in water extracts considering the relatively high
158 solubility (grams per 100 mL water) of Si-SOA. On the other hand, primary
159 organosilicon compounds are hydrophobic, and polydimethylsiloxanes are almost
160 insoluble in water (R cker and K mmerer, 2015). Therefore, the water-soluble Si-
161 containing organic compounds are considered to be secondary reaction products. By
162 subtracting water-soluble inorganic Si from total water-soluble Si, the remainder is
163 water-soluble organic Si, and can be treated as SO-Si. This can provide a conservative

164 estimate of Si-SOA concentrations in fine particles. Advantages of this method include
165 the practicable quantification of Si-SOA without the necessity to identify and quantify
166 all oxidation products of VMS, ease and speed of analysis; no organic solvents are
167 required, and there is no need to know the concentrations of VMS.

168 The total water-soluble Si can be analysed by Inductively Coupled Plasma- Optical
169 Emission Spectrometer (ICP-OES). Inorganic Si-containing compounds like silica
170 (SiO_2) or its polymeric solid form- (SiO_2)_x are almost insoluble in water. Soluble
171 inorganic Si compounds or molybdate-reactive silica include dissolved simple silicates,
172 monomeric silica and silicic acid, and an undetermined fraction of polymeric silica. The
173 pH of the solution and the type and composition of the silicon-containing aerosols are
174 the primary factors controlling both the form and solubility of silica in the resulting
175 solution. It can exist as silicic acid or silicate ion in solution depending upon pH. For
176 example, silica presents predominantly as silicic acid at $\text{pH} < 9$ (Martin, 2007), and
177 almost completely as silicic acid at $\text{pH} < 7$, while silicate ions become increasingly
178 more abundant when pH is increased to around 10 (Annenkov et al., 2017). Hence, in
179 acidic solution ($\text{pH} < 7$), they can be determined by the traditional colorimetric method
180 based on molybdenum blue, shown as Eq. (1) and (2) (Giacomelli et al., 1999; ASTM,
181 1990):



185 In Eq. (2), the reducing agent could be 1-amino-2-naphthol-4-sulphonic acid (ANS,
186 applied in this study) or ascorbic acid or *p*-methylaminophenol sulfate. Turbidity and
187 colour will interfere in the colorimetric analysis, and they should be removed by
188 filtration and dilution. Phosphate is the only specific compound known to interfere in
189 the colour reaction, and its interference is eliminated by adding oxalic acid (Giacomelli
190 et al., 1999).

191

192 2.2 Sampling

193 In this work, summer and winter PM_{2.5} samples collected in Beijing were chosen and
194 compared for better understanding of Si-SOA formation under different atmospheric
195 conditions. PM_{2.5} samples were collected on 47 mm PTFE filters at an urban site located
196 at the Institute of Atmospheric Physics (IAP: 116.39°E, 39.98°N) of the Chinese
197 Academy of Sciences in Beijing, China during summer (8th-21st August 2018) and
198 winter (3rd-23rd January 2019) for 23 hours each day by medium volume samplers
199 (Zambelli, Italy) at a flow rate of 38.3 L min⁻¹. The 47 mm PTFE filters were chosen
200 because the Si background from the filter-making materials is extremely low and they
201 have low water uptake and can be used for weighing. Other commonly used filter
202 materials, such as quartz or cellulose filters cannot be used either because they are
203 composed of silicon dioxide or are not suitable for weighing. Due to a sampler
204 connection problem, the sampling on 4th January was not successful, and hence, this
205 day was excluded for analysis. Field blanks were collected every five days. All chemical

206 concentrations were corrected by the values obtained from field blanks. Hourly $PM_{2.5}$
207 mass concentrations were obtained via the China National Environmental Monitoring
208 Network (CNEM) website from a nearby Olympic Park station which is around 1km
209 away from the sampling site of IAP, and the original hourly data was averaged to 24 h
210 for daily comparison. Our previous study has showed that the $PM_{2.5}$ data at this station
211 are close to those observed at IAP (Shi et al., 2019). The closeness of observed $PM_{2.5}$
212 concentrations at different air quality stations in Beijing also provides further
213 reassurance of the representative nature of the observed $PM_{2.5}$ concentration at the
214 Olympic Park station (Shi et al., 2019; Xu et al., 2020b).

215 2.3 Meteorological data

216 Hourly meteorological data, including wind speed (ws), air temperature (temp), and
217 relative humidity (RH), were obtained from the NOAA National Center for
218 Environmental Information for the Beijing-Capital international airport station, which
219 is around 20km away from the sampling site of IAP (available at:
220 <https://gis.ncdc.noaa.gov/maps/ncei/cdo/hourly>; last access: May 2020). ERA5 hourly
221 data of surface net solar radiation (ssr), downward UV radiation at the surface (uvb)
222 (this parameter is the amount of ultraviolet (UV) radiation reaching the surface.), total
223 cloud cover (tcc), and total precipitation (tp) were acquired from the Copernicus
224 Climate Change Service (C3S), available at:
225 [https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-single-](https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-single-levels?tab=form)
226 [levels?tab=form](https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-single-levels?tab=form) (last access: May 2020). All hourly data were averaged as daily data,
227 corresponding to the sampling times.

228 2.4 Reagents and solutions preparation

229 All solutions were prepared with reagent grade chemicals and stored in clean
230 polyethylene or plastic bottles at 4°C. Milli Q water (Millipore Corp.) was used for the
231 preparation of all solutions and dilutions. All chemical solutions were filtered through
232 0.22 µm filters before use.

233 (1) Silicon standard solution

234 The 1000 ± 2 mg Si L⁻¹ silicon standard for ICP in 2% NaOH (Sigma-Aldrich) and the
235 silicon standard solution containing 1000 ± 4 mg Si L⁻¹ in 2% NaOH (Silicon standard
236 for AAS, Sigma-Aldrich) were cross-calibrated by using both UV/Vis and ICP-OES,
237 giving identical results. Hence, in order to eliminate the impact of using two different
238 Si standards, the 1000 ± 4 mg Si L⁻¹ silicon standard in 2% NaOH (Silicon standard for
239 AAS, Sigma-Aldrich) was selected to prepare the standard solutions for external
240 calibrations of both UV/Vis and ICP-OES.

241 (2) Ammonium molybdate solution

242 Ammonium molybdate solution (75 g L⁻¹) was prepared by dissolving 7.5 g of
243 ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) in 50 mL of water, adding
244 8.5 mL of H₂SO₄ (96%) and adding water to a total volume of 100 mL.

245 (3) Amino-2-naphthol-4-sulfonic acid (ANS) solution

246 The reducing solution was prepared by dissolving 0.5 g of 1-amino-2-naphthol-4-
247 sulfonic acid (ANS) in 50 mL of a solution containing 1 g of sodium sulfite (Na₂SO₃).

248 After dissolving, the solution was added to a 100 mL solution containing 30 g of sodium
249 hydrogen sulfite (NaHSO_3). The mixed was made up to 200 mL with water and stored
250 in a dark, plastic bottle.

251 (4) Oxalic acid

252 Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) is used to minimize the phosphate response, whilst having
253 little effect on the silicate response (Giacomelli et al., 1999). 100 g L^{-1} oxalic acid
254 solution was prepared by dissolving 10 g of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) in 100 mL of
255 water (ASTM-International, 2016).

256 2.5 Sample extraction

257 One half of the 47mm PTFE filter (including samples and field blanks) was extracted
258 ultrasonically with 10 mL water for 30 minutes at room temperature and stood for
259 another 30 minutes before filtered with $0.22 \mu\text{m}$ filters. Blank filters of the same size
260 were spiked with $20 \mu\text{L}$ of 100 mg L^{-1} standard solution. After dryness, the spiked filters
261 were extracted with 10 mL water applying the same extraction method for a recovery
262 test. The sample extracts were analysed within 2 days by both ICP-OES and UV/Vis.

263 2.6 UV/Vis analysis

264 5 mL of the extracts was transferred into 15 mL polyethylene metal free centrifuge
265 tubes and diluted to 10 mL. The interference of the colour of the extracts was removed
266 by further dilution until the extracts were nearly colorless and transparent using white
267 paper as the background. After this step, 0.4 mL of the ammonium molybdate solution
268 was added and mixed well with the diluted extracts. After 5 minutes, 0.3 mL of the

269 oxalic acid solution was added and mixed well with the solutions. After 1 minute, 0.4
270 mL of the ANS solution was added and mixed well, and further stood for 10 minutes.
271 Reagent blank and standards were prepared by treating 10 mL aliquots of Milli Q water
272 and silicon standards of different levels (1~200 $\mu\text{g Si L}^{-1}$) in the same procedure as
273 mentioned above. The absorbance of the samples and standards was measured at 815
274 nm against the reagent blank by a spectrophotometer (JENWAY 6800 UV/Vis). Longer
275 path length cells (4 cm) which were recommended for concentrations below 100 $\mu\text{g L}^{-1}$
276 were used for the test (ASTM-International, 2016). A good calibration curve was
277 obtained between 1~200 $\mu\text{g Si L}^{-1}$ with $R^2 = 0.9999$ between absorbance and
278 concentration (Fig. S1). The recoveries of spiked filter blanks were 100.0%~109.9%
279 (mean: 104.5%) (Table S1). Blanks, standards and duplicates were run every 10
280 samples. Each sample was tested 3 times and their average was used for the calculation
281 of the concentration. The calculated detection uncertainty (standard deviation of
282 standards run every 10 samples) was less than 0.1 $\mu\text{g Si L}^{-1}$. Two sets of standards were
283 made before the sample extraction and before UV/Vis detection, and the differences of
284 the concentrations calculated using the two calibration curves were $< 0.39 \mu\text{g Si L}^{-1}$.
285 The detection limit (DL), calculated as 3 times the standard deviation (SD) of blanks
286 was 1.4 $\mu\text{g Si L}^{-1}$, corresponding to approximately 0.6 ng m^{-3} . Each sample and standard
287 were measured three times, the relative standard deviation (RSD) ranged between 0.1
288 ~ 7.8% (mean: 2.0%) for samples and 0.0 ~ 3.1% (mean: 1.2%) for standards. Two
289 identical filter cuts from each sample (n=8) were extracted separately in the same
290 manner to test the repeatability, which ranged between 0.1 ~ 16.2% (mean: 8.8%).

291 Standard tests were also run for the water-soluble organic Si compound-
292 Heptamethylcyclotetrasiloxan-2-ol (D3D^{OH}), and the results showed < DL on UV/Vis
293 for inorganic Si concentrations (Table S2).

294 2.7 ICP-OES analysis

295 Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES, Optima 8000)
296 was applied to investigate the total water-soluble Si concentrations. The extraction
297 recovery ranged between 110.3%~116.2% (mean: 113.1%). A good calibration curve
298 was obtained between 10-200 $\mu\text{g Si L}^{-1}$ with $R^2 = 0.9999$ (Fig. S2). The detection limit,
299 calculated as 3 times the standard deviation (SD) of blanks, was $4.8 \mu\text{g L}^{-1}$,
300 approximately 2.0 ng m^{-3} . Each sample and standard were measured three times, and
301 the relative standard deviation (RSD) ranged between 0.2~8.8% (mean: 2.0%) for
302 samples and 0.6~8.7% (mean: 3.0%) for standards. Two identical filter cuts from each
303 sample (n=8) were extracted separately in the same manner to test the repeatability,
304 which ranged between 4.8~16.9% (mean: 10.5%). The uncertainty budget for the
305 estimation of total water-soluble Si, total water-soluble inorganic Si and SO-Si is
306 provided in the supplemental information. The combined standard uncertainty of SO-
307 Si as a percentage (u_{or}) is 27.2%, which is calculated using the combined standard
308 uncertainty of total water-soluble Si (u_{t}) and total water-soluble inorganic Si (u_{in}).

309 2.8 Backward trajectory and cluster analysis

310 The air mass backward trajectories were obtained from the Hybrid Single-Particle
311 Lagrangian Integrated Trajectory (HYSPLIT) model, which was developed by the

312 NOAA Air Resources Lab (Stein et al., 2015; Rolph et al., 2017). Each trajectory was
313 computed from archived global data assimilation system (GDAS1, 2006-present)
314 meteorological data with a duration of 72h. The trajectories started at 8:00 am local
315 time with 6-h intervals on each sampling day at 500 m above ground level (AGL). Then
316 these computed trajectories were clustered in a geographic information system (GIS)
317 based software, namely TrajStat 1.2.1.0 (Wang et al., 2009b). The Euclidean distance-
318 based calculation was applied to merge those trajectories with similar origins.

319 **3. Results and Discussion**

320 3.1 Atmospheric lifetimes and backward trajectory analysis

321 Before conducting the backward trajectory analysis of air masses at the IAP site in
322 Beijing, the approximate lifetimes of VMS compounds and their oxidation products
323 were calculated based on the average OH radical concentrations measured in Beijing.
324 As the OH concentrations varies significantly ($<1 \times 10^6$ – 1.7×10^7 molecules cm^{-3})
325 during different hours of the day, and also varies in different seasons and under different
326 weather conditions (Lu et al., 2013; Chu et al., 2021), the OH concentrations used for
327 the calculation of atmospheric lifetimes are daily averaged concentrations during each
328 season. The average OH concentrations for the calculation of VMS lifetimes in this
329 study were assumed to be 4.9×10^6 mol cm^{-3} in summer (Rao et al., 2016), and $1.5 \times$
330 10^6 mol cm^{-3} in winter (Chu et al., 2021). However, it should be noted that the OH
331 concentration applied for summer (4.9×10^6 mol cm^{-3}) was not a daily average, but a
332 modeled daytime average in a non-haze period. Apart from OH concentration as an

333 important factor affecting VMS atmospheric lifetimes, the sensitivity of their
 334 atmospheric lifetimes to other factors such as variation in the time-of-day for VMS
 335 emissions, and to relative humidity dependent heterogeneous uptake and/or reactions
 336 on mineral dusts are assessed in Navea et al. (2011). They found that VMS lifetime was
 337 insensitive to urban OH concentrations due to limited residence time, and somewhat
 338 sensitive to enhanced OH levels in the transition area between the urban and rural
 339 locations.

340

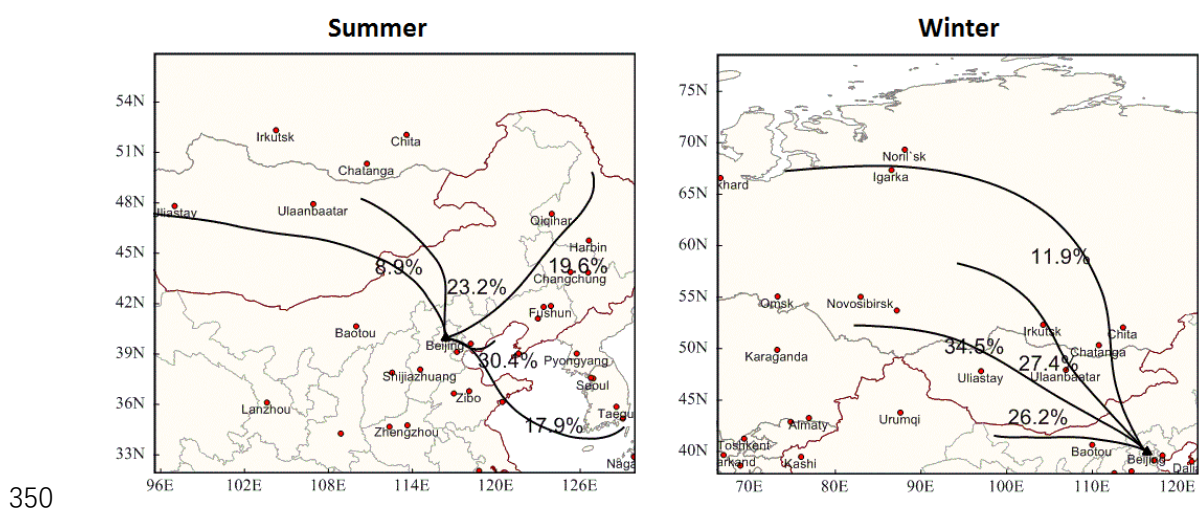
341

Table 2 Calculated lifetimes of VMS compounds and oxidation products in Beijing

| Molecule | k_{OH} ($\times 10^{-12}$ $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) | Approximate lifetime (t; days) | | References |
|----------|--|--------------------------------|--------|----------------------------|
| | | Summer | Winter | |
| L1 | 1.0 ± 0.27 | 2.36 | 7.72 | (Atkinson, 1991) |
| | 1.28 ± 0.46 | 1.85 | 6.03 | (Sommerlade et al., 1993) |
| L2 | 1.38 ± 0.36 | 1.71 | 5.59 | (Atkinson, 1991) |
| | 1.19 ± 0.30 | 1.98 | 6.48 | (Sommerlade et al., 1993) |
| | 1.32 ± 0.05 | 1.79 | 5.85 | (Markgraf and Wells, 1997) |
| | 1.20 ± 0.09 | 1.97 | 6.43 | (Alton and Browne, 2020) |
| L3 | 1.83 ± 0.09 | 1.29 | 4.22 | (Markgraf and Wells, 1997) |
| | 1.7 ± 0.1 | 1.39 | 4.54 | (Alton and Browne, 2020) |
| L4 | 2.66 ± 0.13 | 0.89 | 2.90 | (Markgraf and Wells, 1997) |
| | 2.5 ± 0.2 | 0.94 | 3.09 | (Alton and Browne, 2020) |
| L5 | 3.4 ± 0.5 | 0.69 | 2.27 | (Alton and Browne, 2020) |
| D3 | 0.86 ± 0.09 | 2.75 | 8.97 | (Alton and Browne, 2020) |
| D4 | 1.01 ± 0.32 | 2.34 | 7.64 | (Atkinson, 1991) |
| | 1.26 ± 0.40 | 1.87 | 6.12 | (Sommerlade et al., 1993) |
| | 1.3 ± 0.1 | 1.82 | 5.94 | (Alton and Browne, 2020) |
| D5 | 1.55 ± 0.49 | 1.52 | 4.98 | (Atkinson, 1991) |
| | 2.1 ± 0.1 | 1.12 | 3.67 | (Alton and Browne, 2020) |
| MDOH | 1.89 ± 0.60 | 1.25 | 4.08 | (Whelan et al., 2004) |
| MOH | 3.95 ± 0.95 | 0.60 | 1.95 | (Sommerlade et al., 1993) |

342 Note: L1: Tetramethylsilane; L2: Hexamethyldisiloxane; MDOH: Pentamethyldisiloxanol; MOH: Trimethylsilanol. K_{OH} is the
 343 rate constant for oxidation by OH radicals; The approximate lifetimes of these compounds were calculated as: $t =$
 344 $[1/(K_{OH} \times C_{OH})]/(60 \times 60 \times 24)$; C_{OH} is the average concentration of OH radicals in Beijing, which is 4.9×10^6 (Rao et al., 2016),
 345 and 1.5×10^6 (Chu et al., 2021) mol cm^{-3} in summer and winter, respectively.

346 As shown in Table 2, the lifetimes of these compounds ranged from 1.95~7.72 and
 347 0.60~2.75 days in summer and winter, respectively. For the most abundant species D4
 348 and D5, their lifetimes range from 1.12~2.34 and 3.67~7.64 days in summer and winter,
 349 respectively.



350
 351 Figure 1. Air mass backward trajectory clusters arriving at IAP during summer and winter in Beijing
 352 The cluster results of the 72-hr backward trajectories are shown in Fig. 1. In summer,
 353 the cluster results of the backward trajectory analysis show that around half of the
 354 trajectories (30%+18%) were ocean originated, while 32% (9%+23%) and 20% of the
 355 trajectories were from Mongolia and Helongjiang Province, respectively. The
 356 trajectories in summer did not pass heavily polluted cities such as Ulaanbaatar or
 357 Baotou (Hasenkopf et al., 2016; Zhou et al., 2016). However, all of the backward
 358 trajectories in winter had terrestrial origins, and 26% of the trajectories were from inner
 359 Mongolia and passed Baotou before arriving Beijing. The remaining trajectories (74%)

360 were from Russia and passed Mongolia, and 27% of them passed Ulaanbaatar. In
361 addition, all trajectories also passed heavily polluted northern Hebei province in winter,
362 while only half of them passed this region in summer. Hence, apart from local sources,
363 the aerosol levels in winter of Beijing may be more influenced by long-range transport,
364 especially from heavily polluted regions.

365

366 3.2 PM_{2.5} and total Si concentrations

367 In summer (August 2018), daily PM_{2.5} concentrations ranged from 10.9 to 55.3 $\mu\text{g m}^{-3}$
368 (mean: $29.4 \pm 15.9 \mu\text{g m}^{-3}$). While in winter (January 2019), daily PM_{2.5} concentrations
369 ranged from 8.4 to 260.8 $\mu\text{g m}^{-3}$, with an average of $57.5 \pm 56.2 \mu\text{g m}^{-3}$, approximately
370 double that in the summer period. The highest daily concentration of PM_{2.5} in winter
371 was 260.8 $\mu\text{g m}^{-3}$, much higher than the China National Ambient Air Quality Standard
372 (CNAAQs) (BG3095-12) Grade II for 24 h average PM_{2.5} concentration ($75 \mu\text{g m}^{-3}$).
373 Elevated PM_{2.5} levels in winter could be attributed to regional transport, stagnant
374 weather and increased local emissions due to house heating, etc.

375 As total Si was not determined in this study, it is estimated by applying a total-Si/PM_{2.5}
376 ratio. In our previous study (Xu et al., 2020a), PM_{2.5} samples were collected in the same
377 sampling location and the mean total-Si/PM_{2.5} ratios in winter 2016 and summer 2017
378 were 1.14% and 1.95%, respectively. Both ratios (overall mean: 1.55%) are comparable
379 to the annual mean Si abundance in PM_{2.5} samples (1.56%) collected in Beijing in 2013
380 (Lu et al., 2019). Hence, the total-Si/PM_{2.5} ratios of 1.14% and 1.95% were applied to

381 estimate the total Si concentrations in winter and summer in this study, respectively.

382 The estimated total-Si concentrations ranged between 0.21~1.08 and 0.10~2.97 $\mu\text{g m}^{-3}$

383 in summer and winter, respectively. The average concentrations of total-Si in summer

384 and winter were 0.57 ± 0.31 and 0.66 ± 0.64 $\mu\text{g m}^{-3}$, respectively. These results are lower

385 than those reported in Beijing during 2000, which showed the total-Si in $\text{PM}_{2.5}$ during

386 July and January were 1.87 and 0.99 $\mu\text{g m}^{-3}$, respectively, accounting for 1.9% and 1.6%

387 of $\text{PM}_{2.5}$ (Song et al., 2006). These are also lower than those from another study carried

388 out at an urban site of Beijing, in which the total Si concentration was 1.0 ± 0.9 $\mu\text{g m}^{-3}$,

389 accounting for 1.2% of $\text{PM}_{2.5}$ (Li et al., 2017b). This is consistent with the reduction in

390 $\text{PM}_{2.5}$ levels (Vu et al., 2019) and in the emissions of crustal compounds.

391

392 3.3 Total water-soluble Si, water-soluble inorganic and organic Si

393 Fig. 2 shows total water-soluble Si (i.e., water-soluble inorganic and organic Si)

394 determined through the ICP-OES analysis of water-extracted aerosol samples. The

395 water-soluble inorganic Si measured by UV-Vis ranged from <DL to 3.5 ng m^{-3} , with

396 an average of 1.0 ± 0.8 ng m^{-3} in summer. In winter, water-soluble inorganic Si was in

397 the range of 1.0-16.1 ng m^{-3} , with an average of 3.6 ± 3.9 ng m^{-3} . The mean total water-

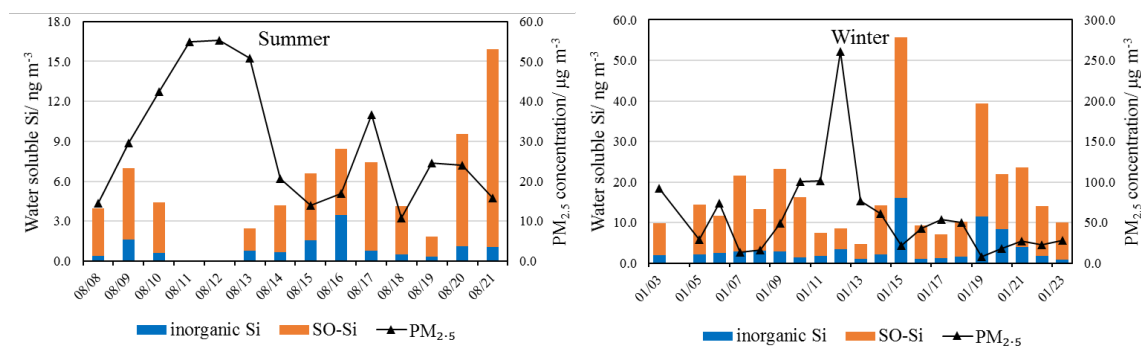
398 soluble Si in winter was 16.8 ± 12.2 ng m^{-3} , approximately 3 times higher than that of

399 summer (5.6 ± 4.0 ng m^{-3}). As mentioned in the method introduction, the difference

400 between total water-soluble Si and water-soluble inorganic Si is water-soluble organic

401 Si (SO-Si). The SO-Si concentrations ranged from <DL to 14.9 ng m^{-3} (mean: 4.6 ± 3.7

402 ng m^{-3}) and 3.5 to 39.6 ng m^{-3} (mean: $13.2 \pm 8.6 \text{ ng m}^{-3}$) in summer and winter,
 403 respectively. They account for approximately $80.1 \pm 10.1 \%$ and $80.2 \pm 8.7 \%$ of the total
 404 water-soluble Si, $1.2 \pm 1.2 \%$ and $5.0 \pm 6.9 \%$ of the total Si, and $0.023 \pm 0.024\%$ and
 405 $0.057 \pm 0.079\%$ of $\text{PM}_{2.5}$ mass.



406

407 Fig. 2 Daily $\text{PM}_{2.5}$ concentrations, water-soluble inorganic Si (Si-inorganic) and secondary organic Si

408 (SO-Si) concentrations at IAP, Beijing during (a) summer (August 2018) and (b) winter (January 2019)

409 (Concentrations on 11th and 12th August are < DL)

410 Si accounts for around 38% of cVMS and 36% of IVMS according to their molecular
 411 weights (Table 3). Assuming the oxidation of VMS by OH radical would replace one
 412 H-atom in one CH_3 group with only one OH group, as D5 is the most abundant pollutant
 413 among these VMS (Ahrens et al., 2014; Genualdi et al., 2011; Kierkegaard and
 414 McLachlan, 2013), the Si-SOA concentration is conservatively estimated as the Si
 415 concentration dividing by the mass ratio of Si to D5-OH (one H-atom in one CH_3 group
 416 in D5 was replaced by one OH group) (36.2%) (Table 3). The estimated Si-SOA
 417 concentrations in summer and winter were $12.7 \pm 10.2 \text{ ng m}^{-3}$ and $36.6 \pm 23.9 \text{ ng m}^{-3}$,
 418 respectively, accounting for $0.06 \pm 0.07\%$ (range $< 0.003 \sim 0.26\%$), and $0.16 \pm 0.22\%$
 419 ($0.006 \sim 0.92\%$) of $\text{PM}_{2.5}$. Even though summer is expected to have VMS emissions due

420 to evaporation under higher temperature, the synoptic scale stagnant weather conditions
 421 during winter in Northern China may have contributed to the accumulation of VMS.
 422 More VMS may have been converted to Si-SOA in this season in wider Northern China
 423 and transported to Beijing.

424 Table 3 Si abundance (%) in molecules of major IVMS and cVMS compounds

| | Full name | Molecular formula | Molecular weight (g/mol) | Si abundance in molecule (%) | Si abundance in molecule after replacing one H-atom in CH ₃ group with one OH group (%) |
|----|-------------------------------|--|--------------------------|------------------------------|--|
| L3 | Octamethyltrisiloxane | C ₈ H ₂₄ O ₂ Si ₃ | 236.53 | 35.5 | 33.3 |
| L4 | Decamethyltetrasiloxane | C ₁₀ H ₃₀ O ₃ Si ₄ | 310.69 | 36.0 | 34.3 |
| L5 | Dodecamethylpentasiloxane | C ₁₂ H ₃₆ O ₄ Si ₅ | 384.84 | 36.4 | 34.9 |
| L6 | Tetradecamethylhexasiloxane | C ₁₄ H ₄₂ O ₅ Si ₆ | 458.99 | 36.6 | 35.4 |
| D3 | Hexamethylcyclotrisiloxane | C ₆ H ₁₈ O ₃ Si ₃ | 222.46 | 37.8 | 35.2 |
| D4 | Octamethylcyclotetrasiloxane | C ₈ H ₂₄ O ₄ Si ₄ | 296.62 | 37.8 | 35.8 |
| D5 | Decamethylcyclopentasiloxane | C ₁₀ H ₃₀ O ₅ Si ₅ | 370.77 | 37.8 | 36.2 |
| D6 | Dodecamethylcyclohexasiloxane | C ₁₂ H ₃₆ O ₆ Si ₆ | 444.92 | 37.8 | 36.4 |

425
 426 Janecek et al. (2017) estimated the concentrations of D4, D5, and D6 oxidized by OH
 427 radicals using the 3-D atmospheric chemical transport model (CMAQ). The inputs of
 428 the model included emissions of D4, D5, D6, and their first oxidative species by OH
 429 radicals. Meteorological conditions, wet and dry deposition of the primary species were
 430 also considered. Reactions of the oxidation products are not included in the model, but
 431 the rate constants for the parent cyclic siloxanes reacting with OH radical were applied.
 432 The computed concentrations of the oxidation products of D5 (namely o-D5) ranged
 433 between 0.37~0.81 ng m⁻³ when the modeled concentration of D5 ranged between
 434 4.04~6.82 ng m⁻³ in the USA (Janecek et al., 2017). D5 was the predominant VMS,

435 which accounted for around 60-90% of the sum of L3~L6 and D3~D6 (Ahrens et al.,
436 2014; Genualdi et al., 2011; Kierkegaard and McLachlan, 2013). The estimated o-D5
437 should represent the majority of VMS oxidation products. Hence, the concentrations of
438 SOA in our study are higher than that reported by Janecek et al. (2017), which is
439 reasonable as VMS concentrations in China are much higher than those in the USA
440 (Table 1) (Wang et al., 2001; Kierkegaard and McLachlan, 2013). Milani et al. (2021)
441 also investigated the SOA concentration formed from oxidation of VMS. However,
442 they only quantified one specific SOA compound –
443 hydroxynonamethylcyclopentasiloxane (D4TOH), which is an oxidation product of D5
444 with one CH₃ group in D5 replaced by OH radical, in PM_{2.5} samples collected at two
445 urban locations in the United States. The D4TOH concentration in the samples ranged
446 from 16 to 185 pg m⁻³ in Atlanta and 19–206 pg m⁻³ in Houston.

447 On 11th and 12th August, the SO-Si (<DL) and its relative abundance in water-soluble
448 Si were much lower than those of the other days. The surface net solar radiation on 11th
449 (3.8×10^5 J m⁻²) and 12th (2.8×10^5 J m⁻²) were the third lowest and the lowest during
450 summer days, respectively, while the total cloud cover was 0.98 and 0.94, respectively,
451 which were the highest during the summer campaign. Lower surface net solar radiation
452 and higher total cloud cover hinder the formation of Si-SOA. In the following, we
453 further explored the relationship to secondary inorganic ions (sulfate and nitrate), and
454 possible effects of meteorological conditions on the formation of Si-SOA.

455

456 3.4 Relationship between SO-Si and secondary inorganic ions

457 The correlation between SO-Si and secondary inorganic ions (sulfate and nitrate) and
458 sulfur conversion ratio was investigated. The sulfur conversion ratio was calculated as
459 the sulfur concentration in sulfate divided by its concentration in the sum of sulfur
460 dioxide and sulfate. As shown in Table 4, PM_{2.5} and secondary inorganic ions are all
461 negatively correlated with SO-Si and SO-Si/PM_{2.5}, suggesting SO-Si is unlikely to
462 share the same sources and/or formation mechanisms as secondary inorganic ions. Kim
463 and Xu (2016) reported that VMS can be sorbed to atmospheric aerosols by partitioning,
464 and also interact with them like other volatile species through sorption processes on the
465 particle surfaces and the subsequent heterogeneous reactions. Some of aerosols such as
466 carbon black and sea salts reversibly interacted with VMS whereas other aerosols such
467 as sulfates showed highly irreversible sorption for the VMS, especially at low
468 concentrations. It is interesting to note that ammonium sulfate can significantly increase
469 aerosol yield in very low RH conditions (RH <10%) in an environmental chamber, as
470 it can act as seed particle to form Si-SOA (Wu and Johnston, 2017). However, the
471 negative correlations between sulfate with SO-Si ($r=-0.57$), and sulfate with SO-
472 Si/PM_{2.5} ($r=-0.71$) suggest that formation mechanisms of Si-SOA is different under the
473 high RH during our study periods (50-60%). A less negatively correlated SO₄²⁻ with
474 SO-Si ($r=-0.36$) and SO-Si/PM_{2.5} ($r=-0.36$) in winter could be the combined result of
475 more in-situ Si-SOA formation during the accumulation phase in stagnant winter
476 conditions and/or more external inputs from upwind areas (due to a longer lifetime, see
477 Table 2). However, due to limited samples and investigations into the Si-SOA formation

478 mechanisms in this study, more work is needed to clarify these mechanistic issues.

479 Table 4 The correlations (r) between SO-Si and SO-Si/PM_{2.5} with sulfate, nitrate and sulfur conversion
480 ratio

| | Summer | | Winter | |
|--|--------|-------------------------|--------|-------------------------|
| | SO-Si | SO-Si/PM _{2.5} | SO-Si | SO-Si/PM _{2.5} |
| PM _{2.5} | -0.51 | -0.64 | -0.44 | -0.46 |
| SO ₄ ²⁻ | -0.57 | -0.71 | -0.36 | -0.36 |
| NO ₃ ⁻ | -0.60 | -0.56 | -0.42 | -0.50 |
| S-SO ₄ ²⁻ /(S-SO ₄ ²⁻ +S-SO ₂) | -0.56 | -0.74 | -0.33 | -0.28 |

481

482 3.5 Relationship between SO-Si and meteorological parameters

483 The Pearson correlation coefficients (r) of SO-Si and SO-Si/PM_{2.5} ratio with different
484 meteorological parameters in summer and winter are presented in Table 5.

485 Table 5 Correlation coefficient (r) between SO-Si concentration and meteorological data in summer and
486 winter

| | Summer | | Winter | |
|--------------------------------------|---------|--------------------------|----------------|--------------------------|
| | SO-Si | SO-Si/ PM _{2.5} | SO-Si | SO-Si/ PM _{2.5} |
| Wind speed | 0.28 | 0.26 | 0.51* | 0.49* |
| Temperature | 0.37 | 0.14 | -0.01 | 0.19 |
| Relative humidity | -0.75** | -0.69** | -0.47* | -0.46* |
| Surface net solar radiation | 0.76** | 0.57* | -0.02 | -0.20 |
| Downward UV radiation at the surface | 0.75** | 0.54* | -0.01 | -0.11 |
| Total cloud cover | -0.52 | -0.39 | 0.10 | 0.20 |
| Total precipitation | -0.55* | -0.46 | - ^a | - |

487 * Correlation is significant at the 0.05 level ($p < 0.05$; two-tailed); ** Correlation is significant at the 0.01
488 level ($p < 0.01$; two-tailed); ^a There is no precipitation in winter sampling period

489 SO-Si was positively correlated with surface net solar radiation (ssr, $r=0.76$) and
490 downward UV radiation at the surface (uvb, $r=0.75$) in summer (Table 5). Its relative
491 abundance in PM_{2.5} was also positively correlated with net solar radiation ($r=0.57$) and
492 downward UV radiation ($r=0.54$) in summer. These results indicate that higher solar
493 radiation may favour the formation of Si-containing SOAs. Temperature showed no

494 correlation with SO-Si, suggesting that temperature-dependent emissions of VMS are
495 unlikely to be a key factor in influencing SO-Si concentration. Wind speed was also
496 correlated with SO-Si and SO-Si/PM_{2.5} in winter. This is in contrary to the negative
497 correlation between wind speed and PM_{2.5} concentrations. This may be due to the
498 higher wind speeds facilitating the transport of VMS and SO-Si from surrounding areas
499 to the sampling location in central Beijing. Relatively humidity (RH), total cloud cover
500 (tcc), and total precipitation (tp, summer only) were all negatively correlated with Si-
501 SOA in summer; only RH is correlated (but weakly) with SO-Si and Si-Si/PM_{2.5} in
502 winter. These results suggest that high RH and total cloud cover may hinder the Si-SOA
503 formation or accumulation in the air. Precipitation may enhance wet deposition of Si-
504 SOA. Because the major degradation pathway of atmospheric VMS is through
505 oxidation by hydroxyl radical, which produces hydroxylated methyl groups with lower
506 hydrophobicity than the VMS (Xiao et al., 2015), the Si-SOA can be readily removed
507 from the atmosphere by wet deposition (Atkinson, 1991; Xiao et al., 2015). It is not
508 totally clear why high RH may suppress Si-SOA formation. This may be related to the
509 OH radical concentration, but we do not have data to investigate this further. No
510 previous chamber studies have looked at VMS oxidation under high RH conditions.

511 In Table 5, no strong correlation was observed between SO-Si and meteorological
512 parameters, except wind speed, in winter. This suggests different factors control the
513 abundance of Si-SOA in summer and winter.

514 3.6 Atmospheric implications

515 Si-SOA contribute to $0.06\pm 0.07\%$ and $0.16\pm 0.22\%$ of $PM_{2.5}$ mass in winter and summer,
516 but it could contribute up to 0.9% during certain days (Fig. 2). The mass concentration
517 of Si-SOA in Beijing is comparable to widely studied isoprene oxidation products such
518 as 2-methyltetrol organosulfate but lower than total isoprene organosulfates (Bryant et
519 al., 2020). The relative contribution to $PM_{2.5}$ mass will likely increase in the future as
520 the $PM_{2.5}$ in Beijing is decreasing while no regulation is in place for Si-containing
521 VOCs. The relative importance of Si-SOA to $PM_{2.5}$ in more remote locations, such as
522 over the open ocean downwind major Si-VOC source regions, may be much higher,
523 considering the longer lifetime of VMS (days) at more remote locations (i.e., due to
524 lower OH concentrations) (Table 1). Li et al (2017a) revealed through chemical
525 mapping of individual particles collected during a research cruise over the Yellow Sea
526 that, the sulfate was coated with a layer of Si. Such coatings of Si on sulfate could not
527 possibly be primary silicon which is extremely insoluble. The coating suggests that they
528 must be secondary Si, formed from VMS. Back trajectory analyses indicated that air
529 masses reaching the cruise were mainly from mainland China (Li et al., 2017a). More
530 work is needed to quantify the concentration of Si-SOA in remote atmospheres as well
531 as their relative abundance in $PM_{2.5}$. In addition, as it exists in fine particles and is much
532 more water soluble than the VMS, Si-SOA could potentially cause greater
533 environmental risks. However, current knowledge on the potential toxicity of the Si-
534 SOA compounds is limited. Furthermore, this study also provides a quantitative method
535 for investigating the oxidation efficiency of VMS through the quantification of SO-Si

536 concentrations directly. Such a method can be used to quantify Si-SOA yield under
537 different environmental conditions in chamber studies.

538

539 **Conclusions**

540 This work provided a conservative estimation of SO-Si and Si-SOA for the first time
541 with no requirements for information on the precursor concentrations. The estimated
542 Si-SOA concentrations were 12.7 ± 10.2 and 36.6 ± 23.9 ng m⁻³ in summer and winter,
543 respectively, accounting for $0.06 \pm 0.07\%$ and $0.16 \pm 0.22\%$ of PM_{2.5}. High surface net
544 solar radiation favours the formation of Si-SOA, especially in summer. Gas-phase
545 oxidation is the predominant Si-SOA formation pathway, rather than the formation on
546 particle surfaces, such as those of SO₄²⁻. Long-range transport is potentially an
547 important source of Si-SOA in Beijing, especially during winter.

548

549 **Competing interests**

550 The authors have no conflict of interests.

551

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558

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