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A New Structural Classification Scheme for Dissolved Organic Sulfur in Urban Snow from North China

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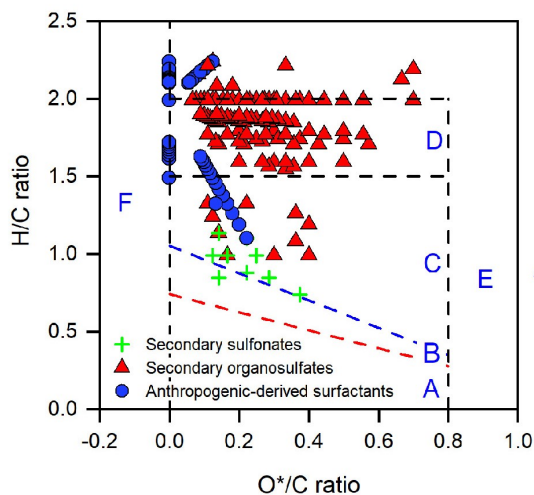
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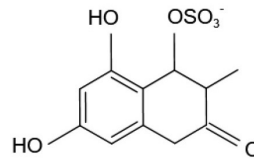
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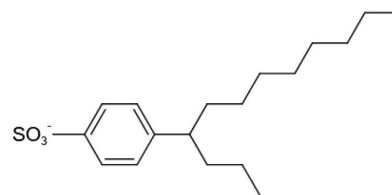
FT-ICR MS



Secondary organosulfates



Anthropogenic-derived surfactants



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18 The authors confirmed that the submitted image was created by an author and has never been
19 published.

20

21 **ABSTRACT**

22 The chemical composition of dissolved organic sulfur in snow is important in understanding the
23 sources and scavenging processes of atmospheric organic matter. Snow samples collected
24 simultaneously from four megacities in North China were analyzed using ultrahigh-resolution
25 Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The modified oxygen
26 (O^*) and redefined aromaticity index (AI^*) help interpret the possible structural information and
27 evaluate the aromaticity of sulfur-containing molecules. By extending these parameters, we
28 provide a new structural classification for organic sulfur species in the atmosphere. With the new
29 classification, the oxidized ($O/S > 3$) and less oxidized state ($O/S \leq 3$) sulfur-containing molecules
30 can be easily distinguished. Typical known secondary organosulfates and sulfonates, and

31 anthropogenic-derived anionic surfactants verified the validity of this new classification. The new
32 classification was applied to the molecular characterization of dissolved organic sulfur in snow
33 samples. More than one hundred (138–150) of the molecules with medium O/S ratios of 5–11 and
34 low-medium mass range < 500 Da are related with typical known secondary organosulfates and
35 anthropogenic-derived anionic surfactants. Our study provides new insights into the molecular
36 compositions of organic sulfur species in the ambient air, although their atmospheric behaviors
37 between the snow-aerosol interfaces warrant further studies.

38

39 **KEYWORDS**

40 Dissolved organic sulfur, wet deposition, snow, organosulfates, classification criterion, FT-ICR
41 MS

42

43 **SYNOPSIS**

44 Molecular composition of dissolved organic sulfur in urban snow obtained by ultra-high resolution
45 mass spectrometry is classified by a new structural scheme.

46 INTRODUCTION

47 A variety of physical and chemical processes occurring in the Earth's atmosphere and cryosphere
48 act as important elements of global biogeochemical cycles of organic matter.¹ Snow plays an
49 important role in scavenging atmospheric organic matter.² Over the last decade, many studies have
50 been conducted to illustrate the unique role of snow in the transport and fate of organic
51 contaminants in polar and high mountain areas.³⁻⁷ The presence of snow can alter the aerosol size
52 distributions of gasoline engine exhausts, while the organic composition of snow is affected by
53 exposure to exhausts.⁸ Vehicle exhaust-derived benzene, toluene and polycyclic aromatic
54 hydrocarbons were found to accumulate at the air-snow interface.⁹ Carboxylic acids, amino acids,
55 sugars and phenolic compounds were used as chemical markers to investigate the aerosol-snow
56 transfer processes.¹⁰ Shahpoury et al.¹¹ suggested that the interplay between gas-particle
57 partitioning in the aerosol and dissolution during in- or below-cloud scavenging determines the
58 phase distribution of polar particulate substances.

59 Recently, with the development of analytical instruments, various organic sulfur molecules
60 referred to here as CHOS, have been detected in atmospheric aerosols¹²⁻¹⁷ and fog or cloud water¹⁸⁻
61 ²¹. Among these compounds, organosulfates (R-O-SO₃⁻) and sulfonates (R-SO₃⁻) are of particular
62 concern.¹⁵ Organosulfates are tracers of the formation of secondary organic aerosols (SOA), while
63 sulfonates might be related to anthropogenic origins.^{22,23} The temporal^{24,25} and spatial²⁶⁻²⁸ variations
64 in CHOS in rainwater or snow have been investigated focusing on molecules within the low and
65 medium mass range (200–500 Da). However, the higher molecular weight species of CHOS (≥500
66 Da) remain poorly characterized. With a resolution improvement of high-field Fourier transform
67 ion cyclotron resonance mass spectrometry (FT-ICR MS),²⁹⁻³¹ more reliable assignments of high
68 mass multiple elemental formulas became possible,^{32,33} especially for non-oxygen heteroatom-rich

69 (such as nitrogen, sulfur or phosphorus) dissolved organic matter. The characteristics of high mass
70 CHOS in biodiesel and diesel fuel SOA,³⁴ and methacrolein and methylvinyl ketone-derived
71 products¹³ were reported previously.

72 In recent years, North China has been suffering from frequent severe haze events, especially in
73 winter. To obtain a better understanding of the aerosol-snow interactions in the urban atmosphere,
74 snow samples were collected from four megacities in North China. By compiling thousands of
75 CHOS, this study provides a new structural classification of CHOS for atmospheric samples. Our
76 results indicate that low-medium mass CHOS species (< 500 Da) in snow, with medium O/S ratio
77 (5–11), are related with typical known secondary organosulfates and anthropogenic-derived
78 anionic surfactants. The feasibility of the new classification on CHONS molecules will be
79 performed in another study by taking consideration of variety oxidation states of sulfur and
80 nitrogen.

81

82 **MATERIALS AND METHODS**

83 Fresh surface snow samples were collected from urban areas of four megacities in North China
84 (Table S1 and Figure S1). The four samples were collected during the same regional precipitation
85 event in urban Beijing, Tianjin, Shijiazhuang, and Taiyuan on 21 February 2017. Melted snow was
86 preconcentrated using solid phase extraction and stored at –20°C prior to measurement using the
87 ESI-FT-ICR MS (15T, Bruker Daltonik, Germany). Detailed information about the sampling,
88 pretreatment processes and data managements could be found in the supporting information text
89 (Text S1).

90 This study mainly focuses on water soluble CHOS groups within the mass range (m/z) of 180–
91 700 Da. From herein, the mass ranges are referred to as low-mass (180–300 Da), medium-mass

92 (300–500 Da), and high-mass (500–700 Da). Due to the possible existence of numerous isomers
93 represented by each formula, the compound classes or functional groups identified in this study
94 only indicate the most likely categorization.^{35,36}

95 The sample specific average number of oxygen atoms between the range from CHO_iS_1 to
96 CHO_jS_1 formulas (average oxygen number density, Num_Density_{i-j}) was calculated according to
97 Equation 1:

$$98 \quad \text{Num_Density}_{i-j} = \frac{\sum_i^j \text{Num_CHO}_n\text{S}_1}{j-i+1}, j \geq i \geq 1, \quad (1)$$

99 where $\text{Num_CHO}_n\text{S}_1$ is the CHO_nS_1 formula number in the specific sample, and the oxygen
100 variation range of Num_Density_{i-j} is from i to j .

101 For CHO_iS_1 (containing one sulfur atom), if $i > 3$ (with more than three oxygen atoms) in the
102 formula, it represents that CHO_iS_1 contains one sulfate group or one sulfonate group coupled with
103 an additional oxygen containing functional group (such as -OH, -(C=O), -OR, and -COOH).^{23, 34,}
104 ³⁷⁻³⁹ For CHO_iS_1 formulas, an alternative notation was introduced using O^* , which acquires a value
105 of $\text{O}^* = i-3$, where i is the number of oxygens in the formula.³⁸ For organic sulfur molecules
106 containing less than 3 oxygen atoms, O^* could have values ($= i-3$) ≤ 0 and consequently also the
107 ratio O^*/C is ≤ 0 .

108 By subtracting SO_3 from CHO_iS_1 , CHO_iS_1 formulas could be viewed as oxygen-containing
109 hydrocarbon molecules with a new formula of CHO_{i-3} . The oxygen in sulfate group or sulfonate
110 group could not contribute to the double-bond equivalent (DBE), therefore, subtracting SO_3 from
111 CHO_iS_1 ensures that the transition from CHO_iS_1 to CHO_{i-3} does not affect the aromaticity of the
112 rest of the formula. AI^* (the modified aromaticity index, see Equation 2) helps evaluate the
113 aromaticity of sulfur containing molecules more accurate than AI (the aromaticity index).³⁴ For
114 example, for benzene-sulfonic acid, $\text{C}_6\text{H}_6\text{SO}_3$, $\text{AI}=0$, the benzene ring is underestimated. By

115 subtracting SO_3 , the new formula transition into C_6H_6 , $\text{AI}^*=0.67$, the aromaticity of benzene ring
116 is accurately estimated as expected. A detailed interpretation of this formalism could be found in
117 previous studies.^{34,38}

118 By introducing $\text{DBE}=(1+c-h/2)$ and $\text{O}^*(=i-3)$ of $\text{C}_c\text{H}_h\text{O}_{i-3}$, AI^* could be simplified into
119 following equation 2. Text S1 provides detailed mathematical calculations of AI^* .

$$120 \quad \text{AI}^*=(\text{DBE}-\text{O}^*)/(\text{c}-\text{O}^*) \quad (2)$$

121

122 RESULTS AND DISCUSSION

123 **Variations in Oxygen to Sulfur Ratios.** The oxygen to sulfur (O/S) ratio of CHOS is widely
124 used for elucidating the possible structure and origin of organic sulfur-containing molecules
125 identified using FT-ICR MS.^{14, 24, 28, 39, 40} An O/S ratio being lower than 3 indicates reduced S-
126 containing molecules. The O/S ratio equals to 3 indicates organic sulfonates. While an O/S being
127 higher than 3 indicates an organosulfate or sulfonate with an additional oxygen containing function
128 group/s (such as hydroxyl, carboxyl and so on).

129 According to Figure S4, CHOS_2 molecules contributed negligibly to the number and relative
130 intensity abundance of CHOS molecules. The following discussion only focused on the more
131 abundant CHOS_1 molecules. The radar distribution in oxygen atoms illustrates the variation in O/S
132 ratios of CHOS_1 molecules (Figure 1b). CHOS_1 in the Beijing sample differed from the rest with
133 the highest abundance in the O_{4-13} groups (number of formulas *Num_Density*₄₋₁₃: 227), while the
134 other three samples were similar among them, largely consisting of O_{5-12} with a lower number of
135 formulas (*Num_Density*₅₋₁₂ varying from 166 to 202).

136 To further analyze similarities and differences of CHOS_1 molecules, these were divided into two
137 mass ranges (< 500 Da and \geq 500 Da) in Figure 1b. For the low and medium mass range of CHOS_1

138 molecules (< 500 Da), the four snow samples showed a same pattern with the number of oxygen
139 atom mainly between 5 and 11. That is, $\text{CHO}_{5-11}\text{S}_1$ formulas constituted 82–89% of the identified
140 CHOS_1 formulas in the low and medium mass range, with $\text{Num_Density}_{5-11}$ ranging from 133 to
141 176. However, for the high mass range (≥ 500 Da), the oxygen distribution presented a totally
142 different pattern. The Beijing sample showed higher abundance in the O_{9-14} range with a higher
143 $\text{Num_Density}_{9-14}$ (117). In contrast, the other three snow samples were mainly composed of O_{9-13}
144 with a lower $\text{Num_Density}_{9-13}$ (varying from 54 to 61).

145 The similarity in the low-medium mass range versus the difference in the high mass range of
146 CHOS_1 molecules indicates distinct origins of molecules in these two mass ranges. Song et al.⁴¹
147 identified $\text{O}_4\text{S}_1\text{--O}_9\text{S}_1$ (≤ 500 Da) as the most abundant water-soluble CHOS species emitted from
148 coal combustion. Jiang et al.³⁷ reported that numerous S-containing molecules in aerosols on clean
149 days were also observed on haze days, although Wang et al.⁴⁰ demonstrated that organic sulfur
150 containing molecules on haze days were of higher mass than those on clean days in Beijing. A
151 previous laboratory study showed that the methacrolein-derived organic sulfur molecules were of
152 high mass (300–650 Da) in the presence of a high concentration (10 mM) of methacrolein.⁴² As
153 discussed in the Text S2, the snow event occurred in Beijing coupled with high concentrations of
154 $\text{PM}_{2.5-24\text{h}}$, DOC and SO_4^{2-} (Figure 1a). Although the $\text{PM}_{2.5-24\text{h}}$ levels of Tianjin and Shijiazhuang
155 samples were almost the same with the Beijing sample (about $60 \mu\text{g m}^{-3}$), but the DOC and SO_4^{2-}
156 concentrations of the Beijing sample was about 1–2 times higher than those from Tianjin and
157 Taiyuan. In addition, according to our previous optical results (UV–vis and excitation-emission
158 matrix fluorescence) on these samples, the Beijing one exhibited higher UV-vis absorbance and
159 higher fluorescence intensity at humic-like substance peaks (peak A and M) than other samples.⁴³
160 These results indicate that high mass (≥ 500 Da) organic sulfur containing molecules might be

161 largely attributed to the higher formation propensity or greater accumulation potential of these
162 molecules in snow during haze episodes. Furthermore, our previous study on wintertime aerosols
163 in Beijing confirms that high mass (≥ 500 Da) CHOS molecules with oxygen atoms ranged from
164 10–15 were significantly enhanced during haze events than clean days.⁴⁴

165 **A Classification of Organic Sulfur Species and its Validation.** Previous classification of
166 atmospheric organic sulfur species did not include all molecules, particularly those CHO_iS_1
167 molecules with $i \leq 3$.^{34,38} The modified subgroups, introduced in our study, provide a new way for
168 identification of the origins of the natural organic sulfur molecules. By combining the modified
169 van Krevelen (VK) plots that use O^*/C in place of the O/C ratio³⁸ and the AI^* values³⁴, the CHOS_1
170 molecules could be divided into six subgroups (*Subgroup A to F*) (Table S2 and Figure 2a). It
171 should be noted that the CHOS_1 molecules with $\text{AI}^* = 0.5$ and $\text{AI}^* = 0.67$ scatter among a wide
172 range in the modified VK diagram (Figure S5). To make the boundary of $\text{AI}^* = 0.5$ and $\text{AI}^* = 0.67$
173 visual, hypothetical boundaries are used according to Figure S5. However, in making this
174 classification, the actual value of AI^* of one molecule were considered, rather than the location of
175 the molecule situated in the modified VK diagram.

176 *Subgroups A to E* are comprised of CHOS_1 molecules containing more than three oxygen atoms.
177 Outdoor smog chamber experiments together with field observations of urban fine aerosols
178 demonstrated that organosulfates and sulfonates could be significant products of polycyclic
179 aromatic hydrocarbons derived SOA.²³ Thus, the possibility of the presence of sulfonate combined
180 with another oxygen containing functional group should not be ignored when interpreting the
181 possible structures of CHOS_1 .^{34,37-39} Molecular H/C ratios (hydrogen saturation index), O^*/C ratios
182 (oxygen saturation index) and AI^* values (aromaticity index), as significant structural information,
183 help in mapping CHOS formulas into subgroups with distinguishable structural moiety (e.g.,

184 aromatic carbon backbone, and aliphatic carbon backbone). *Subgroup A* includes polycyclic
185 aromatics molecules (PCAs) with $AI^* > 0.67$ and $0 < O^*/C < 0.8$.⁴⁵ *Subgroup B* contains highly
186 aromatic molecules with $0.5 < AI^* \leq 0.67$ and $0 < O^*/C < 0.8$.⁴⁵ *Subgroup C* is composed of highly
187 unsaturated molecules with $AI^* \leq 0.5$ and $H/C < 1.5$ and $0 < O^*/C < 0.8$.⁴⁶ *Subgroup D* is
188 comprised of unsaturated aliphatic molecules with $1.5 \leq H/C < 2.0$ and $0 < O^*/C < 0.8$.⁴⁷ *Subgroup*
189 *E* includes saturated molecules with $H/C \geq 2.0$ or $O^*/C \geq 0.8$.⁴⁷ A similar classification of CHO
190 molecules in dissolved organic matter derived from groundwater was made by Seidel et al.⁴⁸

191 *Subgroup F* is defined as containing low oxidation state sulfur containing organic molecules
192 with $O^*/C \leq 0$ (organic sulfur molecules containing less than 4 oxygen atoms). Thus, *Subgroup F*
193 may be composed of sulfoxides, sulfones, sulfonates. The sulfidic and thiophenic molecules in
194 petroleum could be oxidized into sulfoxides and sulfones molecules,⁴⁹ acting as potential sources
195 for low oxidation state S-containing molecules in atmospheric precipitation.²⁸

196 The $CHOS_2$ molecules, i.e., two-sulfur-containing functional groups, such as thiosulfates,
197 disulfides, and polysulfides, make up the seventh subgroup (*Subgroup G*). Organosulfate dimers
198 ($C_{20}H_{34}O_9S_2$) and trimers ($C_{30}H_{50}O_{10}S_2$) were formed by the reactions of α -pinene oxide ($C_{10}H_{16}O$)
199 with ammonium sulfate particles using Quasi-Static reactor and chamber experiments.⁵⁰ Liberatore
200 et al.⁵¹ reported C_{12} -olefin disulfonate ($C_{12}H_{22}S_2O_6^{2-}$, as surfactant) and bromosulfone sulfonate
201 ($C_{12}H_{22}BrS_2O_6^-$, as disinfection byproducts) from laboratory-disinfected gas extraction wastewater.

202 To verify the validity of our modified classification of CHOS molecules, a number of known
203 organosulfates and sulfonates detected in previous studies were placed on the modified VK
204 diagram and previously unmodified VK diagram used in atmospheric studies (Figure 2a).^{52,53} The
205 detection of these organosulfates and sulfonates in our snow samples is listed in Table S5, Table

206 S6 and Table S7, according to the origins of these molecules (SOA and anionic surfactants emitted
207 by anthropogenic sources).

208 The known SOA molecules in Figure 2a include long-chain alkanes-derived, isoprene /
209 glyoxyal-derived, monoterpenes-derived, sesquiterpenes-derived, benzene-derived, naphthalene-
210 derived, unsaturated fatty acids-derived organosulfates, and naphthalene-derived sulfonates that
211 have been detected in smog-chamber experiments.^{14, 22, 23, 39, 42, 54-65} Linear alkyl benzene sulfonates
212 (LAS), sulfophenyl carboxylic acids (SPC), dialkyl tetralin sulfonates (DATS), and dialkyl tetralin
213 sulfonate intermediates (DATSI) (in Figure 2a) are typical anionic surfactants (used in domestic
214 detergents),^{3, 66-69} which have been detected in wastewaters, surface waters, sediments, soils,
215 atmospheric precipitation and aerosols.⁶⁶⁻⁷⁷ In addition, alkyl sulfates, alkane sulfonates, and alpha-
216 olefin sulfonates, as anionic surfactants precursors,⁷⁸ are also placed in Figure 2a. Anthropogenic
217 activities release anionic surfactants into the aquatic environment through wastewater treatment
218 plant.⁷⁹ Anionic surfactants (such as LASs) can migrate from water to the atmosphere, especially
219 from the sea-surface microlayer and ultimately into sea spray aerosol.^{66, 79, 80} A series of LASs (C₁₆-
220 C₂₀) were identified in fine and coarse sea spray particles.⁶⁶ Surfactants found in tropospheric
221 aerosol can affect the formation and development of clouds, and become organic contaminants in
222 wet and dry deposition.^{66, 79} Altieri et al.²⁴ reported four molecules consistent with LASs in
223 rainwater using a 7T FT-ICR MS.

224 By locating the known sulfonates in the modified VK diagram, organic sulfonates are in
225 *subgroups B, C, D, and F* (Figure 2a), which are consistent with our hypothesis that when O/S is
226 higher than 3, the molecule may be an organosulfate or sulfonate with an additional oxygen
227 containing functional group. The modified VK diagram can more easily distinguish the oxidized
228 (O/S >3) and less oxidized state (O/S ≤3) sulfur-containing molecules than the unmodified one.

229 For example, alkane sulfonates, alpha-olefin sulfonates, and linear alkyl benzene sulfonates ideally
230 situate at the line $O^*/C=0$ in the modified VK diagram, rather than scatter in the unmodified one.

231 **Molecular Classification of CHOS Molecules in Snow Samples.** The CHOS molecules
232 observed in snow samples were displayed by modified VK diagram of Figure 1c. The Beijing
233 snow sample differed from the other three samples in *subgroups C* and *D* in formula number
234 proportions, centralized mass range, and O/S composition (Table S4). High O/S molecules (10–16)
235 with high mass (≥ 500 Da) made a significant contribution to this difference. To be specific, the
236 high mass organic sulfur containing molecules, as discussed above, were largely distributed in
237 *subgroups C* and *D*. Highly unsaturated molecules (*subgroup C*) might be related to SOA
238 compounds from biomass burning.⁸¹ In contrast, unsaturated aliphatic molecules (*subgroup D*) are
239 largely attached to biogenic VOCs.^{23, 60, 81} In addition, the Beijing snow sample exhibited a high
240 level of K^+ ,⁴³ which acted as chemical tracer of biomass burning.⁸² Wang et al.³⁹ also found that
241 the abundance fraction of CHOS molecules with longer carbon chains ($C \geq 10$) was higher in
242 aerosols in haze days than in clean days in Beijing. Similar phenomena were observed when
243 comparing the CHOS molecules in aerosols between Shanghai and Los Angeles.³⁸ High O/S
244 molecules with high mass CHOS molecules in Beijing snow samples might be largely related to
245 the high contribution of biomass burning and biogenic VOCs in ambient aerosols during a haze
246 episode. However, on the account of the small sample number of this study, the atmospheric
247 behaviors of organic sulfur containing compounds between aerosol-snow interfaces still need
248 further investigation.

249 As shown in Table S4, the Beijing sample contained the most abundant molecules in *subgroup*
250 *F* among snow samples, and the CHOS molecules are clustered in the medium and high mass
251 ranges (429–598 Da). For the other urban snow samples, the molecules mainly centered on the

252 medium mass range (321–452 Da). There were some sulfonate-like molecules ($O^*/C = 0$) in each
253 sample with the formula number ranged from 15 to 86. High-resolution X-ray photoelectron
254 spectra identified sulfur species of humic-like substances in ambient aerosols, suggesting the
255 existence of thiophenes, thioesters, mercaptanes, sulfones, and sulfates.⁸³

256 Eleven hundred common CHOS molecules (the intersection molecules of four snow CHOS sets)
257 were assigned in the snow samples, contributing 43.2–71.1% to the formula numbers and
258 69.9–85.0% to the total intensity abundance of CHOS molecules (Figure S6b). The classification
259 of the common molecules is shown in Figure 2b and 2c. Detailed molecular classification of
260 common CHOS in the snow samples could be found in Text S3. It should be noted that these
261 common CHOS molecules are largely in medium O/S ratios (5–11) with low-medium mass (< 500
262 Da) (Figure 2b and 2c). More than one hundred (138–150) organosulfate and sulfonate formulas
263 were detected in each snow sample (Figure S8), contributing about 10% of the common CHOS
264 molecules. Besides, 60 unsaturated fatty acids-derived organosulfate formulas were detected as
265 common molecules (Table S5), which might be derived from sulfation processes of chemical
266 species from cooking and/or biogenic primary emissions.⁶⁵

267 The classification of the unshared $CHOS_1$ molecules of the four snow samples (those left behind
268 after the removal the common CHOS) are shown in Figures S6 and S7. The unshared $CHOS_1$
269 molecules exhibited quite different patterns among four cities. Previous studies indicated that
270 CHOS molecules in urban organic aerosols are highly related to anthropogenic emissions.^{38, 39}
271 Beijing, a megacity with the population of twenty million, is located at the northwest part of the
272 North China Plain where is influenced by a combination of fossil fuel combustion and other
273 anthropogenic emissions such as agricultural activities.^{84, 85} In contrast, Taiyuan is a megacity with
274 five million population and is the capital of a coal-rich province. The spectrum of anthropogenic

275 VOCs produced by both anthropogenic and biogenic emissions might be largely different and thus
276 influence the potential formation of organic sulfur compounds in the atmosphere.^{38,39,86} In addition,
277 CHOS molecules could act as condensation nuclei, being incorporated during crystal growth, or
278 scavenged during precipitation.^{2,52,87} The meteorological conditions during the precipitation event
279 in the four cities also illustrate a difference between Beijing and Taiyuan, according to our previous
280 air mass trajectories results.⁴³

281 This work introduces a new classification scheme to sort organic sulfur-containing compounds
282 by distinguishable structural moiety in the ambient air, providing a toolbox in discerning their
283 source origins. Typical known secondary organosulfates and anthropogenic-derived anionic
284 surfactants (with medium O/S ratio and low-medium mass range) are significant components of
285 the common CHOS molecules in our snow samples. Nevertheless, the absence of structural
286 information on these isomers leads to the uncertainty of the connection between the aerosols and
287 precipitation. Future work using FT-ICR MS with hyphenated techniques, such as MSⁿ and trapped
288 ion mobility spectrometry (TIMS), is needed to uncover the mechanisms of scavenging processes
289 of organic compounds during atmospheric precipitation.

290

291 **ASSOCIATED CONTENT**

292 **Supporting Information.**

293 Detailed descriptions of the analytical methods, the mass distribution of CHOS molecules, and
294 detailed molecular classification of common CHOS in snow samples, additional 8 figures and 7
295 tables are given in the Supporting Information (PDF).

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328 **Author Contributions**

329 P.F. designed the study. The manuscript was written by S.S. through contributions from all authors.

330 All authors have given approval to the final version of the manuscript.

331 **Notes**

332 The authors declare no competing financial interest.

333 **Data availability statements**

334 The data used in this manuscript will be available in the data repository website at the time of
335 publication.

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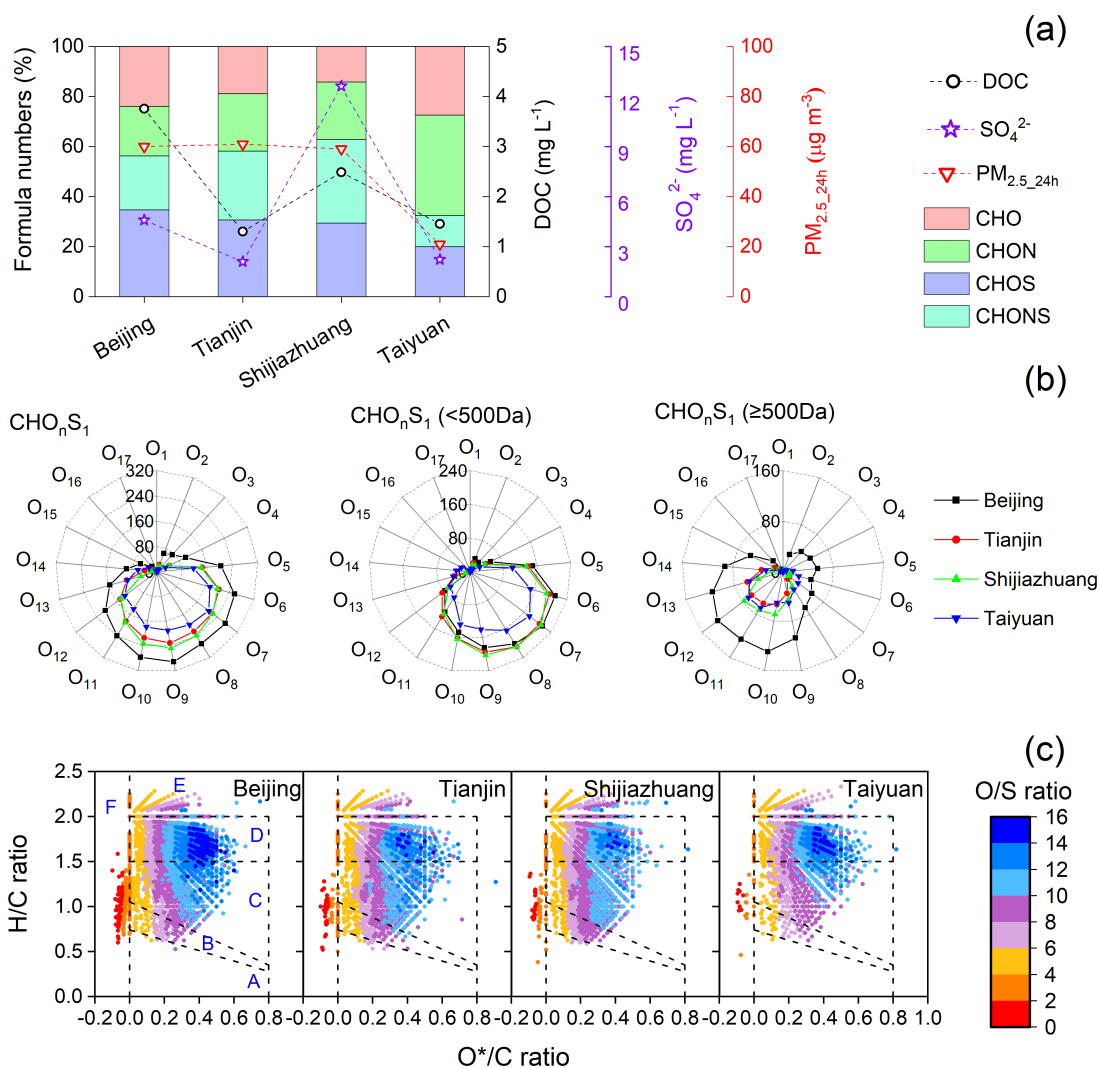
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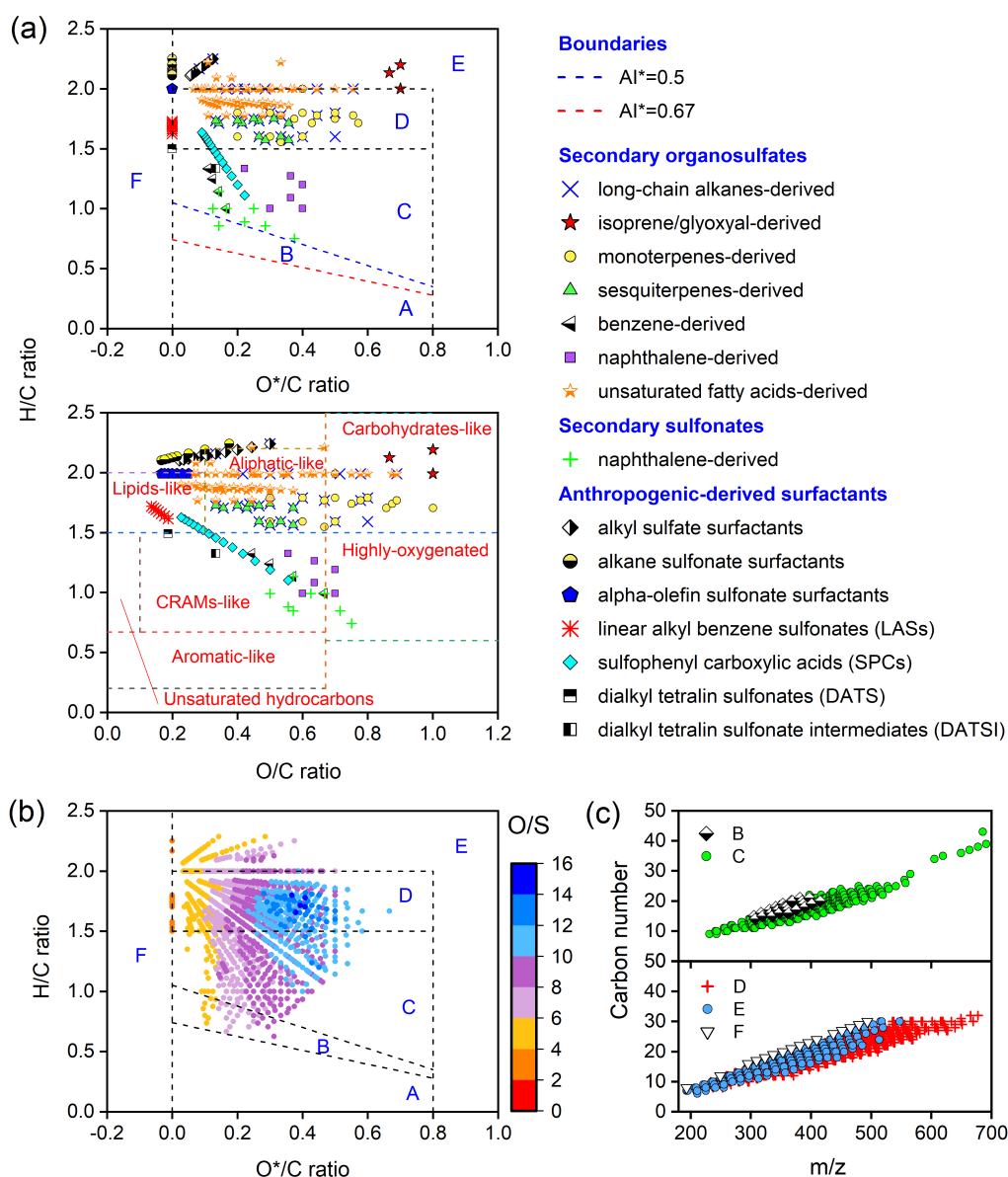
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 654 **Figure 1.** (a) Formula number proportion distribution of different elemental groups, along with
 655 dissolved organic carbon (DOC) of melted snow, inorganic sulfate (SO_4^{2-}) of melted snow and
 656 $\text{PM}_{2.5_24h}$ (daily average mass concentration of the particulate matter $< 2.5\mu\text{m}$ during the snow
 657 event). (b) Radar distribution map of oxygen atoms of CHOS_1 molecules within different mass
 658 range, including the whole mass range (left), molecules with $m/z < 500\text{ Da}$ (middle), and $m/z \geq 500$
 659 Da (right). (c) Modified van Krevelen diagrams of CHOS_1 in the four snow samples. The O/S ratio
 660 of molecules are color-coded. Region A represents polycyclic aromatic molecules, B - highly
 661 aromatic molecules, C - highly unsaturated molecules, D - unsaturated aliphatic molecules, E -
 662 saturated molecules, F - lower oxidation state sulfur containing molecules.

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 665 **Figure 2.** Modified van Krevelen diagrams of CHOS₁ compounds. (a) The modified classification
 666 of typical known organosulfates and sulfonates (detected in previous studies). The classification
 667 criteria of CHOS subgroups are shown in Table S2. The hypothetical boundaries of AI* according
 668 to Figure S5. The lower plot shows the unmodified classification by Bianco et al.⁵² using the O/C
 669 ratio. (b) Modified classification for the common CHOS molecules in the four snow samples (the
 670 intersection molecules of four snow CHOS sets). The O/S ratio of molecules are color-coded. (c)
 671 The molecular mass and carbon number distribution of common molecules in *subgroups B to F*.
 672 Region *A* represents polycyclic aromatic molecules, *B* - highly aromatic molecules, *C* - highly
 673 unsaturated molecules, *D* - unsaturated aliphatic molecules, *E* - saturated molecules, *F* - lower
 674 oxidation state sulfur containing molecules.