A new structural classification scheme for dissolved organic sulfur in urban snow from North China

Sihui Su\textsuperscript{1,2}, Qiaorong Xie\textsuperscript{1}, Alan J. Smith\textsuperscript{2}, Yunchao Lang\textsuperscript{1}, Wei Hu\textsuperscript{1}, Dong Cao\textsuperscript{1}, Siyao Yue\textsuperscript{4}, Shuang Chen\textsuperscript{1}, Jialei Zhu\textsuperscript{1}, Yisheng Xu\textsuperscript{5}, Nicholle G. A. Bell\textsuperscript{2}, Dušan Uhrín\textsuperscript{2}, and Pingqing Fu\textsuperscript{1}\textsuperscript{*}

\textsuperscript{1}Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China

\textsuperscript{2}EaStCHEM School of Chemistry, Joseph Black Building, University of Edinburgh, Edinburgh EH9 3FJ, UK

\textsuperscript{3}State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, China

\textsuperscript{4}Minerva Research Group, Max Planck Institute for Chemistry, Mainz 55128, Germany

\textsuperscript{5}State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

*Corresponding author: Pingqing Fu (fupingqing@tju.edu.cn)
The authors confirmed that the submitted image was created by an author and has never been published.

**ABSTRACT**

The chemical composition of dissolved organic sulfur in snow is important in understanding the sources and scavenging processes of atmospheric organic matter. Snow samples collected simultaneously from four megacities in North China were analyzed using ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The modified oxygen (O*) and redefined aromaticity index (AI*) help interpret the possible structural information and evaluate the aromaticity of sulfur-containing molecules. By extending these parameters, we provide a new structural classification for organic sulfur species in the atmosphere. With the new classification, the oxidized (O/S >3) and less oxidized state (O/S ≤3) sulfur-containing molecules can be easily distinguished. Typical known secondary organosulfates and sulfonates, and
anthropogenic-derived anionic surfactants verified the validity of this new classification. The new classification was applied to the molecular characterization of dissolved organic sulfur in snow samples. More than one hundred (138–150) of the molecules with medium O/S ratios of 5–11 and low-medium mass range < 500 Da are related with typical known secondary organosulfates and anthropogenic-derived anionic surfactants. Our study provides new insights into the molecular compositions of organic sulfur species in the ambient air, although their atmospheric behaviors between the snow-aerosol interfaces warrant further studies.

KEYWORDS

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

SYNOPSIS

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

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

Recently, with the development of analytical instruments, various organic sulfur molecules referred to here as CHOS, have been detected in atmospheric aerosols and fog or cloud water. Among these compounds, organosulfates (R-O-SO$_3^-$) and sulfonates (R-SO$_3^-$) are of particular concern. Organosulfates are tracers of the formation of secondary organic aerosols (SOA), while sulfonates might be related to anthropogenic origins. The temporal and spatial variations in CHOS in rainwater or snow have been investigated focusing on molecules within the low and medium mass range (200–500 Da). However, the higher molecular weight species of CHOS (≥500 Da) remain poorly characterized. With a resolution improvement of high-field Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), more reliable assignments of high mass multiple elemental formulas became possible, especially for non-oxygen heteroatom-rich
(such as nitrogen, sulfur or phosphorus) dissolved organic matter. The characteristics of high mass CHOS in biodiesel and diesel fuel SOA, and methacrolein and methylvinyl ketone-derived products were reported previously.

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

MATERIALS AND METHODS

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

This study mainly focuses on water soluble CHOS groups within the mass range (m/z) of 180–700 Da. From herein, the mass ranges are referred to as low-mass (180–300 Da), medium-mass
Due to the possible existence of numerous isomers represented by each formula, the compound classes or functional groups identified in this study only indicate the most likely categorization.\textsuperscript{35, 36}

The sample specific average number of oxygen atoms between the range from CHO\textsubscript{S\textsubscript{1}} to CHO\textsubscript{S\textsubscript{j}} formulas (average oxygen number density, $\text{Num}_\text{Density}_{i,j}$) was calculated according to Equation 1:

$$\text{Num}_\text{Density}_{i-j} = \frac{\sum_{j=i}^{j+1} \text{Num}_\text{CHO}_{n S_1}}{j-i+1}, \quad j \geq i \geq 1, \quad (1)$$

where $\text{Num}_\text{CHO}_{n S_1}$ is the CHO\textsubscript{S\textsubscript{1}} formula number in the specific sample, and the oxygen variation range of $\text{Num}_\text{Density}_{i,j}$ is from $i$ to $j$.

For CHO\textsubscript{S\textsubscript{1}} (containing one sulfur atom), if $i>3$ (with more than three oxygen atoms) in the formula, it represents that CHO\textsubscript{S\textsubscript{1}} contains one sulfate group or one sulfonate group coupled with an additional oxygen containing functional group (such as -OH, -(C=O), -OR, and -COOH).\textsuperscript{23, 34, 37-39}

For CHO\textsubscript{S\textsubscript{1}} formulas, an alternative notation was introduced using $O^*$, which acquires a value of $O^* = i-3$, where $i$ is the number of oxygens in the formula.\textsuperscript{38} For organic sulfur molecules containing less than 3 oxygen atoms, $O^*$ could have values ($= i-3$) $\leq 0$ and consequently also the ratio $O^*/C$ is $\leq 0$.

By subtracting SO\textsubscript{3} from CHO\textsubscript{S\textsubscript{1}}, CHO\textsubscript{S\textsubscript{1}} formulas could be viewed as oxygen-containing hydrocarbon molecules with a new formula of CHO\textsubscript{i-3}. The oxygen in sulfate group or sulfonate group could not contribute to the double-bond equivalent (DBE), therefore, subtracting SO\textsubscript{3} from CHO\textsubscript{S\textsubscript{1}} ensures that the transition from CHO\textsubscript{S\textsubscript{1}} to CHO\textsubscript{i-3} does not affect the aromaticity of the rest of the formula. AI$^*$ (the modified aromaticity index, see Equation 2) helps evaluate the aromaticity of sulfur containing molecules more accurate than AI (the aromaticity index).\textsuperscript{34} For example, for benzene-sulfonic acid, C\textsubscript{6}H\textsubscript{4}SO\textsubscript{3}, AI=0, the benzene ring is underestimated. By
subtracting \( \text{SO}_3 \), the new formula transition into \( \text{C}_6\text{H}_6 \), \( \text{AI}^* = 0.67 \), the aromaticity of benzene ring is accurately estimated as expected. A detailed interpretation of this formalism could be found in previous studies.\textsuperscript{34, 38}

By introducing \( \text{DBE} (=1+c−h/2) \) and \( \text{O}^* (=i−3) \) of \( \text{C}_6\text{H}_6\text{O}_{i−3} \), \( \text{AI}^* \) could be simplified into following equation 2. Text S1 provides detailed mathematical calculations of \( \text{AI}^* \).

\[
\text{AI}^* = (\text{DBE}−\text{O}^*)/(c−\text{O}^*)
\] (2)

\section*{RESULTS AND DISCUSSION}

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

According to Figure S4, CHOS\textsubscript{2} molecules contributed negligibly to the number and relative intensity abundance of CHOS molecules. The following discussion only focused on the more abundant CHOS\textsubscript{1} molecules. The radar distribution in oxygen atoms illustrates the variation in O/S ratios of CHOS\textsubscript{1} molecules (Figure 1b). CHOS\textsubscript{1} in the Beijing sample differed from the rest with the highest abundance in the O\textsubscript{4-13} groups (number of formulas \textit{Num\_Density\textsubscript{4-13}}: 227), while the other three samples were similar among them, largely consisting of O\textsubscript{5-12} with a lower number of formulas (\textit{Num\_Density\textsubscript{5-12}} varying from 166 to 202).

To further analyze similarities and differences of CHOS\textsubscript{1} molecules, these were divided into two mass ranges (\(<500 \text{ Da and } \geq 500 \text{ Da}\)) in Figure 1b. For the low and medium mass range of CHOS\textsubscript{1}
molecules (< 500 Da), the four snow samples showed a same pattern with the number of oxygen atom mainly between 5 and 11. That is, CHO$_{5-11}$S$_1$ formulas constituted 82–89% of the identified CHOS$_1$ formulas in the low and medium mass range, with Num$_{Density}_{5-11}$ ranging from 133 to 176. However, for the high mass range (≥ 500 Da), the oxygen distribution presented a totally different pattern. The Beijing sample showed higher abundance in the O$_{9-14}$ range with a higher Num$_{Density}_{9-14}$ (117). In contrast, the other three snow samples were mainly composed of O$_{9-13}$ with a lower Num$_{Density}_{9-13}$ (varying from 54 to 61).

The similarity in the low-medium mass range versus the difference in the high mass range of CHOS$_1$ molecules indicates distinct origins of molecules in these two mass ranges. Song et al. identified O$_3$S$_1$–O$_9$S$_1$ (≤500 Da) as the most abundant water-soluble CHOS species emitted from coal combustion. Jiang et al. reported that numerous S-containing molecules in aerosols on clean days were also observed on haze days, although Wang et al. demonstrated that organic sulfur containing molecules on haze days were of higher mass than those on clean days in Beijing. A previous laboratory study showed that the methacrolein-derived organic sulfur molecules were of high mass (300–650 Da) in the presence of a high concentration (10 mM) of methacrolein. As discussed in the Text S2, the snow event occurred in Beijing coupled with high concentrations of PM$_{2.5, 24h}$, DOC and SO$_4^{2-}$ (Figure 1a). Although the PM$_{2.5, 24h}$ levels of Tianjin and Shijiazhuang samples were almost the same with the Beijing sample (about 60 µg m$^{-3}$), but the DOC and SO$_4^{2-}$ concentrations of the Beijing sample was about 1–2 times higher than those from Tianjin and Taiyuan. In addition, according to our previous optical results (UV−vis and excitation-emission matrix fluorescence) on these samples, the Beijing one exhibited higher UV-vis absorbance and higher fluorescence intensity at humic-like substance peaks (peak A and M) than other samples. These results indicate that high mass (≥ 500 Da) organic sulfur containing molecules might be
largely attributed to the higher formation propensity or greater accumulation potential of these molecules in snow during haze episodes. Furthermore, our previous study on wintertime aerosols in Beijing confirms that high mass (≥ 500 Da) CHOS molecules with oxygen atoms ranged from 10–15 were significantly enhanced during haze events than clean days.\textsuperscript{44}

**A Classification of Organic Sulfur Species and its Validation.** Previous classification of atmospheric organic sulfur species did not include all molecules, particularly those CHOS\textsubscript{1} molecules with i ≤ 3.\textsuperscript{34,38} The modified subgroups, introduced in our study, provide a new way for identification of the origins of the natural organic sulfur molecules. By combining the modified van Krevelen (VK) plots that use O*/C in place of the O/C ratio\textsuperscript{38} and the AI* values\textsuperscript{34}, the CHOS\textsubscript{1} molecules could be divided into six subgroups (*Subgroup A to F*) (Table S2 and Figure 2a). It should be noted that the CHOS\textsubscript{1} molecules with AI* = 0.5 and AI* = 0.67 scatter among a wide range in the modified VK diagram (Figure S5). To make the boundary of AI* = 0.5 and AI* = 0.67 visual, hypothetical boundaries are used according to Figure S5. However, in making this classification, the actual value of AI* of one molecule were considered, rather than the location of the molecule situated in the modified VK diagram.

*Subgroups A to E* are comprised of CHOS\textsubscript{1} molecules containing more than three oxygen atoms. Outdoor smog chamber experiments together with field observations of urban fine aerosols demonstrated that organosulfates and sulfonates could be significant products of polycyclic aromatic hydrocarbons derived SOA.\textsuperscript{23} Thus, the possibility of the presence of sulfonate combined with another oxygen containing functional group should not be ignored when interpreting the possible structures of CHOS\textsubscript{1}.\textsuperscript{34,37,39} Molecular H/C ratios (hydrogen saturation index), O*/C ratios (oxygen saturation index) and AI* values (aromaticity index), as significant structural information, help in mapping CHOS formulas into subgroups with distinguishable structural moiety (e.g.,
aromatic carbon backbone, and aliphatic carbon backbone). **Subgroup A** includes polycyclic aromatics molecules (PCAs) with AI* > 0.67 and 0 < O*/C < 0.8. **Subgroup B** contains highly aromatic molecules with 0.5 < AI* ≤ 0.67 and 0 < O*/C < 0.8. **Subgroup C** is composed of highly unsaturated molecules with AI* ≤ 0.5 and H/C < 1.5 and 0 < O*/C < 0.8. **Subgroup D** is comprised of unsaturated aliphatic molecules with 1.5 ≤ H/C < 2.0 and 0 < O*/C < 0.8. **Subgroup E** includes saturated molecules with H/C ≥ 2.0 or O*/C ≥ 0.8. A similar classification of CHO molecules in dissolved organic matter derived from groundwater was made by Seidel et al.

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

The CHOS₂ molecules, i.e., two-sulfur-containing functional groups, such as thiosulfinates, disulfides, and polysulfides, make up the seventh subgroup (**Subgroup G**). Organosulfate dimers (C₅₀H₈₀O₉S₂) and trimers (C₅₀H₈₀O₁₆S₂) were formed by the reactions of α-pinene oxide (C₁₀H₁₆O) with ammonium sulfate particles using Quasi-Static reactor and chamber experiments. Liberatore et al. reported C₁₂-olein disulfonate (C₁₂H₂₂S₂O₆²⁻, as surfactant) and bromosultone sulfonate (C₁₂H₂₂BrS₂O₆, as disinfection byproducts) from laboratory-disinfected gas extraction wastewater.

To verify the validity of our modified classification of CHOS molecules, a number of known organosulfates and sulfonates detected in previous studies were placed on the modified VK diagram and previously unmodified VK diagram used in atmospheric studies (Figure 2a). The detection of these organosulfates and sulfonates in our snow samples is listed in Table S5, Table.
S6 and Table S7, according to the origins of these molecules (SOA and anionic surfactants emitted by anthropogenic sources).

The known SOA molecules in Figure 2a include long-chain alkanes-derived, isoprene / glyoxyal-derived, monoterpenes-derived, sesquiterpenes-derived, benzene-derived, naphthalene-derived, unsaturated fatty acids-derived organosulfates, and naphthalene-derived sulfonates that have been detected in smog-chamber experiments. Linear alkyl benzene sulfonates (LAS), sulfophenyl carboxylic acids (SPC), dialkyl tetralin sulfonates (DATS), and dialkyl tetralin sulfonate intermediates (DATSI) (in Figure 2a) are typical anionic surfactants (used in domestic detergents), which have been detected in wastewaters, surface waters, sediments, soils, atmospheric precipitation and aerosols. In addition, alkyl sulfates, alkane sulfonates, and alpha-olefin sulfonates, as anionic surfactants precursors, are also placed in Figure 2a. Anthropogenic activities release anionic surfactants into the aquatic environment through wastewater treatment plant. Anionic surfactants (such as LASs) can migrate from water to the atmosphere, especially from the sea-surface microlayer and ultimately into sea spray aerosol. A series of LASs (C_{16}-C_{20}) were identified in fine and coarse sea spray particles. Surfactants found in tropospheric aerosol can affect the formation and development of clouds, and become organic contaminants in wet and dry deposition. Altieri et al. reported four molecules consistent with LASs in rainwater using a 7T FT-ICR MS.

By locating the known sulfonates in the modified VK diagram, organic sulfonates are in subgroups B, C, D, and F (Figure 2a), which are consistent with our hypothesis that when O/S is higher than 3, the molecule may be an organosulfate or sulfonate with an additional oxygen containing functional group. The modified VK diagram can more easily distinguish the oxidized (O/S >3) and less oxidized state (O/S ≤3) sulfur-containing molecules than the unmodified one.
For example, alkane sulfonates, alpha-olefin sulfonates, and linear alkyl benzene sulfonates ideally situate at the line O*/C=0 in the modified VK diagram, rather than scatter in the unmodified one.

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

As shown in Table S4, the Beijing sample contained the most abundant molecules in *subgroup F* among snow samples, and the CHOS molecules are clustered in the medium and high mass ranges (429–598 Da). For the other urban snow samples, the molecules mainly centered on the
medium mass range (321–452 Da). There were some sulfonate-like molecules (O*/C = 0) in each sample with the formula number ranged from 15 to 86. High-resolution X-ray photoelectron spectra identified sulfur species of humic-like substances in ambient aerosols, suggesting the existence of thiophenes, thioesters, mercaptanes, sulfones, and sulfates.¹³

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

The classification of the unshared CHOS₁ molecules of the four snow samples (those left behind after the removal the common CHOS) are shown in Figures S6 and S7. The unshared CHOS₁ molecules exhibited quite different patterns among four cities. Previous studies indicated that CHOS molecules in urban organic aerosols are highly related to anthropogenic emissions.³⁸, ³⁹ Beijing, a megacity with the population of twenty million, is located at the northwest part of the North China Plain where is influenced by a combination of fossil fuel combustion and other anthropogenic emissions such as agricultural activities.⁸⁴, ⁸⁵ In contrast, Taiyuan is a megacity with five million population and is the capital of a coal-rich province. The spectrum of anthropogenic
VOCs produced by both anthropogenic and biogenic emissions might be largely different and thus influence the potential formation of organic sulfur compounds in the atmosphere. In addition, CHOS molecules could act as condensation nuclei, being incorporated during crystal growth, or scavenged during precipitation. The meteorological conditions during the precipitation event in the four cities also illustrate a difference between Beijing and Taiyuan, according to our previous air mass trajectories results.

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

ASSOCIATED CONTENT

Supporting Information.

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

AUTHOR INFORMATION

Corresponding Author
Pingqing Fu – Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China; orcid.org/0000-0001-6249-2280; Email: fupingqing@tju.edu.cn

Authors

Sihui Su – Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China; EaStCHEM School of Chemistry, Joseph Black Building, University of Edinburgh, Edinburgh EH9 3FJ, UK

Qiaorong Xie – Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China

Alan J. Simth – EaStCHEM School of Chemistry, Joseph Black Building, University of Edinburgh, Edinburgh EH9 3FJ, UK

Yunchao Lang – Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China

Wei Hu – Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China

Dong Cao – State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Centre for Eco-Environmental –

Siyao Yue – Minerva Research Group, Max Planck Institute for Chemistry, Mainz 55128, Germany
Shuang Chen – Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China

Jialei Zhu – Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China

Yisheng Xu – State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

Nicholle G. A. Bell – EaStCHEM School of Chemistry, Joseph Black Building, University of Edinburgh, Edinburgh EH9 3FJ, UK

Dušan Uhrín – EaStCHEM School of Chemistry, Joseph Black Building, University of Edinburgh, Edinburgh EH9 3FJ, UK

Author Contributions

P.F. designed the study. The manuscript was written by S.S. through contributions from all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Data availability statements

The data used in this manuscript will be available in the data repository website at the time of publication.
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Figure 1. (a) Formula number proportion distribution of different elemental groups, along with dissolved organic carbon (DOC) of melted snow, inorganic sulfate (SO$_{4}^{2-}$) of melted snow and PM$_{2.5,24h}$ (daily average mass concentration of the particulate matter < 2.5μm during the snow event). (b) Radar distribution map of oxygen atoms of CHOS$_1$ molecules within different mass range, including the whole mass range (left), molecules with m/z< 500 Da (middle), and m/z≥ 500 Da (right). (c) Modified van Krevelen diagrams of CHOS$_1$ in the four snow samples. The O/S ratio of molecules are color-coded. Region A represents polycyclic aromatic molecules, B - highly aromatic molecules, C - highly unsaturated molecules, D - unsaturated aliphatic molecules, E - saturated molecules, F - lower oxidation state sulfur containing molecules.
Figure 2. Modified van Krevelen diagrams of CHOS$_1$ compounds. (a) The modified classification of typical known organosulfates and sulfonates (detected in previous studies). The classification criteria of CHOS subgroups are shown in Table S2. The hypothetical boundaries of AI* according to Figure S5. The lower plot shows the unmodified classification by Bianco et al.$^{52}$ using the O/C ratio. (b) Modified classification for the common CHOS molecules in the four snow samples (the intersection molecules of four snow CHOS sets). The O/S ratio of molecules are color-coded. (c) The molecular mass and carbon number distribution of common molecules in subgroups B to F. Region A represents polycyclic aromatic molecules, B - highly aromatic molecules, C - highly unsaturated molecules, D - unsaturated aliphatic molecules, E - saturated molecules, F - lower oxidation state sulfur containing molecules.