RE: A point-to-point response to reviewers' comments

"Molecular Characterization of Atmospheric Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River" (acp-2015-393R1) by X. K. Wang, S. Rossignol, Y. Ma, L. Yao, M. Y. Wang, J. M. Chen, C. George, and L. Wang

We are grateful to the helpful comments from the editor and the anonymous referees, and have carefully revised our manuscript accordingly. A point-to-point response to their comments, which are repeated in italic, is given below.

Editor

Minor points:

1. *Line 557: Replace "J.-L. and Wortham" by "J.-L., and Wortham".*

Reply: We have replaced "J.-L. and Wortham" with "J.-L., and Wortham" (Page 20, Line 581).

2. *Lines 635-637: There is no reference made within the text to "Nizkodorov et al. (2011)".*

Reply: The reference is not cited in the main text and has been removed from the reference list.

3. *Lines 656-658: Titles of journal articles should be in lower case instead of in Title Case.*

Reply: Titles of journal articles are now in lower case (Page 23, Line 687-690).

4. *Line 701: Replace "Goldsteint" by "Goldstein".*

Reply: We have replaced "Goldsteint" with "Goldstein" (Page 24, Line 746).

5. *For the Supplement: Last page, for "Riva et al. (2015b)": Titles of journal articles should be in lower case instead of in Title Case.*

Reply: Titles of journal articles are now in lower case.

Anonymous Referee #1

1. *Although the manuscript was significantly improved there are still major issues with employed formulae assignment approach. Considering that there are no authentic standards available for the majority of the tentatively assigned OSs, the authors should at least make an effort to improve their formulae assignment methodology. I strongly suggest including isotopes 13C, 34S and at least 31P into the formulae assignments constrains. I failed to see any justification*

> *for not using these isotopes in the selected references mentioned in the authors responses. Polyisotopic formula assignments containing naturally occurring 13C and 34S are abundant in aerosol samples (e.g., Mazzoleni et al., 2012, Dzepina et al., 2015) and their ratios are widely used to check the validity of the assigned formulae.*
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> *Mazzoleni, L. R., Saranjampour, P., Dalbec, M. M., Samburova, V., Hallar, A. G., Zielinska, B., Lowenthal, D., and Kohl, S.: Identification of water-soluble organic carbon in nonurban aerosols using ultrahigh-resolution FT-ICR mass spectrometry: organic anions, Environ. Chem., 9, 285–297, 2012.*
>
> *Dzepina, K., Mazzoleni, C., Fialho, P., China, S., Zhang, B., Owen, R. C., Helmig, D., Hueber, J., Kumar, S., Perlinger, J. A., Kramer, L. J., Dziobak, M. P., Ampadu, M. T., Olsen, S., Wuebbles, D. J., and Mazzoleni, L. R.: Molecular characterization of free tropospheric aerosol collected at the Pico Mountain Observatory: a case study with a long-range transported biomass burning plume, Atmos. Chem. Phys., 15, 5047-5068, doi:10.5194/acp-15-5047-2015, 2015.*

Reply: Mazzoleni et al. and Dzepina et al. used FT-ICR MS to characterize aerosol components. FT-ICR MS indeed offers higher mass resolving power and mass accuracy, and also can improve the signal-to-noise ratio of cumulative data (Marshall, 2000). However, in our case, the isotopic peak is not usually detected by Orbitrap MS due to the low intensity of the quasi-molecular ion. Nevertheless, we are confident in our assignments as, within an error of 2 ppm, only one molecular formula is generally chemically relevant. One can thus consider that our assignments were done using the standard rules currently available in the literature of our field (Tao et al., 2014; Fuller et al., 2012; Lin et al., 2012a; Lin et al., 2012b).

Anonymous Referee #2

> *The paper by Wang et al. tackles a key issue of the identification of organosulfates in three megacities at the middle and lower reaches of the Yangtze river. At the early stage I reviewed the paper by these authors submitted to ACPD. At that time I was highly critical about the way of presentation and the lacking of a number of analytical data. Now, I can say the authors made the major revision of the ACPD manuscript addressing the most controversial points. Taking into account my review report (please see in the separate document), I would suggest the manuscript to be accepted for publication for ACP, however considering a minor revision.*

Reply: We are very grateful to referee #2 for his/her positive viewing of our study and we revised the manuscript thoroughly according to the comments of all reviewers.

Minor comments:

1. *p. 3, line 42: "Organosulfates (OSs)—i.e., sulfate esters and…"*
   In my opinion the analyzed and discussed throughout the text are compounds that are sulfate monoesters and/or nitroxy derivatives thereof. Thus, I would suggest replacing sulfate esters for sulfate monoesters.

Reply: Here we introduce the definition of OS, and “sulfate esters” is more appropriate.

2. *p. 3, line 54-64: The authors are presenting the pathways how OSs could be formed. However, the state of the knowledge on this subject is incomplete. There is no single word about other mechanisms published recently to rationalize the formation of organosulfates through the aqueous phase chemistry. In my opinion the authors are discussing the fragmentary data ignoring the route of the addition of sulfate radical anions to the C=C bonds. Was it made intentionally? If no, I would suggest completing the state of the knowledge by stressing the aqueous-phase processing of organic precursors with sulfate radical anions. For example refer to the papers by Szmigielski (Atmos Environ, 2015), Schoene et al. (Phys Chem Chem Phys, 2014); Szmigielski (Chemistry of Organic Sulfates and Nitrates in the Urban Atmosphere; NATO Science for Peace and Security Series C-Environmental Security, p 211-226); Noziere et al., (Geoph Res Lett, 2010); Rudzinski et al. (Atmosph Chem Phys, 2009).*

Reply: We now state that “Sulfate/sulfite radical-induced oxidation reactions with unsaturated organic compounds including isoprene, methyl vinyl ketone, methacrolein, and α-pinene in the aqueous phase represent another potential formation route of OSs (Szmigielski, 2015; Rudzinski et al., 2009; Noziere et al., 2010; Schindelka et al., 2013)” (Page 3, Line 62-66).

3. *p. 7, line 176-182: Were MS parameters, such as spray voltage, gas flows etc., optimized? If yes, please add this info to the text.*

Reply: The ionization conditions were not specifically optimized for OSs detection as standard settings provided very good performances.

4. *p. 7, line 180: “The Q-Exactive mass spectrometer was externally mass calibrated daily…” Does it mean the mass spectrometer was calibrated before each analysis?*

Reply: The Q-Exactive mass spectrometer was externally mass calibrated daily, whatever the number of samples analyzed each day. The mass deviation remained within 2 ppm on 24 hours.

5. *p. 8, line 192: Why mass tolerance was set at plus/minus 2? Was there a difference if this parameter was lowered to 1 unit, a sit is a case of Orbitrap MS analysis?*

Reply: The mass accuracy of this Orbitrap MS is ±2 ppm. Hence, all mathematically possible formulas for detected ions were calculated using a mass tolerance of ±2 ppm. If this value is lowered to 1 ppm, correct formulas may be discarded.

6. *Line 201-212: “In this study, the abundance of an OS refers to the area of its chromatographic peak, and the number of isomers for an OS is based on the number of chromatographic peaks observed for given m/z values.”*
   This approach might lead to a systematic error since no response from internal standard was

considered. I realize this approach is popular in the literature. However, the replication of the risky method is not a good manner in the analytically-oriented paper. My doubts are also about the assumption that the number of isomers for an OS is based on the number of chromatographic peaks observed for given m/z values. What happens when peak overlapping occurs? The latter is a common case of analysis of SOA extracts!

Reply: If two peaks overlap, the number of isomers will be smaller than the actual value. Therefore, we have stated in the manuscript (Page 9, Line 222-223) that "Note that the obtained number of isomers may vary significantly when the separation method is further optimized".

7. p. *9, line 233: "Not taking into account the two double bonds involved in each sulfate group…"*
   Why DBE does not involve each sulfate group? Does it apply when nitroxy-organofulfates are considered?

Reply: The DBE values of both OSs and nitrooxy-OSs were calculated based on the Eq. 1 (Page 9, Line 242), which does not take the double bonds of sulfate group into account.

8. *p. 10, line 266-269: Again, in this paragraph the authors are missing the recently obtained data regarding the WM 182 OS from aqueous-phase-generated secondary organic aerosols and/or ambient SOA from Diabla Gora rural site (Szmigielski Atmos Environ 2015; DOI:10.1016/j.atmosenv.2015.10.072). In my opinion it should be taken into account while discussing the number of isomers in Riva's samples. Did the authors record the ESI spectrum (first order or MS/MS) for the isomers of the MW 182 OSs? If so, it would be benefitable to put these data in the supplementary text to let the reader see the isomeric differences*

Reply: We now state in the manuscript (Page 10-11, Line 276-284) that "An OS with this molecular formula has recently been identified in laboratory-generated secondary organic aerosols either from the ozonolysis of isoprene in the presence of sulfate aerosols or from the transformations of isoprene coupled with S(IV)-autoxidation in the aqueous-phase, but only one and two isomers were detected by UPLC-high-resolution MSs, respectively (Riva et al., 2015a; Szmigielski, 2015). From our ambient samples, 11 isomers were detected in total, with varying numbers of isomers in each sample (see Figure 2 and Table S3). On the other hand, only two isomers were detected in the ambient $PM_{2.5}$ samples from Diabla Gora rural site (Szmigielski, 2015)".
LC chromatograms of the MW 182 OSs are presented in figure 2. Tandem MS experiments were not conducted due to the limited amount of solutions. See also our reply to comment #1 from Anonymous Referee #5.

9. *p. 16, line 438 onward: The author should also refer to other documented pathways of the OSs formation from isoprene through aqueous-phase processing (please see my comments above).*

Reply: We now state in the manuscript (Page 17, Line 462-467) that "C_5 and C_4 OSs could also be formed from sulfate/sulfite radical-induced oxidation reactions with isoprene and its oxidation products (i.e., methyl vinyl ketone, and methacrolein) in the aqueous phase, respectively (Schone et al., 2014; Noziere et al., 2010). Since the liquid water content is not available for our ambient samples, these aqueous reaction pathways are not considered here".

Anonymous Referee #3

> *I applaud the authors for thoroughly addressing the review comments. I only have a few minor comments on the revise ms as given below.*

Reply: We are very grateful to referee #3 for his/her positive viewing of our study and we revised the manuscript thoroughly according to the comments of all reviewers.

Specific comments:

1. *In comparison with earlier studies using LC/MS for detecting OS compounds in ambient samples, one notable difference is that a significantly higher number of isomers were detected in this work (Section 3.1). The authors suggest that different chromatographic conditions and additional precursors available at the sampling sites in this study are the causes for the observed difference. Could different detection sensitivity between Orbitrap MS and the lower resolution MS another contributing cause? It will be helpful if the authors could report the detection limits by the Orbitrap-MS of the few OS standards used in their work. This will add value to the study by providing guidance to future LC/MS analysis of OS compounds.*

Reply: The estimated limits of detection are now reported in Table S2 of the Supporting Information. These values are in agreement with the rare ones that can be found in the literature (Zhang et al, 2012 ; Staudt et al., 2014) and we can thus conclude that the number of isomers reported here is probably not related to a gain in sensitivity. As a consequence, no modification was made in the main text of the manuscript.

2. *Isomeric pattern differs significantly among locations. For example, in the WH samples, OSs with six isomers account for the largest proportion; in contrast, in the SH and NJ samples, OSs with one isomer only are dominant (Lines 304-309). Does this reflect diversity in precursors or oxidation mechanism or both? This may suggest that simultaneous measurements of VOCs and semi-volatile organic compounds may shed more insights in future studies. Some discussion on this will be useful. I also feel the point of isomeric pattern difference among the sites is a noteworthy point to include in the abstract. This finding is something unique and certain coming out of this study, while the statements on OS reaction pathways are largely speculative due to the limited sample size and lack of other collaborative measurements.*

Reply: We now state that "Clearly, the isomeric pattern differs significantly in WH compared to the other two megacities, probably due to the diversity in precursors and/or oxidation mechanism"

(Page 12, Line 322-324).

We now state in the abstract (Page 2, Line 24-27) that "OSs with two to four isomers accounted for about 50% of the total OSs on average in these megacity samples, and the percentage of OSs with six and more isomers in WH sample was more significant than those in SH and NJ samples".

Minor comments:

1. *Abstract: specify the percentage is by number of formulas or by intensity.*

Reply: We now state in our revised manuscript (Page 2, Line 22-24) that "The number of aliphatic OS formulas represented more than 78% of the detected OSs at the three locations, while aromatic OSs were much less numerous."

2. *Line 74: less abundant --> more abundant*

Reply: We have replaced "less abundant" with "more abundant" (Page 4, Line 81).

Anonymous Referee #4

accept as is

Reply: We are very grateful to referee #4 for his/her positive viewing of our study.

Anonymous Referee #5

> *The authors have done a very good job in addressing all the reviewer comments and short comments posted during the discussion. Most of the issues, including the English writing, have been resolved enough to warrant publication. However, there remain a few minor issues that need to be resolved before full publication is considered in ACP.*

Reply: We are very grateful to referee #5 for his/her positive viewing of our study and we revised the manuscript thoroughly according to the comments of all reviewers.

Specific comments:

1. *Specifically, I still wonder why the authors did not consider conducting tandem MS experiments to confirm the presence of organosulfates versus sulfonates? Also, tandem MS experiments could have provided deeper insights into the the structures of some of these OSs. The authors need to specifically say in the discussion of the results that "one limitation of this work is the lack of using tandem MS experiments to provide insights into the structures of these organosulfates." Although high-resolution MS was used, and in many instances consistent with prior studies, it is not enough on its own to fully identify these organosullfur*

compounds as organosulfates or sulfonates, especially since sulfonates recently identified in Riva et al. (2015, ES&T) can be multifunctional and thus contain many O atoms. I highly recommend that a word of caution is added in the text about this. The authors now rightly emphasize throughout many places in the text now that these are "tentative assignments."

Reply: We do agree that having conducted tandem MS experiment would have provided more information. Nevertheless, we have not conducted such experiments here as the objective was to get a global fingerprint of the sulfur containing organic compounds present in the samples and not to answer the specific question of the presence of sulfonates. We now state in the revised manuscript :

- Material and methods, section 2.3 (Page 8-9, Line 214-219): "However, tandem MS experiments were not conducted on the S- and N-containing ions detected in these eight ambient samples. Therefore, other S- and N-containing compounds, such as sulfonates or compounds bearing nitro groups, may also be involved (e.g., Riva et al., 2015b; El Haddad et al., 2013) due to the lack of using tandem MS experiments to provide insights into the structures of these ions."
- Results, beginning of section 3.3 (Page 13 Line 352-356) "Table 1 summarizes the average characteristics (molecular weight, DBE, and elemental ratios) of tentatively assigned CHOS and CHONS compounds. These CHOS and CHONS compounds were here tentatively regarded as organosulfates and nitrooxy-organosulfates respectively, but other S- and N- containing functional groups could be involved as well in small amount (Lin et al., 2012b)."
- Conclusion (Page 19 Line 538-541): "More than 100 formulas of CHOS and dozens of formulas of CHONS with various numbers of isomers were tentatively determined in each sample. These CHOS and CHONS compounds were here tentatively regarded as organosulfates and nitrooxy-organosulfates respectively."

2. *Lastly, I think the authors need to be really careful when using words like "abundant, more abundant, or less abundant" when describing the differences in types of organosulfates or differences between sites. For example, in the abstract the authors state "Aliphatic OSs represented more than 78% of the detected OSs at the three locations, while OSs were much less abundant." Statements like this are not good since you don't know the response factor of aromatic organosulfates versus aliphatic organosulfates. Thus, I suggest using words like "numerous, less numerous, or more numerous" when trying to describe differences between sites or types of OSs.*

Reply: We now state (Page 2, Line 22-24) that "The number of aliphatic OS formulas represented more than 78% of the detected OSs at the three locations, while aromatic OSs were much less numerous". In addition, we have replaced "less abundant" with "less numerous" (Page 12, Line 322).

Minor comments:

1. *Page 3, Line 50: Change "isoprene-derived epoxide (IEPOX)" to isomeric isoprene*

epoxydiols (IEPOX) to be consistent with the original paper by Paulot et al. (2009, Science).

Reply: "isoprene-derived epoxide (IEPOX)" has been replaced by "isomeric isoprene epoxydiols (IEPOX)" (Page 3, Line 53).

2. *Page 3, Lines 52-54: The authors state that "subsequent acid catalyzed reactions of IEPOX and MAE in the presence of sulfates can lead to the formation of OSs" but the fail to cite Lin et al. (2013, PNAS). Lin et al. (2013, PNAS) demonstrated for the first time that MAE in fact does this. Further, Lin et al. (2012, ES&T) was the first study to demonstrate with "true" IEPOX that it does in fact produce OSs. These papers should be cited here in the introduction.*

Reply: These papers have been cited in the introduction (Page 3, Line 56-57).

Reference:

Marshall, A. G.: Milestones in Fourier transform ion cyclotron resonance mass spectrometry technique development, International Journal of Mass Spectrometry, 200, 331-356, doi:10.1016/s1387-3806(00)00324-9, 2000.

Fuller, S. J., Zhao, Y. J., Cliff, S. S., Wexler, A. S., and Kalberer, M.: Direct Surface Analysis of Time-Resolved Aerosol Impactor Samples with UltrahighResolution Mass Spectrometry, Anal. Chem., 84, 9858-9864, doi:10.1021/ac3020615.

Lin, P., Rincon, A. G., Kalberer, M., and Yu, J. Z.: Elemental composition of HULIS in the Pearl River Delta Region, China: results inferred from positive and negative electrospray high resolution mass spectrometric data, Environ. Sci. Technol., 46, 7454-7462, doi:10.1021/es300285d, 2012a. Lin, P., Yu, J. Z., Engling, G., and Kalberer, M.: Organosulfates in humic-like substance fraction isolated from aerosols at seven locations in East Asia: a study by ultra-high-resolution mass spectrometry, Environ. Sci. Technol., 46, 13118-13127, doi:10.1021/es303570v, 2012b.

Staudt, S., Kundu, S., Lehmler, H. J., He, X. R., Cui, T. Q., Lin, Y. H., Kristensen, K., Glasius, M., Zhang, X. L., Weber, R. J., Surratt, J. D., and Stone, E. A.: Aromatic organosulfates in atmospheric aerosols: Synthesis, characterization, and abundance, Atmos. Environ., 94, 366-373, doi:10.1016/j.atmosenv.2014.05.049, 2014.

Tao, S., Lu, X., Levac, N., Bateman, A. P., Nguyen, T. B., Bones, D. L., Nizkorodov, S. A., Laskin, J., Laskin, A., and Yang, X.: Molecular Characterization of Organosulfates in Organic Aerosols from Shanghai and Los Angeles Urban Areas by Nanospray Desorption Electrospray Ionization High-Resolution Mass Spectrometry, Environmental science technology, 48, 10993-11001, doi:10.1021/es5024674, 2014.

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Molecular Characterization of Atmospheric Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River

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Abstract. $PM_{2.5}$ filter samples have been collected in three megacities at the middle and lower reaches of the Yangtze River: Wuhan (WH), Nanjing (NJ), and Shanghai (SH). The samples were analyzed using ultra-high-performance liquid chromatography (UHPLC) coupled with Orbitrap mass spectrometry (MS), which allowed for detection of about 200 formulas of particulate organosulfates (OSs), including dozens of formulas of nitrooxy-organosulfates, with various numbers of isomers for each tentatively determined formula at each location. The number of a~~A~~liphatic OS~~s~~ formulas represented more than 78% of the detected OSs at the three locations, while aromatic OSs were much less ~~abundant~~numerous. OSs with two to four isomers accounted for about 50% of the total OSs on average in these megacity samples, and the percentage of OSs with six and more isomers in WH sample was more significant than those in SH and NJ samples. Additionally, t~~T~~he molecular formula,~~ number of isomers,~~ average molecular weight, and degrees of oxidation and unsaturation of tentatively assigned OSs were compared. The results indicate that the OSs between NJ and SH shared higher similarity, and the characteristics of OSs in SH varied diurnally and seasonally. OSs derived from isoprene, monoterpenes, and sesquiterpenes were abundant in samples from the three megacities and could be produced through both daytime photochemistry and NO_3 night-time chemistry. The reaction pathways leading to isoprene-derived OSs probably varied in those locations because of the different NO_x levels. In addition, a number of OSs that might be formed from polycyclic aromatic hydrocarbons were also detected, which underlies the importance of anthropogenic sources for this class of compounds.

1. Introduction

Atmospheric aerosols can scatter and absorb sunlight and provide cloud condensation nuclei. Hence, they have significant impacts on air quality and climate (Andreae and Crutzen, 1997; Hallquist et al., 2009). Aerosol particles contain a large fraction of toxic chemical substances and are harmful to human health (Magari et al., 2002; Ostro et al., 2007). Organosulfates (OSs)—i.e., sulfate esters and their derivatives formed from atmospheric heterogeneous and multiphase chemical reactions (Ma et al., 2012)—are a class of organic compounds that contribute to the total abundance of atmospheric aerosol particles (Tolocka and Turpin, 2012).

Surratt et al. (2007) were the first to identify isoprene- and α-pinene-derived OSs in ambient aerosols in the southeast US using high-performance liquid chromatography coupled with electrospray mass spectrometry. Since then, tremendous progress has been made in the understanding of the formation mechanisms of OSs. Experimental studies show that isomeric isoprene epoxydiols ~~isoprene-derived epoxide~~ (IEPOX) and methacrylic acid epoxide (MAE) are formed during the oxidation of isoprene under low- and high-NO_x conditions, respectively. Subsequent acid catalyzed-reactions of IEPOX and MAE in the presence of sulfates can lead to the formation of OSs (Darer et al., 2011; Lin et al., 2012c; Lin et al., 2013; Surratt et al., 2010; Paulot et al., 2009). OSs can be formed from reactions between α-pinene and OH radicals, NO_3 radicals, and O_3 in the presence of sulfates, from β-pinene under high-NO_x conditions, from ozonolysis and photochemical reactions of other monoterpenes (α-terpinene and γ-terpinene), and from sesquiterpene (i.e., β-caryophyllene) under acidic conditions (Surratt et al., 2008; Iinuma et al., 2007a; Iinuma et al., 2007b; Chan et al., 2011). Sulfate/sulfite radical-induced oxidation reactions with unsaturated organic compounds including isoprene, methyl vinyl ketone, methacrolein, and α-pinene in the aqueous phase represent another potential formation route of OSs (Szmigielski, 2015; Rudzinski et al., 2009; Noziere et al., 2010; Schindelka et al., 2013). In addition, both reactive uptake of carbonyl compounds on sulfuric acid or sulfates (Liggio et al., 2005) and hydrolysis reactions of organonitrates can lead to formation of OSs (Darer et al., 2011; Hu et al., 2011).

Very recently, OSs and sulfonates were revealed to form from photo-oxidation of polycyclic aromatic hydrocarbons (PAHs) in the presence of sulfate seed (Riva et al., 2015b).

Identification and quantification of OSs in atmospheric particulate samples have been widely performed around the world (e.g., Kristensen and Glasius, 2011; Stone et al., 2009; Olson et al., 2011; Zhang et al., 2012). Many studies indicate that the total abundance of OSs varies from one region to another. OSs accounted for about 4% of the total organic mass in ambient aerosols over the southeast Pacific Ocean (Hawkins et al., 2010), whereas this contribution was estimated to be about 30% at the forested site of K-puszta in Hungary during summer (Surratt et al., 2008). The abundance of a given OS also shows clear variation between different sampling locations. The level of four aromatic OSs was estimated to be 234.4 pg m^{-3} in atmospheric $PM_{2.5}$ in Pakistan, which were much ~~less~~ more abundant than those in California (8.9 pg m^{-3}) or Nepal (3.9 pg m^{-3}) (Staudt et al., 2014).

In a given location, there are seasonal variations of OSs. For example, the α-pinene-related nitrooxy-OSs were detected at high concentrations during the winter period, followed by autumn, spring, and summer at a rural background site in Hamme, Belgium (Kahnt et al., 2013). Ma et al. (2014) also showed that the total mass concentration of 17 OSs was the highest in summer and lowest in winter, while no clear seasonal trend was observed in the mass concentration of benzyl sulfate (BS). However, BS showed the highest concentration in winter and the lowest one in summer in Lahore, Pakistan (Kundu et al., 2013), which underlies the role of both regional constraints and meteorological conditions.

Recently, ultra-high-resolution mass spectrometry has been applied for tentative determination of the molecular formulas of OSs in atmospheric aerosols samples. Owing to the high mass resolution and mass accuracy of the ultra-high-resolution mass spectrometer, the molecular formulas of analytes can be tentatively determined without the authentic standards required with low-resolution mass spectrometers. Lin et al. (2012a, 2012b) studied aerosols sampled at a rural location of the Pearl River Delta Region in China and suggested that the arbitrary signal intensities of OSs obtained from the humic-like fraction are often the strongest in the electrospray ionization ultra-high resolution mass spectra, and that the degrees of oxidation of OSs and nitrooxy-OSs are quite high. Using a similar approach, O'Brien et al. (2014) showed that a significant portion of OSs was formed from biogenic precursors through the epoxide pathway in Bakersfield, CA, USA. In addition, by using a mixture of acetonitrile and toluene instead of a mixture of acetonitrile and water as the working solvent for nano-DESI ionization, Tao et al. (2014) tentatively determined many OSs with long aliphatic carbon chains and low degrees of oxidation and unsaturation, which were presumably formed from anthropogenic precursors emitted by cars in Shanghai (SH).

Although it has been accepted that OSs are an important component of ambient particulate matter, studies on their characteristics are rather sparse in China, especially in the Yangtze River region. Ma et al. (2014) identified and quantified 17 OSs in SH. As mentioned, Tao et al. (2014) compared OS characteristics such as the degrees of oxidation and saturation between samples from SH and Los Angeles. While SH has been a relative hotspot for OS characterization, the characteristics of OSs in the general Yangtze River region have yet to be elucidated. Wuhan (WH), Nanjing (NJ), and SH are three megacities at the middle and lower reaches of the Yangtze River with populations of over 10, 8, and 24 million, respectively (as of 2014). Tremendous amounts of energy are consumed owing to the large population and rapid economic development, leading to extensive emissions of anthropogenic pollutants including particulate matter, volatile organic compounds (VOCs), sulfur dioxide, and nitrogen oxides (Huang et al., 2011; Wang et al., 2013). At the same time, these three cities are located in the subtropical zone with high emissions of biogenic VOCs (Guenther et al., 1995). Hence, substantial amounts of OSs are likely to exist in WH, NJ, and SH aerosol particles. In this study, OSs, including nitrogen-containing OSs, were specifically searched for in WH, NJ, and SH $PM_{2.5}$ samples using an UHPLC coupled to an Orbitrap-MS. Characteristics of OSs including the molecular formula, number of isomers, molecular weight, and the degrees of oxidation and unsaturation were analyzed and compared. The potential precursors in the megacities are also discussed.

2．Material and methods

2.1 Collection of $PM_{2.5}$ samples

Eight $PM_{2.5}$ samples were collected at three locations: two in WH, two in NJ, and four in SH, as shown in Figure 1 and Table 1. Samples covering 24 h were collected in WH from January 26 to 27 (sample ID: WH winter, WHW) and from June 15 to 16, 2012 (sample ID: WH summer, WHS). The WH site was located on the rooftop of a dormitory building (30°29′N, 114°24′E) that is about 20 m above ground at ZhongNan University of Economics and Law near a commercial street. NJ samples were collected from August 29 to 30, 2012, for 12 h for each sample (samples ID: NJ summer daytime, NJSD; NJ summer nighttime, NJSN). The NJ site was located in the Chinese national meteorology observatory facility at the Nanjing University of Information Science and Technology (32°12′N，118°42′E), which is about 15 km north of the downtown area and about 2 km west of clusters of steel mills and petrochemical refinery facilities (Zheng et al., 2015).

SH samples were collected for 12 h from January 17 to 18, 2013 (sample ID: SH winter daytime, SHWD; SH winter nighttime, SHWN), and July 28 to 29, 2013 (sample ID: SH summer daytime, SHSD; SH summer nighttime, SHSN). The SH site was located on the rooftop of a teaching building at Fudan University (31°18′N，121°30′E) about 20 m above ground with surrounding residential and commercial properties and a major highway to the south of the site (Xiao et al., 2015; Ma et al., 2014). Table S1 provides a comparison of air quality and meteorological conditions between the sampling days and the seasonal average in SH.

$PM_{2.5}$ was collected on 90 mm quartz-fiber filters (Whatman Company, UK) using a middle-flow impact aerosol sampler (Qingdao Hengyuan Tech Co., Ltd., HY-100) operating at 100 lpm. All filters were prebaked at 500°C for 5 h to remove residual organics before use. After sample collection, filters were wrapped in prebaked aluminum foil and stored at -20°C before further analysis.

2.2 Sample analysis

One-fourth of each filter was put into an amber vial with 6 mL of methanol (Optima® LC/MS, Fischer Scientific, UK) and shaken for 20 min on an orbital shaker set to 1000 rpm. The extract was then filtered through a glass syringe on a 0.2μm PTFE membrane (13 mm, Pall Corporation, USA). These two steps were performed twice, and the extracts of each filter were recombined and blown almost to dryness under a gentle stream of nitrogen. The extracts were then reconstituted in 1 mL of a 1:1 v/v mixture of water (Optima® LC/MS, Fischer Scientific, USA) and acetonitrile (Optima® LC/MS, Fischer Scientific, USA). For the analysis, 100 μL of the final reconstituted extract was diluted by adding 100 μL of water. 5μL of these diluted solutions (50 μL in the case of the NJSD sample) were analyzed by UHPLC (Dionex 3000, Thermo Scientific, USA) coupled to a Q-Exactive Hybrid Quadrupole-Orbitrap MS (Thermo scientific, USA). The efficiency and the repeatability on three replicates of the extraction protocol were checked using four standards: methyl sulfate, octyl sulfate, dodecyl sulfate, and camphor sulfonic acid. The results showed that their average extraction efficiencies were 71.4, 95.0, 97.7, and 94.0%, respectively (Table S2). Analytical replicates were not considered because the final sample extract volume was quite low (200 μL), and the remaining volume after the first injection was preferentially kept in case of specific analytical doubt rather than systematically injected.

Analytes were separated using a Waters Acquity HSS T3 column (1.8μm, 100×2.1mm) with mobile phases consisting of (A) 0.1% formic acid in water (Optima® LC/MS, Fischer Scientific, USA) and (B) 0.1% formic acid in acetonitrile (Optima® LC/MS, Fischer Scientific, USA). The concentration of eluent B was initially kept at 1% for 2 min, then increased to 100% in 11 min, kept at 100% for 2 min, decreased to 1% in 0.1 min, and kept at 1% for 6.9 min. The Q-Exactive Hybrid Quadrupole-Orbitrap mass spectrometer was equipped with a heated electrospray ionization source. It was operated in the negative ion mode with a spray voltage of -3.0kV, a mass resolving power of 140 000 at m/z 200, and a scanning range of 50–750 m/z. The Q-Exactive mass spectrometer was externally mass calibrated daily using a 2 mM sodium acetate solution that provides a series of negative adduct ions in the range of 50–750 m/z.

2.3 Data processing

The obtained chromatograms were analyzed with Progenesis QI software (V1.0, Waters Corporation) by assuming that the extracted ions in the range of 50–750 m/z [M-H] were formed from loss of a proton from the analytes. In contrast to direct infusion, the LC separation provides meaningful help in distinguishing quasi-molecular ions and potential in-source formed adducts for the same chromatographic retention time. A molecular formula calculator was then used to mathematically assign all possible formulas for an extracted quasi-molecular ion with a mass tolerance of ±2 ppm. These molecular formulas can be expressed as $C_cH_hO_oN_nS_s$, where c is the number of carbon atoms in the range of 1–40, h is the number of hydrogen atoms in the range of 2–80, o is the number of oxygen atoms in the range of 0–40, n is the number of nitrogen atoms in the range of 0–3, and s is the number of sulfur atoms in the range of 0–2. Formulas were further constrained by setting H/C, O/C, N/C, S/C, and double bond equivalent to carbon number ratios (DBE/C) in the ranges of 0.3–3.0, 0–3, 0–0.5, 0–0.2, and 0–1, respectively. This was done to ensure that the retrieved molecular formula do exist in nature (Fuller et al., 2012; Lin et al., 2012a; Lin et al., 2012b).

The number of ions with more than one reasonable formula within 2 ppm mass tolerance accounted only for 1.5% of the total number of tentatively determined ions, and the formulas with the best accuracy are listed in Table S3. The peak intensities of isotopically substituted ions were constrained by their low abundance and were hence not systematically checked. Compounds that satisfy these criteria and present a number of oxygen atoms greater than or equal to 4s+3n ($4s+3n \leq o$) were tentatively regarded as OSs or nitrooxy-OSs. However, tandem MS experiments were not conducted on the S- and N-containing ions detected in these eight ambient samples. Therefore, other S- and N-containing compounds, such as sulfonates or compounds bearing nitro groups, may also be involved (e.g., Riva et al., 2015b; El Haddad et al., 2013) due to the lack of using tandem MS experiments to provide insights into the structures of these ions.

In this study, the abundance of an OS refers to the area of its chromatographic peak, and the number of isomers for an OS is based on the number of chromatographic peaks observed for given m/z values. Note that the obtained number of isomers may vary significantly when the separation method is further optimized. Then, the arbitrary abundances of all isomers for a given m/z value are added up. The arbitrary abundance of the most abundant OS or nitrooxy-OS in each sample is defined as 100%, and only OSs and nitrooxy-OSs with an arbitrary abundance larger than 0.5% of the most abundant one in the same sample are presented. The signal-to-noise ratios of the least abundant OSs in each sample are greater than 10 with a noise level of ca. 1×10^4 arbitrary units. Note that the arbitrary abundance of a given OS does not directly reflect its concentration compared to others in the same sample because the ionization efficiency is compound and solvent specific in electrospray ionization. Also, similar ionization efficiency is assumed for a given OS in different samples as similar retention times are observed and as UHPLC separation resolves most of the matrix components.

Blank filters were processed and analyzed in an identical way, and blank correction was made as follows. The presence of targeted quasi-molecular ions in the blanks was systematically verified, and if a chromatographic peak was indeed detected, then it was retained (i.e., considered as real) only if the sample-to-blank ratio of the peak area was greater than 10, with the blank value being subtracted prior to further processing. The DBE value of a molecule reflects the degree of its unsaturation. The DBE value is usually calculated as:

$$\mathrm{DBE} = \frac{2c+2+n-h}{2} \qquad \text{(Eq. 1)}$$

Not taking into account the two double bonds involved in each sulfate group, the DBE values of OSs calculated by Eq. 1 represent the unsaturation degree of the side carbon chain (eventually bearing oxygen and nitrogen atoms). In addition, one can note that this equation adds one DBE unit for each nitrate group. Molecular formulas with DBE<0 and formulas that disobey the nitrogen rule were discarded. The difference between the DBE value and the number of N atoms (DBE-n) is the most conservative criterion to determine whether a compound is aliphatic: the number of OSs with (DBE-n) < 4 can be regarded as the minimum number of aliphatic OSs (Lin et al., 2012b).

Both DBE/C and the aromaticity index (AI) could be used as criteria to determine whether a compound contains aromatic rings with thresholds of DBE/C > 0.67 and AI > 0.5, respectively. However, AI is more conservative (Koch and Dittmar, 2006). The value of AI can be calculated according to:

$$\mathrm{AI} = \frac{\mathrm{DBE_{AI}}}{\mathrm{C_{AI}}} = \frac{1+c-o-s-(0.5h)}{c-o-s-n} \qquad \text{(Eq. 2)}$$

where $\mathrm{DBE_{AI}}$ represents the sum of the minimum number of C=C double bonds and the number of rings in a formula containing heteroatoms, and $\mathrm{C_{AI}}$ represents the difference between the number of carbon and the number of potential double bonds caused by heteroatoms. If $\mathrm{DBE_{AI}} \leq 0$ or $\mathrm{C_{AI}} \leq 0$, then AI is defined to be zero. In contrast, AI>0.5 and AI≥0.67 indicate the existence of aromatic and fused aromatic ring structures in a compound, respectively (Koch and Dittmar, 2006).

In the Kendrick mass defect diagram (KMD diagram), CH_2 (14.00000) was chosen as a base unit. The Kendrick mass ($\mathrm{KM_{CH2}}$) and the Kendrick mass defect ($\mathrm{KMD_{CH2}}$) can be determined by Eq. 3 and Eq. 4, respectively:

$$\mathrm{KM_{CH_2}} = \text{Observed Mass} \times \left(\frac{14.00000}{14.01565}\right) \quad \text{(Eq. 3)}$$

$$\mathrm{KMD_{CH_2}} = \text{Nominal Mass} - \mathrm{KM_{CH_2}} \quad \text{(Eq. 4)}$$

where “Observed Mass” is the mass measured by the mass spectrometer, and “Nominal Mass” is the rounded integer mass of a compound.

3. Results and discussion

3.1 Isomers

UHPLC separation was applied prior to MS analysis for detection of potential isomers hidden behind a given m/z value and to provide another dimension of the ambient aerosol composition complexity. As an example, Figure 2 shows the extracted ion chromatograms for $C_5H_{10}O_5S$. An OS with this molecular formula has recently been identified in laboratory-generated secondary organic aerosols either from the ozonolysis of isoprene in the presence of sulfate aerosols or from the transformations of isoprene coupled with S(IV)-autoxidation in the aqueous-phase, but only one and two isomers were~~as~~ detected by UPLC-high-resolution MSs, respectively (Riva et al., 2015a; Szmigielski, 2015). From our ambient samples, 11 isomers were detected in total, with varying numbers of isomers in each sample (see Figure 2 and Table S3). On the other hand, only two isomers were detected in the ambient $PM_{2.5}$ samples from Diabla Gora rural site (Szmigielski, 2015). The reason for this difference in the number of isomers ~~between~~ among ~~the two~~these studies might arise from the different chromatographic conditions and additional precursors, including different terpenes. In addition, it is difficult to assign which isomer has been detected by Riva et al. (2015a) and Szmigielski (2015) due to different chromatographic conditions and detectors.

Additional extracted ion chromatograms are presented in the supplement for $C_5H_{12}O_7S_1$, $C_{10}H_{17}O_7N_1S_1$, and $C_{16}H_{32}O_6S_1$ (Figure S1). Two and four isomers were detected for $C_5H_{12}O_7S_1$ and $C_{10}H_{17}O_7N_1S_1$, respectively, whereas Surratt et al. (2008) detected one and six isomers for these OSs, also from ambient samples. A thorough analysis of UHPLC-Orbitrap MS data leads to the tentative determination of more than 100 CHOS formulas and dozens of CHONS formulas, with various numbers of isomers in each sample. The full list of the neutral mass, molecular formula, number of isomers, retention times, and potential precursors for these assigned OSs is tabulated in Table S3. Having access to the isomeric pattern of significant OSs could be very helpful in the future for identifying possible OS sources. Thus, Table S3 provides one of the first data sets of OS isomers in ambient samples.

The full mass spectra in summer samples from the three megacities, including all tentatively assigned OSs, have been reconstructed to present the samples' general characteristics. In Figure 3, the X-axis corresponds to the neutral molecular weight of detected OSs, the Y-axis represents their arbitrary abundances, and the number of isomers per detected mass is color-coded. Comparison of the reconstructed mass spectra shows that the number of OSs with an identical formula and the same number of isomers that could be observed in all three megacities accounted for only 17.6% of all the tentatively assigned OS molecular formulas. Between WHS and NJSN, the proportion of OSs sharing identical formulas reached 50.3%, but only 27.9% also possessed the same number of isomers. Quite similarly, between NJSN and SHSD+SHSN, the proportion of OSs sharing identical formulas reached 62.8%, but only 39.4% also had the same number of isomers. Between WHS and SHSD+SHSN, this proportion reached 51.5%, with only 32.3% having the same number of isomers. Therefore, one can consider that the samples from NJ and SH showed greater similarity, especially from their isomeric patterns. This observation is in agreement with the proximity of the two megacities compared to the more distant megacity of WH.

As shown in Figure 3, OSs with two to four isomers accounted for about 50% of the total detected OSs. Those with more than six isomers accounted for the largest proportion, and OSs with one isomer were insignificant in WH. In contrast, in SH and NJ, OSs with one isomer only were preponderant, while those with more than six isomers were much less numerous~~abundant~~. Clearly, the isomeric pattern differs significantly in WH compared to the other two megacities, probably due to the diversity in precursors and/or oxidation mechanism.

3.2 Tentative assignment and potential precursors of major OSs

The gaseous precursors of many OSs in Figure 3 can be tentatively assigned, since identical formulas of OSs have been observed in chamber studies. In Figure 3, OSs with strong arbitrary intensities have been labeled with a letter as follows: A: $C_5H_8O_3SO_4$; B: $C_5H_{12}O_3SO_4$; C: $C_6H_{10}O_3SO_4$; D: $C_7H_{12}O_3SO_4$; E: $C_9H_{18}O_2SO_4$; F: $C_5H_{11}O_2NO_3SO_4$; G: $C_9H_{16}O_3SO_4$; H: $C_{10}H_{17}NO_3SO_4$; I: $C_5H_{10}O_1(NO_3)_2SO_4$; J: $C_{16}H_{32}O_2SO_4$; and K: $C_{15}H_{25}NO_3SO_4$. Among these OSs, A, C, D, and G are a series of homologues, and so are E and J. A, B, F, and I could be derived from isoprene, whereas D and G could be derived from limonene, C from 3-Z-hexenal, K from β-caryophyllene, and H from various monoterpenes (i.e., α-pinene, β-pinene, α-terpinene and terpinolene) (Chan et al., 2011; Shalamzari et al., 2014; Surratt et al., 2008; Gomez-Gonzalez et al., 2008). E and J were characterized by high molecular weights and degrees of saturation, presumably being long-chain aliphatic OSs. In general, many abundant OSs could be derived from isoprene, monoterpenes, and sesquiterpenes in these three megacities.

The relative abundance of J was the highest in WH but much lower in NJSN and SHSD+SHSN samples. H was the highest in the SHSD+SHSN samples, while I was the most abundant in the NJSN sample. It is doubtless that I bears two nitrate groups (two nitrogen atoms in its formula that fulfill the 4s+3n≤o rule) and is the most abundant in the NJSN sample, likely due to active NO_3 radical chemistry at night. F and K, which bear one nitrate group, were also quite abundant in the NJSN sample, underlying the role of NO_3 chemistry at night. The isomer ratios vary from sample to sample and therefore certainly carry information about their origin. These ratios and possible VOC precursors for these most abundant OSs are summarized in Table S4.

3.3 Comparison of OS characteristics

Table 1 summarizes the average characteristics (molecular weight, DBE, and elemental ratios) of tentatively assigned CHOS and CHONS compounds. These CHOS and CHONS compounds were here tentatively regarded as organosulfates and nitrooxy-organosulfates respectively, but other S- and N- containing functional groups could be involved as well in small amount (Lin et al., 2012b).~~OSs and nitrooxy-OSs in each sample.~~ In addition, (o-3s)/c (Tao et al., 2014) and (o-3s-2n)/c have been calculated to illustrate the number of oxygen-containing functional groups per carbon atom. These two values are derived from the fact that each sulfate and nitrate group respectively contains three and two oxygen atoms more than do common oxygen-containing groups, such as a hydroxyl or a carbonyl moiety. (o-3s)/c and (o-3s-2n)/c can therefore be regarded as measures of the degree of oxidation of CHOSs and CHONS compounds, respectively.

The average molecular weight and DBE value of CHONS species were generally larger than those of CHOS analogues, because CHONS contains one or two more nitrate groups (the presence of one nitrate group adding one DBE unit). Measurement of the O/C ratio of OSs in Bakersfield (CA, USA) indicated that the degree of oxidation of CHONS was larger than that of CHOS throughout the day (O'Brien et al. 2014). A similar trend has been observed for $CHONS_1$ and $CHOS_1$ in SH and Los Angeles aerosol samples but using the (o-3)/c ratio to measure the degree of oxidation (Tao et al., 2014). In this study, however, the average degree of oxidation of CHONS was only slightly larger than that of CHOS during the daytime and slightly smaller at night. The use of the (o-3s)/c and (o-3s-2n)/c ratios to evaluate the degrees of oxidation of the CHOS and CHONS carbon chain, respectively, allows for precise comparison of the oxidation states of these two classes of compounds. The values of the oxidation states for OSs and nitrooxy-OSs on a same sample (0.01 to 0.14 units of difference) suggest that the presence of the sulfate and/or nitrate groups is not determinant.

The OSs with (DBE-n) < 4 accounted for 86.2, 78.5, and 78.3% of total OSs in WH, NJ, and SH, respectively, suggesting tentatively assigned OSs were mainly aliphatic OSs. Also, the number of OSs with (DBE-n) ≥ 4 can be regarded as the maximum number of aromatic OSs. This value appears to be slightly higher in SH (21.7%) and NJ (21.5%) compared to WH (13.8%), possibly indicating a slightly more significant anthropogenic influence for the first two cities.

The number of OSs with DBE/C > 0.67 accounted for 2.2, 5.2, and 7.1% of total OSs, and their abundance accounted for 0.6, 1.4, and 8.0% of total abundances of OSs in WHS, NJSD+NJSN, and SHSD+SHSN, respectively. Only a few aromatic OSs with AI > 0.5 were detected, but it could be due to the fact that this value takes into account carbon-bounded S and N but not sulfate and nitrate groups (and the related oxygen atoms), underestimating the aromatic ring content. BS and its analogues were nevertheless detected in most of the samples of the three megacities.

Figure 4 shows the CH_2-Kendrick diagrams and Van Krevelen (VK) diagrams for CHOS species for the WHS, NJSD+NJSN, and SHSD+SHSN samples, respectively, and the variation in DBE is color-coded. In the CH_2-Kendrick diagram, compounds in a homologue series of compounds with identical KMD_{CH2} values form a horizontal line. The molecular formula of the homologue series 1 and 2, which have DBE values equal to zero, can be written as $C_nH_{2n+2}SO_4$ and $C_nH_{2n+2}O_1SO_4$ (n>4), respectively. Hence, the OS in the homologue series 2 contained one more hydroxyl group or ether group than the corresponding one in the homologue series 1. Similarly, molecular formula of the homologue series 3, 4, and 7 with DBE=1 can be written as $C_nH_{2n}O_1SO_4$, $C_nH_{2n}O_2SO_4$, and $C_nH_{2n}O_3SO_4$; those for series 6, 9, 11, and 13 with DBE=2 can be written as $C_nH_{2n-2}O_2SO_4$, $C_nH_{2n-2}O_3SO_4$, $C_nH_{2n-2}O_4SO_4$, and $C_nH_{2n-2}O_5SO_4$; and those for series 5, 8, 10, 12, 14, and 15 with DBE=3 can be written as $C_nH_{2n-4}O_1SO_4$, $C_nH_{2n-4}O_2SO_4$, $C_nH_{2n-4}O_3SO_4$, $C_nH_{2n-4}O_4SO_4$, $C_nH_{2n-4}O_5SO_4$, and $C_nH_{2n-4}O_6SO_4$, respectively. For the homologue series with DBE=2 or 3, the oxygen atoms other than those in the sulfate group probably belonged to hydroxyl, carbonyl, or carboxylic groups, because it is unlikely that a compound in this range of molecular weight would contain so many ether groups. CHOS with DBE=4 or 5 represented 9.9, 12.2, and 9.5% of the total CHOS species in the WHS, NJSD+NJSN, and SHSD+SHSN samples, respectively.

The region of the CH_2-Kendrick diagrams where KM_{CH2} is between 350 and 750 and KMD_{CH2} is larger than 0.38 appears to be of particular interest. No CHOS was observed in this region in WHS, whereas up to 6.5 and 9.5% of the total CHOS were detected there in the NJSD+NJSN and SHSD+SHSN samples, respectively. The CHOS species in this region were characterized by a high molecular weight, high degrees of unsaturation and oxidation (DBE > 5 and (o-3s)/c > 0.5), and a minimum amount of isomers (one isomer for 79% of CHOS in this region). Moreover, these CHOS are located in the lower right region of the VK diagrams that plot H/C versus (o-3s)/c ratios (Figure 4, Wu et al. 2004; Kim et al, 2003). They are thus likely to contain one or more aromatic rings (DBE/C > 0.67, but AI<0.5) and come most certainly from anthropogenic precursors.

Fewer CHONS than CHOS species were observed (Figure 5). In the CH_2-Kendrick diagram, the KMD_{CH2} values of CHONS were generally larger than those of CHOS because of the presence of one or two additional nitrate group contributing to these KMD_{CH2} values. Similarly to CHOS species, CHONS species in a homologue series with identical KMD_{CH2} values form a horizontal line. Molecular formula of the homologue series 1 and 3 with DBE=1 can be written as $C_nH_{2n+1}NO_3SO_4$ and $C_nH_{2n+1}ONO_3SO_4$; those for homologue series 2, 4, 5, and 8 with DBE=2 can be written as $C_nH_{2n-1}NO_3SO_4$, $C_nH_{2n-1}ONO_3SO_4$, $C_nH_{2n-1}O_2NO_3SO_4$, and $C_nH_{2n-1}O_3NO_3SO_4$; those for series 7, 9, and 10 with DBE=3 can be written as $C_nH_{2n-3}O_2NO_3SO_4$, $C_nH_{2n-3}O_3NO_3SO_4$, and $C_nH_{2n-3}O_4NO_3SO_4$; and those series 6 with DBE=4 can be written as $C_nH_{2n-5}ONO_3SO_4$ (n>4). By comparing the molecular formulas of CHOS and CHONS species, it appears that most of CHONS could correspond to the addition of nitrate groups on the detected CHOS. In the VK diagrams, the homologue series 1 and 3 constitute upward lines and the other ones constitute downward lines. In the region where KM_{CH2} is between 500 and 700 and KMD_{CH2} is larger than 0.6, CHONS species with DBE values larger than 5, a high molecular weight and a high degree of oxidation ((o-3s-2n)/c > 0.5) were detected in NJSD+NJSN and SHSD+SHSN, but not in WHS. According to the formulas of those CHONS species, their precursors were different from those for any CHOS species. On the other hand, a few additional CHONS species with DBE values also larger than 5, relatively low molecular weight and low degrees of saturation and oxidation ((o-3s-2n)/c < 0.3) were present in the three megacities.

Figure S2 shows the numbers of CHOS and CHONS species in different mass ranges. Generally, OSs in the mass range of 250–300 Da showed the greatest variety. The number of OSs in the mass range of 200–400 Da accounted for 90.5, 83.1, and 85.4% of determined OSs in WHS, NJSD+NJSN, and SHSD+SHSN, respectively. OSs with molecular weights larger than 500 Da characterized by high degrees of unsaturation in the KMD diagrams existed in the NJ and SH samples, whereas the molecular weight of all OSs in the WH sample was less than 500 Da. In summary, the molecular characteristics of tentatively assigned OSs between NJSD+NJSN and SHSD+SHSN shared better similarity, probably because NJ and SH are geographically closer at the lower reach of the Yangtze River, whereas WH is at the middle reach of the Yangtze River.

3.4 Formation pathways of isoprene-derived OSs in three megacities

Isoprene has been shown to be an important precursor of OSs in the three megacities. Previous studies suggest that IEPOX ($C_5H_{10}O_3$) and MAE ($C_4H_6O_3$) are two key reactive intermediates that are formed during isoprene oxidation under low- and high-NO_x conditions, respectively. Subsequent acid catalyzed-reactions of IEPOX and MAE in the presence of sulfates lead to the formation of $C_5H_{12}O_3SO_4$ and $C_4H_8O_3SO_4$, respectively (Surratt et al., 2010; Worton et al., 2013), with the C_4 OS being promoted under high-NO_x conditions compared to the C_5 OS. C_5 and C_4 OSs could also be formed from sulfate/sulfite radical-induced oxidation reactions with isoprene and its oxidation products (i.e., methyl vinyl ketone, and methacrolein) in the aqueous phase, respectively (Schone et al., 2014; Noziere et al., 2010). Since the liquid water content is not available for our ambient samples, these aqueous reaction pathways are not considered here.

In this study, the S/C ratio has been limited to 0–0.2 to assure that the obtained compound exists in nature (Lin et al., 2012a; Tao et al., 2014; Wozniak et al., 2008). As a result, $C_4H_8O_3SO_4$ has been eliminated by this criterion. Manually extracted ratios of the abundances of $C_4H_8O_3SO_4$ to $C_5H_{12}O_3SO_4$ (denoted hereafter as C_4/C_5 ratios) were used to elucidate the major formation pathway of isoprene-derived OSs in the three megacities.

In SH winter daytime samples, the C_4/C_5 ratio was 8.9 and decreased to 0.20 during summer. In WH, the C_4/C_5 ratio was equal to 0.22 in winter and 0.13 in summer. In both cases, these observations are consistent with the C_4 OS being promoted with higher winter NO_x levels but also suggest that even in winter, isoprene OSs are formed under low-NO_x conditions. In the NJSD sample, the C_4/C_5 ratio was about 2.5, suggesting that the high-NO_x pathway might dominate in summer in NJ (Dong et al., 2013).

3.5 Comparison of OSs in the SH samples

For a more accurate comparison, the abundance of $C_{10}H_{17}NO_3SO_4$ in the SHSN sample (the highest one from all the SH samples) was set arbitrarily to 100%, and an abundance limit corresponding to 0.5% of this value was used to include or exclude the OSs from the four SH samples in the following comparison. Figure 6 shows that the number of OSs in the SHSD and SHSN samples was much larger than those in the SHWD and SHWN samples, respectively, consistent with a higher photochemical activity and/or higher precursor emissions in summer than in winter. The number of OSs in the SHSN and SHWN samples, especially the number of CHONS, was much larger than that in the SHSD and SHWD samples, respectively, consistent with the previous observation in Figure 3 (see section 3.2) that much more CHONS is present during nighttime.

As shown in Figure 7, the total arbitrary abundances of OSs in the SHSD and SHSN samples were 2.1 and 3.0 times higher than in the SHWD and SHWN samples. The total arbitrary abundances of CHOS did not display significant differences between SHSD and SHSN or between SHWD and SHWN. However, the arbitrary abundances of CHONS in these SHSN and SHWN samples were 5.0 times and 2.2 times higher than in the SHSD and SHWD samples. This is consistent with an expected nighttime chemistry of NO_3. Moreover, the variety (Figure 6) and the abundance (Figure 7) of CHONS in both SHWN and SHSN samples were far larger than those in SHWD and SHSD.

The fact that the SHSN sample showed higher abundance and variety of CHONS than the SHWD sample seems to point toward a CHONS formation driven by both daytime photochemistry (and/or precursor emission) and subsequent nighttime NO_3 chemistry. Similar trends of higher CHONS abundance during nighttime than during daytime were observed in Beijing, China (van Pinxteren et al., 2009), Atlanta, GA (Hatch et al., 2011), and Bakersfield, CA, USA (O'Brien et al., 2014). However, He et al. (2014) observed a reverse trend at a regional background site in the Pearl River Delta region (concentrations of nitrooxy-OSs were higher during daytime), concluding that photochemical reactions could also lead to the formation of a significant amount of nitrooxy-OSs. This photochemical pathway could contribute to the formation of the nitrooxy-OSs detected during daytime, even if they showed only relatively low abundances in this study.

Figure 7 shows the carbon number-based arbitrary abundance of CHOS and

CHONS. In all four samples, more than 60% of the OSs were characterized by 5 to 10 carbon atom chains. In the SHSD and SHSN samples, C_5 and C_{10} were the most abundant. Isoprene and monoterpenes could be the main precursors for most of the C_5 and C_{10} OSs (Riva et al., 2015a; Surratt et al., 2008). On the other hand, a recent work (Riva et al., 2015b) suggests that a number of observed C_{10} OSs (e.g., $C_{10}H_{12}O_7S_1$) might be derived from PAHs. In addition to C_5 and C_{10}, the relative abundances of C_8, C_9, and C_{14+} were also high in the SHWD and SHWN samples, hinting at additional precursors. In contrast, C_{10} derived from monoterpenes always represented the dominant category in spring, autumn, and winter in the Pearl River Delta, South China, and in Taiwan (Lin et al., 2012b), underlying a lesser anthropogenic influence in these two regions than in the Yangtze River region.

The VK diagrams of CHOS and CHONS in the SH samples are presented in Figure S3, which represents a combination of Figure 4 and Figure 5 (with a lesser number of OSs accounted for). OSs in the four samples were characterized by similar degrees of saturation. OSs with a low degree of saturation and a high molecular weight existed in all four samples. Table 1 and Figure S3 show that the average degree of oxidation of OSs in the SHSD and SHSN samples was higher than those in the SHWD and SHWN samples, which is consistent with a promoted photochemical activity in summer.

4. Conclusions

In this study, atmospheric $PM_{2.5}$ samples in WH, NJ, and SH were analyzed using an UHPLC-Orbitrap MS. More than 100 formulas of CHOS and dozens of formulas of CHONS with various numbers of isomers were tentatively determined in each sample. These CHOS and CHONS compounds were here tentatively regarded as organosulfates and nitrooxy-organosulfates respectively.

Aliphatic OSs represented at least 78% of the tentatively determined OSs in the three megacity summer samples, while there was much less aromatic OSs. Comparison of the molecular formula, number of isomers, average molecular weight, and degrees of saturation and oxidation suggests that OSs in aerosol samples from NJ and SH shared more similarities.

Major OSs in these ambient samples could be derived from biogenic precursors (isoprene, monoterpenes, and sesquiterpenes), but also from PAHs. Isoprene appeared to be most likely one of the important precursors in the three megacities, and the influence of NO_x level on the nature of isoprene-derived OSs is consistent with the literature. Clearly, the identity, precursors, and formation mechanisms of many OSs have yet to be positively elucidated. The systematic use of chromatographic separation prior to MS detection appears essential given the variety of the precursors and the resulting isomers.

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Table 1. Summary of sampling location, sampling time, Molecular Weight (MW), Double Bond Equivalents (DBE), and Elemental Ratios (arithmetic mean ± standard deviation) of tentatively assigned CHOS and CHONS.

Location	Sample ID	Sampling time	Number of formulas (CHOS/CHONS)	CHOS [a]				CHONS [b]			
				MW	DBE	(o-3s)/c [c]	H/C [d]	MW	DBE	(o-3s-2n)/c [e]	H/C
Wuhan	WHW	9:00 a.m., Jan. 26 - 9:00 a.m., Jan 27, 2012	149/43	266.6±57.2	2.56±2.60	0.37±0.25	1.68±0.44	311.0±60.5	3.61±2.57	0.35±0.13	1.58±0.46
	WHS	8:30 a.m., Jun. 15 - 8:30 a.m., Jun. 16, 2012	213/55	287.9±60.8	2.16±1.64	0.39±0.23	1.75±0.36	318.1±53.8	2.98±1.52	0.40±0.17	1.69±0.34
Nanjing	NJSD	7:30 a.m. - 7:30 p.m., Aug. 29, 2012	139/54	288.9±67.9	1.82±1.32	0.39±0.25	1.83±0.27	313.6±48.2	2.56±1.08	0.44±0.21	1.79±0.23
	NJSN	7:30 p.m., Aug. 29 - 7:30 a.m., Aug. 30, 2012	160/72	294.0±97.3	3.21±3.84	0.46±0.34	1.65±0.45	335.2±74.3	3.46±2.30	0.43±0.20	1.66±0.37
	NJSD+NJSN	Combination [f]	205/83	304.8±93.5	3.00±3.47	0.43±0.32	1.68±0.41	332.5±70.7	3.28±2.21	0.44±0.21	1.69±0.35
Shanghai	SHWD	7:30 a.m. - 7:30 p.m., Jan. 17, 2013	125/32	274.3±81.1	2.38±2.56	0.39±0.31	1.72±0.46	328.7±132.2	4.22±3.95	0.44±0.33	1.53±0.57
	SHWN	7:30 p.m., Jan. 17 - 7:30 a.m., Jan. 18, 2013	159/54	270.0±71.1	2.54±2.39	0.40±0.29	1.69±0.44	303.9±51.9	2.98±2.50	0.38±0.17	1.71±0.46
	SHWD+SHWN	Combination [f]	168/59	277.2±71.2	2.63±2.59	0.40±0.29	1.68±0.46	325.8±92.0	3.59±3.50	0.42±0.27	1.64±0.52
	SHSD	8:00 a.m. - 8:00 p.m., Jul. 28, 2013	165/40	296.4±84.7	2.76±2.66	0.47±0.32	1.68±0.42	348.2±115.4	4.03±3.48	0.61±0.43	1.55±0.52
	SHSN	8:00 p.m., Jul. 28 - 8:00 a.m., Jul. 29, 2013.	122/51	278.1±73.9	2.36±2.48	0.48±0.29	1.74±0.40	319.2±73.0	3.26±2.93	0.45±0.22	1.69±0.44
	SHSD+SHSN	Combination [f]	168/58	296.3±84.7	2.77±2.65	0.47±0.31	1.68±0.42	337.6±102.2	3.52±3.04	0.53±0.38	1.64±0.47

[a] Molecules with (o-4s)/c<0 were not included.

[b] Molecules with (o-4s-3n)/c<0 were not included.

[c] (o-3s)/c infers to the extent of oxidation for a CHOS molecule.

[d] H/C refers to the ratio between hydrogen atom and carbon atom in a molecule.

[e] (o-3s-2n)/c refers to the extent of oxidation for a CHONS molecule.

[f] Combination of two samples for a comparison purpose.

Figure Captions

Figure 1. Locations of Wuhan (WH), Nanjing (NJ), and Shanghai (SH) in China.

Figure 2. LC chromatograms of tentatively determined $C_5H_{10}O_5S_1$ (potentially from isoprene). A chromatogram for the NJSD sample is not included because a large amount of sample injection led to corruption of peaks and hence inaccurate retention times and worse peak resolution.

Figure 3. Mass spectra of detected CHOS and CHONS reconstructed from extracted ion chromatograms (UHPLC-Orbitrap MS analysis, negative ionization mode). X-axis corresponds to the molecular weight (Da) of identified species. The number of isomers for a given formula is marked by colors. A, neutral mass = 211.9993 Da, $C_5H_8O_7S_1$; B, neutral mass=216.0306 Da, $C_5H_{12}O_7S_1$; C, neutral mass=226.0150 Da, $C_6H_{10}O_7S_1$; D, neutral mass=240.0307 Da, $C_7H_{12}O_7S_1$; E, neutral mass=254.0827 Da, $C_9H_{18}O_6S_1$; F, neutral mass=261.0157 Da, $C_5H_{11}O_9N_1S_1$; G, neutral mass=268.0620 Da, $C_9H_{16}O_7S_1$; H, neutral mass=295.0729 Da, $C_{10}H_{17}O_7N_1S_1$; I, neutral mass=306.0007 Da, $C_5H_{10}O_{11}N_2S_1$; J, neutral mass=352.1922 Da, $C_{16}H_{32}O_6S_1$; K, neutral mass=363.1356 Da, $C_{15}H_{25}O_7N_1S_1$.

Figure 4. (a–c) CH_2-Kendrick diagrams and (d–e) Van Krevelen diagrams for CHOS. The color-coding indicates the DBE values calculated from Eq. 1. The molecular formula of the homologue series 1 to 15 can be written as $C_nH_{2n+2}SO_4$, $C_nH_{2n+2}O_1SO_4$, $C_nH_{2n}O_1SO_4$, $C_nH_{2n}O_2SO_4$, $C_nH_{2n-4}O_1SO_4$, $C_nH_{2n-2}O_2SO_4$, $C_nH_{2n}O_3SO_4$, $C_nH_{2n-4}O_2SO_4$, $C_nH_{2n-2}O_3SO_4$, $C_nH_{2n-4}O_3SO_4$, $C_nH_{2n-2}O_4SO_4$, $C_nH_{2n-4}O_4SO_4$, $C_nH_{2n-2}O_5SO_4$, $C_nH_{2n-4}O_5SO_4$, and $C_nH_{2n-4}O_6SO_4$, respectively (n>4).

Figure 5. (a–c) CH_2-Kendrick diagrams and (d–e) Van Krevelen diagrams for CHONS. The color-coding indicates the DBE values calculated from Eq 1. The molecular formula of the homologue series 1 to 10 can be written as $C_nH_{2n+1}NO_3SO_4$, $C_nH_{2n-1}NO_3SO_4$, $C_nH_{2n+1}ONO_3SO_4$, $C_nH_{2n-1}ONO_3SO_4$, $C_nH_{2n-1}O_2NO_3SO_4$, $C_nH_{2n-5}ONO_3SO_4$, $C_nH_{2n-3}O_2NO_3SO_4$, $C_nH_{2n-1}O_3NO_3SO_4$, $C_nH_{2n-3}O_3NO_3SO_4$, and $C_nH_{2n-3}O_4NO_3SO_4$, respectively (n>4).

Figure 6. Number of C atoms of CHOS and CHONS as a function of molecular weight in the Shanghai samples. Note that only compounds with a relative abundance greater than or equal to 0.5% of that of $C_{10}H_{17}O_7N_1S_1$ in the SHSN sample are shown in this figure.

Figure 7. Relative abundance distributions of CHOS and CHONS in the Shanghai samples. Note that only compounds with a relative abundance greater than or equal to 0.5% of that of $C_{10}H_{17}O_7N_1S_1$ in the SHSN sample are shown in this figure.

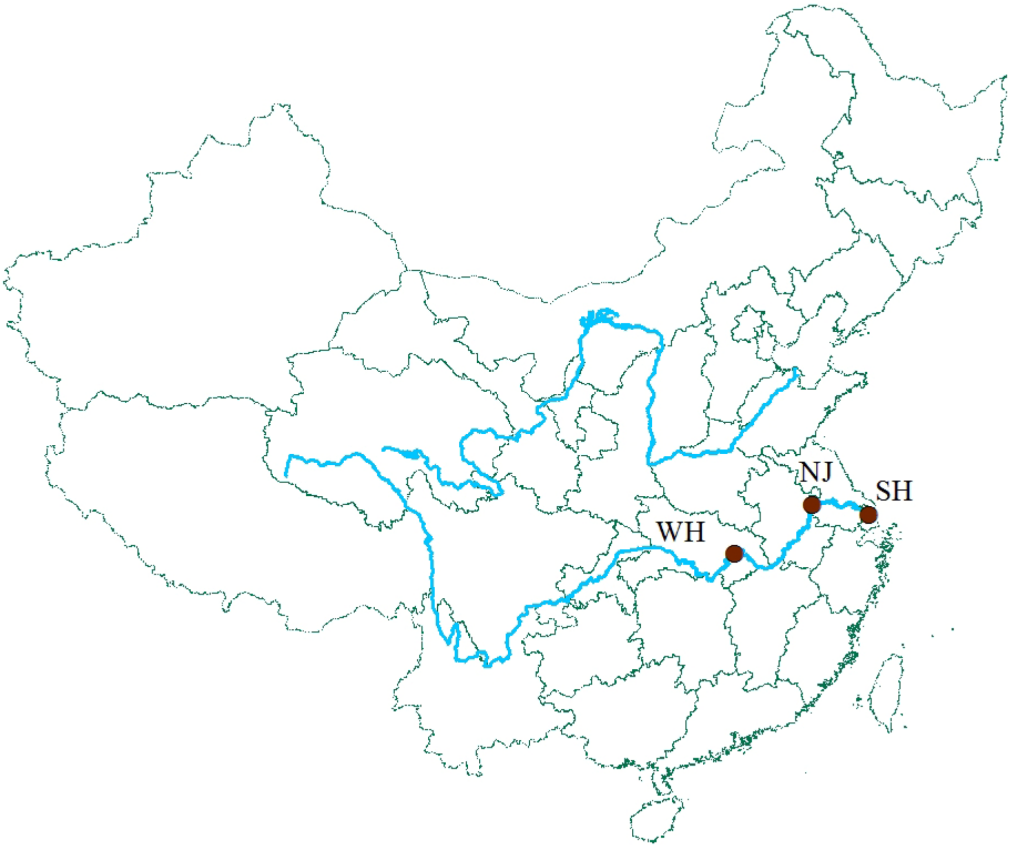


Figure 1

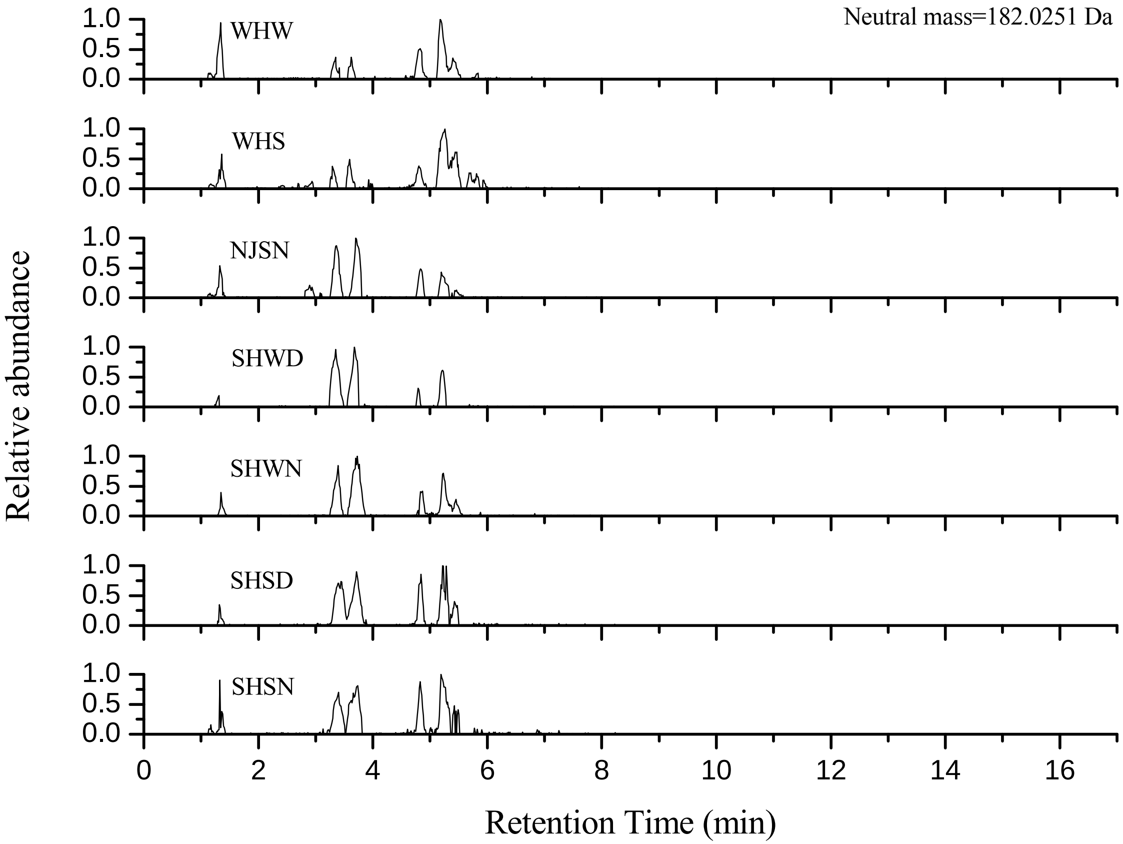
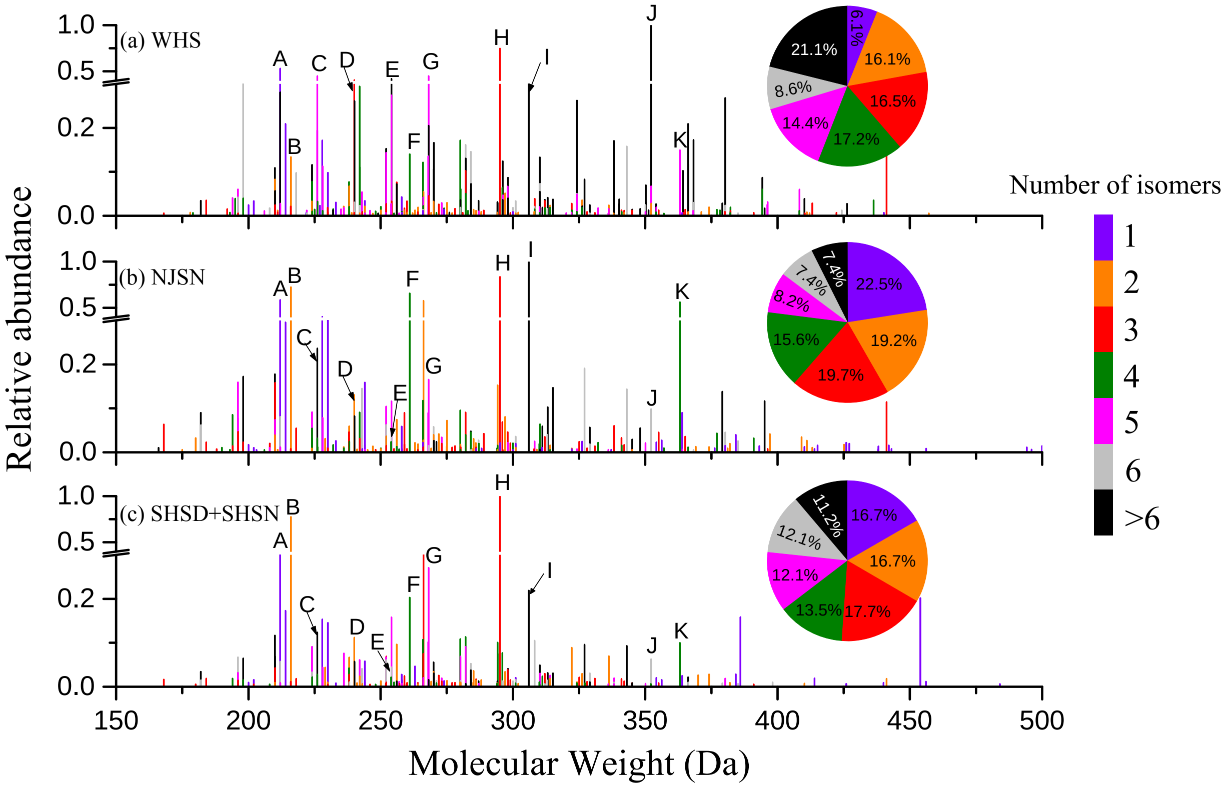

Neutral mass=182.0251 Da
WHW
WHS
NJSN
SHWD
SHWN
SHSD
SHSN
1.0
0.5
0.0
Relative abundance
0
2
4
6
8
10
12
14
16
Retention Time (min)

Figure 2



1.0
0.5
0.2
0.0
(a) WHS
A
B
C
D
E
F
G
H
I
J
K
6.1%
16.1%
16.5%
17.2%
14.4%
8.6%
21.1%
(b) NJSN
22.5%
19.2%
19.7%
15.6%
8.2%
7.4%
7.4%
(c) SHSD+SHSN
16.7%
16.7%
17.7%
13.5%
12.1%
12.1%
11.2%
Relative abundance
150
200
250
300
350
400
450
500
Molecular Weight (Da)
Number of isomers
1
2
3
4
5
6
>6

Figure 3

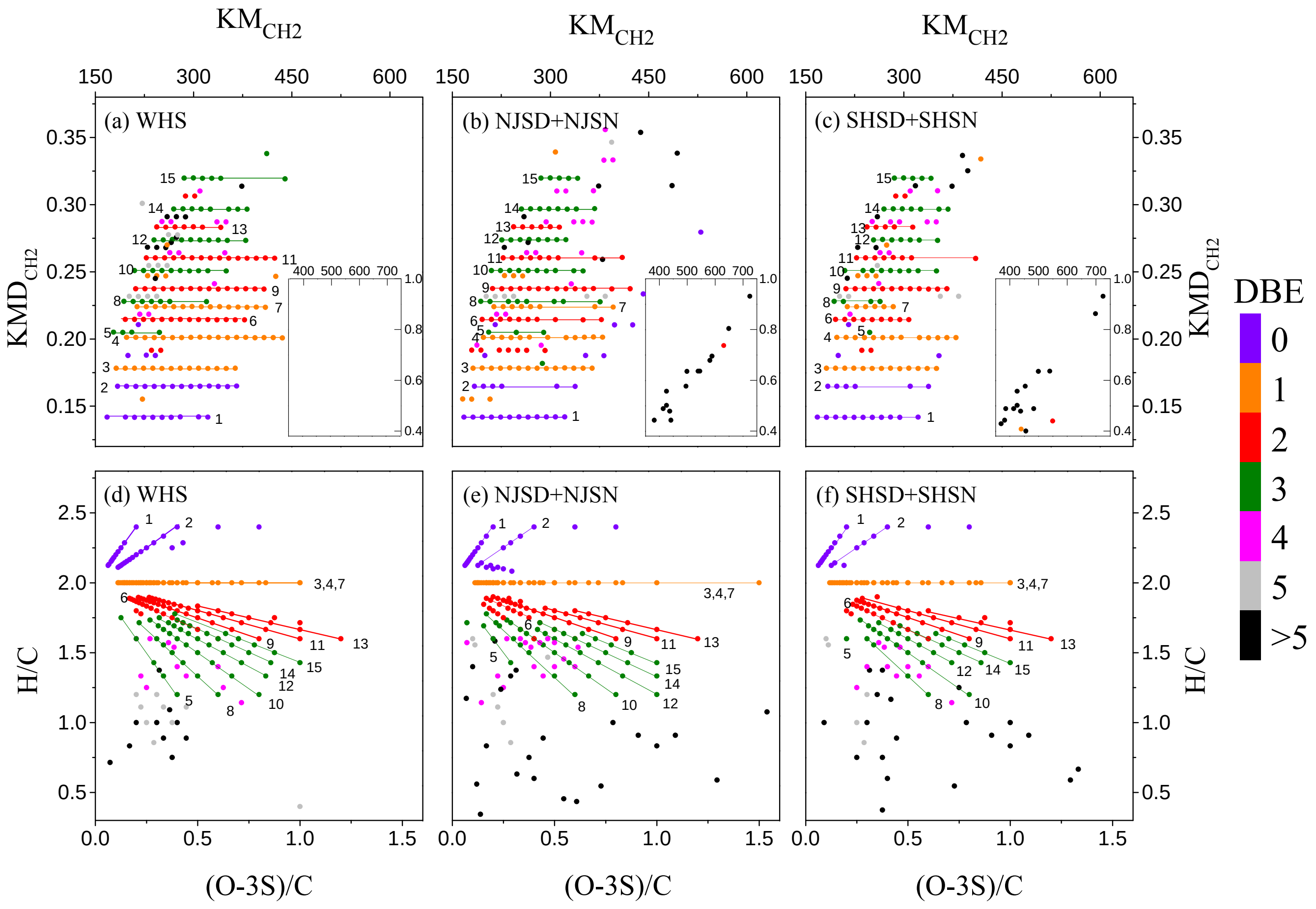

KM$_{CH2}$
150
300
450
600
(a) WHS
(b) NJSD+NJSN
(c) SHSD+SHSN
KMD$_{CH2}$
0.35
0.30
0.25
0.20
0.15
400 500 600 700
1.0
0.8
0.6
0.4
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
(d) WHS
(e) NJSD+NJSN
(f) SHSD+SHSN
H/C
2.5
2.0
1.5
1.0
0.5
3,4,7
0.0
0.5
1.0
1.5
(O-3S)/C
DBE
0
1
2
3
4
5
>5

Figure 4

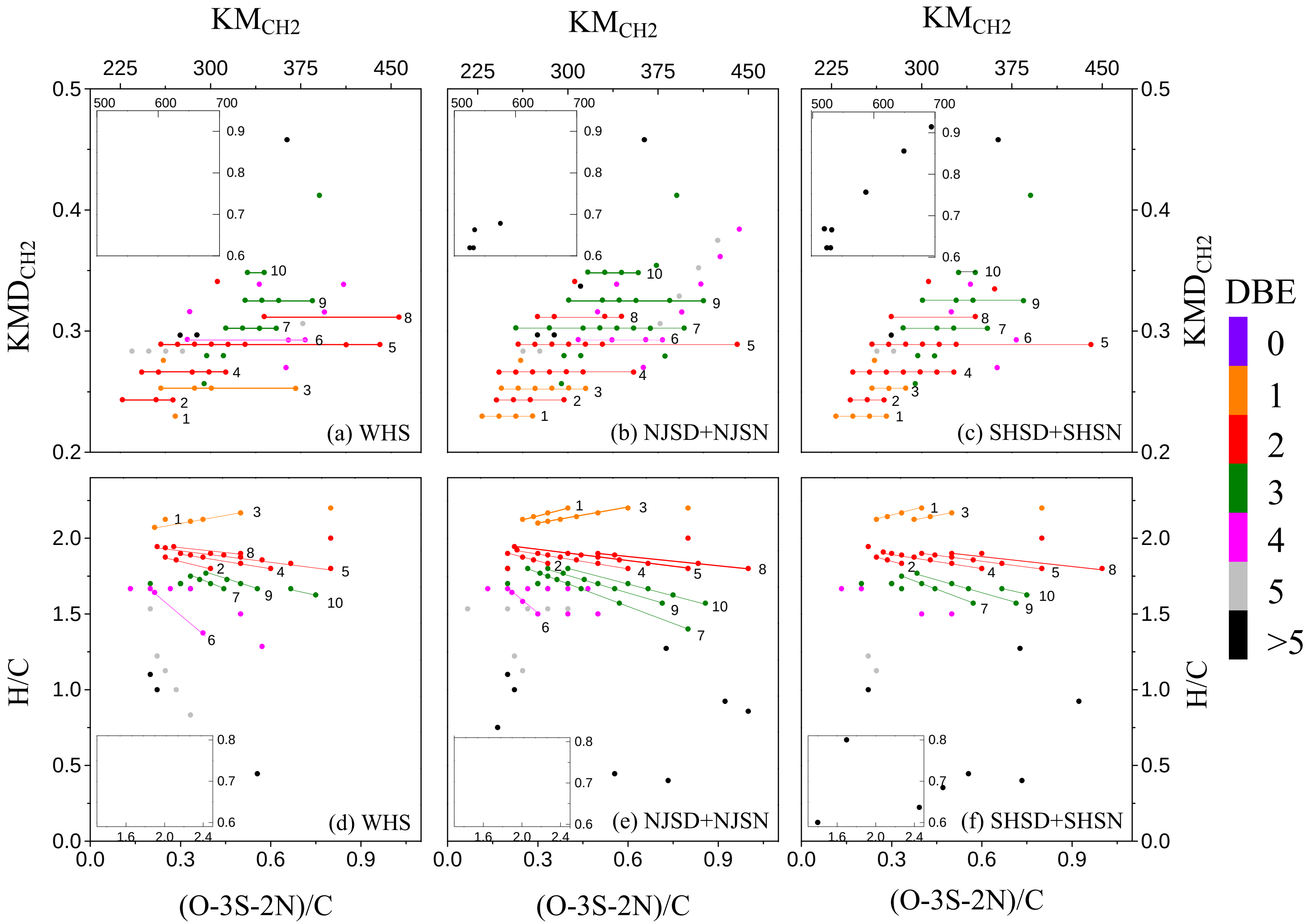

KM$_{CH2}$
225
300
375
450
KMD$_{CH2}$
0.2
0.3
0.4
0.5
500
600
700
0.6
0.7
0.8
0.9
(a) WHS
(b) NJSD+NJSN
(c) SHSD+SHSN
(d) WHS
(e) NJSD+NJSN
(f) SHSD+SHSN
H/C
0.0
0.5
1.0
1.5
2.0
1.6
2.0
2.4
(O-3S-2N)/C
0.0
0.3
0.6
0.9
1
2
3
4
5
6
7
8
9
10
DBE
0
1
2
3
4
5
>5

Figure 5

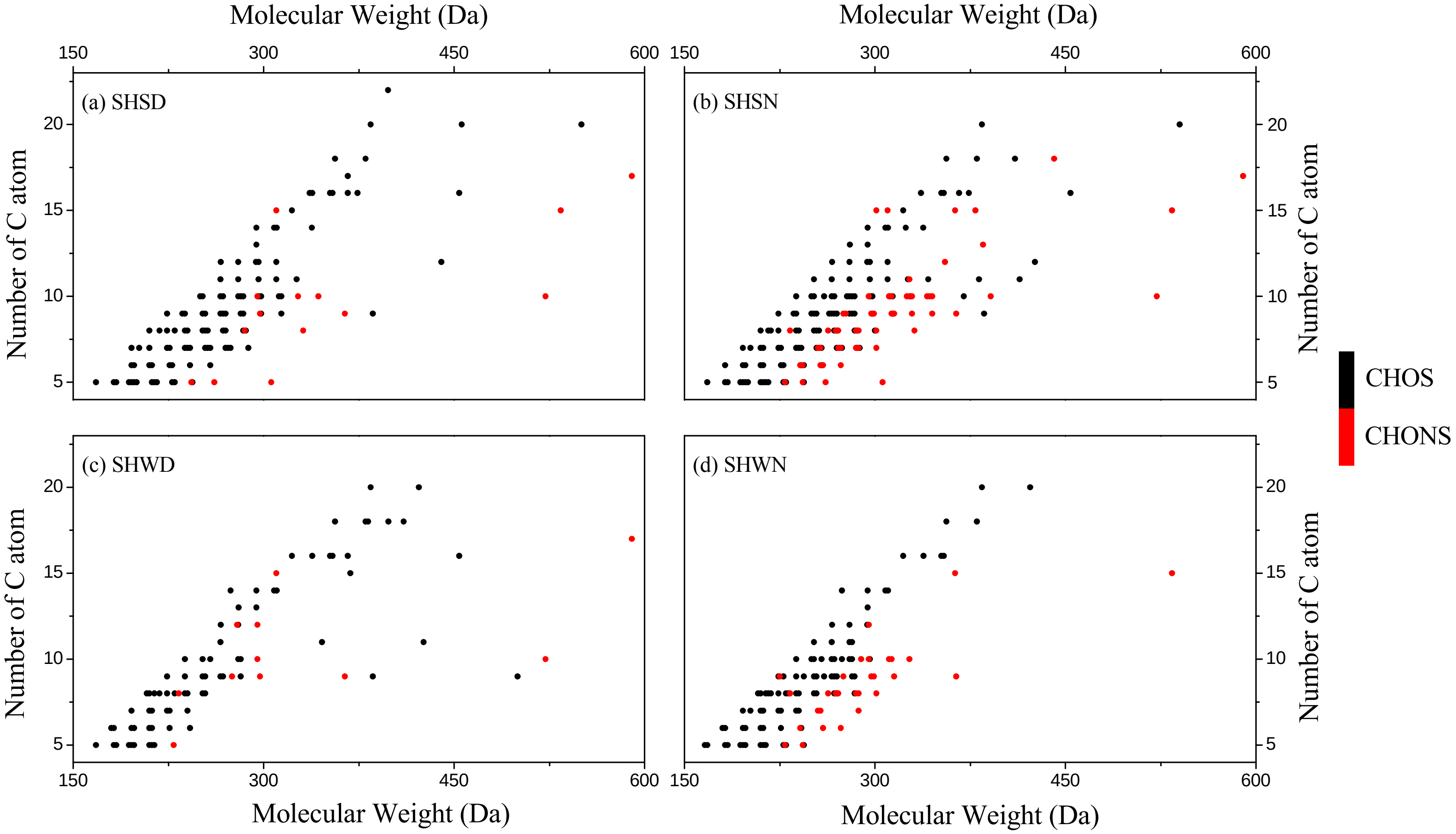

Molecular Weight (Da)
150
300
450
600
(a) SHSD
(b) SHSN
(c) SHWD
(d) SHWN
Number of C atom
5
10
15
20
CHOS
CHONS

Figure 6

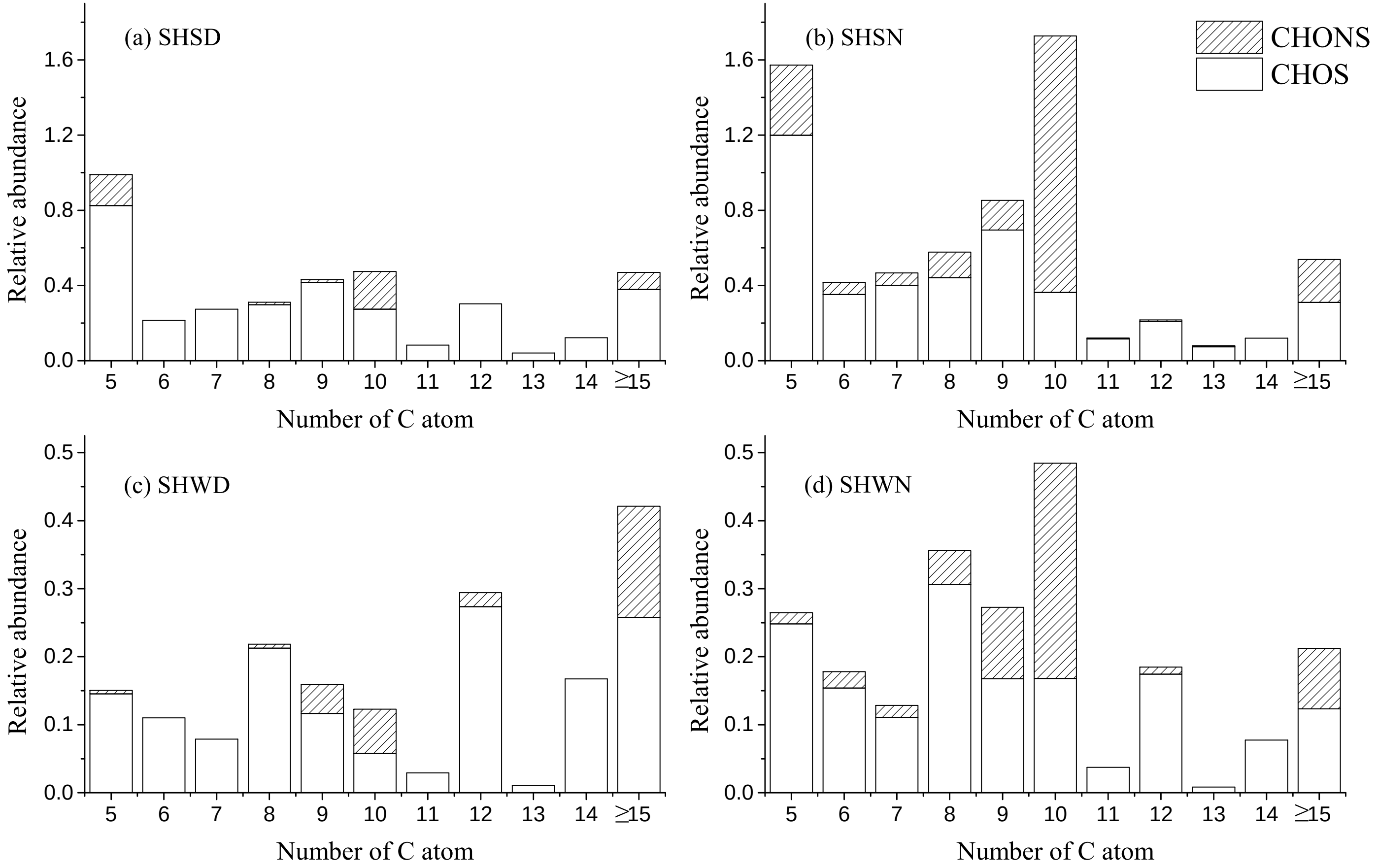

(a) SHSD
(b) SHSN
(c) SHWD
(d) SHWN
CHONS
CHOS
Relative abundance
Number of C atom
0.0
0.4
0.8
1.2
1.6
0.1
0.2
0.3
0.4
0.5
5
6
7
8
9
10
11
12
13
14
≥15

Figure 7

Supplement for

Molecular Characterization of Atmospheric Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River

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This supplementary information document contains three figures and five tables, totaling 42 pages.

Table S1. A comparison of air quality and meteorological conditions (arithmetic mean ± standard deviation) between the SH sampling days and the seasonal average.

Time	Air quality [a]						Meteorological conditions [b]		
	$PM_{2.5}$ $\mu g\ m^{-3}$	PM_{10} $\mu g\ m^{-3}$	O_3 $\mu g\ m^{-3}$	SO_2 $\mu g\ m^{-3}$	NO_2 $\mu g\ m^{-3}$	CO $mg\ m^{-3}$	Wind speed $m\ s^{-1}$	Temperature ℃	Relative humidity %
28 - 29 Jul, 2013	52.5	75.0	184.5	19.0	38.5	0.69	1.7±0.8	34.8±2.2	49.4±8.3
1 Jun - 31 Aug, 2013	43.4±24.5	59.9±26.1	136.0±58.0	14.6±5.2	34.0±11.7	0.67±0.16	2.5±1.2	28.7±5.1	70.1±16.0
17 - 18 Jan, 2013	77.0	90.5	68.0	32.5	57.5	1.01	2.9±1.8	0.9±1.1	58.3±3.2
26 Dec, 2012 –28 Feb, 2013	78.4±48.1	84.4±46.6	72.0±23.1	27.5±15.0	54.7±21.5	0.99±0.40	2.3±1.1	5.8±3.9	71±16.5

[a] Arithmetic mean of 24h average concentrations

[b] Arithmetic mean of hourly average concentrations

Extraction efficiency and repeatability of the extraction protocol ~~— Protocol~~

5 µL of a 200 µM solution of methyl sulfate, octyl sulfate, dodecyl sulfate and camphor sulfonic acid, were deposited on a quartz filter that was then extracted and analyzed as described in the main text. Three replicates were performed. The average chromatographic peak area obtained for each compound was compared to the average value obtained for three injections of a 1 µM standard solution (1µM being the theoretical final concentration of the extract) to assess the extraction efficiencies. The repeatabilities were determined as the standard deviation obtained from the injection of the three replicates. LOD were estimated from calibration curves (0 to 2 µM) as $3.3*(\sigma_{slope}/a)$ with a the slope of the calibration curve and σ_{slope} standard deviation on the slope. They are reported in Table S2.

Table S2. Extraction efficiencies and repeatabilities of the extraction protocol and estimated limits of detection.~~.~~

	Standard solution		Filter extract		Ext. Eff.	Estimated LOD (ng)
	Average area	Std. Dev.	Average area	Std. Dev.		
Methyl sulfate	4.6 108	1.6%	3.3 108	5.6%	71.4%	0.019
Octyl sulfate	3.2 1011	2.4%	3.0 1011	2.3%	95.0%	0.012
Dodecyl sulfate	5.9 1011	2.3%	5.7 1011	3.1%	97.7%	0.24*
Camphor sulfonic acid	1.3 1011	0.9%	1.2 1011	1.7%	94.0%	0.032

* High LOD due to the presence of dodecyl sulfate in the blank analysis.

Table S3. List of tentatively assigned OSs. Below are OSs and nitrooxy-OSs with an arbitrary intensity larger than 0.5% of the most abundant one in the same sample. Data for the NJSD sample is not included because a large amount of sample injection led to corruption of peaks and hence inaccurate retention times and worse peak resolution.

Neutral mass	Formula	Number of isomers	Retention times (min)	Sample ID	Potential precursor	Ref.
166.0301	$C_5H_{10}O_4S_1$	8	1.45	NJSN, SHWN	Isoprene	Szmigielski, 2015
			4.68; 4.85; 5.59; 5.82; 6.11; 7.58	NJSN, SHWD, SHWN		
			7.44	SHWD, SHWN		
168.0458	$C_5H_{12}O_4S_1$	3	6.18; 6.41; 6.78	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
177.9937	$C_5H_6O_5S_1$	3	2.95; 3.37	WHS, SHWN		
			1.31	SHWN		
180.0458	$C_6H_{12}O_4S_1$	3	6.48; 6.66	NJSN, WHW, SHWD, SHWN		
			8.31	WHW, SHWD, SHWN		
182.0251	$C_5H_{10}O_5S_1$	11	1.15	WHW, WHS, NJSN, SHSN	Isoprene	Riva et al., 2015a
			1.33; 3.35; 3.63; 4.85; 5.26	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			2.94	WHS, NJSH		
			5.40	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
			5.48; 5.98	WHS		
			5.89	WHW, WHS		
182.0615	$C_6H_{14}O_4S_1$	6	6.86; 7.05; 7.23; 7.44; 7.56; 7.65	WHW, NJSN, SHWD, SHWN, SHSD, SHSN		
184.0407	$C_5H_{12}O_5S_1$	3	3.62; 4.57; 4.97	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
188.0145[p]	$C_7H_8O_4S_1$	4	5.40; 6.61	NJSN, SHWN	2-methylnaphthalene	Riva et al., 2015b
			6.60	SHWN		
			4.80	NJSN		
189.9939	$C_6H_6O_5S_1$	3	1.25; 4.26; 5.84	WHW		

192.0095	$C_6H_8O_5S_1$	4	1.38	WHW		
			4.65; 4.93; 5.14	WHS, WHW		
193.9886	$C_5H_6O_6S_1$	5	1.15	WHW, WHS, SHWD, SHWN		
			1.33; 3.38; 4.34; 4.76	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
194.0250	$C_6H_{10}O_5S_1$	4	4.92; 5.31; 5.86	NJSN, SHWD, SHWN		
			6.09	SHWD,SHWN		
194.0614	$C_7H_{14}O_4S_1$	7	5.17	SHWD		
			5.28; 6.09; 6.93; 8.98	SHWD, SHWN		
			7.94; 8.21	SHWN		
196.0043	$C_5H_8O_6S_1$	5	1.34; 3.68; 4.69; 5.40	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			6.18	WHS, NJSN, SHWN, SHSN		
196.0407	$C_6H_{12}O_5S_1$	6	2.82	WHW, WHS, NJSN, SHWD, SHWN, SHSN		
			1.34; 5.18; 5.44 6.05	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			7.05	WHW, WHS, SHWN, SHSN		
196.0771	$C_7H_{16}O_4S_1$	3	8.00; 7.79; 8.42	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
198.0200	$C_5H_{10}O_6S_1$	7	1.34; 4.10; 4.74; 5.13; 5.30; 6.10	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	Isoprene	Riva et al., 2015a
			5.84	NJSN, SHWD, SHWN, SHSD, SHSN		
198.0564	$C_6H_{14}O_5S_1$	4	5.89; 5.19; 6.06	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			6.19	WHW, WHS, SHWD, SHWN, SHSD, SHSN		
200.0146^{p}	$C_8H_8O_4S_1$	5	5.40; 5.51; 5.89; 6.98; 7.95	SHWN	2-methylnaphthalene	Riva et al., 2015b

200.0357	$C_5H_{12}O_6S_1$	1	1.36	WHW, WHS, NJSN, SHWN, SHSD, SHSN	Isoprene	Riva et al., 2015a
201.9938 ^{p}	$C_7H_6O_5S_1$	1	4.56	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	2-methylnaphthalene	Riva et al., 2015b
204.0096	$C_7H_8O_5S_1$	3	5.28; 6.94; 7.31	WHW		
206.0251	$C_7H_{10}O_5S_1$	5	4.81	WHS		
			5.19; 5.70; 5.85; 6.11	WHS, NJSN		
208.0043	$C_6H_8O_6S_1$	6	1.97	WHW, WHS, SHWD		
			1.34; 2.21; 4.53; 5.78	WHW, WHS, NJSN, SHWD, SHWN, SHSD		
			6.22	WHW, NJSN, WHS		
208.0771	$C_8H_{16}O_4S_1$	5	7.18	WHW, NJSN, SHWD		
			6.93	WHW, SHWD, SHWN		
			7.73; 8.34	WHW, NJSN, SHWD, SHWN		
			10.33	WHW		
209.9836	$C_5H_6O_7S_1$	2	0.98; 1.33	WHW, WHS, NJSN, SHWD, SHWN, SHSN		
210.0200	$C_6H_{10}O_6S_1$	8	1.36; 3.92; 4.65; 4.99; 5.27; 5.53	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			5.70	WHS, SHSN		
			6.19	WHS, NJSN, SHWN, SHSD,SHSN		
210.0563	$C_7H_{14}O_5S_1$	7	5.39	WHW, WHS, NJSN, SHWD, SHWN, SHSN		
			5.92; 6.13; 6.35; 6.77	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			8.13; 8.52	WHW, WHS, SHSD, SHSN, SHWD		
210.0928	$C_8H_{18}O_4S_1$	3	8.48; 8.76; 9.09	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
211.9993	$C_5H_8O_7S_1$	1	1.36	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	Isoprene	Surratt et al., 2008
212.0356	$C_6H_{12}O_6S_1$	8	1.36; 5.24; 5.72; 6.06; 6.34	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		

			6.78	WHW, NJSN, SHWD, SHWN, SHSD, SHSN		
			7.01; 7.15	WHS, SHWD, SHWN		
212.0721	$C_7H_{16}O_5S_1$	5	5.59; 5.80; 6.48; 6.95; 7.10	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
213.9939	$C_8H_6O_5S_1$	1	5.86	WHW, SHWD, SHWN, SHSD		
214.0150	$C_5H_{10}O_7S_1$	1	1.34	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	Isoprene	Surratt et al., 2008
216.0095^p	$C_8H_8O_5S_1$	3	5.39; 5.76; 6.56	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	2-methylnaphthalene	Riva et al., 2015b
216.0306	$C_5H_{12}O_7S_1$	2	1.15; 1.29	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	Isoprene	Surratt et al., 2008
217.9888	$C_7H_6O_6S_1$	5	1.34; 5.05; 5.24; 5.65; 6.99	WHW		
218.0251	$C_8H_{10}O_5S_1$	6	5.19; 5.73; 5.98	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			6.30; 7.86	WHW, WHS, SHWN		
			8.16	WHW, WHS		
221.9470	$C_5H_2O_8S_1$	1	0.92	WHS		
222.0200	$C_7H_{10}O_6S_1$	5	1.36; 1.62; 1.95; 2.42; 4.76	WHW, WHS		
222.0928	$C_9H_{18}O_4S_1$	6	12.36	WHW, WHS, SHWD		
			7.66; 8.72; 10.46; 12.87	WHW, WHS, SHWD, SHWN		
			12.44	WHW, WHS		
223.9993	$C_6H_8O_7S_1$	2	1.14; 1.34	WHW, WHS, NJSN, SHWD, SHWN		
224.0357	$C_7H_{12}O_6S_1$	5	1.37	WHW, NJSN, SHWD, SHSN	α-pinene	Surratt et al., 2008
			2.65	WHW, WHS, NJSN, SHSN		
			3.19	WHW, WHS, NJSN, SHWD, SHSN		
			5.17; 5.93	WHW, WHS, NJSN,		

				SHWD, SHWN, SHSD, SHSN		
224.0720	$C_8H_{16}O_5S_1$	7	5.72; 5.95; 6.44; 7.60	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			9.21	WHW, WHS, SHWD, SHWN, SHSN		
			9.74	WHW, WHS, SHWN, SHSN		
			10.35	WHS		
224.1085	$C_9H_{20}O_4S_1$	4	9.00; 9.16; 9.37; 9.81	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
225.9785	$C_5H_6O_8S_1$	2	0.97	WHW, SHWD, SHWN		
			1.25	SHWN		
226.0150	$C_6H_{10}O_7S_1$	7	1.36; 2.72; 3.25; 4.57; 4.98	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	3-Z-Hexenal	Shalamzari et al., 2014
			6.41; 7.02	NJSN, SHWD, SHWN, SHSD, SHSN		
226.0514	$C_7H_{14}O_6S_1$	5	5.84; 6.10; 6.56; 7.19	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			8.01	WHS, SHWD, SHWN		
226.0878	$C_8H_{18}O_5S_1$	4	6.73; 7.47; 7.73; 7.86	WHW, WHS, NJSN, SHWD, SHWN, SHSD		
227.0102	$C_5H_9O_7N_1S_1$	1	1.15	WHW, WHS		
227.9943	$C_5H_8O_8S_1$	1	1.34	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	α-pinene	Surratt et al., 2008
228.0096^{p}	$C_9H_8O_5S_1$	4	5.80; 6.31; 6.69	WHW, SHWD, SHWN	2-methylnaphthalene	Riva et al., 2015b
			8.86	SHWD		
228.0306	$C_6H_{12}O_7S_1$	5	1.36; 1.97; 2.38; 2.87; 4.76	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	Isoprene	Riva et al., 2015a
228.0667	$C_7H_{16}O_6S_1$	4	5.57	WHS		
			4.97; 5.42; 5.76	WHS, SHWN		
229.0260	$C_5H_{11}O_7N_1S_1$	2	6.82; 7.22	WHW, NJSN, SHWD, SHWN, SHSD, SHSN		
229.9886^{p}	$C_8H_6O_6S_1$	4	3.49; 3.79	WHW, WHS	2-methylnaphthalene	Riva et al., 2015b
			5.68	WHW, SHWD, SHWN		

			6.57	WHW, WHS, NJSN, SHWD, SHWN, SHSD		
230.0098	$C_5H_{10}O_8S_1$	1	1.11	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
230.0251[p]	$C_9H_{10}O_5S_1$	3	5.94; 6.17; 6.40	WHW, WHS, NJSN, SHWD, SHWN	2-methylnaphthalene	Riva et al., 2015b
232.0044	$C_8H_8O_6S_1$	7	6.84	WHW, WHS		
			5.74; 6.10; 6.31; 7.29	WHW, WHS, SHWD, SHWN		
			5.30; 7.86	WHW, WHS, SHWN		
232.0407	$C_9H_{12}O_5S_1$	4	6.30	WHS, NJSN, SHWD	2-methylnaphthalene	Riva et al., 2015b
			6.41; 6.61; 6.82	WHS, NJSN, SHWD, SHWN		
232.0772	$C_{10}H_{16}O_4S_1$	1	6.86	WHW		
234.9789	$C_6H_5O_7N_1S_1$	5	1.36	WHW, WHS, SHWD		
			5.61; 6.74; 7.11; 7.27	WHW, WHS, SHWD, SHWN		
236.0357	$C_8H_{12}O_6S_1$	2	4.98; 5.67	WHW, WHS, NJSN, SHWN		
236.0721	$C_9H_{16}O_5S_1$	5	5.73	WHW, WHS, SHWD, SHSD, SHSN		
			6.44; 7.35; 7.58; 7.91	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
238.0149	$C_7H_{10}O_7S_1$	4	1.36; 3.87; 4.81	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			5.55	WHW, WHS, SHWN, SHSD, SHSN		
238.0514	$C_8H_{14}O_6S_1$	2	5.24; 5.65	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	α-pinene	Surratt et al., 2008
238.0877	$C_9H_{18}O_5S_1$	4	6.52; 7.23; 9.12	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			10.18	WHW, WHS		
238.1242	$C_{10}H_{22}O_4S_1$	4	9.57; 9.88; 10.10; 10.61	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
239.9942	$C_6H_8O_8S_1$	3	1.15; 5.10; 5.20	WHS		
240.0307	$C_7H_{12}O_7S_1$	3	4.84; 5.27	WHW, WHS, NJSN,	Limonene	Surratt et

				SHWD, SHWN, SHSD, SHSN	al., 2008
			6.64	WHS	
240.0671	$C_8H_{16}O_6S_1$	11	4.92; 5.47; 6.35; 6.52; 6.84; 7.29; 7.91; 8.17	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	
			8.27	WHS, SHWN, SHSD, SHSN	
			8.81	WHS	
			9.72	WHW, WHS, SHWD	
240.1034	$C_9H_{20}O_5S_1$	6	6.68; 7.39; 8.01; 8.41; 8.54	WHS, SHWD, SHWN	
			7.92	WHS, SHWN	
241.0259	$C_6H_{11}O_7N_1S_1$	2	7.22; 7.32	NJSN, SHWD, SHWN, SHSN	
242.0099	$C_6H_{10}O_8S_1$	5	1.28	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	
			4.84; 5.43	WHW, WHS, NJSN, SHWN, SHSD, SHSN	
			5.73	SHSD, SHSN	
			5.85	WHW, WHS, NJSN, SHWD, SHSD, SHSN	
242.0251	$C_{10}H_{10}O_5S_1$	3	6.64	SHWN	
			5.90; 6.89	WHS, SHWN	
242.0463	$C_7H_{14}O_7S_1$	4	1.36; 4.97; 5.84	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	
			6.05	WHS, SHSN	
242.0826	$C_8H_{18}O_6S_1$	6	5.05; 5.53; 6.22; 6.47; 6.69; 7.10	WHS, SHWN, WHW	
243.0052	$C_5H_9O_8N_1S_1$	6	1.12	WHW, WHS, NJSN, SHWN, SHSN	
			5.40	WHW, WHS, NJSN, SHWN, SHSD, SHSN	
			5.63; 6.18; 6.80	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	
			6.03	NJSN, SHSN	
243.0416	$C_6H_{13}O_7N_1S_1$	2	7.50	NJSN, SHWN, SHSN	

			8.07	SHWN, SHSN		
243.9890	$C_5H_8O_9S_1$	1	1.05	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
244.0044	$C_9H_8O_6S_1$	4	5.14; 5.55; 6.86; 7.10	WHW, WHS, SHWD, SHWN		
244.0254	$C_6H_{12}O_8S_1$	2	1.34	WHW, WHS, NJSN, SHSD, SHWN, SHSN		
			1.80	WHS, SHSN		
244.0407	$C_{10}H_{12}O_5S_1$	6	6.59; 6.89; 6.97; 7.03; 7.20	WHS, NJSN, SHWN		
			6.06	SHWN		
245.0207	$C_5H_{11}O_8N_1S_1$	2	5.74; 5.95	NJSN	Isoprene	Surratt et al., 2008
246.0200	$C_9H_{10}O_6S_1$	5	5.52; 6.27; 6.39; 6.69; 6.88	WHS, SHWN		
246.0565	$C_{10}H_{14}O_5S_1$	3	6.28; 7.23; 8.95	WHW		
248.0357	$C_9H_{12}O_6S_1$	4	5.17; 5.34; 5.70	WHW, SHWN		
			8.21	WHW		
248.0721	$C_{10}H_{16}O_5S_1$	4	5.88	WHW, WHS	α-pinene	Surratt et al., 2008
			6.30; 6.91; 7.49	WHW, WHS, NJSN, SHWN, SHSD		
248.9945	$C_7H_7O_7N_1S_1$	7	4.95; 6.59; 6.93; 7.05; 7.75; 8.38	WHW, WHS		
			5.59	WHW		
250.0514	$C_9H_{14}O_6S_1$	2	5.22; 6.17	WHW, WHS, NJSN, SHSD, SHSN	Limonene; Terpinolene	Surratt et al., 2008
250.0877	$C_{10}H_{18}O_5S_1$	5	6.34; 6.70; 7.03; 7.23	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	α-pinene; β-pinene; Terpinolene	Surratt et al., 2008
			5.27	WHW		
250.1243	$C_{11}H_{22}O_4S_1$	1	8.93	SHWD, SHWN		
251.9940	$C_7H_8O_8S_1$	5	5.01; 5.49	WHS		
			1.36; 2.39; 4.88	WHS, SHSD		
252.0306	$C_8H_{12}O_7S_1$	5	1.34; 1.85; 4.80; 5.53; 6.24	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	Isoprene	Schindelka et al., 2013

252.0670	$C_9H_{16}O_6S_1$	7	5.98; 6.24; 7.61; 7.96; 8.08	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	Limonene; β-caryophyllene	Chan et al., 2011
			4.90	WHW, WHS, NJSN, SHWD, SHWN, SHSN		
			10.26	WHW, WHS		
252.1035	$C_{10}H_{20}O_5S_1$	3	7.86	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			8.93	WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			10.75	WHS, SHSD		
252.1399	$C_{11}H_{24}O_4S_1$	3	10.57; 10.91; 11.39	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
254.0099	$C_7H_{10}O_8S_1$	5	1.36; 2.63; 4.97; 5.55	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			6.02	WHS		
254.0463	$C_8H_{14}O_7S_1$	5	1.34	WHW, WHS, NJSN, SHWD, SHSD, SHSN	Isoprene; α-terpinene	Schindelka et al., 2013; Surratt et al., 2008
			5.13; 5.35; 5.55; 6.15	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
254.0827	$C_9H_{18}O_6S_1$	8	5.52; 6.89; 7.16; 7.50; 7.96; 8.56	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			8.99; 9.59	WHW, WHS, SHWN		
254.1190	$C_{10}H_{22}O_5S_1$	3	8.69; 8.80; 9.07	WHS		
255.0414	$C_7H_{13}O_7N_1S_1$	4	1.34	WHW, WHS, SHWD, SHSN		
			7.47; 7.71; 7.92	WHW, WHS, NJSN, SHWD, SHWN, SHSN		
256.0256	$C_7H_{12}O_8S_1$	3	1.36; 4.85	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
			5.95	WHS		
256.0618	$C_8H_{16}O_7S_1$	7	3.29	WHW, WHS, SHSD, SHSN		
			3.85	WHW, WHS, NJSN, SHSD, SHSN		
			5.53; 5.80; 6.34	WHW, WHS, NJSN, SHWD, SHWN, SHSD,		

				SHSN		
			6.55	WHS, SHSD, SHSN		
			6.81	WHW, WHS, SHWN, SHSD, SHSN		
256.9845	$C_5H_7O_9N_1S_1$	1	6.49	NJSN		
257.0208	$C_6H_{11}O_8N_1S_1$	5	1.15	WHS, SHWN, SHSN		
			6.15; 6.43; 7.05; 7.23	WHS, NJSN, SHWN, SHSN		
257.0572	$C_7H_{15}O_7N_1S_1$	3	8.17; 8.35	SHWD, SHWN, SHSN		
			8.56	SHWN, SHSN		
258.0048	$C_6H_{10}O_9S_1$	1	1.34	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
258.0201	$C_{10}H_{10}O_6S_1$	5	4.94; 5.95; 6.70; 6.85	WHW, WHS, SHWD, SHWN, SHSD	naphthalene	Riva et al., 2015b
			5.45	WHW, SHWD, SHWN, SHSD		
258.0412	$C_7H_{14}O_8S_1$	1	1.34	WHS, NJSN, SHSD, SHSN		
259.0000	$C_5H_9O_9N_1S_1$	3	4.43; 5.14	WHS, NJSN, SHSD		
			5.81	NJSN, SHSD		
259.0364	$C_6H_{13}O_8N_1S_1$	3	5.84; 6.05; 6.55	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
259.9993	$C_9H_8O_7S_1$	3	5.56; 5.94; 6.18	WHW, WHS, NJSN, SHWD, SHWN, SHSD		
260.0203	$C_6H_{12}O_9S_1$	2	1.02; 1.16	WHS		
260.0357	$C_{10}H_{12}O_6S_1$	2	6.86; 7.28	WHS, SHSN		
261.0157	$C_5H_{11}O_9N_1S_1$	4	2.46; 2.94; 3.53; 4.43	WHS, NJSN, SHWN, SHSD, SHSN	Isoprene	Surratt et al., 2008
262.0149	$C_9H_{10}O_7S_1$	2	5.03; 5.39	WHS		
262.0513	$C_{10}H_{14}O_6S_1$	5	6.03; 6.22; 6.47; 6.84	WHW, SHSD		
			9.00	WHW		
263.0102	$C_8H_9O_7N_1S_1$	4	7.37	WHW, WHS, NJSN, SHWN		
			7.99	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			7.65; 8.60	WHW		
264.0306	$C_9H_{12}O_7S_1$	3	5.07; 6.07; 6.28	WHS, NJSN, SHSD, SHSN		
264.0670	$C_{10}H_{16}O_6S_1$	2	5.49; 6.60	WHW, WHS, NJSN, SHSD	β-pinene	Surratt et al., 2008

264.1034	$C_{11}H_{20}O_5S_1$	2	7.32; 7.83	WHW		
266.0099	$C_8H_{10}O_8S_1$	6	2.16	WHS		
			1.36; 5.14; 5.45; 5.60; 6.11	WHS, SHWN		
266.0252	$C_{12}H_{10}O_5S_1$	1	7.43	WHW, WHS, NJSN, SHWD, SHWN		
266.0462	$C_9H_{14}O_7S_1$	4	2.68; 5.51; 6.18; 6.56	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
266.0826	$C_{10}H_{18}O_6S_1$	5	6.24; 6.77; 6.93	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	α-pinene; α-terpinene; Terpinolene	Surratt et al., 2008
			8.80	WHS, SHSD, SHSN		
			9.37	WHS		
266.1190	$C_{11}H_{22}O_5S_1$	4	7.73	WHW, WHS, SHWD, SHWN, SHSD, SHSN		
			8.51; 8.90	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			12.27	WHS		
266.1554	$C_{12}H_{26}O_4S_1$	3	12.24; 12.54	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			16.75	SHWD, SHSN		
268.0253	$C_8H_{12}O_8S_1$	5	1.37; 4.93; 5.57	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			6.31	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
			6.55	WHW, WHS, NJSN, SHWD, SHWN, SHSN		
268.0620	$C_9H_{16}O_7S_1$	5	5.74; 6.30; 7.02	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	Isoprene; Limonene	Riva et al., 2015a
			7.47	WHW, WHS, NJSN, SHWD, SHSD, SHSN		
			7.74	WHS, NJSN, SHSN		
268.0983	$C_{10}H_{20}O_6S_1$	10	7.40; 7.62; 7.77; 8.12; 8.57; 9.21	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			8.30	WHS, SHWN, SHSD, SHSN		

			8.80	WHS, SHSD, SHSN
			9.70; 10.36	WHW, WHS, SHWN
268.1347	$C_{11}H_{24}O_5S_1$	3	9.20; 9.39; 9.77	WHS
269.0572	$C_8H_{15}O_7N_1S_1$	2	8.22; 8.61	WHW, WHS, NJSN, SHWD, SHWN, SHSN
270.0048	$C_7H_{10}O_9S_1$	2	1.36; 2.98	WHS, NJSN, SHWN, SHSD, SHSN
270.0411	$C_8H_{14}O_8S_1$	8	1.36; 4.85; 5.22; 5.39; 5.63; 7.28	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN
			1.79	WHW, WHS, SHWN, SHSD, SHSN
			6.39	WHS, SHWD, SHSD
270.0776	$C_9H_{18}O_7S_1$	9	4.93; 5.03; 5.49; 5.97; 6.10; 6.40; 6.91	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN
			7.33	WHW, WHS, SHSN
			7.60	WHW, WHS, NJSN, SHSN
271.0364	$C_7H_{13}O_8N_1S_1$	7	4.81	WHW, NJSN, SHWN, SHSN
			5.09	WHW, NJSN, SHSN
			5.28; 5.77	WHW, NJSN, SHWN, SHSN
			6.45	WHW, NJSN, SHWN
			6.56; 6.74	WHW, NJSN, SHWN, SHSD, SHSN
271.0729	$C_8H_{17}O_7N_1S_1$	4	8.46	WHW, WHS, SHWD, SHWN, SHSN
			8.60; 8.82; 9.19	WHW, WHS, SHWD, SHWN, SHSD, SHSN
272.0205	$C_7H_{12}O_9S_1$	3	2.50	WHW, WHS, SHSD
			1.36; 5.07	WHW, WHS, NJSN, SHWN, SHSD, SHSN
272.0357	$C_{11}H_{12}O_6S_1$	3	5.45; 5.99; 6.22	WHW, SHWN
273.0158	$C_6H_{11}O_9N_1S_1$	5	5.11; 5.89; 6.11; 6.59; 6.78	WHS, NJSN, SHWN, SHSD, SHSN
273.0522	$C_7H_{15}O_8N_1S_1$	3	6.13; 6.35; 6.86	NJSN, SHWN, SHSN

274.0150	$C_{10}H_{10}O_7S_1$	4	4.92; 5.42; 5.67; 6.64	WHW, WHS, SHWD, SHWN	naphthalene	Riva et al., 2015b
274.0303	$C_{14}H_{10}O_4S_1$	1	9.26	WHW, WHS, SHWD, SHWN		
274.0362	$C_7H_{14}O_9S_1$	1	1.36	SHSD, SHSN		
274.9951	$C_5H_9O_{10}N_1S_1$	2	2.72; 3.68	NJSN, SHSD		
275.0104	$C_9H_9O_7N_1S_1$	2	8.04; 8.31	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
276.0307	$C_{10}H_{12}O_7S_1$	7	5.10; 5.44; 5.70; 5.81; 6.02; 6.15; 6.39	WHS	naphthalene	Riva et al., 2015b
277.0259	$C_9H_{11}O_7N_1S_1$	4	6.05	NJSN, SHWN, SHSN		
			8.14	WHW		
			8.42; 8.61	WHW, WHS, NJSN, SHWN, SHSN		
278.0463	$C_{10}H_{14}O_7S_1$	3	5.18; 5.39; 5.78	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
280.0255	$C_9H_{12}O_8S_1$	2	5.09; 6.18	SHSD, SHSN		
280.0619	$C_{10}H_{16}O_7S_1$	4	5.44; 6.01; 6.35; 7.47	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	α-pinene; β-pinene; Limonene; α-terpinene; γ-terpinene	Surratt et al., 2008
280.0982	$C_{11}H_{20}O_6S_1$	7	6.69; 7.11; 7.56; 7.96	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			8.86	WHW, WHS, SHWN, SHSD, SHSN		
			9.09	WHW, WHS, SHWD, SHWN, SHSN		
			9.53	WHW WHS		
280.1347	$C_{12}H_{24}O_5S_1$	6	7.98;10.10	WHW, WHS, SHWD, SHWN, SHSD, SHSN		
			9.13; 9.63	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			10.66	WHS, SHSD		
			11.26	WHS		
280.1709	$C_{13}H_{28}O_4S_1$	4	12.36	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		

			13.08	WHW, WHS, NJSN, SHWD, SHWN, SHSN		
			13.69	WHS, NJSN, SHWD, SHWN		
			14.28	WHW, WHS, SHWD		
281.0207	$C_8H_{11}O_8N_1S_1$	3	1.37; 6.81; 7.11	WHS		
282.0412	$C_9H_{14}O_8S_1$	4	1.37	WHW, WHS, NJSN, SHWD, SHSD, SHSN		
			5.31; 6.52	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			7.12	WHW, WHS, SHWD, SHWN, SHSD, SHSN		
282.0776	$C_{10}H_{18}O_7S_1$	6	6.24; 6.52; 6.80; 7.06	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	α-pinene; β-pinene; Limonene; α-terpinene; Terpinolene	Surratt et al., 2008
			7.79	WHW, WHS, SHWD, SHWN, SHSD, SHSN		
			8.18	WHW, WHS		
282.1139	$C_{11}H_{22}O_6S_1$	11	6.45; 6.57; 7.86; 8.09; 8.35; 8.72; 9.00; 9.19	WHW, WHS, SHWD, SHWN, SHSD		
			9.87	WHW, WHS, SHWD, SHWN		
			10.46; 11.18	WHW, WHS		
282.1503	$C_{12}H_{26}O_5S_1$	4	8.52; 9.81; 10.14; 10.51	WHS		
283.0000	$C_7H_9O_9N_1S_1$	4	6.76	WHS		
			7.12	WHS, SHWN		
			7.48; 7.61	WHS, SHWD, SHWN		
283.0729	$C_9H_{17}O_7N_1S_1$	1	8.72	SHWD, SHWN		
284.0203	$C_8H_{12}O_9S_1$	9	1.36; 3.82; 4.68; 4.99; 5.39; 6.10	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			3.70	WHW, WHS, NJSN, SHSD, SHSN		
			3.91	WHW, WHS, SHSD, SHSN		
			5.94	WHW, WHS, NJSN		
284.0566	$C_9H_{16}O_8S_1$	6	5.31; 5.57; 5.88; 6.24	WHW, WHS, NJSN, SHWD, SHWN, SHSD,	α-terpinene	Surratt et al., 2008

				SHSN		
			6.59	WHS, SHSD		
			6.64	WHW, WHS, SHWN, SHSD, SHSN		
284.0932	$C_{10}H_{20}O_7S_1$	10	5.13; 5.99; 6.22; 6.64; 7.09; 7.41	WHW, WHS, NJSN, SHWN, SHSD, SHSN	β-pinene; Terpinolene	Surratt et al., 2008
			5.27	WHW, WHS, SHWN, SHSD, SHSN		
			8.16; 8.25	WHS, SHSD		
			8.00	WHS		
284.9946	$C_{10}H_7O_7N_1S_1$	3	5.51; 5.73; 9.34	WHW, SHWN		
285.0156	$C_7H_{11}O_9N_1S_1$	2	6.35	NJSN, SHSD, SHSN		
			7.06	NJSN, SHSN		
285.0522	$C_8H_{15}O_8N_1S_1$	2	6.99; 7.28	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
285.9997	$C_7H_{10}O_{10}S_1$	2	1.16;1.34	WHS, NJSN, SHSD, SHSN		
286.0360	$C_8H_{14}O_9S_1$	3	1.37; 3.12; 5.51	WHS, NJSN, SHSD, SHSN		
286.1242	$C_{14}H_{22}O_4S_1$	1	11.35	NJSN		
287.0313	$C_7H_{13}O_9N_1S_1$	7	5.59	WHW, WHS, NJSN, SHWN, SHSN		
			5.70; 6.07; 6.35; 6.52; 6.98	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			7.33	WHS, SHWN, SHSD, SHSN		
287.0677	$C_8H_{17}O_8N_1S_1$	5	8.30	WHS, SHWN, SHSN		
			6.99; 7.48; 8.13; 8.64	WHW, WHS, NJSN, SHWD, SHWN, SHSN		
288.0153	$C_7H_{12}O_{10}S_1$	2	1.16; 1.36	WHS, SHSD, SHSN		
288.0307	$C_{11}H_{12}O_7S_1$	2	7.23; 7.45	WHS	2-methylnaphthalene	Riva et al., 2015b
288.0459	$C_{15}H_{12}O_4S_1$	1	9.79	WHW, SHWN		
288.1399	$C_{14}H_{24}O_4S_1$	1	8.31	NJSN		
289.0259	$C_{10}H_{11}O_7N_1S_1$	5	5.94	WHW, SHWD, SHWN		
			6.36	WHW, SHWD		
			8.38; 8.60; 8.85	WHW, WHS, NJSN, SHWD, SHWN		
291.0417	$C_{10}H_{13}O_7N_1S_1$	4	6.53; 8.85;	WHW		

			8.98; 9.20			
292.1711	$C_{14}H_{28}O_4S_1$	1	12.54	WHW		
294.0412	$C_{10}H_{14}O_8S_1$	4	5.24; 5.99; 6.13; 7.24	NJSN, SHSD		
294.0777	$C_{11}H_{18}O_7S_1$	2	5.82; 6.36	WHS, NJSN, SHWN, SHSD		
294.1141	$C_{12}H_{22}O_6S_1$	9	6.91; 7.11; 7.35; 7.62; 7.78; 8.16; 8.61	WHW, WHS, SHWD, SHWN, SHSD, SHSN		
			9.03	WHS, SHSD		
			9.77	WHW, WHS, SHWD, SHSN		
294.1503	$C_{13}H_{26}O_5S_1$	7	8.42	WHW, WHS, SHWD		
			9.56; 9.82	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			10.39	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
			10.88	WHW, WHS, NJSN, SHWN, SHSD		
			11.19, 12.45	WHS		
294.1868	$C_{14}H_{30}O_4S_1$	4	9.43	WHW, NJSN, SHWD, SHWN, SHSD, SHSN		
			13.60	WHW, NJSN, SHWD, SHSD, SHSN		
			13.83	SHSN		
			16.52	WHW, SHWD, SHWN, SHSD, SHSN		
295.0729	$C_{10}H_{17}O_7N_1S_1$	4	8.37; 8.82; 8.95	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	α-pinene; β-pinene; α-terpinene; Terpinolene	Surratt et al., 2008
			9.17	SHWD, SHWN		
296.0567	$C_{10}H_{16}O_8S_1$	4	5.38; 6.70	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			6.59	WHS, NJSN, SHWN, SHSD, SHSN		
			7.78	WHW, WHS, SHWD, SHWN, SHSD, SHSN		
296.0931	$C_{11}H_{20}O_7S_1$	7	5.93; 6.59; 7.15	WHS, NJSN, SHSD, SHSN, SHWN		
			7.78	WHS, SHSD, SHSN,		

				SHWN		
			8.01	WHS		
			8.14	WHS, SHSN, SHWN		
			8.48	WHS, SHSN		
296.1295	$C_{12}H_{24}O_6S_1$	8	7.73; 8.33; 8.57; 8.93; 9.31	WHW, WHS, SHWD, SHWN, SHSD, SHSN		
			9.81	WHW, WHS, SHWN, SHSD, SHSN		
			10.60	WHW, WHS		
			11.27	WHW, WHS, SHWN		
296.1660	$C_{13}H_{28}O_5S_1$	5	9.56; 9.85; 10.62; 10.89; 11.35	WHS		
297.0520	$C_9H_{15}O_8N_1S_1$	2	6.94; 7.43	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN	Limonene	Surratt et al., 2008
297.0884	$C_{10}H_{19}O_7N_1S_1$	2	9.56; 9.70	WHW, SHWN		
298.0301	$C_{16}H_{10}O_4S_1$	1	9.77	WHW, SHWN		
298.0360	$C_9H_{14}O_9S_1$	5	1.34; 5.06; 5.24	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
			6.65	WHW, WHS, SHWN		
			6.73	WHW, WHS		
298.0724	$C_{10}H_{18}O_8S_1$	8	5.53; 5.97; 6.11; 6.40; 7.22	WHW, WHS, NJSN, SHWN, SHSD, SHSN	α-pinene; α-terpinene	Surratt et al., 2008
			6.77	WHW, WHS, SHWN, SHSD, SHSN		
			6.93; 7.39	WHW, WHS, SHSD, SHSN		
298.1087	$C_{11}H_{22}O_7S_1$	10	5.88; 6.19; 6.51; 6.61; 7.16; 7.44; 7.60; 7.73; 8.87; 8.98	WHS		
298.1241	$C_{15}H_{22}O_4S_1$	1	9.72	WHW		
299.0677	$C_9H_{17}O_8N_1S_1$	3	7.57; 8.12	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			8.58	WHS, NJSN, SHSN		
300.0152	$C_8H_{12}O_{10}S_1$	6	1.19; 1.36; 1.61; 5.09	WHS, NJSN, SHSD, SHSN		
			1.80, 1.93	WHS, SHSN		

300.0516	$C_9H_{16}O_9S_1$	1	4.85	WHS, NJSN		
300.1399	$C_{15}H_{24}O_4S_1$	3	8.98; 10.96; 11.83	WHW		
300.9894	$C_{10}H_7O_8N_1S_1$	1	5.84	WHW		
301.0106	$C_7H_{11}O_{10}N_1S_1$	4	5.57; 5.77; 6.01; 6.40	SHSD, SHSN		
301.0468	$C_8H_{15}O_9N_1S_1$	6	5.93; 6.23; 6.86; 7.14; 7.67; 7.87	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
301.0833	$C_9H_{19}O_8N_1S_1$	2	7.23; 7.96	WHS, NJSN, SHWN		
302.0097	$C_{11}H_{10}O_8S_1$	4	6.41; 6.59; 7.33; 7.40	SHWN		
302.0309	$C_8H_{14}O_{10}S_1$	2	1.16; 1.34	WHS, SHSD	Isoprene	Surratt et al., 2008
302.1190	$C_{14}H_{22}O_5S_1$	1	12.08	WHW		
306.0007	$C_5H_{10}O_{11}N_2S_1$	7	6.22; 6.44; 6.63; 6.80; 6.98; 7.61; 7.45	WHS, NJSN, SHWD, SHWN, SHSD, SHSN	Isoprene	Surratt et al., 2008
308.0048	$C_6H_{12}O_{12}S_1$	3	6.61; 6.80; 6.99	NJSN		
308.0933	$C_{12}H_{20}O_7S_1$	2	6.99; 7.49	WHS, SHSD, SHWN		
308.1296	$C_{13}H_{24}O_6S_1$	4	8.31; 8.54; 9.22	WHS, SHSD		
			10.44	WHS		
308.1659	$C_{14}H_{28}O_5S_1$	6	9.24; 10.53	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			10.88	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
			11.22	WHW, WHS, NJSN, SHSD, SHSN		
			11.85	WHW, WHS, NJSN, SHWD, SHSD, SHSN		
			12.11	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
308.2021	$C_{15}H_{32}O_4S_1$	3	10.96; 12.18	WHS, WHW		
			16.74	WHS		
309.0521	$C_{10}H_{15}O_8N_1S_1$	2	8.00; 8.37	NJSN		
310.0361	$C_{10}H_{14}O_9S_1$	4	4.76; 5.45; 5.86; 6.22	WHS, NJSN, SHSD		
310.0726	$C_{11}H_{18}O_8S_1$	5	5.17; 5.92; 6.64; 7.12	WHS, NJSN, SHWN, SHSD, SHSN		

			7.24	WHS, SHSD, SHSN		
310.1088	$C_{12}H_{22}O_7S_1$	11	6.31; 6.48; 6.97; 7.44; 7.75; 7.95; 8.16	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			8.33	WHS, SHWD, SHSD, SHSN		
			8.69	WHW, WHS, NJSN, SHWD, SHSD, SHSN		
			8.86	WHW, WHS, SHSD		
			9.17	WHS,, SHSD, SHSN		
310.1450	$C_{13}H_{26}O_6S_1$	12	6.99; 7.64; 8.72; 9.06; 9.22; 9.52; 9.95	WHS, SHWN		
			10.16; 10.49; 11.39; 12.22; 13.49	WHS		
310.1815	$C_{14}H_{30}O_5S_1$	7	9.72	WHW, WHS, NJSN, SHWD, SHWN, SHSD		
			10.17	WHW, WHS, NJSN, SHWD, SHWN, SHSD		
			11.27	WHW, WHS, SHWD, SHWN, SHSD		
			11.47	WHW, WHS, SHWN		
			12.40	WHW, WHS, NJSN, SHWN, SHSN		
			14.63	WHW, WHS, SHWD, SHWN		
			15.14	NJSN, SHSD, SHSN, SHWN		
311.0102	$C_{12}H_9O_7N_1S_1$	1	9.28	NJSN, SHWD, SHWN		
311.0677	$C_{10}H_{17}O_8N_1S_1$	7	6.60	WHW, WHS, NJSN	α-pinene; β-pinene; α-terpinene; γ-terpinene	Surratt et al., 2008
			6.73	WHW, WHS, NJSN, SHWN, SHSN		
			7.05; 7.69; 7.84	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
			8.73	WHW, WHS, NJSN, SHWN, SHSN		
			8.96	WHW, WHS, NJSN, SHWN		
312.0518	$C_{10}H_{16}O_9S_1$	3	6.44	WHW, WHS, NJSN, SHSD, SHSN		

			5.45; 6.55	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
312.0882	$C_{11}H_{20}O_8S_1$	8	5.18; 6.40; 6.59; 6.89; 7.29	WHS, SHWN, SHSD		
			7.54; 7.69; 7.91	WHS		
312.1245	$C_{12}H_{24}O_7S_1$	4	6.66; 7.65; 8.17; 8.85	WHS		
313.0470	$C_9H_{15}O_9N_1S_1$	6	6.07; 6.36; 6.82; 7.05; 7.29; 7.53	WHW, WHS, NJSN, SHWN, SHSD, SHSN	Limonene	Surratt et al., 2008
313.0834	$C_{10}H_{19}O_8N_1S_1$	7	6.70; 6.85	WHW, WHS, NJSN, SHWN, SHSN		
			7.06; 7.45; 7.67; 8.37; 8.72	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
314.0310	$C_9H_{14}O_{10}S_1$	2	1.36; 5.28	WHS, NJSN, SHSD, SHSN		
314.0675	$C_{10}H_{18}O_9S_1$	5	5.17; 5.51; 5.88; 6.07	WHS, NJSN, SHSD, SHSN		
			6.66	SHSD		
315.0627	$C_9H_{17}O_9N_1S_1$	9	6.41; 6.68; 7.03; 7.43	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			8.00	WHW, WHS, SHWD, SHWN, SHSD, SHSN		
			8.25, 8.60	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
			8.41	WHS, SHWN, SHSD, SHSN		
			8.81	WHW, WHS, NJSN, SHSD, SHSN		
315.0992	$C_{10}H_{21}O_8N_1S_1$	1	8.14	SHWN		
318.0412	$C_{12}H_{14}O_8S_1$	2	6.99; 7.26	SHSD		
320.1298	$C_{14}H_{24}O_6S_1$	5	7.41; 7.91; 8.17 8.29; 8.76;	WHS	β-caryophyllene	Chan et al., 2011
321.0157	$C_{10}H_{11}O_9N_1S_1$	1	6.06	SHWN	naphthalene	Riva et al., 2015b
321.0521	$C_{11}H_{15}O_8N_1S_1$	1	6.60	WHW		
322.1090	$C_{13}H_{22}O_7S_1$	5	6.65; 6.97; 7.71; 7.98	WHS, SHSD		

			8.22	WHS
322.1453	$C_{14}H_{26}O_6S_1$	4	7.95; 9.37; 9.88; 11.31	WHS
322.1817	$C_{15}H_{30}O_5S_1$	3	11.32	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN
			11.76	WHS, SHWN, SHSD, SHSN
			12.37	WHS
322.2179	$C_{16}H_{34}O_4S_1$	4	12.15; 16.71	WHW, WHS, NJSN, SHWD, SHWN, SHSD
			14.91	WHW, WHS, SHWD
			16.40	WHW, WHS
324.0883	$C_{12}H_{20}O_8S_1$	4	6.26; 7.10; 7.36; 7.47	WHS, SHSD
324.1245	$C_{13}H_{24}O_7S_1$	6	9.07; 9.83	WHS
			7.43; 7.98; 8.31	WHS, SHWN, SHSD
			8.52	WHS, SHSD
324.1608	$C_{14}H_{28}O_6S_1$	10	9.20; 9.59; 10.62; 11.11	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN
			9.83; 11.24	WHW, WHS, NJSN, SHWN, SHSD, SHSN
			10.14	WHW, WHS, SHWN, SHSD, SHSN
			10.89; 12.37	WHW, WHS
			13.68	WHS
324.1971	$C_{15}H_{32}O_5S_1$	5	9.86; 10.89; 11.35; 12.76; 14.51	WHS
325.0470	$C_{10}H_{15}O_9N_1S_1$	3	6.56; 6.95; 7.43	NJSN, SHSN
326.0133	$C_{10}H_{14}O_8S_2$	1	7.58	WHW
326.0675	$C_{11}H_{18}O_9S_1$	2	5.70	WHS, NJSN, SHSD, SHSN
			6.64	WHS, SHSD, SHSN
326.1040	$C_{12}H_{22}O_8S_1$	4	6.84; 7.06; 7.36; 8.42	WHS
326.1403	$C_{13}H_{26}O_7S_1$	7	7.24; 7.75; 7.66; 8.12; 8.38; 8.70; 8.85	WHS

327.0626	$C_{10}H_{17}O_9N_1S_1$	7	5.19	WHS, SHSD, SHSN	β-pinene; Limonene; Terpinolene	Surratt et al., 2008
			6.27; 6.63; 7.49; 7.74; 8.50	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			8.73	WHS, NJSN, SHSD, SHSN		
327.0992	$C_{11}H_{21}O_8N_1S_1$	4	8.56; 8.78; 9.28	SHWN, SHSD, SHSN		
			9.60	SHSN		
327.1356	$C_{12}H_{25}O_7N_1S_1$	1	11.02	SHWN		
328.0467	$C_{10}H_{16}O_{10}S_1$	3	4.71; 5.02; 5.82	WHS, NJSN, SHSD, SHSN		
328.1345	$C_{16}H_{24}O_5S_1$	1	14.48	SHWD		
329.0419	$C_9H_{15}O_{10}N_1S_1$	6	6.19; 6.43; 6.53; 6.80; 7.06; 7.50	WHS, NJSN, SHSD, SHSN		
329.0783	$C_{10}H_{19}O_9N_1S_1$	9	5.70; 5.85; 6.01; 6.41; 7.01; 7.29; 7.49; 8.11	WHW, WHS, NJSN, SHSN, SHWN	Limonene	Surratt et al., 2008
			8.89	WHW, WHS, SHSN		
331.0213	$C_8H_{13}O_{11}N_1S_1$	3	5.45	WHS, NJSN, SHWN, SHSD, SHSN		
			5.90; 6.19	WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
332.1298	$C_{15}H_{24}O_6S_1$	6	7.87; 8.16; 8.44; 9.08	WHW, WHS, NJSN		
			9.60	WHW,WHS		
			10.19	WHW		
336.0882	$C_{13}H_{20}O_8S_1$	5	6.05; 6.27; 6.44; 6.86; 6.94	WHS, NJSN, SHSD		
336.1611	$C_{15}H_{28}O_6S_1$	5	8.22; 9.29; 10.01; 10.58; 12.22	WHS		
336.1974	$C_{16}H_{32}O_5S_1$	2	12.15	WHS, SHWD, SHWN, SHSD, SHSN		
			12.68	WHS, SHWN, SHSD, SHSN		
337.0836	$C_{12}H_{19}O_8N_1S_1$	1	7.87	NJSN		
338.1040	$C_{13}H_{22}O_8S_1$	2	6.20; 6.40	WHS		
338.1404	$C_{14}H_{26}O_7S_1$	9	7.03; 7.20; 7.86; 8.52;	WHS, SHWN, SHSD, SHSN		

			8.90			
			9.13	WHS, SHSN		
			9.41; 9.72; 10.57	WHS		
338.1764	$C_{15}H_{30}O_6S_1$	9	8.22	WHS, SHSD		
			9.25; 14.12	WHS		
			9.70; 10.01; 10.84; 11.39	WHW, WHS, SHWN, SHSD		
			10.48	WHW, WHS		
			12.15	WHW,WHS, SHWN		
338.2130	$C_{16}H_{34}O_5S_1$	7	9.28	WHW, WHS, SHWD, SHSD		
			10.84	WHS, SHWN		
			11.01	WHS, SHWD, SHWN, SHSD		
			11.13	WHW, WHS, SHWD, SHWN		
			11.62; 12.48; 12.78	WHW, WHS, NJSN, SHWD, SHWN, SHSD		
340.1195	$C_{13}H_{24}O_8S_1$	9	7.66; 8.22; 8.41; 8.51	WHS		
			7.27; 7.50; 7.81; 8.73; 8.93	WHS, SHWN		
340.1559	$C_{14}H_{28}O_7S_1$	8	7.66; 8.24; 8.56; 8.94; 9.17; 9.30; 9.60; 9.97	WHS		
341.0421	$C_{10}H_{15}O_{10}N_1S_1$	3	6.78; 6.95; 7.29	WHW, WHS, NJSN, SHSD, SHSN		
341.0784	$C_{11}H_{19}O_9N_1S_1$	4	7.57; 7.66; 7.95; 9.08	WHS, NJSN		
341.1511	$C_{13}H_{27}O_7N_1S_1$	1	11.79	SHWN		
342.0624	$C_{11}H_{18}O_{10}S_1$	3	5.45; 5.73; 5.99	WHS, NJSN, SHSD, SHSN		
342.0989	$C_{12}H_{22}O_9S_1$	2	6.60; 7.11	WHS		
343.0576	$C_{10}H_{17}O_{10}N_1S_1$	7	6.44; 6.68; 7.57	WHW, WHS, NJSN, SHWN, SHSD, SHSN	α-pinene; β-pinene; α-terpinene	Surratt et al., 2008
			7.70; 7.77	WHW, WHS, NJSN, SHSD, SHSN		
			8.11	WHS, NJSN, SHSD, SHSN		
			8.21	SHSD, SHSN		

343.1304	$C_{12}H_{25}O_8N_1S_1$	3	8.85; 8.96; 9.22	SHWN		
345.0369	$C_9H_{15}O_{11}N_1S_1$	3	6.05; 6.57; 6.93	WHS, NJSN, SHSN		
345.0733	$C_{10}H_{19}O_{10}N_1S_1$	7	5.39; 5.59; 5.76; 7.07; 7.23; 7.32	WHW, WHS, NJSN, SHWN, SHSN		
			6.93	WHW, WHS, NJSN, SHSN		
346.0760	$C_{11}H_{22}O_8S_2$	1	7.31	SHWD		
348.1246	$C_{15}H_{24}O_7S_1$	10	6.80; 6.89; 6.97; 7.07; 7.33; 7.73; 7.86; 8.03; 8.31; 8.51	WHS, NJSN	β-caryophyllene	Chan et al., 2011
350.1038	$C_{14}H_{22}O_8S_1$	5	6.44; 6.66; 6.93; 7.16; 7.33	WHS, SHSD	β-caryophyllene	Chan et al., 2011
350.1404	$C_{15}H_{26}O_7S_1$	6	7.39; 7.54; 7.74; 8.34; 8.43	WHS, NJSN, SHWN, SHSD	β-caryophyllene	Chan et al., 2011
			8.53	WHS		
350.1766	$C_{16}H_{30}O_6S_1$	7	9.35; 9.90; 10.14; 10.42; 10.71; 11.37; 12.10	WHS, WHW		
350.2130	$C_{17}H_{34}O_5S_1$	7	11.27; 11.49; 11.70; 12.09; 12.42; 13.12; 13.98	WHS		
		4	12.09; 12.42; 13.12; 13.98	SHSD		
352.0829	$C_{13}H_{20}O_9S_1$	4	5.92; 6.23; 6.35; 6.48	SHSD		
352.1198	$C_{14}H_{24}O_8S_1$	2	6.89; 7.74	WHS, SHSD	β-caryophyllene	Chan et al., 2011
352.1557	$C_{15}H_{28}O_7S_1$	5	7.29; 8.30; 9.08	WHS, SHSD		
			9.47; 11.37	WHS		
352.1922	$C_{16}H_{32}O_6S_1$	10	10.25; 10.38; 10.67; 11.27	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			10.50; 10.89	WHW, WHS, SHWD,		

				SHWN, SHSD, SHSN		
			11.63; 12.32	WHW, WHS, NJSN, SHWN		
			13.55	WHS		
			16.75	WHW		
352.2287	$C_{17}H_{36}O_5S_1$	2	11.82; 12.45	WHS		
354.0988	$C_{13}H_{22}O_9S_1$	4	5.99; 6.09; 6.28; 7.09	WHS, SHSD		
354.1353	$C_{14}H_{26}O_8S_1$	9	7.48; 7.67; 7.94; 8.43; 8.54; 8.67; 8.81; 9.09; 9.99	WHS		
354.1718	$C_{15}H_{30}O_7S_1$	5	8.08; 9.04; 9.37; 9.51; 9.77	WHS		
354.2079	$C_{16}H_{34}O_6S_1$	3	15.58	SHWD		
			16.34	WHW, SHWD		
			16.68	NJSN, SHWN, SHSD, SHSN		
355.0942	$C_{12}H_{21}O_9N_1S_1$	3	8.21; 8.46; 8.77	WHW, WHS, NJSN, SHWN, SHSN		
356.1659	$C_{18}H_{28}O_5S_1$	2	7.69	SHWD, SHWN		
			15.77	NJSN, SHWD, SHWN, SHSD ,SHSN		
357.0735	$C_{11}H_{19}O_{10}N_1S_1$	4	6.78; 6.98; 7.22; 7.36	WHS, NJSN		
361.0684	$C_{10}H_{19}O_{11}N_1S_1$	2	6.47; 7.29	SHSD		
363.1356	$C_{15}H_{25}O_7N_1S_1$	6	10.53	WHW, WHS, NJSN, SHWN	β-caryophyllene	Chan et al., 2011
			10.88	WHW, WHS, NJSN, SHWD, SHWN, SHSN		
			11.18	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			11.32	SHSD, SHSN		
			11.50	WHW, WHS, SHSD, SHSN		
			11.93	WHW, WHS, NJSN, SHWN		
363.9484	$C_9H_4O_{12}N_2S_1$	1	0.84	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		

364.1196	$C_{15}H_{24}O_{8}S_{1}$	5	6.76; 7.41; 7.56; 7.77; 7.86	NJSN	β-caryophyllene	Chan et al., 2011
364.1925	$C_{17}H_{32}O_{6}S_{1}$	3	9.72; 9.92; 11.49	WHS		
364.2286	$C_{18}H_{36}O_{5}S_{1}$	8	11.66; 12.01; 12.31; 13.01; 13.45; 13.64; 13.86; 14.76	WHS		
365.1150	$C_{14}H_{23}O_{8}N_{1}S_{1}$	3	8.78; 9.11; 9.29	WHS, NJSN		
366.1715	$C_{16}H_{30}O_{7}S_{1}$	12	7.61	WHS, SHSD		
			8.74; 9.22; 9.65	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			10.08	WHW, WHS, SHWD, SHWN, SHSD, SHSN		
			10.46	WHW, WHS, SHWN		
			10.79	WHW, WHS, SHWD, SHSN		
			11.15	WHW, WHS		
			11.44; 12.50	WHS, SHWD		
			12.36	WHS		
			12.89	NJSN, SHSD, SHSN		
366.2078	$C_{17}H_{34}O_{6}S_{1}$	8	10.86; 11.02; 11.39; 12.35	WHW, WHS, SHSD, SHWN		
			12.64; 13.43	WHW, WHS, SHSD		
			13.23; 13.92	WHW, WHS		
366.2440	$C_{18}H_{38}O_{5}S_{1}$	2	12.89; 16.74	WHS		
368.1144	$C_{14}H_{24}O_{9}S_{1}$	5	6.69; 6.88; 7.09; 7.16; 7.24	WHS, SHSD		
368.1509	$C_{15}H_{28}O_{8}S_{1}$	6	8.11; 8.34	WHW, WHS		
			9.13	WHS		
			10.00	WHW, WHS, SHWN		
			9.52; 10.18	WHW, WHS, SHWD, SHWN		
368.1873	$C_{16}H_{32}O_{7}S_{1}$	8	8.51; 8.93; 9.19; 9.55; 9.82; 10.10	WHW, WHS, NJSN		
			8.31; 10.42	WHW, WHS		
369.1098	$C_{13}H_{23}O_{9}N_{1}S_{1}$	2	8.48; 9.50	NJSN		
369.9841	$C_{10}H_{10}O_{13}S_{1}$	2	10.48; 10.70	SHSD, SHSN		

371.1618	$C_{14}H_{29}O_8N_1S_1$	2	10.27; 11.17	WHS		
374.1041	$C_{16}H_{22}O_8S_1$	2	9.35; 9.60	WHW, WHS, NJSN, SHWN, SHSD, SHSN		
376.1924	$C_{18}H_{32}O_6S_1$	3	9.30	WHW, NJSN		
			9.07; 11.45	WHW		
377.1149	$C_{15}H_{23}O_8N_1S_1$	4	9.03; 9.28; 9.55; 9.88	WHS, NJSN		
378.2081	$C_{18}H_{34}O_6S_1$	4	9.64; 10.95; 12.01; 12.45	WHW, WHS		
379.1305	$C_{15}H_{25}O_8N_1S_1$	8	8.60; 9.06	WHS, NJSN		
			8.77; 9.17; 9.33; 9.75; 10.22; 11.27	WHS, NJSN, SHSN		
380.1511	$C_{16}H_{28}O_8S_1$	3	7.12; 7.43; 9.19	WHS	β-caryophyllene	Chan et al., 2011
380.1652	$C_{20}H_{28}O_5S_1$	1	14.98	NJSN		
380.1871	$C_{17}H_{32}O_7S_1$	6	9.17; 10.27; 11.18; 11.98; 12.48; 12.63	WHS		
380.2233	$C_{18}H_{36}O_6S_1$	11	8.96; 16.68	WHS		
			9.22	WHW, WHS, NJSN, SHWN		
			9.61	WHS, NJSN		
			11.56; 11.78; 12.00; 12.27	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN		
			12.67	WHW, WHS, SHSD		
			13.29; 14.15	WHW, WHS		
381.1463	$C_{15}H_{27}O_8N_1S_1$	2	9.08; 9.97	NJSN		
381.9843	$C_{11}H_{10}O_{13}S_1$	2	7.84; 10.48	NJSN, SHSD, SHSN		
382.1302	$C_{15}H_{26}O_9S_1$	4	6.93; 7.26; 7.07; 7.50	WHS		
382.1666	$C_{16}H_{30}O_8S_1$	3	8.51; 10.07; 10.48	WHS		
382.2031	$C_{17}H_{34}O_7S_1$	4	8.59; 8.94; 10.09; 11.09	WHS		
382.2395	$C_{18}H_{38}O_6S_1$	1	13.24	SHWD		
384.1972	$C_{20}H_{32}O_5S_1$	1	14.12	NJSN, SHWD, SHWN, SHSD, SHSN		
385.1049	$C_{13}H_{23}O_{10}N_1S_1$	6	7.37; 7.53; 7.90; 8.25; 8.47; 8.80	WHS, NJSN, SHSN		
385.9429	$C_9H_6O_{15}S_1$	1	0.85	WHW, SHWD, SHSD,		

				SHSN
390.0991	$C_{16}H_{22}O_9S_1$	1	7.58	SHSD
391.0245	$C_{10}H_{17}O_{11}N_1S_2$	4	6.36	WHW, NJSN
			6.60; 6.91; 7.06	WHW, WHS, NJSN, SHWN, SHSN
393.1100	$C_{15}H_{23}O_9N_1S_1$	1	8.85	NJSN
394.2030	$C_{18}H_{34}O_7S_1$	10	8.83; 12.09; 12.41	WHS
			9.35; 9.66; 10.97; 11.31; 11.50; 11.79; 12.72	WHW, WHS
394.2393	$C_{19}H_{38}O_6S_1$	4	12.33; 12.74; 13.12; 13.41	WHS
395.1255	$C_{15}H_{25}O_9N_1S_1$	7	8.16; 8.63; 8.96; 9.11; 9.69; 9.83; 10.13	WHS, NJSN
396.1823	$C_{17}H_{32}O_8S_1$	5	8.93; 9.22; 10.49; 10.67; 10.89	WHS
396.2186	$C_{18}H_{36}O_7S_1$	5	7.45	WHS
			9.43; 10.47; 10.66	WHS, NJSN
			11.56	WHW, WHS
397.1410	$C_{15}H_{27}O_9N_1S_1$	2	7.92; 8.52	NJSN
398.1194	$C_{22}H_{22}O_5S_1$	1	5.68	SHSD
398.2345	$C_{18}H_{38}O_7S_1$	1	16.42	SHWD
402.1306	$C_{13}H_{26}O_{10}N_2S_1$	1	12.23	SHWD
408.2188	$C_{19}H_{36}O_7S_1$	4	10.18; 10.82; 11.58; 11.75	WHS
408.2548	$C_{20}H_{40}O_6S_1$	5	10.96; 13.50; 13.75; 13.97; 14.76	WHS
409.1048	$C_{15}H_{23}O_{10}N_1S_1$	2	8.77; 9.87	NJSN
410.1978	$C_{18}H_{34}O_8S_1$	6	7.91; 9.70; 10.23; 11.05	WHW, WHS
			10.58	WHS
			11.35	WHW, WHS, NJSN, SHWD, SHWN, SHSD, SHSN
410.2344	$C_{19}H_{38}O_7S_1$	3	9.47; 9.90; 11.37	WHS

411.1205	$C_{15}H_{25}O_{10}N_1S_1$	2	7.86; 8.47	WHS, NJSN
412.1222[a]	$C_{16}H_{28}O_8S_2$	2	4.76; 5.21	WHW, WHS
413.1362	$C_{15}H_{27}O_{10}N_1S_1$	2	7.81; 8.69	NJSN
413.1725	$C_{16}H_{31}O_9N_1S_1$	3	10.17; 10.91; 11.17	WHW, WHS
413.9742	$C_{11}H_{10}O_{15}S_1$	1	10.69	NJSN, SHWN, SHSD, SHSN
417.1464	$C_{18}H_{27}O_8N_1S_1$	1	10.39	WHW
418.1330[b]	$C_{15}H_{30}O_9S_2$	1	1.19	SHSD
422.2342	$C_{20}H_{38}O_7S_1$	3	9.28; 9.44	SHWN
			16.58	SHWD
422.2705	$C_{21}H_{42}O_6S_1$	3	11.08; 12.39; 16.71	WHS
424.2136	$C_{19}H_{36}O_8S_1$	6	9.64; 11.01; 11.35; 11.18; 11.88; 12.11	WHS
425.0998	$C_{15}H_{23}O_{11}N_1S_1$	2	7.86; 8.00	NJSN
425.9192	$C_{11}H_6O_{14}S_2$	1	0.83	WHW, NJSN, SHWD, SHWN, SHSD
425.9743	$C_{12}H_{10}O_{15}S_1$	1	7.84	NJSN, SHSD, SHSN
426.2293	$C_{19}H_{38}O_8S_1$	8	9.60; 9.92; 10.10; 10.34; 10.66; 11.04; 11.80; 12.87	WHS
427.1154	$C_{15}H_{25}O_{11}N_1S_1$	1	6.76	NJSN
436.2864	$C_{22}H_{44}O_6S_1$	4	11.40; 11.79; 12.41; 13.19	WHS
438.0108	$C_{14}H_{14}O_{14}S_1$	1	11.45	NJSN
438.1354	$C_{21}H_{26}O_8S_1$	1	9.64	NJSN
440.0843[c]	$C_{12}H_{24}O_{15}S_1$	1	1.18	SHWD, SHWN, SHSD
440.1724	$C_{18}H_{32}O_{10}S_1$	1	8.65	WHS, SHWD
441.2037	$C_{18}H_{35}O_9N_1S_1$	3	10.39	WHS, NJSN
			12.37; 12.78	WHW, WHS, NJSN, SHWN, SHSN
442.0512[d]	$C_{25}H_{14}O_6S_1$	1	8.29	NJSN
442.2607	$C_{20}H_{42}O_8S_1$	1	16.71	SHWD
443.1106	$C_{15}H_{25}O_{12}N_1S_1$	1	7.92	NJSN
452.0727	$C_{27}H_{16}O_5S_1$	1	11.14	WHW
453.9304	$C_{16}H_6O_{12}S_2$	1	0.86	SHWD, SHSD, SHSN
456.1098	$C_{20}H_{24}O_{10}S_1$	1	1.19	SHWD, SHSD
456.1460	$C_{21}H_{28}O_9S_1$	1	8.09	NJSN
457.1989	$C_{18}H_{35}O_{10}N_1S_1$	2	9.43; 9.88	WHS

484.0526	$C_{16}H_{20}O_{15}S_1$	1	10.75	SHWN, SHSD
494.2136[e]	$C_{29}H_{34}O_5S_1$	1	6.73	NJSN
495.9773	$C_{19}H_{12}O_{12}S_2$	1	11.15	NJSN
499.9235	$C_9H_8O_{22}S_1$	1	0.84	NJSN, SHWD, SHWN, SHSD
521.9178	$C_{10}H_6O_{21}N_2S_1$	1	0.86	SHWD, SHSD, SHSN
525.9679[f]	$C_{11}H_{14}O_{18}N_2S_2$	1	8.91	NJSN, SHSD
531.9747	$C_{13}H_{12}O_{19}N_2S_1$	2	9.55; 12.81	NJSN, SHSD
533.9332	$C_{15}H_6O_{18}N_2S_1$	1	16.22	WHW, NJSN, SHWN, SHSD, SHSN
539.9671	$C_{20}H_{12}O_{14}S_2$	1	8.37	NJSN, SHSD, SHSN
545.9742[g]	$C_{22}H_{10}O_{15}S_1$	1	11.91	NJSN
550.1753[h]	$C_{20}H_{38}O_{13}S_2$	1	1.34	SHSD
575.9650[i]	$C_{14}H_{12}O_{21}N_2S_1$	1	9.53	NJSN
581.9719[j]	$C_{29}H_{10}O_{10}S_2$	1	10.23	NJSN
589.9054	$C_{17}H_6O_{18}N_2S_2$	2	0.86	SHWD, SHSD, SHSN
			10.30	SHWD
589.9641[k]	$C_{23}H_{10}O_{17}S_1$	1	8.91	NJSN
631.9687[l]	$C_{11}H_{20}O_{26}S_2$	1	11.13	NJSN
645.9682[m]	$C_{21}H_{14}O_{18}N_2S_2$	1	13.65	SHWD
649.9218[n]	$C_{13}H_{14}O_{26}S_2$	3	14.21; 14.35; 14.81	NJSN
651.8755	$C_{10}H_8O_{27}N_2S_2$	1	0.85	SHWD, SHSD
696.8671	$C_{11}H_7O_{32}N_1S_1$	1	0.85	SHSD
699.9188	$C_{16}H_{12}O_{29}S_1$	1	16.72	SHSD
725.8798[o]	$C_{17}H_{10}O_{28}S_2$	3	0.86	SHWD, SHSD, SHSN
			16.63	SHSD
			16.75	NJSN, SHWD, SHWN, SHSD, SHSN

[a] Other formula within 2 ppm: $C_{15}H_{24}O_{13}$.

[b] Other formula within 2 ppm: $C_{14}H_{26}O_{14}$.

[c] Other formula within 2 ppm: $C_{33}H_{12}O_2$.

[d] Other formula within 2 ppm: $C_{17}H_{18}O_8N_2S_2$.

[e] Other formula within 2 ppm: $C_{17}H_{38}O_{12}N_2S_1$.

[f] Other formula within 2 ppm: $C_{10}H_{10}O_{23}N_2$..

[g] Other formula within 2 ppm: $C_{14}H_{14}O_{17}N_2S_2$.

[h] Other formulas within 2 ppm: $C_{19}H_{34}O_{18}$.

[i] Other formula within 2 ppm: $C_{22}H_8O_{19}$.

[j] Other formula within 2 ppm: $C_{16}H_{10}O_{22}N_2$.

[k] Other formula within 2 ppm: $C_{15}H_{14}O_{19}N_2S_2$.

[l] Other formulas within 2 ppm: $C_{24}H_{12}O_{15}N_2S_2$; $C_{10}H_{16}O_{31}$.

[m] Other formula within 2 ppm: $C_{29}H_{10}O_{16}S_1$; $C_{20}H_{10}O_{23}N_2$.

[n] Other formula within 2 ppm: $C_{12}H_{10}O_{31}$

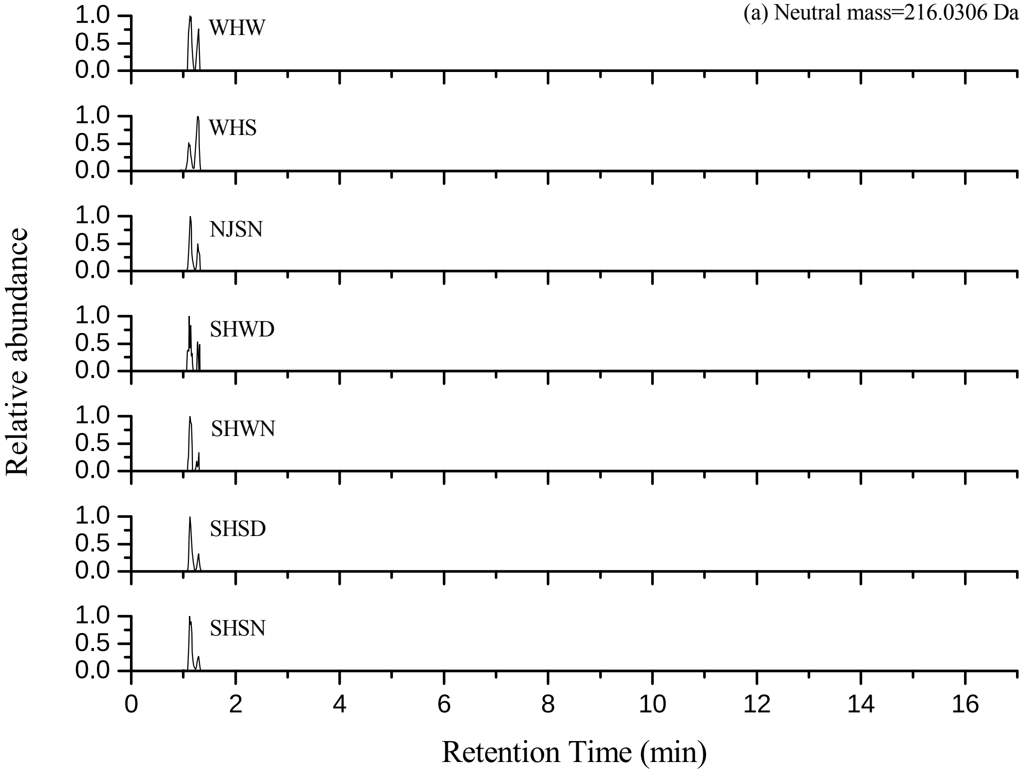
[o] Other formula within 2 ppm: $C_{16}H_6O_{33}$.

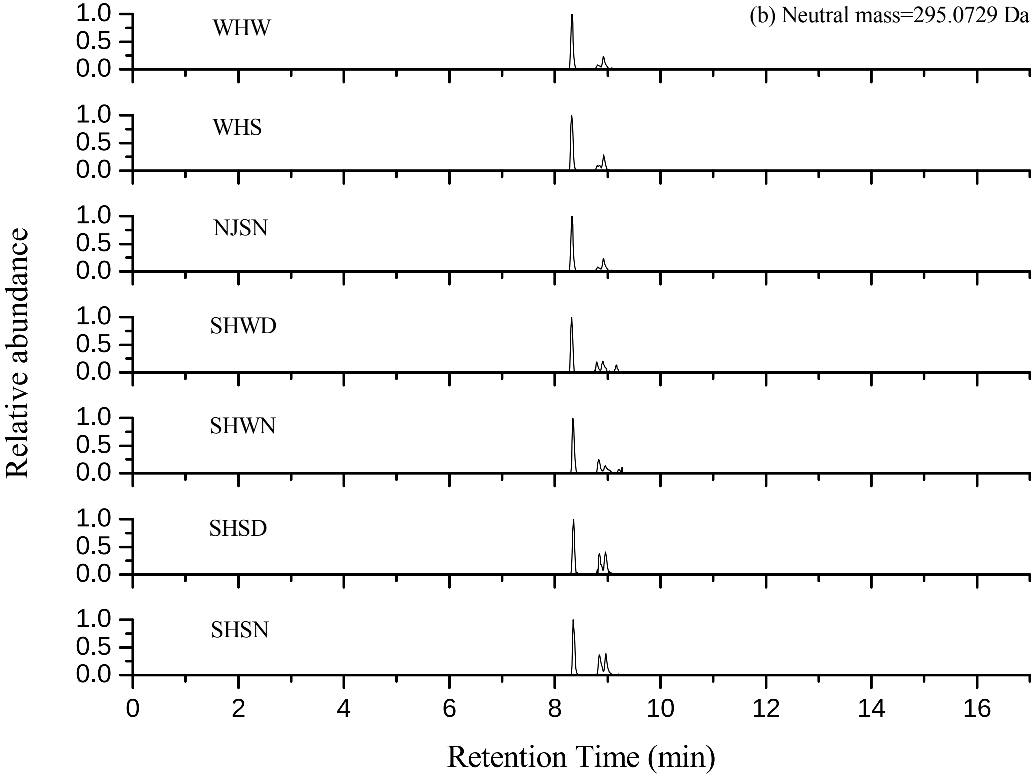
[p] Potentially being sulfonates.

Table S4. The isomer ratios for selected OSs in Figure 3.

ID	Formula	Trace	Number of isomers	Retention times (min)	Intensity ratios of isomers (%)	Potential precursor	Ref.
A	$C_5H_8O_7S_1$	WHS	1	1.36	100	Isoprene	Surratt et al., 2008
		NJSN	1	1.36	100		
		SHSD+SHSN	1	1.36	100		
B	$C_5H_{12}O_7S_1$	WHS	2	1.15; 1.29	37.4: 62.6	Isoprene	Surratt et al., 2008
		NJSN	2	1.15; 1.29	79.4: 20.6		
		SHSD+SHSN	2	1.15; 1.29	73.5: 26.5		
C	$C_6H_{10}O_7S_1$	WHS	5	1.36; 2.72; 3.25; 4.57; 4.98	6.8: 27.8: 52.0: 11.6: 1.8	3-Z-Hexenal	Shalamzari et al., 2014
		NJSN	7	1.36; 2.72; 3.25; 4.57; 4.98; 6.41; 7.02	10.1: 19.8: 41.7: 9.7: 2.1: 6.6: 10.0		
		SHSD+SHSN	7	1.36; 2.72; 3.25; 4.57; 4.98; 6.41; 7.02	10.7: 17.0: 45.7: 9.5: 4.1: 1.0: 2.0		
D	$C_7H_{12}O_7S_1$	WHS	3	4.84; 5.27; 6.64	27.0: 72.9: 0.1	Limonene	Surratt et al., 2008
		NJSN	2	4.84; 5.27	51.4: 48.6		
		SHSD+SHSN	2	4.84; 5.27	44.6: 55.4		
E	$C_9H_{18}O_6S_1$	WHS	8	5.52; 6.89; 7.16; 7.50; 7.96; 8.56; 8.99; 9.59	0.5: 24.6: 45.3: 14.6: 10.5: 3.9: 0.1: 0.5	Not known	
		NJSN	6	5.52; 6.89; 7.16; 7.50; 7.96; 8.56	2.7: 29.0: 46.6: 14.9: 5.9: 0.9		
		SHSD+SHSN	6	5.52; 6.89; 7.16; 7.50; 7.96; 8.56	0.8: 30.5: 46.4: 17.2: 4.4: 0.7		
F	$C_5H_{11}O_9N_1S_1$	WHS	4	2.46; 2.94; 3.53; 4.43	33.8: 13.9: 43.8: 8.5	Isoprene	Surratt et al., 2008
		NJSN	4	2.46; 2.94; 3.53; 4.43	24.7: 17.2: 51.4: 6.7		
		SHSD+SHSN	4	2.46; 2.94; 3.53; 4.43	22.2: 28.6: 42.8: 6.4		

G	$C_9H_{16}O_7S_1$	WHS	5	5.74; 6.30; 7.02; 7.47; 7.74	71.9: 15.4: 11.6: 0.9: 0.2	Limonene	Surratt et al., 2008
		NJSN	5	5.74; 6.30; 7.02; 7.47; 7.74	90.8: 7.4: 1.6: 0.4: 0.1		
		SHSD+SHSN	5	5.74; 6.30; 7.02; 7.47; 7.74	87.4: 8.4: 4.0: 0.1: 0.1		
H	$C_{10}H_{17}O_7N_1S_1$	WHS	3	8.37; 8.82; 8.95	69.1: 10.5: 20.4	α-pinene, β-pinene, α-terpinene and terpinolene	Surratt et al., 2008
		NJSN	3	8.37; 8.82; 8.95	51.4: 38.3: 10.3		
		SHSD+SHSN	3	8.37; 8.82; 8.95	47.8: 25.9: 26.3		
I	$C_5H_{10}O_{11}N_2S_1$	WHS	7	6.22; 6.44; 6.63; 6.80; 6.98; 7.61; 7.45	2.2: 12.9: 26.8: 23.7: 16.0: 10.0: 8.4	Isoprene	Surratt et al., 2008
		NJSN	7	6.22; 6.44; 6.63; 6.80; 6.98; 7.61; 7.45	1.8: 10.4: 25.7: 27.0: 15.1: 13.6: 6.4		
		SHSD+SHSN	7	6.22; 6.44; 6.63; 6.80; 6.98; 7.61; 7.45	1.6: 13.9: 20.0: 24.8: 21.1: 12.7: 5.9		
J	$C_{16}H_{32}O_6S_1$	WHS	9	10.25; 10.38; 10.50; 10.67; 10.89; 11.27; 11.63; 12.32; 13.55	33.3: 16.7: 7.1: 8.1: 6.4: 7.6: 8.6: 9.2: 3.0	Not known	
		NJSN	6	10.25; 10.38; 10.67; 11.27; 11.63; 12.32	42.4: 21.3: 7.8: 7.3: 10.9: 10.3		
		SHSD+SHSN	6	10.25; 10.38; 10.50; 10.67; 10.89; 11.27	43.8: 21.6: 11.0: 10.9: 6.6: 6.1		
K	$C_{15}H_{25}O_7N_1S_1$	WHS	5	10.53; 10.88; 11.18; 11.50; 11.93	0.8: 2.6: 17.4: 77.6: 1.6	β-caryophyllene	Chan et al., 2011
		NJSN	4	10.53; 10.88; 11.18; 11.93	0.2: 26.3: 69.8: 3.7		
		SHSD+SHSN	4	10.88; 11.18; 11.32; 11.50	0.3: 2.8: 96.8: 0.1		


(a) Neutral mass=216.0306 Da
WHW
WHS
NJSN
SHWD
SHWN
SHSD
SHSN
1.0
0.5
0.0
Relative abundance
0
2
4
6
8
10
12
14
16
Retention Time (min)


(b) Neutral mass=295.0729 Da
WHW
WHS
NJSN
SHWD
SHWN
SHSD
SHSN
1.0
0.5
0.0
Relative abundance
0
2
4
6
8
10
12
14
16
Retention Time (min)

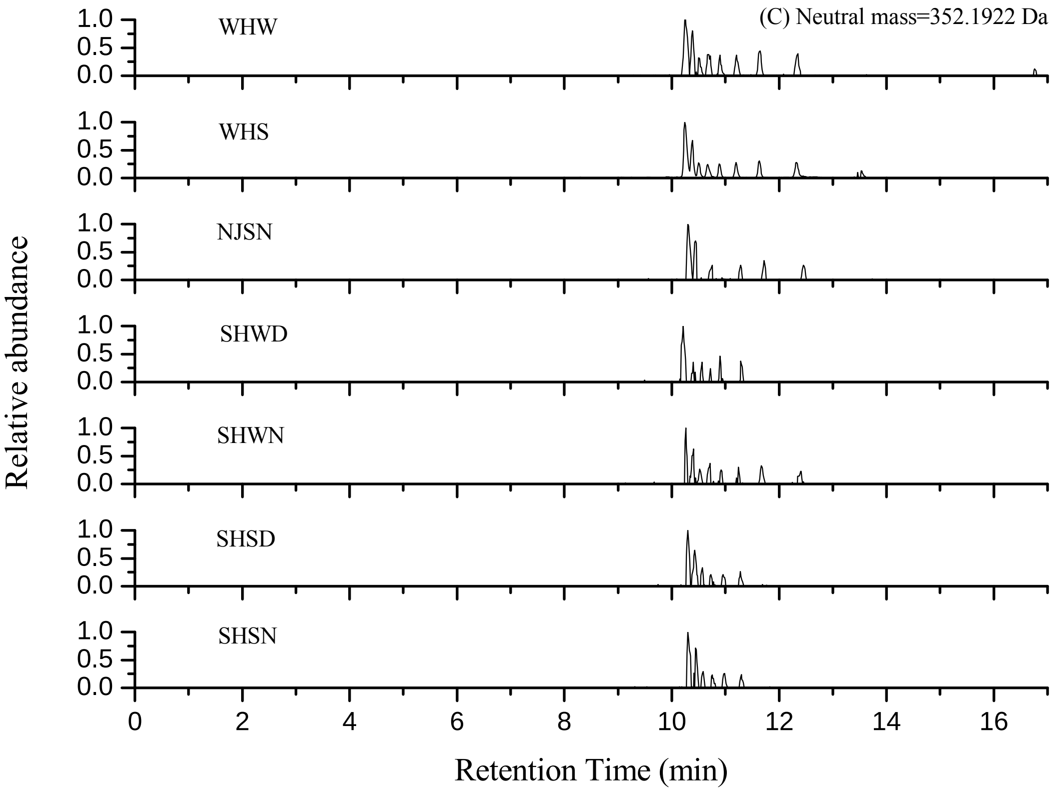


Figure S1. LC chromatograms of three deprotonated OSs (a) $C_5H_{12}O_7S_1$ (potentially from isoprene); (b) $C_{10}H_{17}O_7N_1S_1$ (potentially from various monoterpenes); (C) $C_{16}H_{32}O_6S_1$ (with an unknown precursor). Chromatograms for the NJSD sample is not included because a large amount of sample injection led to corruption of peaks and hence inaccurate retention times and worse peak resolution.

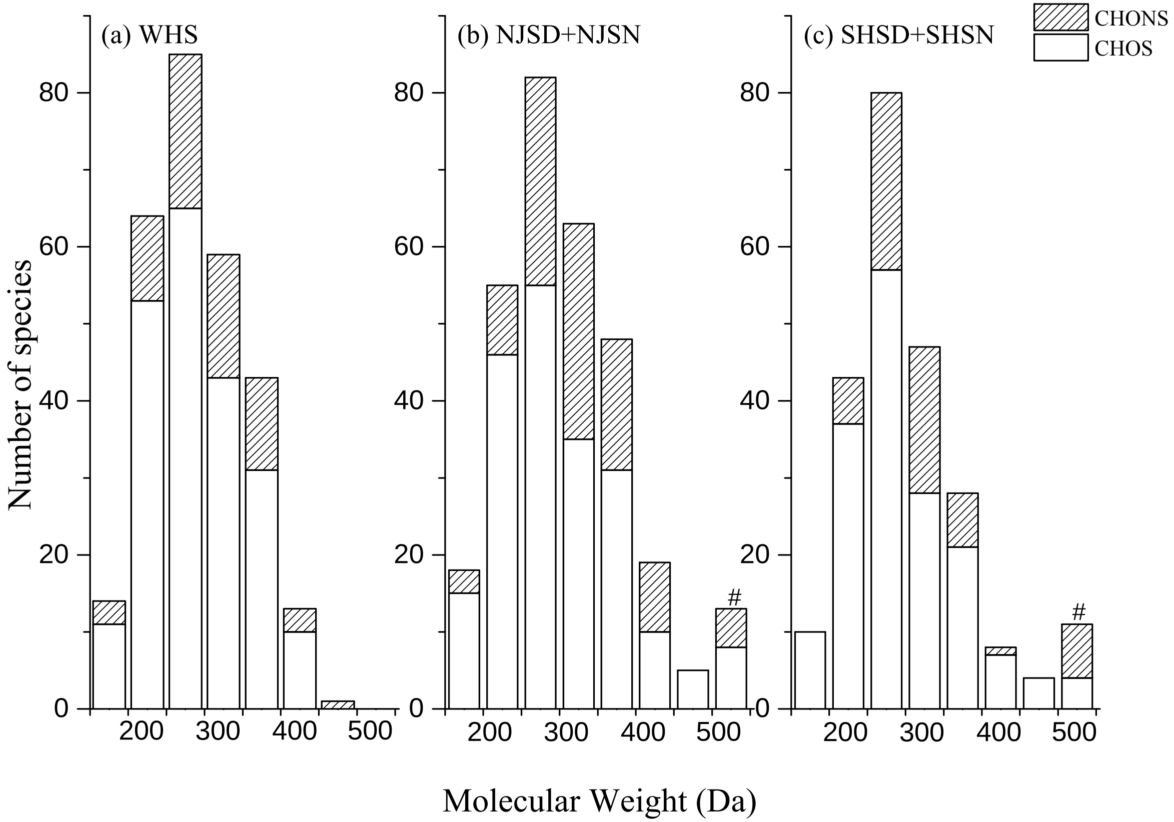


Figure S2. Number of CHOS and CHONS in the different mass ranges. The bins are 50 Da wide. The last bin with a pound sign includes all species with a molecular weight larger than 500 Da.

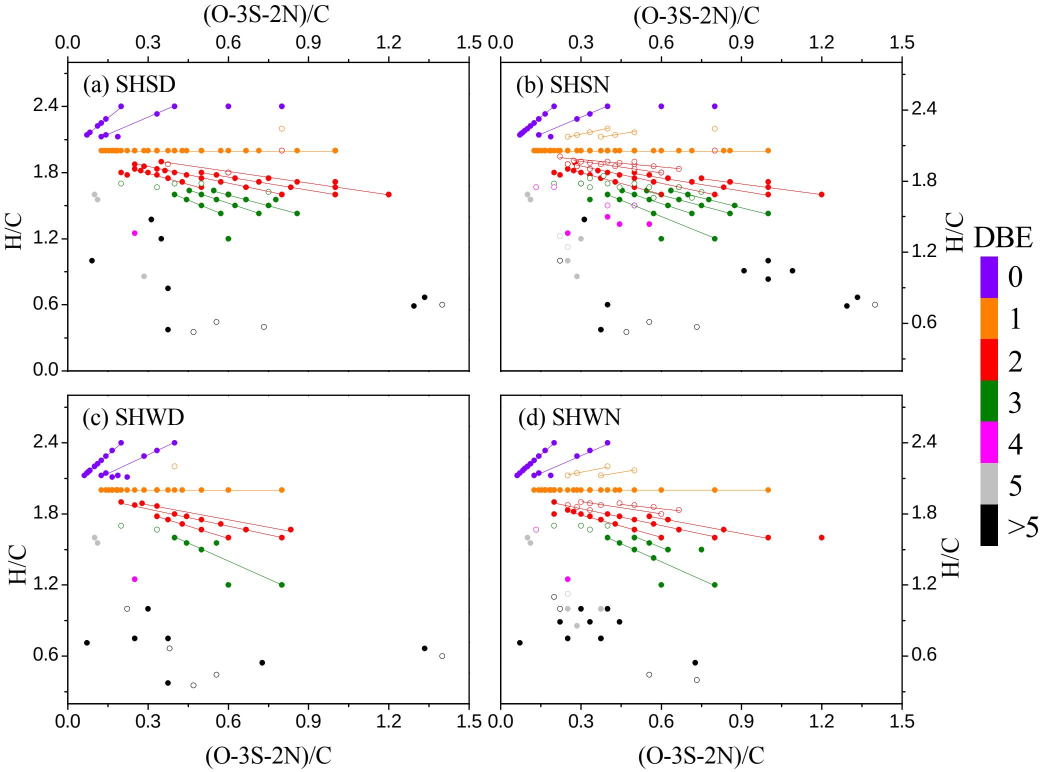


Figure S3. (a-d) Van Krevelen diagrams for CHOS and CHONS detected in Shanghai samples. The filled and open circles denote CHOS and CHONS, respectively. Note that only compounds with a relative abundance greater than or equal to 0.5% of that of $C_{10}H_{17}O_7N_1S_1$ in the SHSN sample are shown in this figure.

Reference:

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