RE: A point-to-point response to referee #1's comments

"Identification of Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River" (acp-2015-393) 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 referee #1 for his/her valuable technical comments, encouraging us to further develop our experimental section. A point-to-point response to this reviewer's comments, which are repeated in italic, is given below.

1. *The work by Wang et al. describes molecular composition of PM2.5 samples from three megacities i.e., Wuhan (WH), Nanjing (NJ), and Shanghai (SH) determined by an UHPLC Orbitrap MS. The authors identified significant number of organosulfates and nitrooxy-organosulfates and discussed their contribution to the PM at these locations. Unfortunately the authors ignored a majority of the very important comments that were given at the initial ACPD review stage. I strongly believe that they have to be addressed before the manuscript could be published in ACP. Unfortunately I cannot support this work for publication in this current form.*

Reply: We are very much surprised by this comment. In fact, during the initial review stage we had already to respond to a full, and quite extensive, review of our paper. We therefore already corrected our paper thoroughly and provided an extensive and constructive point-to-point answer to all comments we received. We therefore honestly believed, as the manuscript was accepted, that the feedbacks we provided have been appreciated. We understand now that referee 1 would like that we revise our manuscript beyond to what has already been done. Naturally, we did so and especially clarified the experimental procedures we used. We believe that our approach and data are convincing enough to warrant publication in ACP.

2. *The methodology section is still confusing. Considering a very large number of detected molecules (>200), I assume the whole results and discussion section is based on the direct infusion analysis. If not, please show the LC/MS chromatogram and describe the methodology more clearly. Please add a citation for the LC/MS method.*

Reply: As mentioned in the manuscript, all the analysis have been performed by LC-MS and not by direct infusion analysis. The associated methodology has been specifically developed for these analysis (therefore we cannot provide an additional reference), but we recognize that we could have still added some details. Especially, we have added some more figures in the manuscript and in the supplement showing some of the chromatograms we obtained.
We now clearly state in our revised manuscript that:

"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.

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 (Page 6-8, Line 152-192).”

3. *It is not clear whether the mass spectra were blank corrected. If yes, please describe how. What was the signal to noise threshold for keeping the formulae for further evaluation? Orbitrap MS is known to result in the formation of shoulder ions, which significantly increase a number of identified molecules. Were the shoulder ions removed from the mass spectra? Were the analytical replicates considered? Were the C, N, P and S isotopes considered for the correct molecular formulae assignment?*

Reply: The way in which the LC/MS dataset was processed is described in section “2.3 Data processing”. The peak search was performed manually. For all the detected m/z, the exact mass was extracted to obtain the extracted ion chromatogram. The occurrence of shoulder peaks eluting at an identical retention time was checked to identify potential “shoulder ions”, that could come from H_2O loss for example, and to determine if the detected m/z corresponds effectively to a $[M-H]^-$ quasi-molecular ion or not. Chromatographic peak areas were then determined from the extracted quasi-molecular ion chromatograms only. The analytical replicates were not considered but one can assume an uncertainty corresponding to the whole analytical process, including the extraction step, which is now given in the supporting information. Molecular formula assignment was performed including the following elements: C, H, N, S and O. Isotopes are a classical way to confirm molecular formula assignments when the resolution of the instrument is not sufficient. Here, in most cases, the isotopic peak is not detected due to the low intensity of the related 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.

We now clearly state in our revised manuscript that:

"These molecular formula 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, 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) (Page 8, Line 192-209)."

"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 (Page 9, Line 225-230)."

"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. (Page 7, Line 163-170)."

4. *What was the mass scan range of the Orbitrap analysis?*

Reply: The mass scan range of the orbitrap analysis was m/z 50 to 750. We have stated that "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" (Page 7, Line 178-180).

5. *Orbitrap is known to have mass dependant ion transmission. Therefore, by selecting either low or high mass range one can miss out high or low molecular weight compounds. The mass*

error of 2 ppm for formulae assignments is rather high, especially considering that the majority of the assigned OSs have MW >200 (see Figure 2). Kind and Fiehn (2007) demonstrated that even at 1 ppm error a very large number of chemically realistic formulae is possible in this mass range.

Reply: 2 ppm was the mass error achieved in this study. As previously discussed at the initial review stage, similar values are reported for a consequent number of recent studies also dealing with chemical analysis of aerosol samples. The rules used here to constrain molecular formula assignments within these 2 ppm (Page 8, Line 190-192), or very closed ones, are also quite common (Fuller et al., 2012; Lin et al., 2012a; Lin et al., 2012b; Tao et al., 2014). Clearly, the accuracy of 2 ppm corresponds already to high resolution analysis on complex dilute samples only available in very low amounts. The study of Kind and Fiehn (2007) is of high interest, and very helpful to constrain the possible identification of chemical formula. Especially, they considered simulated MS spectra at ± 3 ppm mass accuracy and ± 5% isotope ratio measurement errors. In any case, we do agree that all molecular formula are only tentatively assigned and not positively identified. We have added more information about other possible formula within 2 ppm for the major ions in the footnote of Tables S3, as it had been done by Lin et al. (2012b) for example in their supplement. Also, we now state in our manuscript (Page 8, Line 201-203) that “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”.

6. *Please mention reproducibility of the ion appearance in the mass spectra for the ions with low intensity in the replicates.*

Reply: No replicate was performed. Second injections of a larger volume of sample were performed - for which the peak shapes were degraded - allowing to confirm the presence the ions but not to give reproducibility. In any case, even the “low” intensity ions present signal to noise ratios much greater than 10 or, for a very large majority, were not present in the blank at all.

7. *Please also clarify whether the mass spectra (Figure 2) was obtained by integration of chromatographic area of the LC chromatogram or from a direct infusion analysis.*

Reply: The intensity of individual mass spectra in Figure 2 was obtained by integration of chromatographic peaks. We stated in our manuscript (Page 8, Line 210-212) that “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”. Please also refer to our reply to the 2nd comment.

8. *It is important that all extracts have comparable OC or PM load, overwise the comparison of molecular composition in the samples from different sampling locations is highly speculative as such differences could be attributed to the analytical artefacts (e.g., ion suppression which is known to be an issue in the ESI direct infusion analysis). Please justify it.*

Reply: OC data are unfortunately unavailable and PM data are only available for Shanghai (with relatively comparable values, see Table S1). We do agree that these values would have been particularly interesting. Nevertheless, the samples were not analyzed here by ESI direct infusion. LC separation allowed to minimize artifacts due to the matrix, diluting the low amount of sample injected (5μL) in the LC solvent flow (300 μL min^{-1}) and resolving most the matrix components (these latter being previously solvent extracted and filtered).

Reference:

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.

Kind, T., and Fiehn, O.: Seven Golden Rules for heuristic filtering of molecular formulas obtained by accurate mass spectrometry, Bmc Bioinformatics, 8, doi:10.1186/1471- 2105-8-105, 2007.

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, Environmental science technology, 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-highresolution mass spectrometry, Environmental science technology, 46, 13118-13127, doi: 10.1021/es303570v, 2012b.

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 NanosprayDesorption Electrospray Ionization High-Resolution Mass Spectrometry, Environmental science technology, 48, 10993-11001, doi: 10.1021/es5024674, 2014.

RE: A point-to-point response to referee #1's second comments

"Identification of Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River" (acp-2015-393) 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 referee #1 for his/her valuable comments. A point-to-point response to this reviewer's comments, which are repeated in italic, is given below.

1. *I have a short remark to the authors comment on 'Bearing in mind the availibility of instruments having resolutions better than 1 ppm, and the availablitly of the environmental samples as those considered here, we do believe having conducted our study according to the best available standards.'*

   As mentioned in the main the text of the paper-the authors used a mass tolerance of 2 ppm and only C, H, O, N, and S elements for their formulae assignments. This would be valid if you have authentic standards or/and compared your chromatographic RTs as well as the MSn fragmentation patterns with the literature data for all of the suggested OSs. The riverine environments (including Yangtze River region) are not only rich in nitrogen but also phosphorous (e.g. Li et al., 2007, Duan et al., 2009, Hou et al., 2009). Therefore, not considering phosphorous and isotopic ratios for the most abundant elements (i.e. C, N, S and P) could lead to significant formulae misassignments, especially for the ions with m/z >300. The authors describe their formulae assignment procedure by referring to Wozniak et al. (2008). However, the work by Wozniak et al. (2008) does consider phosphorous and isotopic ratios in their molecular formulae assignment procedure.

   References:

   M. Li et al. Long-term variations in dissolved silicate, nitrogen, and phosphorus flux from the Yangtze River into the East China Sea and impacts on estuarine ecosystem, Estuar. Coast. Shelf Sci., 71 (2007), pp. 3–12;

   S.W. Duan, et al. Seasonal changes in nitrogen and phosphorus transport in the lower Changjiang River before the construction of the Three Gorges Dam, Estuar. Coast. Shelf Sci., 79 (2008), pp. 239–250

   L.J. Hou, et al. Phosphorus speciation and availability in intertidal sediments of the Yangtze Estuary, China. Appl. Geochem., 24 (2009), pp. 120–128; A.S. Wozniak et al. Technical Note: Molecular characterization of aerosol-derived water soluble organic carbon using ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, Atmos. Chem. Phys., 8 (2008), pp. 5099-5111.

Reply: Thank you very much for your interest. It is perfectly correct that the work by Wozniak et al. (2008) does consider phosphorous and isotopic ratios in their molecular formulae assignment procedure. However they concluded (Page 5102, Section 3.1.1): "Phosphorous is typically not a quantitatively significant component of atmospheric materials (Chen et al., 2002; Grimshaw and Dolske, 2002; Baker et al., 2006); therefore all molecular formulas containing phosphorous were eliminated for ease of processing". We therefore indeed just followed their recommendations.
Phosphorus should be considered when dealing with sediment and water samples (e.g. Li et al.,

2007, Duan et al., 2009, Hou et al., 2009) because this element is rich in riverine environment. However, here we focus on analysis of organics organosulfates in atmospheric aerosol samples. We revised our title into “Molecular Characterization of Atmospheric Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River” to avoid this misunderstanding.

RE: A point-to-point response to referee #1's third comments

"Identification of Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River" (acp-2015-393) 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 referee #1 for his/her valuable comments. A point-to-point response to this reviewer's comments, which are repeated in italic, is given below.

1. *Unfortunately I failed to find any recommendations on not considering phosphorous for molecular formulae assignment in Wozniak et al paper. The authors did consider this element and eliminated all molecular formulas containing phosphorous from the final list of formulae as they found them insignificant in their environment (and those environments considered by Wozniak et al references). As emphasised in my previous comment, this may not be the case for Yangtze river environment.*

Reply: The referee is right in saying that Wozniak et al. not recommend to not consider phosphorous. Nevertheless, these authors clearly state that this element is insignificant and that a large majority of compounds can be assigned using only C, H, O, N and S elements. The statement that phosphorous is typically not a quantitatively significant component of atmospheric materials is supported by the literature (Chen et al., 2002; Grimshaw and Dolske, 2002; Baker et al., 2006). In addition, our sampling locations are away from the river and atmospheric aerosol samples are unlikely to be significantly impacted by the river spray, if there was any. Therefore, we choose to process our data similarly to recent studies dealing with environmental aerosol samples from various environments (rural, suburban, urban, Los Angeles, Shanghai, Pearl River Delta Region in China, East Asia) that is to say only involving C, H, O, N and S elements for molecular mass assignment (Fuller et al., 2012; Lin et al., 2012a; Lin et al., 2012b; Tao et al., 2014). In any case, if we do agree that the fact to take or not take into account phosphorous for molecular formula assignment in the case of environmental aerosol samples can be under debate, we think that it cannot be a reasonable reason to reject the present manuscript, given the recent literature on the subject.

2. *Moreover, neither Fuller et al nor Wozniak et al (referenced paper in this section) provide any recommendation for not considering isotopic patterns. For molecular formulae assignment procedure, I strongly recommend considering isotopic pattern/ratio section of the highly cited work by Kind and Fiehn (2007) and references therein, which strongly emphasise the importance of this step for accurate molecular formulae assignment.*

Reply: Similarly, the referee is right in saying that neither Fuller et al. nor Wozniak et al. recommend to not consider isotopic pattern. Nevertheless, neither studies effectively used isotopic pattern for molecular formula assignment. In these studies, if a given m/z refers to a C^{13}-containing compound (Fuller et al., 2012) or is 1.003 mass units greater than another detected peak (Wozniak et al, 2008), the peak is not further considered. Lin et al. (2012a) used C^{13} isotopic peaks only to determine the charge status of the ions. Tao et al. (2014) did not mention isotopic pattern at all. Only Lin et al. (2012b) mentioned isotopic pattern to support the assignment of S-containing formulae. But it is clearly stated that this is done only for intensive ions. In our study, in most cases, the isotopic peak is not detected due to the relatively low intensity of the quasi-molecular ion. One can thus consider that our assignments were done using the standard rules currently available in the literature of our field.

Reference:

Baker, A. R., Jickells, T. D., Witt, M., and Linge, K. L.: Trends in the solubility of iron, aluminum, manganese and phosphorous in aerosol collected over the Atlantic Ocean, Mar. Chem., 98, 43-58, 2006.

Chen, L.-W. A., Doddridge, B. G., Dickerson, R. R., Chow, J. C., and Henry, R. C.: Origins of fine aerosol mass in the Baltimore-Washington corridor: implications from observation, factor analysis, and ensemble air parcel back trajectories, Atmos. Environ., 36, 4541- 4554, 2002.

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 Ultrahigh-Resolution Mass Spectrometry, Anal. Chem., 84, 9858-9864, doi: 10.1021/ac3020615, 2012.

Grimshaw, H. J. and Dolske, D. A.: Rainfall concentrations and wet atmospheric deposition of phosphorous and other constituents in Florida, U. S. A., Water Air Soil Poll., 137, 117–140, 2002

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.

Nizkorodov, S. A., Laskin, J., and Laskin, A.: Molecular chemistry of organic aerosols through the application of high resolution mass spectrometry, Phys. Chem. Chem. Phys., 13, 3612-3629, doi:10.1039/c0cp02032j, 2011.

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, Environ. Sci. Technol., 48, 10993-11001, doi:10.1021/es5024674, 2014.

RE: A point-to-point response to referee #2's comments

"Identification of Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River" (acp-2015-393) 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 referee #2 for his/her valuable comments, encouraging us to further improve our manuscript. A point-to-point response to this reviewer's comments, which are repeated in italic, is given below.

The manuscript presents results from high-resolution mass spectrometric analysis of 8 particle samples collected in three chinese cities, and the main objective of the study is to investigate occurrence of organosulfates and nitrooxy-organosulfates. As such, the study should be very interesting, but unfortunately the presentation needs to be improved in order to communicate the findings adequately. There are numerous grammatical errors, which need to be corrected carefully before resubmission. The study is interesting and should be published once the authors has improved it according to the comments of all reviewers.

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.

General comments:

1. *The study is based on eight samples, which is OK, given that the authors remember this limitation in their discussion of the findings. Examples where this need to be improved are found e.g. on pages 21428 and 21431 as well as the discussion of Fig. 5 on page 21433.*

Reply: The manuscript has been thoroughly edited and improved to limit the conclusions about seasonal trends and urban variations, preferentially highlighting the nature/variety of the detected OSs rather than their temporal and spatial variations. For example, new section 3.5 is now titled with "Comparison of OSs in the SH samples" (Page 17, Line 460).

2. *The introduction should refer to the first findings of organosulfates and nitrooxy-organosulfates before more recent papers (first paragraph).*

Reply: We now state, before other recent papers, that "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" (Page 3, Line 46-48).

3. *I support the discussion brought forward by other reviewers regarding use of the word "identification". This word should only be used, when the finding has been supported by analysis of an authentic standard.*

Reply: We revised our title into "Molecular Characterization of Atmospheric Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River". In addition, we now state in our revised manuscript (Page 4, Line 85-86) that "Recently, ultra-high-resolution mass spectrometry has been applied for tentative determination of the molecular formulas of OSs in atmospheric aerosols samples" to avoid any misinterpretation of the term "identification".

4. *Number of isomers: It is not clear what the scientific explanation and interpretation is of these numbers, and why this is relevant (text + Fig. 2).*

Reply: The number of isomers for a tentatively determined OS is based on the number of chromatographic peaks with the same m/z value. It corresponds to the number of molecular structures detected for a given molecular formula, and reflects another dimension of the complexity of the aerosol composition, hidden by more common direct high resolution MS analysis. In the revised manuscript, we started our discussion with chromatograms that show the presence of different numbers of isomers of $C_5H_{10}O_5S$ (neutral mass 182.0251 Da) in seven ambient samples. In addition, the retention times of isomers for all observed OSs have been included in the supplement for future comparison (new Table S3).

Specific comments:

1. *page 21418 line 7: Find a better reference than Lee et al, 2013 for this statement.*

Reply: Two new references have been cited (Page 3, Line 40-42).

Magari, S. R., Schwartz, J., Williams, P. L., Hauser, R., Smith, T. J., and Christiani, D. C.: The association of particulate air metal concentrations with heart rate variability, Environmental Health Perspectives, 110, 875-880, 2002

Ostro, B., Feng, W. Y., Broadwin, R., Green, S., and Lipsett, M.: The effects of components of fine particulate air pollution on mortality in California: Results from CALFINE, Environmental Health Perspectives, 115, 13-19, doi:10.1289/ehp.9281, 2007

2. *BS -> OS several places: particulate matters -> particulate matter*

Materials and methods: Please add some more information on the cities and the surrounding areas.

Reply: "BS" is the abbreviation for benzyl sulfate.

"particulate matters" has been replaced by "particulate matter" throughout the manuscript (Page 5, Line 103, 113).

We added the population and typical metrological conditions of the three cities. The detailed information on the surrounding areas of the three sampling sites can be found in the previous studies (Zheng et al., 2015; Xiao et al., 2015; Ma et al., 2014).

3. *21422 lines 4 + 5: Ficher -> Fischer*

Reply: “Ficher” has been replaced by “Fischer” throughout the manuscript (Page 6, Line 153, Page 7, Line 158, 159, 173,174).

4. *21422 line 14: Please state at least the recovery percentage here. Use of the word daily: In most places it should be replaced by “daytime”.*

Reply: We have stated (Page 6, Line 163-167) that “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)”.
In the present manuscript, “daily sample” has been replaced by the sample IDs.

5. *21426 line 18: Do you mean that C (C6H10O3SO4) could come from isoprene with 5 C-atoms?*

Reply: C ($C_6H_{10}O_3SO_4$) could be derived from 3−Z−hexenal (Shalamzari et al., 2014). The manuscript has been revised accordingly (Page 12, Line 319).

6. *21428 line 7: “so closed values” – do you mean so similar or?*

Reply: The term “so closed values” has been replaced by “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.” (Page 13, Line 357).

7. *21428 lines 10-25: This discussion should focus on differences between samples not cities (due to the very low number of samples).*

Reply: Please refer to our reply to the 1st general comment from referee #2.

8. *21429 line 26: Add reference to Fig. 3 here.*

Reply: The manuscript has been revised accordingly (Page 15, Line 401).

9. *21432 line 1-2: This statement seems out of context and should be elaborated further, preferably with reference to relevant sources.*

Reply: We now state that “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” (Page 16, Line 432-436).

10. *21433 line 4-5: This statement is too strong (given the few samples) and should be softened.*

Reply: As stated in our reply to comments from other referees, the manuscript have been thoroughly edited to limit the conclusions about seasonal trends.

11. *21434 line 11: How can these pathways lead to low abundance of CHONS during daytime? A better statement would be that they lead to a higher abundance during night.*

Reply: The statement refers to the potential photochemical pathway of nitrooxy-OS formation. This pathway should thus contribute to daytime N-OS, detected here at relatively low abundances. We thus maintain our statement but it is now clarified to avoid any misinterpretation: “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 (Page 18, Line 490-492).”

Reference:

Shalamzari, M. S., Kahnt, A., Vermeylen, R., Kleindienst, T. E., Lewandowski, M., Cuyckens, F., Maenhaut, W., and Claeys, M.: Characterization of polar organosulfates in secondary organic aerosol from the green leaf volatile 3-Z-hexenal, Environmental science & technology, 48, 12671-12678, doi:10.1021/es503226b, 2014.

RE: A point-to-point response to referee #3's comments

"Identification of Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River" (acp-2015-393) 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 referee #3 for his/her valuable comments, encouraging us to further improve our manuscript. A point-to-point response to this reviewer's comments, which are repeated in italic, is given below.

This is the first study combining UPLC separation with UHRMS (Orbitrap) to characterize organosulfates (OSs) present in ambient samples. The UPLC separation allows detection of isomers, which offers another dimension of information in comparison with the previous fused-injection UHRMS studies of OSs. Such data is valuable in advancing our understanding of OSs, although the authors could have done a better job exploring information derived from this unique combination of information (see details in specific comments).

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

General comments

The uses of wording such as "seasonal" and "diurnal" are misleading as a very small number of samples (a total of 8 samples spread over three cities and two seasons) were characterized and it is over-stretched to argue these snapshots represent seasonal and diurnal variation for a location. The authors also noted that the NJ daytime sample was different from other (pp21425, lines 18-19), illustrating the danger of using one single sample to represent one type of atmospheric conditions). In related to this concern, the abstract needs re-phrasing to indicate sample-to-sample variation, instead of generalizing as seasonal or diurnal variation.

Reply: Our point of view was not to infer any general conclusion about seasonal or diurnal trends of OSs in China but more to describe our observations and suggest some explanations. Nevertheless, we agree that seasonal/diurnal comparisons from average values in Table 1 are not so relevant and should come along with moderate conclusions. For the Shanghai samples and corresponding manuscript section, even if we do agree that no definitive conclusion can be made about seasonal/diurnal trends with such a small dataset, we think that describing our results this way is informative and could help future more complete field campaign to identify specific points to clarify, as the presence of nitrooxy-OSs during daytime or the importance of the precursors' seasonality in different locations. The manuscript was nevertheless be thoroughly edited to limit the conclusions about seasonal trends preferentially highlighting the nature/variety of the detected OSs rather than their seasonal/diurnal trends. For example, new section 3.5 is now entitled with "Comparison of OSs in the SH samples" (Page 17, Line 460)
The abstract was revised accordingly

Specific comments:

1. *Abstract: "… detection of about two hudred particulate organosulfates (OSs), including dozens of nitroxy-organosulfates…". This statement appears to refer to the number of unique formulas, not counting isomers sharing the same formula. This needs to be clarified. It will also be good to indicate the number of OS chromatographic peaks detected (i.e, counting the isomers).*

Reply: We now state that "…allowed for detection of about 200 formulas of particulate organosulfates (OSs), including dozens of formulas of nitrooxy-organosulfates…" (Page 2, Line 21-22).

2. *Abstract: winter versus summer comparison for WH and SH is better removed or rephrased as sample-to-sample variation instead of generalizing as seasonal variation considering the small number of samples at each location and in each season (as there is only one 24-h summer sample and one 24-h winter sample in WH, one day sample and one night sample in SH in each season).*

Reply: Please refer to our reply to the general comment from referee #3.

3. *Considering the ability of detecting isomers is a unique result with this work, Fig. S1 deserves to be shown in the main text. I also suggest that the authors include example chromatograms showing isomer presence for a few monoterpene-derived OSs that have been reported in the smog chamber experiments and other ambient studies. For example, [M-H]- at m/z =251.0595 (or neutral mass 252.0673) could be a limonene derived OS. In current work, 5-7 of isomers at this neutral mass were detected, possibly indicating VOCs other than limonene could also be precursors. Such information is useful in guiding future LC/MS quantification of common OSs.*

Reply: In the revised manuscript, we start our discussion with chromatograms that show the presence of different numbers of isomers of $C_5H_{10}O_5S_1$ (neutral mass = 182.0251 Da) in seven samples. Some more extracted ion chromatograms have been included in the supplement (Figure S1), including those for species H (neutral mass=295.0729 Da) derived from monoterpenes.

4. *For the abundant OS formulas shown in Fig. 2 (i.e., A, B… J, K), I suggest including a table to show the isomer ratios in the samples and possible VOC precursors for these abundant OS formulas. Also comment on the ratio variability among different samples. This information can be useful for LC/MS quantification studies of OSs with lower mass resolution instruments.*

Reply: This table has been added in the Supplement (new Table S4). Discussion on the isomer ratios has been added in the manuscript (Page 12, Line 332-334).

5. *Figure 2 caption, line 4: a given species -> a given formula*

Reply: “species” has been replaced by “formula” (Page 25, Line 11).

6. *Re-organize Tables S3-S10 to list the formulas from the three sites side by side. I suggest combining into one single table to facilitate cross-sample comparison. Also include the retention time data as this also offers information on the compound polarity. It will be also helpful to label the formulas that match those reported in the smog chambers of known precursors.*

Reply: Tables S3-S4 and S6-S10 were combined into one single table (new Table S3 in the supplement), to facilitate cross-sample comparison. However, data for the Nanjing daytime sample is not included because a large amount of injection (50 ul) led to corruption of peaks and hence inaccurate retention times and worse peak resolution.

7. *As sulfate is the common precursor for all the OSs, the level of sulfate in each sample could be useful to understand the sample-to-sample variation of OSs detected. I suggest including sulfate data in the manuscript.*

Reply: Unfortunately, the concentration of sulfate is not available.

8. *Figs. 3 and 4: please add a brief note in the caption to indicate what the series (1, 2, 3,…) are.*

Reply: We have added “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)”, and “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)”, in the captions of Figs. 3 and 4, respectively.

9. *Fig. 4 (f): series (3) appear twice but series (2) is missing.*

Reply: This typo has been corrected. One mis-labelled “3” in the Fig. 4 (f) has been replaced by ”2” (Page 30).

RE: A point-to-point response to referee #4's comments

"Identification of Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River" (acp-2015-393) 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 referee #4 for his/her valuable technical comments, encouraging us to further develop our experimental section. A point-to-point response to this reviewer's comments, which are repeated in italic, is given below.

General comments:

1. *"I feel that the manuscript is not suitable for publication in its current form for a number of reasons. My first concern is lack of chromatograms and mass spectra in the manuscript or supporting information. I understand that showing a large number of extracted ion chromatograms is not practical. However, the authors need to show at least chromatograms from major peaks in the main manuscript or supporting information. The authors can discuss about the differences in organosulfates at different locations directly using chromatograms. That is far more effective than descriptive texts."*

Reply: We do share with the referee his/her concern about the practical aspects of adding too many chromatograms. However, as recommended we have added extracted ion chromatograms of major m/z in the main text and in the supplement and now start our discussion around those. In addition, we have also added retention times in the supporting information (new Table S3). Nevertheless, a figure such as Figure 3 or Figure 6 appears more appropriated to discuss the complete dataset.

2. *"Second, the authors discuss about seasonal and diurnal variations from extremely small sets of data. While the authors can discuss about the differences in these sampling days, they should not be discussed as seasonal or diurnal patterns."*

Reply: Our point of view was not to infer any general conclusion about seasonal or diurnal trends of OSs in China but more to describe our observations and suggest some explanations. Nevertheless, we agree that seasonal/diurnal comparisons from average values in Table 1 are not so relevant and should come along with moderate conclusions. For the Shanghai samples and corresponding manuscript section, even if we do agree that no definitive conclusion can be made about seasonal/diurnal trends with such a small dataset, we think that describing our results this way is informative and could help future more complete field campaign to identify specific points to clarify, as the presence of nitrooxy-OSs during daytime or the importance of the precursors' seasonality in different locations. The manuscript was nevertheless thoroughly edited to limit the conclusions about seasonal trends i.e., preferentially highlighting the nature/variety of the detected OSs rather than their seasonal/diurnal trends. For example, new section 3.5 is now entitled with "Comparison of OSs in the SH samples" (Page 17, Line 460).

3. *"Third, I find the manuscript extremely difficult to follow. It is extremely densely written. The authors should seek a language editing service to make sure that the manuscript can be read smoothly."*

Reply: The manuscript have been lightened and clarified as much as possible and reviewed by a language editing service. Naturally all technical comments will be implemented in the revised version.

Technical comments:

4. *Page 21419 line 13 onwards: The authors should also address Kahnt et al (2015) here. Kahnt, A., Behrouzi, S., Vermeylen, R., Shalamzari, M. S., Vercauteren, J., Roekens, E., Claeys, M., and Maenhaut, W.: One-year study of nitroorganic compounds and their relation to wood burning in PM10 aerosol from a rural site in Belgium, Atmos. Environ., 81, 561-568, Doi 10.1016/J.Atmosenv.2013.09.041, 2013.*

Reply: The reference was addressed. We now state in our revised manuscript (Page 4, Line 76-79) that "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)".

5. *Page 21420 line 10: Do the authors mean 'OS' measurements instead of identification? I am not aware of a study dealing with OS identification from Shanghai aerosols.*

Reply: Ma et al. (2014) have identified 17 OSs in SH with the corresponding authentic standard compounds.

6. *Page 21421 line 4: Do the authors mean 24 h samples? Daily samples mean a sampling was performed every day. I can only find two 24 h samples in the Table 1.*

Reply: In the present manuscript, "daily sample" has been replaced by the sample IDs.

7. *Page 21422 line 11: 'Th' and 'm/z' are used simultaneously. Both are a unit of massto-charge ratio, and it is redundant here. I recommend using 'm/z' as recommended by IUPAC.*

Reply: Only "m/z" is used in the revised manuscript (Page 7, Line 179-180).

8. *Page 21423 line 1 and throughout the manuscript: A term 'identification' should be reserved for a compound that is positively identified from the comparison to an authentic standard compound. 'Pseudo-molecular ion' should be 'quasi-molecular ion'.*

Reply: We revised our title into "Molecular Characterization of Atmospheric Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River". Also, we now state in our revised manuscript (Page 4, Line 85-86) that "Recently, ultra-high-resolution mass spectrometry has been applied for tentative determination of the molecular formulas of OSs in atmospheric aerosols samples" to avoid any misinterpretation of the term "identification". "Pseudo-molecular ion" has been replaced with "quasi-molecular ion" throughout the manuscript.

9. *Page 21423 line 16: The authors claim the detection of about 200 organosulfates from the UHPLC/(-)ESI-MS analysis but I am a little skeptical if these compounds eluted from the column as peaks. The authors mush show more extracted ion chromatograms in the main manuscript and supporting information. In supporting information, the authors show only four extracted ion chromatograms for an m/z value range between m/z 351.1849 and m/z 351.1853 without showing their mass spectra. From the description of the data processing, the authors did not seem to consider an isotope distribution of a detected compound, and relied solely on the ratio of H/C, O/C, N/C, S/C, and DBE. The authors should show corresponding mass spectra to assure readers that the compounds shown here are indeed organosulfates.*

Reply: We have added some more ion chromatograms in the manuscript and in the supplement (new Figure S1). Showing additional ion chromatograms and mass spectra would be just overwhelming and unpractical. However, retention times, potential precursors, and corresponding references for the identified OSs have been included in the supplement (new Tables S3). Molecular formula assignment was performed including the following elements: C, H, N, S and O. Isotopes are a classical way to confirm molecular formula assignments when the resolution of the instrument is not sufficient. Here, in most cases, the isotopic peak is not detected due to the low intensity of the related 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. Please also refer to our reply to the very last comment of referee #1 on this point.

10. *Pages 21422-21423: In connection to the previous concern, how did the authors calibrate m/z values? Have the authors used a lock mass function or were they calibrated externally? This should be clearly stated in the manuscript.*

Reply: We apologize for not having provided this information before and have amended the manuscript accordingly. We now state in our revised manuscript (Page 7, Line 180-182) that "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".

11. *Figure S1 in supporting information: Figure S1 should show the intensity of the peak.*

Reply: Figure S1 is shown to illustrate the separation of various OSs. Due to the different PM loadings in the samples, the intensity of the peaks in Figure S1 varies significantly but does not deliver additional useful information. Therefore, in our opinion, relative abundance is retained for the y-axis.

12. *Page 21425 line 10: How do the authors know that they are all nitrooxyorganosulfates? They are other structures that can contain nitrogen such as heterocyclic compounds, nitrophenolic*

compounds, etc.

Reply: MSn experiments were not performed in our study, and hence we cannot exclude other possibilities such as heterocyclic compounds, nitrophenolic compounds, etc. We now state (Page 8, Line 205-209) that "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, 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)".

13. *Figure 2. The authors should caution the readers that these are a number of isomers separated by the authors' method. For example, the C10H17O7N1S1 compounds show only three isomers for a certain method but it can be separated into six isomers when the method is further optimized.*

Reply: We now state in our revised manuscript (Page 8, Line 212-213) that "Note that the obtained number of isomers may vary significantly when the separation method is further optimized".

14. *Page 21426 line 27-29 and throughout manuscript: Is it a nitrate group or nitrooxy group? How do the authors know without MSn experiments?*

Reply: Please refer to our reply to the 12th comments from the referee #4.

15. *Page 21427: The authors cannot discuss seasonal differences from such a limited number of samples.*

Reply: The manuscript was thoroughly edited to limit the conclusions about seasonal trends, preferentially highlighting the nature/variety of the detected OSs rather than their trends. For example, new section 3.5 is now entitled with "Comparison of OSs in the SH samples" (Page 17, Line 460). In addition, air quality and meteorological data on the sampling days have been compared with the seasonal averages in the supplement (new Table S1), indicating that those parameters on the sampling days are quite close to the seasonal average.

16. *Page 21429 onwards about KMD and VK diagrams: I find this section very difficult to read and get information out of it. I recommend the authors summarizing most important information here instead of describing every single detail about the diagrams.*

Reply: The manuscript was lightened and clarified as much as possible and reviewed by a language editing service.

17. *Page 21432: These isoprene originating organosulfates tend to elute very early in the chromatogram, and their MS intensities can be potentially influenced by co-eluting compounds in this region (ion suppression). How have the authors corrected for this? If not, how do the authors know that they are not affected by the ion suppression?*

Reply: No correction has been made. We do agree that co-eluting compounds may lead to ion suppression. However, the samples were not analyzed here by ESI direct infusion. LC separation allowed to minimize artifacts due to the matrix, diluting the low amount of sample injected (5µL) in the LC solvent flow (300 µL min-1) and resolving most the matrix components (these latter being previously solvent extracted and filtered). In addition, By extracting early-eluting inorganics from our mass spectra, we found that their retention times were much earlier than those of isoprene OSs. Hence, the ion suppression would be minimum under our experimental conditions.

18. *Page 21433 onwards: Seasonal and diurnal variations cannot be discussed ˝ when the number of sampling day is so limited even they are similar to average seasonal conditions.*

Reply: Please refer to our reply to the 2nd comment from referee #4.

Reference:

Ma, Y., Xu, X., Song, W., Geng, F., and Wang, L.: Seasonal and diurnal variations of particulate organosulfates in urban Shanghai, China, Atmospheric Environment, 85, 152-160, doi:10.1016/j.atmosenv.2013.12.017, 2014.

RE: A point-to-point response to referee #5's comments

"Identification of Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River" (acp-2015-393) 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 anonymous referee #5, and have carefully revised our manuscript accordingly. A point-to-point response to the reviewers' comments, which are repeated in italic, is given below.

General comments:

In my opinion the manuscript is not suitable for publication in its present shape for at least two reasons.

Reply: We revised our manuscript thoroughly according to comments from all referees. We believe that our approach and data are convincing enough to warrant publication in ACP.

1. *A substantial lack of the analytical data*
   The authors intend to present the data from a few field campaigns in three megacities at the middle and lower reaches of the Yangtze River. A key tool they use is hyphenated mass spectrometry. Here is my first concern: the manuscript (including the supporting info) is lacking of the chromatographic and mass spectrometric data. I am utterly aware of a great number of raw data. However, the most relevant/major LC peaks should be discussed or at least briefly defined. The authors should consider a table as a tool to summarize the most ample organosulfates that contribute to the organic fraction.

Reply: We do share with the referee, his/her concern about the practical aspects of adding too many chromatograms. However, as recommended we have added extracted ion chromatograms of major m/z in the main text and in the supplement and now start our discussion around those.
A table was added in the supplement (new Table S4) summarizing the most ample organosulfates presented in Figure 2 (now Figure 3). In addition, retention times, potential precursors, and corresponding references for observed OSs have been included in the supplement (new Table S3).

2. *A misleading title*
   The title "Identification of particulate organosulfates in three megacities at the middle and lower reaches of the Yangtze" suggests the authors are willing to make a thorough analysis to confirm molecular entities of detected organosulfates in the ambient SOA samples. As an analytical chemist I can not allow for the misuse of the term "identification" by showing only an elemental formula of the detected organosulfate. The elemental formula is a relevant, though not sufficient parameter for the structural elucidation of any organic compound. A term 'identification' should be re- served for a compound that is positively identified from the comparison to an authentic standard compound.

Reply: In this study, the formulas were tentatively determined by applying a number of restrictions to the detected exact m/z values. We do agree with referee #5 that all molecular formulas are only tentatively assigned and not positively identified. We revised our title into "Molecular Characterization of Atmospheric Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River". In addition, we now state in our revised manuscript (Page 4, Line 85-86) that "Recently, ultra-high-resolution mass spectrometry has been applied for tentative determination of the molecular formulas of OSs in atmospheric aerosols samples" to avoid any misinterpretation of the term "identification".

3. Constrained data for seasonal variation

> *The authors make an effort to discuss the seasonal and diurnal variations. However, it is not clear for me how the authors are able to achieve this goal from such a limited number of samples.*

Reply: Our point of view was not to infer any general conclusion about seasonal or diurnal trends of OSs in China but more to describe our observations and suggest some explanations. Nevertheless, we agree that seasonal/diurnal comparisons from average values in Table 1 are not so relevant and should come along with moderate conclusions. For the Shanghai samples and corresponding manuscript section, even if we do agree that no definitive conclusion can be made about seasonal/diurnal trends with such a small dataset, we think that describing our results this way is informative and could help future more complete field campaign to identify specific points to clarify, as the presence of nitrooxy-OSs during daytime or the importance of the precursors' seasonality in different locations. The manuscript will nevertheless be thoroughly edited to limit the conclusions about seasonal trends, preferentially highlighting the nature/variety of the detected OSs rather than their seasonal/diurnal trends. For example, new section 3.5 is now titled with "Comparison of OSs in the SH samples" (Page 17, Line 460).

4. Difficulty in reading

> *The manuscript is written in the unpleasant way for the reader. I found the text difficult to follow, possibly owing to the fact of the data oversaturation. Thus, I would suggest the authors looking for a language editing service to make sure that the manuscript can be read smoothly. Just an example, page 21429 onwards about KMD and/or V K diagrams: I find this section very weird to read and get information out of it.*

Reply: The manuscript was lightened and clarified as much as possible and reviewed by a language editing service.

5. Moreover, there are some errors in terminology. An example, Th' and 'm/z' are used simultaneously. Both are a unit of mass-to-charge ratio, and it is redundant here. I would advise on using "m/z" as recommended by IUPAC provisions. Another example, page 21426 line 27-29 and throughout manuscript: Is it a nitrate group or nitrooxy group? How do the authors know without CID (collision induced dissociation) experiments?

Reply: Only "m/z" is used in the revised manuscript.

Organonitrates ($RONO_2$) are compounds bearing nitrooxy group(s), also called “nitrate group”. Both denominations refer to the same functionality. See for instance “Volatile organic compounds in the atmosphere” from Ralph Koppmann (2007, Blackwell Publishing Ltd) p 283-284. However, it is true that MSn experiments were not performed in our study, and hence we cannot exclude other possibilities such as heterocyclic compounds, nitrophenolic compounds, etc. We now state (Page 8, Line 205-209) that “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, 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)”.
Other errors in terminology have also been revised.

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

"Identification of Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River" (acp-2015-393) 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 JDS Surratt and M Riva, and have carefully revised our manuscript accordingly.

JDS Surratt and M Riva

1. *Although I am not a reviewer for this paper, when my Postdoctoral Scholar (Matthieu Riva) and I saw this published online in ACPD we read this with very high interest. I think the intentions of the authors are very good and this kind of data from China are highly needed in the literature.*

Reply: We are very grateful to JDS Surratt and M Riva for their positive viewing of our study.

2. *I strongly agree with the reviewer comments on the technical aspects they raised in their reviews. Specifically, I do want to point out that I agree that comparing seasonal and site trends really requires more filters, so these comparisons probably need to be modified with this in mind.*

Reply: The manuscript will nevertheless be thoroughly edited to limit the conclusions about seasonal trends, preferentially highlighting the nature/variety of the detected OSs rather than their trends. For example, new section 3.5 is now entitled with "Comparison of OSs in the SH samples" (Page 17, Line 460). In addition, the technical aspects, and especially the LC-MS coupling, have been clarified (Page 6-9, Line 151-224). Bearing in mind the availability of instruments having resolutions better than 1 ppm, and the availability of the environmental samples as those considered here, we do believe having conducted our study according to the best available standards.

3. *However, the degree of characterization provided in this manuscript is very interesting and potentially useful, especially the supplemental tables listing the detailed list of organosulfates (OSs) (including nitrated derivatives) identified from these samples. From carefully reviewing these detailed tables, it is clear that a lot of biogenic VOCs contribute to these OSs.*

Reply: We gratefully thank JDS Surratt and M Riva for their support.

4. *"However, the authors should be aware that a new study by Riva et al. (2015, ES&T) recently published from my group (in collaboration with Professor Eric Villenave's group and Professor Betsy Stone's group) revealed that organosulfur compounds (both organosulfates and sulfonates) form from the photooxidation of PAHs in the presence of sulfate aerosol. Several of the laboratory-generated PAH organosulfur compounds were identified in ambient*

> *samples collected from Pasadena, CA, USA and Lahore, Pakiston. Notably, many of the ions you report in your supplemental tables were recently characterized as sulfonates (i.e., m/z 201 [C7H5O5S-], 215 [C8H7O5S-], 227 [C9H7O5S-], 229 [C9H9O5S-]) and organosulfates (i.e., m/z 231 [C9H11O5S-], 257 [C10H9O6S-], 274 [C10H9O7S-]) from PAH (naphthalene and 2-methylnaphthalene) oxidations in presence of sulfate aerosol (Riva et al., 2015, ES&T). In addition, we noted that many of the OSs you identified were recently observed in Riva et al. (2015, Atmos. Environ.). In that study, OSs distinct to isoprene ozonolysis were identified. Many of these Oss previously observed from isoprene ozonolysis were also identi- fied in your supplemental tables, including m/z 181 [C5H9O5S-], 197 [C5H9O6S-], 199 [C5H11O6S-], 213 [C5H9O7S-], 227 [C6H11O7S-], 249 [C9H13O6S-], and 267 [C9H15O7S-]. One lesson we learned from the isoprene ozonolysis study is that some of the OSs can have similar elemental formulas as monoterpene OSs, and thus, reporting retention times or showing extracted ion chromatograms (as suggested by one of the reviewers) will be very helpful. I also wonder if the authors agree if adding another column to their supplemental tables listing the potential VOC precursor(s) and relevant study(studies) that supports this is useful? The authors may want to add a cautionary note that even if an OS has a C5 or C10 backbone (based on accurate mass measurements), these might not necessarily come from isoprene or monoterpenes as our recent work has shown that PAHs might have similar compositions or nominal masses as these products."*

Reply: This comment on your recent study on the formation of OSs, and more particularly to organo-sulfonates from PAH is of high interest regarding the determination of the nature of sulfur compounds as SOA components and the determination of their formation pathways. In our manuscript, compounds that present a number of oxygen greater than, or equal to, 4s + 3n (s being the number of sulfur atoms and n the number of nitrogen atoms) were tentatively regarded as OSs or nitrooxy-OSs, ignoring the fact that a compound with a number of oxygen atoms greater than, or equal to, 3s could also correspond to a sulfonate. This assumption was similarly used by Lin et al. (2012a and 2012b), for example. We think that it should be kept in the present manuscript for data processing and comparison purposes. However, specific mentions to the possibility of the presence of sulfonate groups instead of sulfate ones were added all along the text appropriately, especially when discussing compounds with high DBE values (i.e., potentially aromatic species), according to your comment.

Mention to possible PAH precursors was also added (Page 3, Line 62-64). Besides, the highly relevant cautionary note that even if an OS has a C_5 or C_{10} backbone these might not necessarily come from isoprene or monoterpenes was introduced. Both of the previous studies, Riva et al. (2015, ES&T) and Riva et al. (2015, Atmos. Environ.), have been of course cited appropriately. We added statements such as "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" (Page 18, Line 495-499).

We have shown more extracted ion chromatograms in the manuscript and in the supplement, as requested by you and a number of other reviewers. Also, we have added retention times, possible precursors and corresponding references of detected OSs (new Table S3) in the supporting information.

Reference:

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, Environmental science & technology, 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-highresolution mass spectrometry, Environmental science & technology, 46, 13118-13127, doi: 10.1021/es303570v, 2012b.

Riva, M., Budisulistiorini, S. H., Zhang, Z., Gold, A., and Surratt, J. D.: Chemical characterization of secondary organic aerosol constituents from isoprene ozonolysis in the presence of acidic aerosol, Atmos. Environ., doi:10.1016/j.atmosenv.2015.06.027, 2015a.

Riva, M., Tomaz, S., Cui, T., Lin, Y.-H., Perraudin, E., Gold, A., Stone, E. A., Villenave, E., and Surratt, J. D.: Evidence for an Unrecognized Secondary Anthropogenic Source of Organosulfates and Sulfonates: Gas-Phase Oxidation of Polycyclic Aromatic Hydrocarbons in the Presence of Sulfate Aerosol, Environ. Sci. Technol., 49, 6654-6664, doi:10.1021/acs.est.5b00836, 2015b.

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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. Aliphatic OSs represented more than 78% of the detected OSs at the three locations, while aromatic OSs were much less abundant. The 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 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; 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). 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 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, 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).

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 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 C_{AI} represents the difference between the number of carbon and the number of potential double bonds caused by heteroatoms. If $DBE_{AI} \leq 0$ or $C_{AI} \leq 0$, 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 (KM_{CH2}) and the Kendrick mass defect (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 from the ozonolysis of isoprene in the presence of sulfate aerosols, but only one isomer was detected by UPLC-high-resolution MS (Riva et al., 2015a). From ambient samples, 11 isomers were detected in total, with varying numbers of isomers in each sample (see Figure 2 and Table S3). The reason for this difference in the number of isomers between the two 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) due to different chromatographic conditions.

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 abundant. Clearly, the isomeric pattern differs significantly in WH compared to the other two megacities.

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 $4s+3n \leq o$ 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 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. 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. 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.

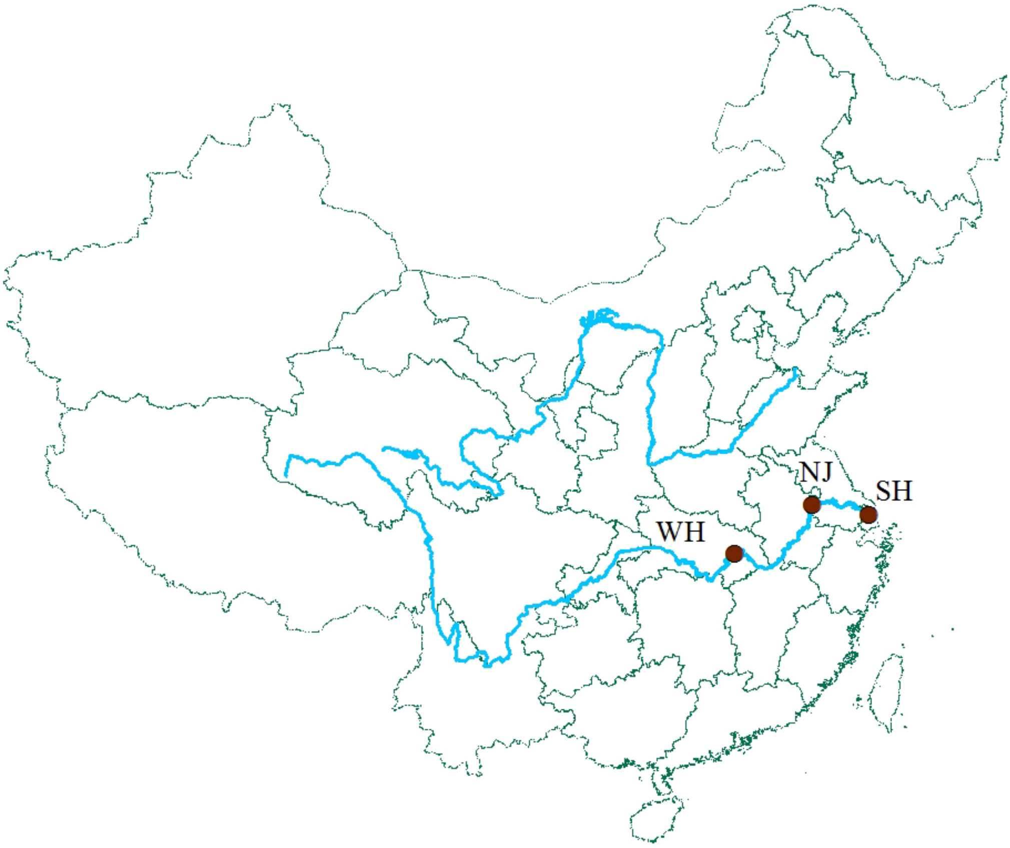

Figure 1

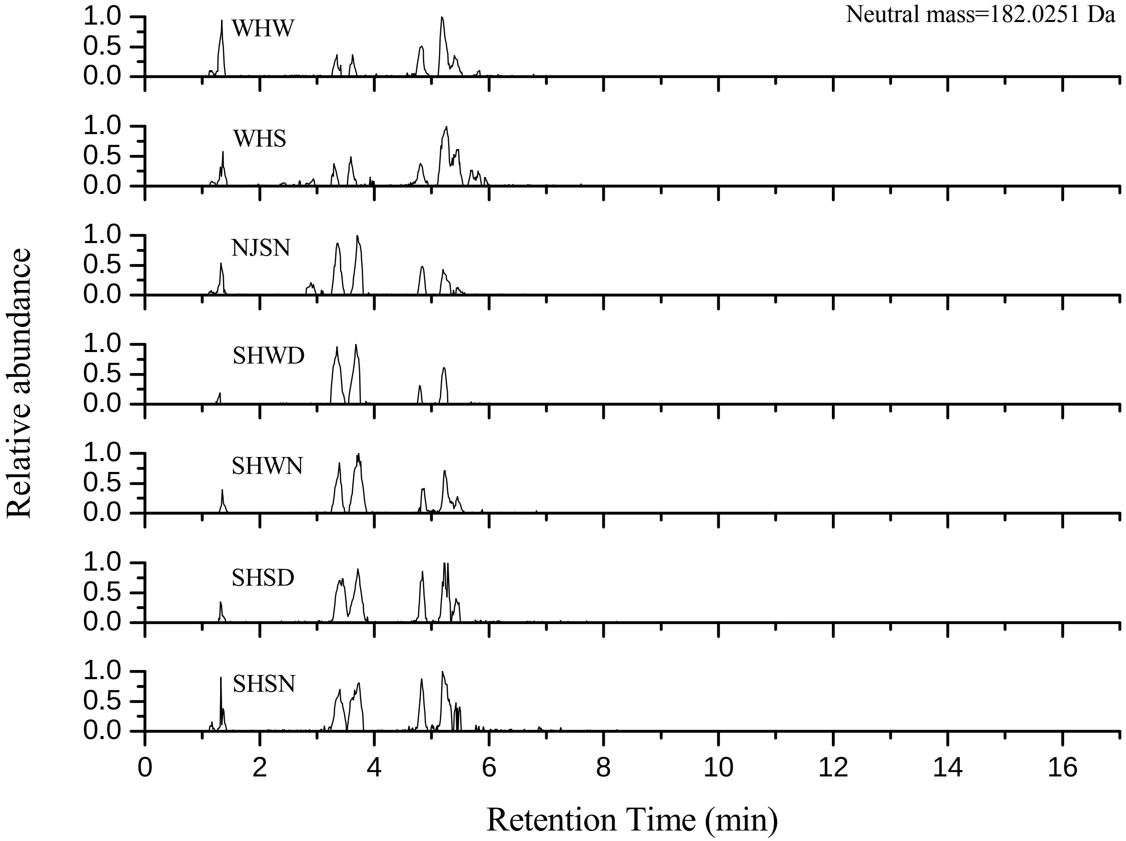
Neutral mass=182.0251 Da
WHW
WHS
NJSN
SHWD
SHWN
SHSD
SHSN
1.0
0.5
0.0
Relative abundance
0
2
4
6
8
10
12
14
16
Retention Time (min)

Figure 2

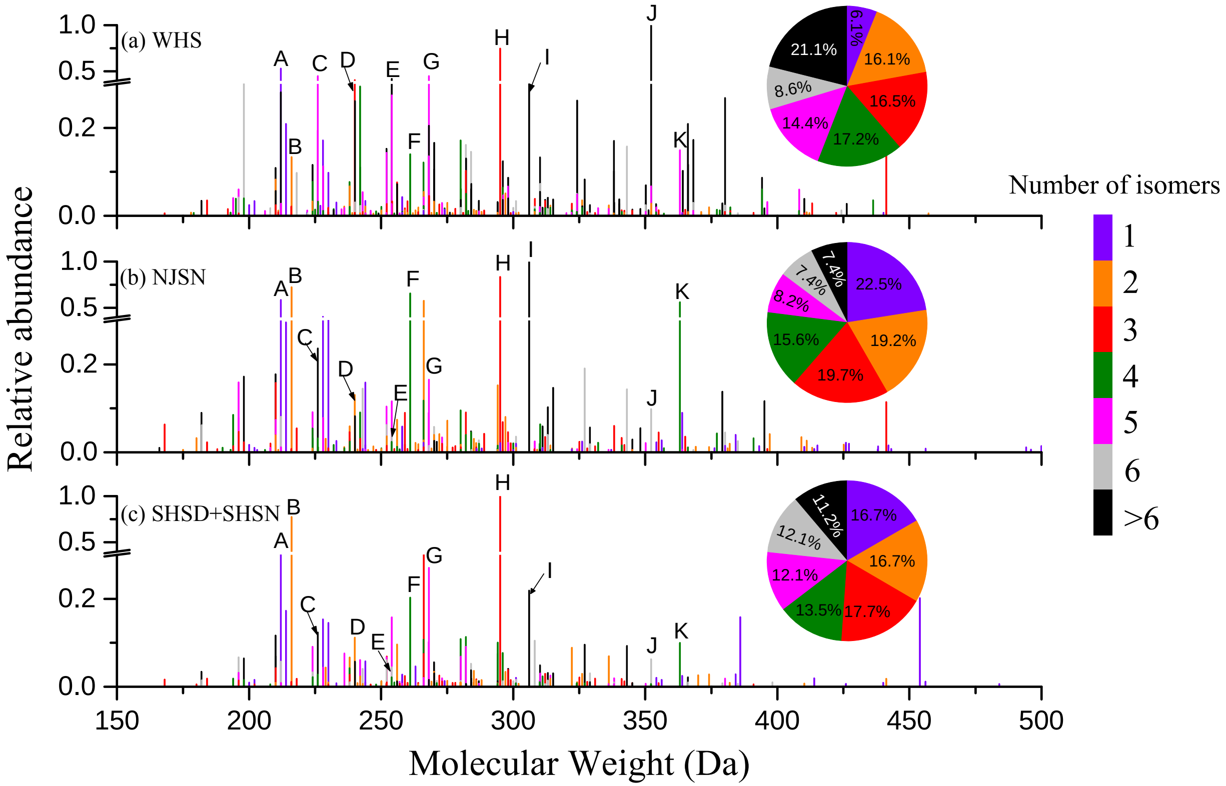
Relative abundance
Molecular Weight (Da)
(a) WHS
(b) NJSN
(c) SHSD+SHSN
1.0
0.5
0.2
0.0
150
200
250
300
350
400
450
500
A
B
C
D
E
F
G
H
I
J
K
6.1%
16.1%
16.5%
17.2%
14.4%
8.6%
21.1%
22.5%
19.2%
19.7%
15.6%
8.2%
7.4%
7.4%
16.7%
16.7%
17.7%
13.5%
12.1%
12.1%
11.2%
Number of isomers
1
2
3
4
5
6
>6

Figure 3

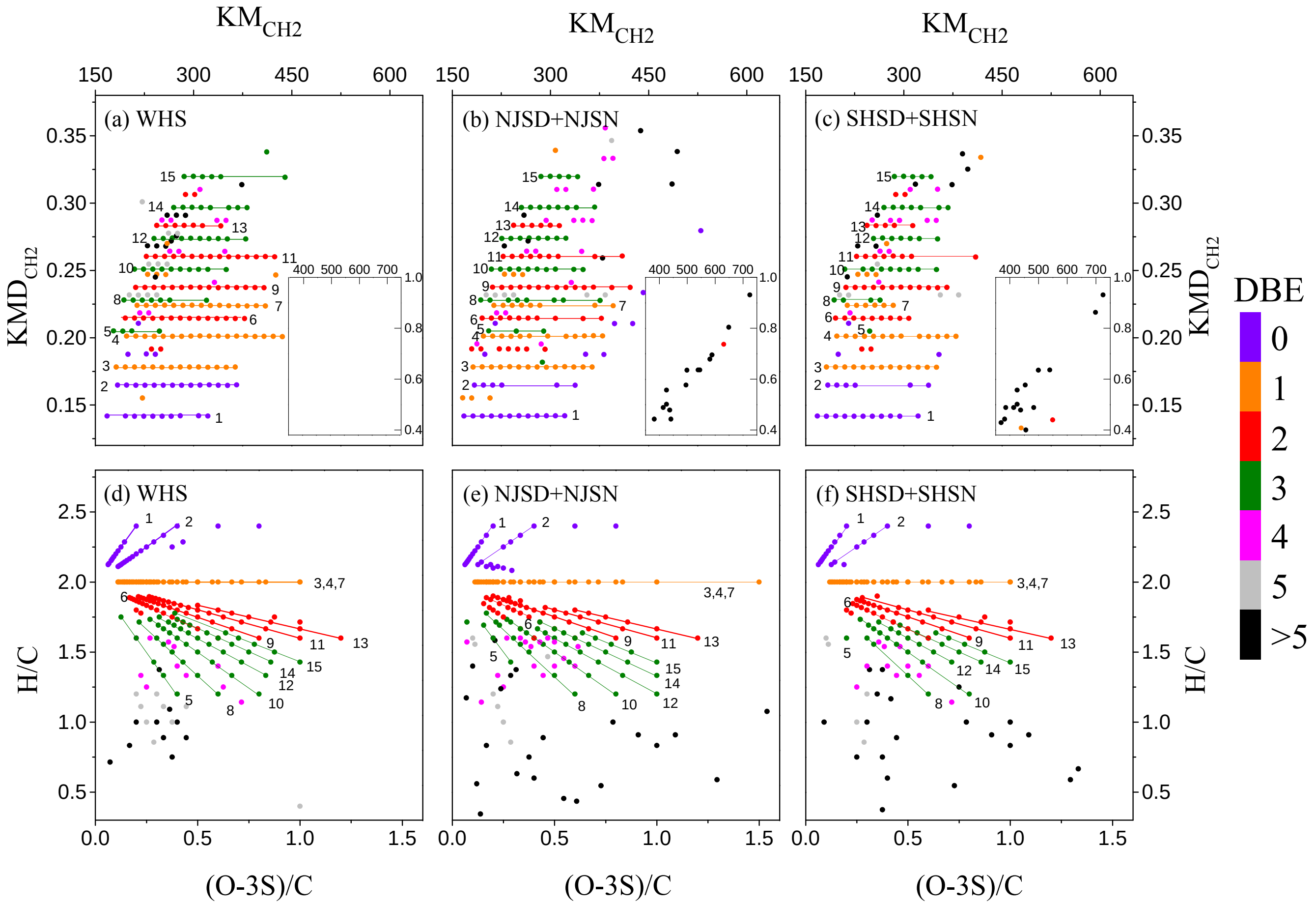
KM$_{CH2}$
150
300
450
600
(a) WHS
(b) NJSD+NJSN
(c) SHSD+SHSN
KMD$_{CH2}$
0.35
0.30
0.25
0.20
0.15
400 500 600 700
1.0
0.8
0.6
0.4
(d) WHS
(e) NJSD+NJSN
(f) SHSD+SHSN
H/C
2.5
2.0
1.5
1.0
0.5
0.0
0.5
1.0
1.5
(O-3S)/C
3,4,7
DBE
0
1
2
3
4
5
>5

Figure 4

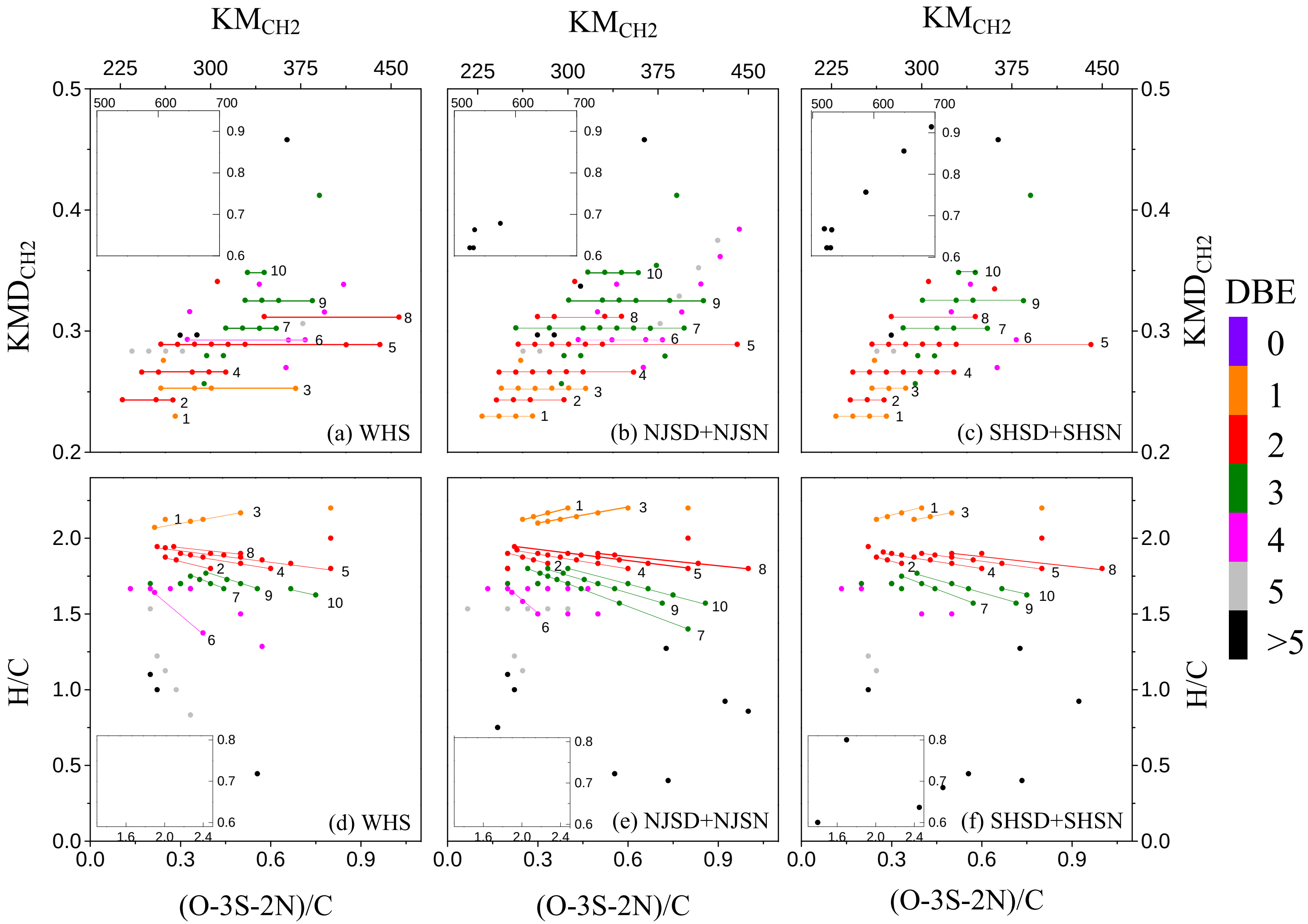
KMCH2
225
300
375
450
500
600
700
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
KMDCH2
(a) WHS
(b) NJSD+NJSN
(c) SHSD+SHSN
(d) WHS
(e) NJSD+NJSN
(f) SHSD+SHSN
H/C
2.0
1.5
1.0
0.5
0.0
1.6
2.0
2.4
0.0
0.3
0.6
0.9
(O-3S-2N)/C
1
2
3
4
5
6
7
8
9
10
DBE
0
1
2
3
4
5
>5

Figure 5

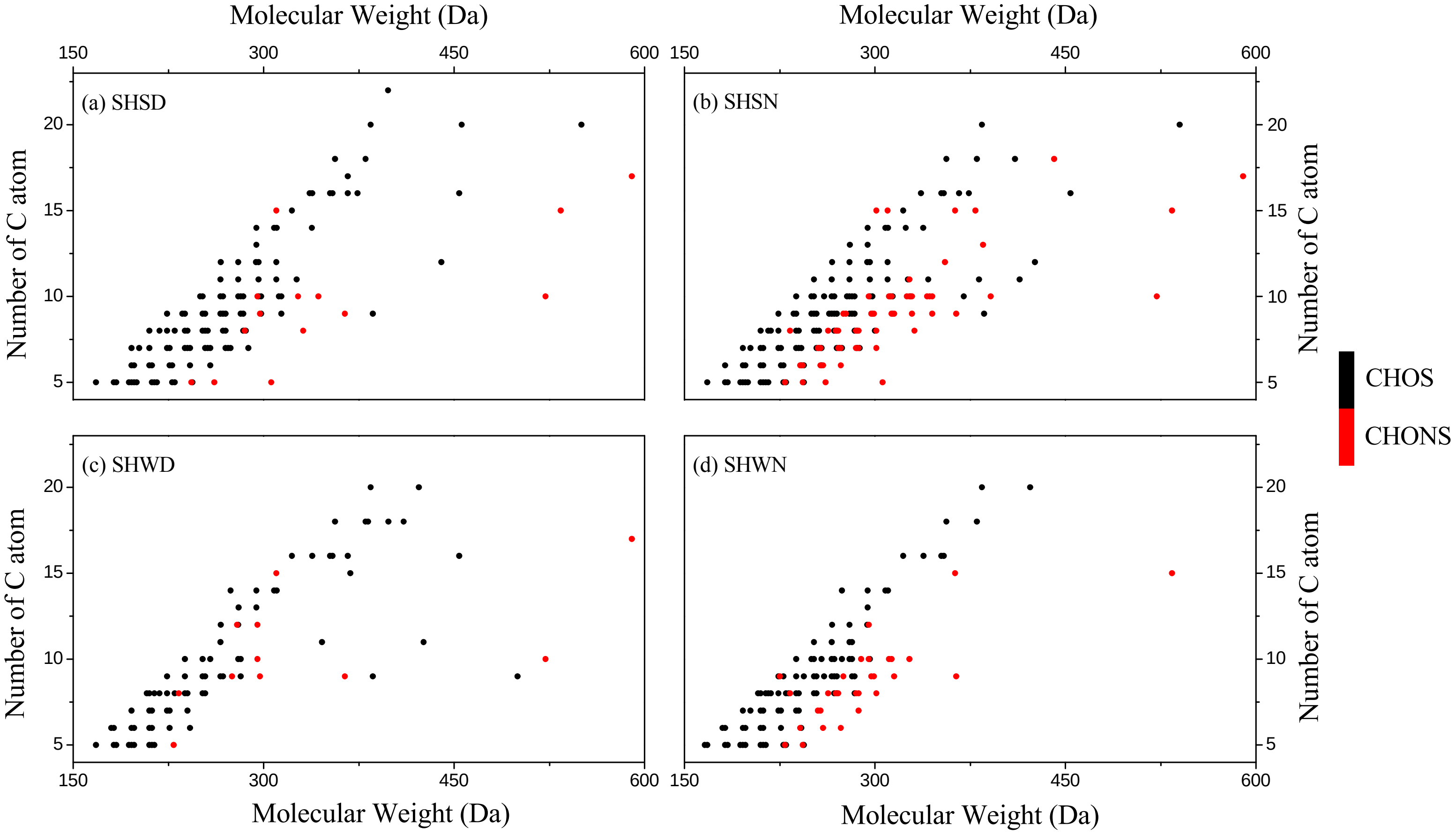
Molecular Weight (Da)
150
300
450
600
(a) SHSD
(b) SHSN
(c) SHWD
(d) SHWN
Number of C atom
5
10
15
20
CHOS
CHONS

Figure 6

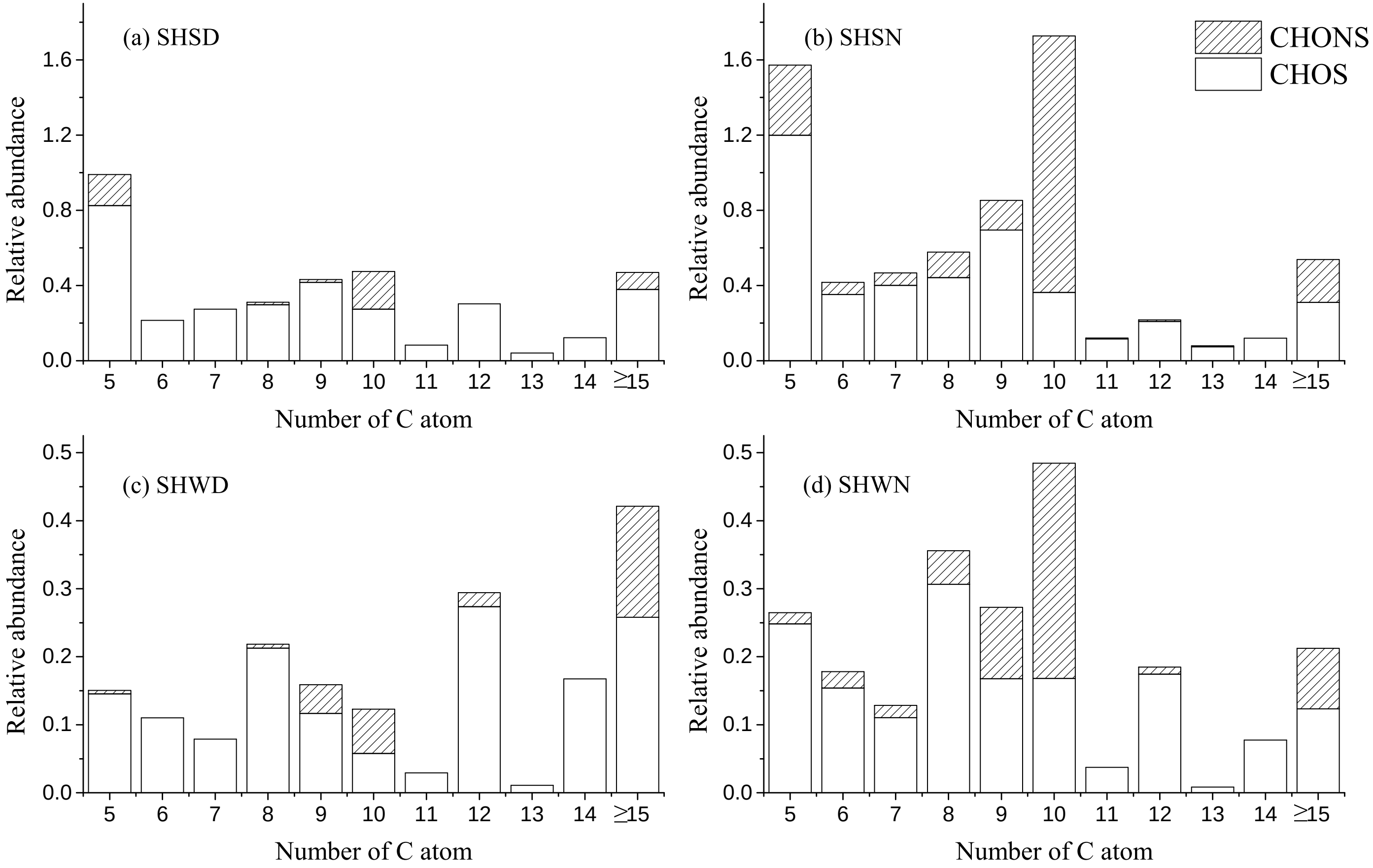
(a) SHSD
(b) SHSN
(c) SHWD
(d) SHWN
CHONS
CHOS
Relative abundance
Number of C atom
0.0
0.4
0.8
1.2
1.6
0.1
0.2
0.3
0.4
0.5
5
6
7
8
9
10
11
12
13
14
≥15

Figure 7